An investigation of sulphur in carbonaceous and enstatite chondrites by stepped combustion

Thesis

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An investigation of sulphur in carbonaceous and enstatite chondrites by stepped combustion

by

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Abstract

A stepped combustion technique has been developed to resolve the different sulphur-bearing components of meteorites. The technique has been applied to studies of carbonaceous and enstatite chondrites.

Stepped combustion of C1 and C2 carbonaceous chondrites provides evidence for the presence of secondary sulphur minerals. Evidence for six different sulphur components has been found (elemental and organic sulphur, sulphides, FESON and sulphates). Most of the sulphur in C1 and C2 meteorites is oxidised and probably formed as aqueous alteration products of precursive sulphide minerals in the meteorite parent bodies. C1 and C2 chondrites both contain the same sulphur components suggesting that hydrothermal alteration may have evolved along a common pathway. Changes in sulphur isotopic composition associated with alteration have led to an enrichment of ^{34}S in elemental sulphur and sulphates compared to the starting sulphide material.

Most of the sulphur in C3, C4 and C5/6 chondrites is present as sulphide, but stepped combustion has demonstrated that there is also a component of preterrestrial oxidised sulphur in these materials. Chemical evidence suggests that oxidised sulphur may occur as FESON or anhydrite. This finding indicates that C3 and C4 chondrites have undergone a small amount of hydrous alteration on the meteorite parent body and this provides an important evolutionary link with C1 and C2 meteorites.

The stepped combustion method has been used as a means of assessing the relative abundances of the two main sulphides (troilite and oldhamite) in enstatite chondrites and aubrites. It was found that troilite and oldhamite abundances both decrease systematically with petrologic grade. The variability of these two minerals provides constraints on models envisaged for the evolution of the enstatite chondrite parent body. Enstatite chondrites have whole-rock $\delta^{34}S$ values of close to 0‰, whereas aubrites are depleted in ^{32}S by up to 2‰.

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Chapter 1

Introduction

1.1 Background

A fundamental principle of the theory of atomic structure, put forward by Dalton in 1803, was that atoms of the same element are equal in weight. This postulate was later challenged by William Crookes in an address to the Chemical Section of the British Association at Birmingham in 1886. In a prophetic statement, Crookes suggested that atoms of any particular element may vary in their atomic weights (these he referred to as meta-elements), and furthermore, that such mass differences could lead to physical fractionation between the light and heavy atoms. In 1913, Soddy proposed the term isotopes (from the Greek iso and topes meaning equal and place) be used for these substances.

The theory of isotopes has its origin in the discovery of radioactivity. In 1896 Becquerel noticed that some photographic plates which had been stored near to a uranium compound had become fogged. He showed that this effect was due to 'radiations' emitted by the uranium. The 'radiations' are particles ejected when an unstable nucleus spontaneously disintegrates to acquire a more stable state, the parent nucleus undergoes a change in atomic number during radioactive decay and therefore, becomes a nucleus of a different element (known as the daughter element). For example, an isotope of rubidium, ^{87}Rb, is unstable and will decay by emission of an electron to stable ^{87}Sr

$$^{87}\mathrm{Rb} \rightarrow {}^{87}\mathrm{Sr} + \bar{e}$$

Stable isotopes, as the name suggests, do not undergo radioactive decay and vary only in atomic weight.

The first indication that isotopes of stable elements exist came in 1912 when J. J. Thompson demonstrated that neon has isotopes with masses 20 and 22. Thompson used a magnetic deflection instrument which constituted the first mass spectrograph and this experiment was the first demonstration of the principle of mass spectroscopy, the separation and recording of the mass of an ionized atom. 'Mass spectrograph' is a term that is nowadays usually employed for instruments that detect ions by a photographic plate, whereas a 'mass spectrometer' uses an electrical method of detection. The first precision spectroscopes were constructed by J. Dempster in 1918 and F. W. Aston in 1919, to measure the relative abundances of some isotopes. Aston's spectrograph was used initially to confirm that neon is composed of two constituents which correspond to Soddy's isotopes, and have mass numbers 20 and 22 (the third stable isotope of mass 21 was discovered by Hogness and Kvalnes in 1928).

In 1920, F. W. Aston discovered that sulphur has three stable isotopes with mass numbers 32,33 and 34 which occur in the approximate abundance ratio of 96:1:3, respectively. Following a calculation by Wigner made in 1937, which showed that mass 36 should also be a stable isotope, Nier (1938), using a high precision mass spectrometer proved the existence of ^{36}S with an abundance of 0.016%. The atomic abundances of sulphur in troilite (FeS) from the Canyon Diablo iron meteorite (CDT), selected as the primary standard to which all sulphur isotope measurements are referred (discussed in Section 1.2.1), were proposed by Ault and Jensen (1962) as follows.

$$^{32}\mathrm{S} = 94.941\%$$
$$^{33}\mathrm{S} = 0.769\%$$
$$^{34}\mathrm{S} = 4.273\%$$
$$^{36}\mathrm{S} = 0.017\%$$

Urey and Grief (1935) predicted that the isotopes of some light elements (H, Li, B, C, N, and O) should vary slightly in their chemical properties and this prompted the first studies of the natural abundance variations of stable isotopes in geological samples (Manian et al., 1934; Nier and Gulbransen, 1939; Murphey and Nier, 1941). Thode (1949) and Thode et al. (1949), utilizing mass spectrometry, pioneered sulphur stable isotope measurements of various natural samples. Thode and his co-workers showed that:

1. Large sulphur isotopic variations exist in nature (Thode et al., 1949).

2. Certain materials have characteristic sulphur isotopic compositions (Thode et al., 1949; Macnamara and Thode, 1950; Szabo et al., 1950; Thode et al., 1958; Thode et al., 1961; Shima et al., 1963; Thode and Monster, 1965).

3. Certain bacteria (e.g. Desulfovibrio desulfuricans) fractionate sulphur isotopes (Thode et al., 1951; Harrison and Thode, 1958).

4. The isotopic composition of meteoritic sulphur is constant (Macnamara and Thode, 1950).

Sulphur isotopic studies are now routinely included in certain aspects of geochemistry, meteoritics, hydrology, meteorology, pollution and environmental control, biochemistry and chemical kinetics.

1.2 Determination of sulphur stable isotopes

1.2.1 Sulphur isotope nomenclature

The absolute abundances of sulphur isotopes are not normally determined. As a convention, the abundance of the heavy isotope (^{33}S, ^{34}S, and ^{36}S) is referred to that of the light isotope (^{32}S), to define a dimentionless parameter, the isotope ratio R.

$$R = {}^{33}S/{}^{32}S \text{ or } {}^{34}S/{}^{32}S \text{ or } {}^{36}S/{}^{32}S$$

The isotope ratios measured for samples can be referred to analogous ratios obtained for a standard using the δ-notation, defined as:

$$\delta = \left[\frac{R_{sample} - R_{standard}}{R_{standard}}\right] \times 1000 \text{ per mil. } (‰)$$

$$\text{e.g. } \delta^{34}S = \left[\frac{({}^{34}S/{}^{32}S)_{sample} - ({}^{34}S/{}^{32}S)_{standard}}{({}^{34}S/{}^{32}S)_{standard}}\right] \times 1000 \ (‰)$$

As natural variations in the minor isotopes of sulphur are small, δ is expressed in parts per thousand or 'per mil' (‰). Essentially, the δ-notation is the per mil deviation in R of the unknown sample from the standard.

Historically troilite (FeS) from all iron meteorites was thought to be isotopically homogeneous and to have a ^{34}S/^{32}S ratio (= 0.04500451) approximately equal to the average of terrestrial samples (Trofimov, 1949; Macnamara and Thode, 1950). However, subsequent isotopic measurements performed on troilite from many different iron meteorite samples has revealed the existence of small variations in δ^{34}S in the order of ± 0.1‰, and so, standard specification was restricted to troilite from the Canyon Diablo iron meteorite abbreviated to CDT (Ault and Jensen, 1962). Unfortunately this standard has not been adopted by scientists working in Eastern Europe where troilite from the Sikhote-Alin meteorite is the accepted standard. Troilite represents an inferior choice for a sulphur isotopic standard because it is chemically impure (containing minor amounts of nickel, cobalt and some carbides) making it difficult to recover 100% of the sulphur using chemical preparations (Nielsen, 1983).

1.2.2 Mass spectrometry

The optical spectrographs developed by Aston, Thompson and others were superceded by higher precision gas source mass spectrometers constructed by Nier and coworkers (e.g. Nier and Gulbransen, 1939; Murphey and Nier, 1941). The origins of the modern mass spectrometers lie in the instrument originally described by Nier (1947) and later improved by McKinney et al. (1950). An instrument especially modified from Nier's design for making sulphur isotope measurements using sulphur dioxide gas has been described by Wanless and Thode (1953). Sulphur dioxide gas is usually obtained by combustion of sulphide samples in oxygen, however, such measurements are restricted to δ^{34}S determinations because isobaric interferences from oxygen isotopes prevent precise δ^{33}S and δ^{34}S measurements. The ratios of the minor isotopes (^{33}S and ^{36}S) are normally analysed using sulphur hexafluoride gas because fluorine is monoisotopic.

The instrument configuration (Figure 1.1) allows highly precise isotope ratio measurements to be obtained by rapid and repeated reference/sample comparisons. The sample and reference gases are continuously (dynamically) leaked through capillaries to a changeover valve (Murphey, 1947) which allows selection of either gas for isotopic analysis. As one gas is directed to the ionization source of the mass spectrometer, the other is bled to waste at the same rate to ensure that any isotopic fractionation occurring during the analysis affects both sample and reference gases to the same extent. The ion beams of interest (for sulphur dioxide m/z 64, 65 and 66) are focussed onto two Faraday buckets and the electronic signals from these are amplified to obtain raw isotope ratio measurements.

1.3 The cosmochemistry of sulphur

1.3.1 Nucleosynthesis

Sulphur is the ninth most abundant element in the solar system having an abundance of 5.0×10^5 (relative to silicon, Si=10^6), and iron is the only heavier element more abundant than sulphur (Cameron, 1982). Explosive nucleosynthesis is the most important stellar process for production of sulphur isotopes (^{32}S, ^{33}S, ^{34}S and ^{36}S) and only ^{32}S is synthesised in hydrostatically stable stars. During explosive carbon burning the main sulphur isotope to be formed is ^{33}S (Arnett, 1973; Wannier, 1980), but under certain conditions synthesis of ^{32}S, ^{34}S and ^{36}S can also occur (Audouze and Vauclair, 1980). Major production of ^{32}S and ^{34}S occurs during explosive oxygen burning as does ^{36}S, but the latter is confined to neutron-rich environments (Arnett, 1973; Cameron, 1982). Only ^{32}S is synthesised in hydrostatically stable stars. During oxygen burning, oxygen nuclei can undergo the following reaction:

$$^{16}\mathrm{O} + {}^{16}\mathrm{O} \rightarrow {}^{32}\mathrm{S} + \gamma$$

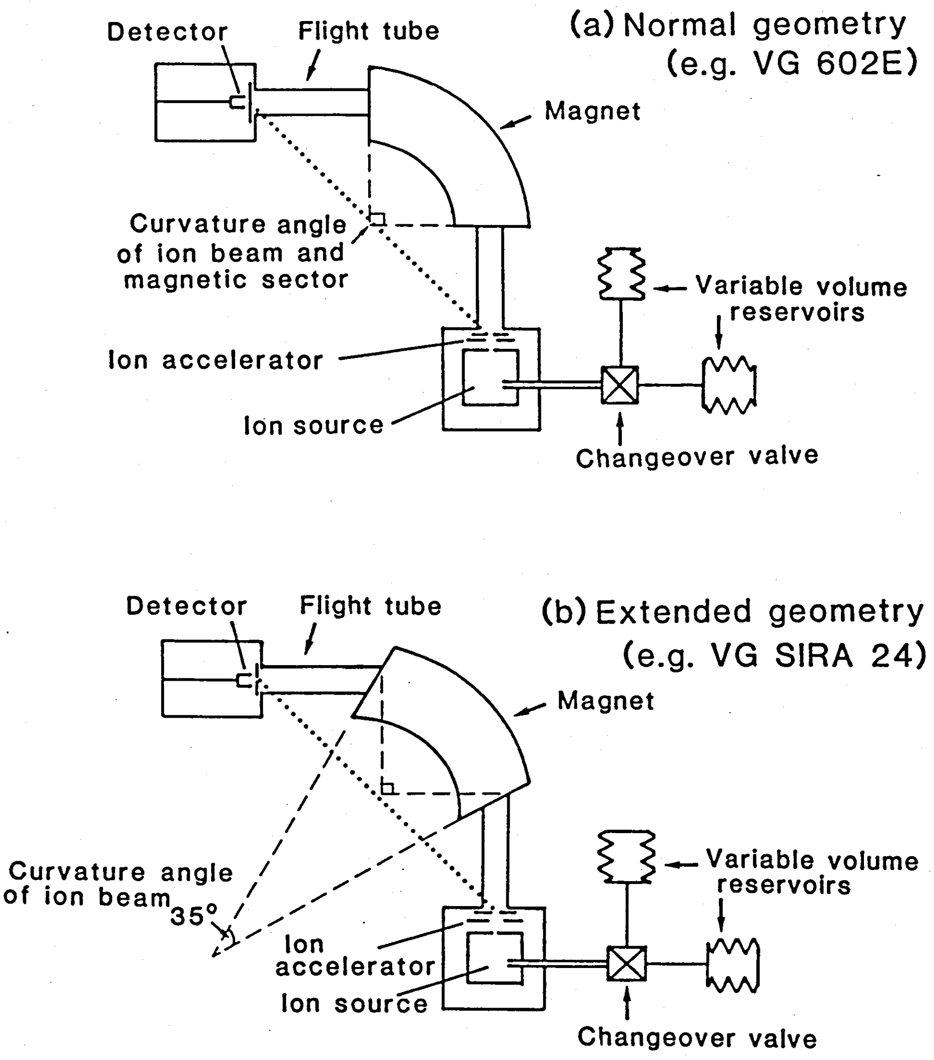


Figure 1.1 Schematic diagram of (a) normal geometry, and (b) extended geometry for ion optics in dynamic mass spectrometers. (VG = Vacuum Generators, Cheshire, England).

Source	$^{34}S/^{33}S$	$^{32}S/^{34}S$
Sgr B	5.3 ± 1.0	17.1 ± 1.0
M17		22.2 ± 1.0
Ori A	4.8 ± 5.0	21.6 ± 1.0
NGC 7538		26.0 ± 2.0
Solar system	5.5	23

Table 1.1 Some examples of sulphur isotope ratios in giant galactic clouds. (From Wannier, 1980).

The silicon quasi-equilibrium process occurring during silicon burning involves the following nuclear reaction:

$$^{28}\text{Si} + ^{4}\text{He} \rightarrow ^{32}\text{S} + \gamma$$

Helium nuclei are captured by silicon nuclei to form sulphur (Audouze and Vauclair, 1980)

1.3.2 Sulphur in the interstellar medium

The chemistry of sulphur in interstellar clouds is complex and has been considered in detail by Oppenheimer and Dalgarno (1974). Sulphur occurs in 17% of known interstellar molecules (e.g. SO_2, SiS, CS, OCS, H_2CS, CH_3CS: Mann and Williams, 1980).

Astronomical observations of sulphur isotope abundances cannot be related directly to a standard so they are conventionally expressed as $^{32}S/^{34}S$ and $^{34}S/^{33}S$ ratios. The observed interstellar ratios (Table 1.1), measured in giant galactic clouds by millimeter-wave and microwave spectroscopy, are consistent with the solar values (solar $^{32}S/^{34}S$ and $^{34}S/^{33}S$ ratios have values of 22.5 and 5.5 respectively) and show little spatial variation within the galaxy (Bertojo et al., 1974; Wannier, 1980). This is in conflict with current theories of nucleosynthesis which predict an increase in metallicity towards the galactic centre, this in turn should lead to an increase in the abundances of the neutron-rich isotopes ^{33}S, ^{34}S and ^{36}S (Wannier, 1980).

1.3.3 Sulphur condensation in the solar nebula

The major gaseous sulphur-bearing species in the solar nebula is hydrogen sulphide (Larimer, 1967). As sulphur is a siderophile element, equilibrium condensation occurs by reaction with metallic iron:

$$H_2S(g) + Fe(s) \rightarrow FeS(s) + H_2(g)$$

Compound	Condensation temperature (K)
MnS	1160
ZnS	730
FeS	680
CdS	570

Table 1.2 Equilibrium condensation temperatures of some sulphide minerals in a solar nebula with a total pressure of 6.6×10^{-3} atmospheres (from Larimer 1967).

Condensation begins at 685 K and is independent of nebula pressure (Wai and Wasson, 1977). Iron metal condenses at around 1375 K (Grossman and Larimer, 1974) and troilite forms by permeation of the metal with sulphur; calculations show that 50% of the sulphur has condensed by 648 K (Wai and Wasson, 1977). It is possible that the reaction between iron and H_2S will cease to occur when available metal surfaces have been coated with FeS (Larimer and Anders, 1967; Kerridge, 1976). If such a kinetic barrier is imposed then some sulphur may condense as either, other metal sulphides, or possibly as solid hydrogen sulphide at about 250 K (Wai and Wasson, 1977).

The equilibrium condensation temperatures of some sulphide minerals are given in Table 1.2. The condensation temperatures of cadmium, manganese and zinc sulphides are higher than those of the corresponding pure elements (Larimer, 1967). Thus, CdS, MnS and ZnS are expected to be nebula condensates forming at similar temperatures to troilite. Wai and Wasson (1977) have calculated the 50% condensation point of sphalerite, as a solid solution in FeS, to be 684 K at 10^{-4} atm.

$$\mathrm{Zn(g)} + \mathrm{FeS(s)} \rightarrow \mathrm{ZnS(sph.)} + \mathrm{Fe(s)}$$

Unlike troilite, the condensation of sphalerite is pressure-dependent, so at higher nebular pressures sphalerite will condense at a temperature higher than that of troilite (e.g. at 10^{-3} atm the condensation point of sphalerite is 710 K: Wai and Wasson, 1977). ZnS is an accessory mineral in enstatite chondrites and achondrites and is commonly found in troilite nodules of iron meteorites.

Larimer (1967) predicted a condensation temperature of 1160 K for MnS in a solar gas at total pressure of 6.6×10^{-3} atm. MnS (as alabandite), MgS (as niningerite) and CaS (as oldhamite) are found almost exclusively in enstatite chondrites and aubrites. It is generally agreed that the occurrence of these three sulphides is related to the highly reducing conditions and high pressures that prevailed in the region of the solar nebula where these meteorites formed (e.g. Keil, 1968; Larimer, 1968; Herndon and Suess, 1976; Larimer and Bartholomay, 1979; Sears, 1980). Sulphides of Ca and Mg are unlikely to form under normally accepted nebular conditions due to the prior condensation (>1300 K) of most of the Ca as perovskite ($CaTiO_3$), gehlinite ($Ca_2Al_2SiO_7$) and diopside ($CaMgSi_2O_6$), and most of the Mg as forsterite ($MgSiO_4$). Oldhamite is thought to condense at high temperatures in the solar nebula under reducing conditions (>2000 K: Herndon and Suess, 1976). Since oldhamite becomes unstable at lower temperatures, its survival depends upon removal from contact with the cooling nebula gas at near-formation temperatures, by enclosure within other early condensates (Larimer and Bartholomay, 1976; Sears, 1980).

CdS is not known from meteorites, although Larimer (1967) has calculated that it is a stable condensate at 570 K from a solar gas with a total pressure of 6.6×10^{-3} atm. The absence of CdS in meteorites is probably due to the relatively low condensation temperature of this mineral, because most of the sulphur (as H_2S) will have previously reacted with Fe, Ca, Mn and Zn.

1.3.4 Sulphur in solar system bodies

Apart from the high level of sulphur in the sun, sulphur compounds are common and often play key-roles in planetary processes on other solar system bodies (Table 1.3).

Venus

Lewis (1972) has predicted that sulphur is virtually absent from Mercury and Venus because material forming these planets accreted at temperatures above the condensation point of troilite. However, the cloud layer which shrouds Venus is known to be laden with sulphuric acid aerosol droplets (Hoffman et al., 1979). Sulphuric acid forms by photochemical oxidation and hydration of sulphur dioxide in the upper cloud regions (Winick and Stewart, 1980). The high surface temperatures of Venus preclude the existence of sulphur compounds as lithospheric components (Lewis, 1969, 1973). However, if Venus received a small amount of troilite during accretion from the solar nebula, or if there was addition of an extra-Venusian component, enough sulphur may have been provided to saturate the atmosphere (Prinn, 1973). Models of atmospheric sulphur chemistry (involving SO_2, COS and H_2SO_4) on Venus existed (Prinn, 1973, 1975) prior to positive detection of sulphur compounds by either the Pioneer Venus mission (Hoffman et al., 1979), or earth-based spectroscopy (Barker, 1979).

Object	Component	Reference
Sun	S/Si $\approx$ 0.5.	Cameron, (1982)
Venus	Atmosphere (H_2SO_4, SO_2, COS).	Hoffman et al. (1979)
Earth	Core, mantle, crust, biosphere, ocean, atmosphere.	Wuensch et al. (1978)
Mars	Core (FeS), regolith (SO_4^{2-}, S^{2-}).	Andersen and Jorden, (1971) Clarke et al. (1976)
Io	Surface (S^0, SO_2).	Warmstecker et al. (1974) Hapke (1979)
Comets	SO_2, H_2S	Frank and Sill, (1982)
Asteroids (meteorites)	S^0, SO_4^{2-}, S^{2-}	Kaplan and Hulston (1966)
Interplanetary dust particles	S^{2-}	Brownlee and Wheelock (1985)

Table 1.3 Sulphur in the solar system

Earth

Sulphur has a widespread and diverse occurrence on earth. Sulphur exists in a number of different oxidation states, the most important of which are S^{2-} (in sulphide, sulphosalts and hydrogen sulphide gas), S^0 (in elemental sulphur), S^{4+} (in sulphur dioxide gas) and S^{6+} (in sulphates and sulphur trioxide gas). Schneider (1978) has listed a total of 310 naturally occurring sulphur-bearing minerals, of these, there are 106 sulphide and 174 sulphate minerals.

The isotopic composition of sulphides in mafic and ultramafic igneous rocks provides the best estimate of the primitive isotopic value of the earth as these rocks are related to a mantle origin. The isotopic composition of primary sulphides gives a global mean $\delta^{34}S$ value of between 0 and +1‰ (Shima et al., 1963; Smitheringdale and Jensen, 1963; Schneider, 1970; Kanehira et al., 1973; Grinenko et al., 1975; Puchelt and Hubberton, 1980; Sakai et al., 1985;), this value is very close to the average for meteorites.

Sulphide minerals which are exposed to the earth's atmosphere or aerated water are soon altered to sulphate by oxidation. The resulting sulphates are relatively soluble and are spatially separated from sulphide, via the transporting medium of water, to the oceans. Present day ocean sulphate has a remarkably uniform isotopic composition with a $\delta^{34}S$ value of +20.99‰ (Rees et al., 1978).

The reduction of sulphate to sulphide is the important step in the "biological sulphur cycle" which is responsible for most of the global sulphur isotope variations. Sulphur is a key element for many biochemical processes, it is present in the sulphur containing amino acids (cysteine and methionine), and is required for production of some co-enzymes (Postgate, 1968). The isotopic selectivity of biological sulphate reduction has been studied extensively (Harrison and Thode, 1958; Kaplan and Rittenburg, 1964; Nakai and Jensen, 1964; Kemp and Thode, 1968; Smejkal et al., 1971) and can give rise to hydrogen sulphide depleted in ^{34}S by between 0 and 60‰ with respect to the sulphate reservoir.

Moon

Although depleted in the moon relative to its cosmic abundance, sulphur is present in all lunar rocks, mainly as troilite. Mare basalts are substantially richer in sulphur than are highland rocks, values of up to 3000 ppm being found in the former and down to 20 ppm in the latter. Soils do not appear to be depleted nor enriched significantly in sulphur with respect to their associated rocks (Moore et al., 1972; Gibson and Moore, 1974; Kerridge et al., 1975). An apparent depletion in soils at Apollo 11 was reported by Kaplan et al. (1970), but this may have been due to incomplete sampling (Kerridge et al., 1975).

Abundance patterns of sulphur in lunar soils have been interpreted in terms of simple mixing models involving contributions from various identifiable major rock-types (e.g. Moore et al., 1972; Gibson and Moore, 1974). An extralunar component of sulphur has been suggested by Kerridge et al. (1975) to explain the isotopic fractionation observed between rocks and soils (Section 1.5)

Mars

Mars is thought to contain a core of FeS (Andersen and Jordon, 1971) and results from the Viking 2 lander showed that the martian regolith contains high levels of sulphur of up to 3.5 wt%. The sulphur minerals (Clarke et al., 1976) include sulphates (possibly kieserite, $MgSO_4.H_2O$: Baird et al., 1976) and sulphides. The SNC meteorites (shergottites, nakhlites and chassignite) are reputed to have a martian origin (Weinke, 1978; Wood and Ashwal, 1981; McSween, 1984), but contain only up to 0.25 wt% sulphur (Gibson et al., 1985) which is notably lower than the measurements made by spacecraft on the martian surface. A detailed examination of Shergottite EETA 79001 has led to the discovery of sulphur-rich aluminosilicate mineraloids which may be martian weathering products (Gooding and Muenow, 1986).

Io

In the outer regions of the solar system Io (a Jovian satellite) is an important site for sulphur. The surface of Io is rich in elemental sulphur and frozen sulphur dioxide (Warmstecker et al., 1974; Hapke, 1979). The results of the Voyager 1 mission showed that intense volcanism is occurring on Io, and sulphur is believed to play a prominent role in this activity (e.g. Smith et al., 1979; Carr et al., 1979). It has been suggested that the surface of Io is covered in a molten layer of sulphur, some kilometers thick resting on a silicate subcrust, which is visible only as occasional mountains (Smith et al., 1979). Surface temperatures of Io are between 400 and 600 K (Carr, 1985) which are above the melting point of sulphur (400 K), but too low for molten silicates to be present (which melt at 1300 K). Lewis (1982) has considered the evolution of sulphur-rich liquids on Io and proposes a starting material with a similar composition to either, metal-free CV3, or CM2 carbonaceous chondrite material. Lewis considers that sulphates are important constituents of the mantle in that they prevent total extraction of sulphur to the core which would otherwise occur during recycling of denser sulphide species.

Comets

Sulphur-containing molecules (e.g. sulphur dioxide and hydrogen sulphide) have been observed from the spectra of comets (Frank and Sill, 1982). Sulphur is considered to be present at near-cosmic abundances in these bodies (Delsemme, 1982).

1.4 The abundance and distribution of sulphur in meteorites

Sulphur occurs in virtually all meteorites and is often the fifth most abundant element after silicon, oxygen, magnesium and iron. The reported range for sulphur in different meteorite groups is shown in Figure 1.2. Carbonaceous and enstatite chondrites are the two most sulphur-rich groups of meteorites. Carbonaceous chondrites contain between 1.31 and 6.70 wt% sulphur (Mason, 1963) and the enstatite chondrites between 2.62 and 6.12 wt% sulphur (Mason, 1966). Ordinary chondrites have average total sulphur contents of about 2 wt% (Cripe and Moore, 1975). H- and L-group chondrites normally contain between 1 and 3 wt% sulphur but the range is slightly larger for LL chondrites (between 1 and 5 wt%: Cripe and Moore, 1975). Sulphur contents of achondritic meteorites are normally below 1 wt%. The aubrites contain the greatest concentrations of any achondrite

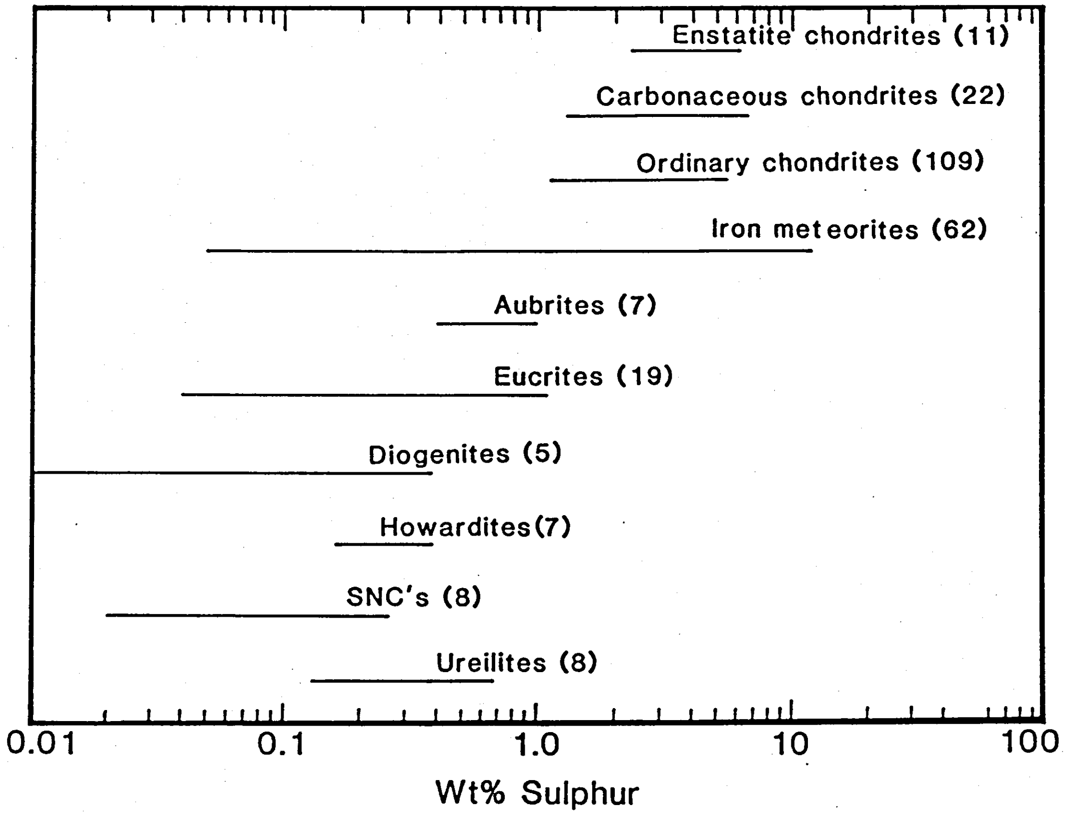


Figure 1.2 The sulphur contents of meteorites. The number of meteorites analysed for each class is given in parentheses. Data is taken from: Buchwald (1975), Cripe and Moore (1975), Gibson et al. (1985) and Mason (1963, 1966).

group, with a range from 0.25 to 0.86 wt% (Gibson et al. 1985). Sulphur in iron meteorites is localized in heterogeneously distributed troilite-rich nodules thus making it somewhat difficult to determine the total sulphur abundances of these materials (Buchwald, 1975). For a true bulk value it is necessary either to dissolve several hundred grams of iron meteorite, or to use planimetry (Buchwald, 1975). Concentrations of sulphur in iron meteorites are normally below 1 wt%, however, Buchwald (1975) reports a value of 12 wt% sulphur for the Soroti meteorite.

Over twenty different sulphur-bearing mineral species have so far been identified in meteorites (Table 1.4). Sulphur has been found in both reduced (sulphides) and oxidised (sulphates) compounds and in elemental form. In addition, some of the sulphur in carbonaceous chondrites is present in organic compounds (Studier et al., 1965; Murphy and Nagy, 1966; Hayes, 1967; Hayes and Biemann, 1968). Many elements in chondrites have a dominant affinity to sulphur: Fe (as troilite), Cu (as chalcopyrite, vallerite and cubanite), Zn (as sphalerite), nickel (as pyrrhotite and pentlandite) are among the most common. Some elements that are normally lithophile can occur as sulphides in meteorites: Ca (as oldhamite), Mn (as niningerite), K and Na (as djerfisherite) and Mg (as alabandite) are present in enstatite chondrites and aubrites. Sulphates (mainly epsomite and gypsum) have been discovered in C1 and C2 carbonaceous chondrites (e.g. DuFresne and Anders, 1962; Bostrom and Fredriksson, 1966; Fuchs et al., 1973; Bunch and Chang, 1980). It has been suggested that the presence of sulphates along with elemental sulphur in carbonaceous chondrites is evidence for oxidation of troilite which occurred by aqueous alteration on the meteorite parent body (Bostrom and Fredriksson, 1966).

By far the most common sulphur-bearing mineral found in meteorites is troilite (FeS), named after Father Demenico Troili who first described iron sulphide nodules in the Albareto meteorite in 1766 (Haidinger, 1863). Ramdohr (1973) has examined the opaque mineralogy of 135 stony meteorites and identified troilite as a constituent of all of them. The concentration of troilite can be high in meteorites, Keil (1968) has reported 12 wt% troilite in the enstatite chondrite Blithfield. Troilite is also the dominant sulphide found in lunar material (Evans, 1970; Mason et al., 1970; Skinner et al., 1970). Troilite is largely absent from terrestrial rocks, but it has been found associated with large serpentine and magnetite masses (Eakle, 1922). On earth, pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$) are common igneous sulphides, and pyrite is the stable iron sulphide mineral in sedimentary rocks.

The composition and structure of meteoritic troilite is surprisingly variable. Troilite is often non-stoichiometric FeS, containing up to 1% of impurities, predominantly of chromium, nickel, copper and zinc (Nichiporuk and Chodos, 1959). In many iron meteorites and enstatite chondrites, where the

Mineral	Formula
Elemental sulphur	S
Troilite	FeS
Oldhamite	CaS
Alabandite	MnS
Sphalerite	ZnS
Pyrrhotite	$Fe_{1-x}S$
Akinaivite	$Fe_{1+x}S$
Pyrite	FeS_2
Molybdenite	MoS_2
Brezinaite	Cr_3S_4
Schreiberoite	Cr_2S_3
Ferroan alabandite	$(Fe,Mn)S$
Pentlandite	$(Fe,Ni)_9S_8$
Chalcopyrrhotite	$(Cu,Fe)S$
Niningerite	$(Fe,Mg,Mn)S$
Daubréelite	$FeCr_2S_4$
Chalcopyrite	$CuFeS_2$
Cubanite	$CuFe_2S_3$
Vallerite	$CuFeS_2$
Djerfisherite	$K_3(Na,Cu)(Fe,Ni)_{12}S_{14}$
Heideite	$(Fe,Cr)_{1-x}(Ti,Fe)_2S_4$
Schöllhornite	$Na_{0.3}(H_2O)[CrS_2]$
Caswellsilverite	$NaCrS_2$
Anhydrite	$CaSO_4$
Bassanite	$CaSO_4.\frac{1}{2}H_2O$
Gypsum	$CaSO_4.2H_2O$
Leonhardtite	$MgSO_4.4H_2O$
Epsomite	$MgSO_4.7H_2O$
Bloedite	$MgSO_4.Na_2SO_4.4H_2O$
Boussingaultite	$(NH_4)_2SO_4.MgSO_4.6H_2O$

Table 1.4 The sulphur minerals of meteorites.

concentration of chromium is high, troilite contains exsolution lamellae of daubréelite ($FeCr_2S_4$) (El Gorsey, 1967; Keil, 1968; Ramdohr, 1973).

Many minor accessory sulphides have been identified in meteorites, e.g. Heideite $(Fe,Cr)_{1+x}(Ti,Fe)_2S_4$, in the Bustee aubrite (Keil and Brett, 1974), caswellsilverite $NaCrS_2$ in the Norton County aubrite (Okada and Keil, 1982), and djerfisherite, $K_3(Na,Cu)(Fe,Ni)_{12}S_{14}$ in Penca Blanca Springs an aubrite, and the enstatite chondrites: St. Marks, Kota-Kota (Fuchs, 1966), Qingzhen (El Gorsey et al., 1983), Indarch and Yamato 691 (El Gorsey et al., 1985). However, some of these minerals appear to have formed by terrestrial weathering of pre-existing meteoritic sulphides, e.g. in Norton County, bassanite ($CaSO4.\frac{1}{2}H_2O$) is a weathering product of oldhamite (Okada et al., 1981), schöllhornite $Na_{0.3},(H_2O)_1[CrS_2]$ from caswellsilverite (Okada et al., 1985) and leonhardtite ($MgSO_4.4H_2O$) has been found on the exposed surfaces of chondrites in Antarctica (Marvin and Motylewski, 1980).

1.5 The sulphur isotopic composition of extraterrestrial materials

The first sulphur isotopic study of meteorites was conducted by Trofimov (1949) on troilite samples from four iron meteorites. Data was presented as $^{34}S/^{32}S$ ratios with ± 10‰ errors. Improved instrument precision enabled Macnamara and Thode (1950) to measure very small variations in the $^{34}S/^{32}S$ ratios of troilite sulphur in iron meteorites. With a precision of ± 0.5‰ the total range in $\delta^{34}S$ values measured in five meteorites was between 0.0 and −1.8‰. Macnamara and Thode noted that the meteoritic $^{34}S/^{32}S$ ratio was constant and approximately equivalent to the average $^{34}S/^{32}S$ ratio of terrestrial sulphur. This led them to suggest that the $^{34}S/^{32}S$ ratio of meteoritic sulphur is the primordial terrestrial value and that variations measured in terrestrial samples represent isotopic fractionations accompanying geological processes occurring within the Earth's crust.

Vinogradov (1957) reported constant $\delta^{34}S$ values for eleven meteorites from the Soviet Union. Ault and Kulp (1959) used troilite from the Canyon Diablo iron meteorite as their primary standard against which all samples were referenced. On the basis of the isotopic consistency of meteoritic sulphur, Thode et al. (1961), suggested that it could be used as a standard of comparison for all sulphur isotopic measurements and set about a careful investigation of constancy of the $^{34}S/^{32}S$ ratio in seventeen stone and iron meteorites. Sulphur in one specimen, the Bella Roca iron meteorite, was subjected to nine separate isotopic analyses to assess whether there are any internal sulphur isotopic variations within a meteorite. With a measurement precision of ± 0.1‰, Thode et al., found that there was a maximum spread

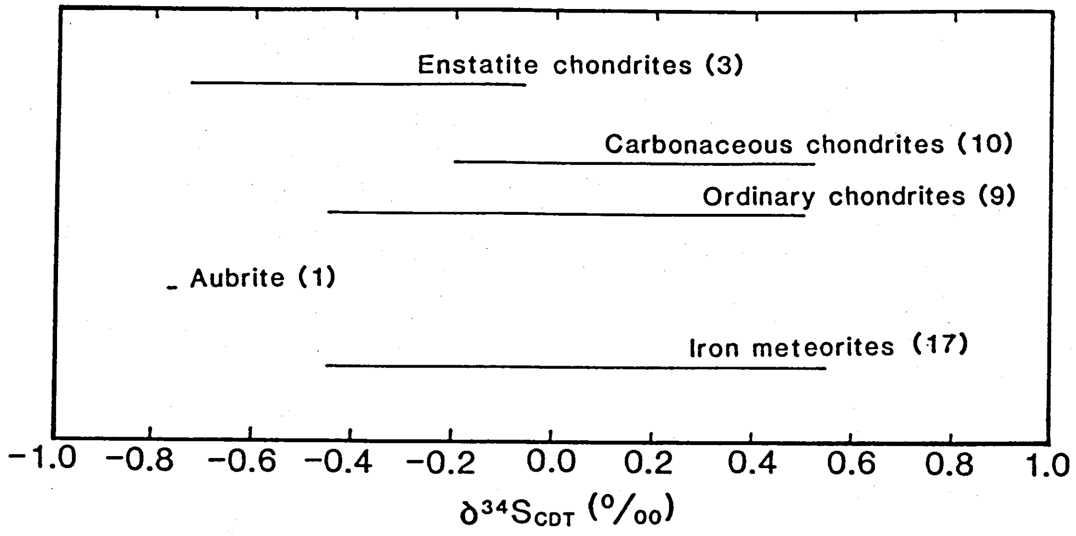


Figure 1.3 Whole-rock $\delta^{34}S$ values for meteorites. The number of meteorites analysed for each class is given in parentheses. Data is taken from Kaplan and Hulston (1966), Thode et al. (1961) and Ueda et al. (1986).

of only ± 0.2‰ from the mean value. These results led to the adoption of troilite from the Canyon Diablo iron meteorite as the primary sulphur standard (Ault and Jensen, 1962).

The first sulphur isotope study which attempted to perform measurements on different sulphur components of meteorites was undertaken by Monster et al. (1965), on the Orgueil carbonaceous chondrite. The results indicated that both elemental and troilite sulphur were enriched in ^{34}S while sulphate was depleted, however, the integrated $\delta^{34}S$ value for bulk Orgueil was close to 0‰. It was suggested by Monster et al., that the sulphur isotopic fractionations, between different sulphur species in Orgueil, were the result of parent body alteration processes.

Kaplan and Hulston (1966) carried-out a detailed investigation of the isotopic composition of sulphur compounds in twenty-two meteorites. Sulphur from different components was extracted by chemical methods. Most sulphur compounds exhibited small variations in $\delta^{34}S$ of between 1 and 2‰ but the averaged data for each meteorite gave whole-rock $\delta^{34}S$ values of between +0.60‰ and −0.76‰ (Figure 1.3). The most significant deviation from the meteoritic average was measured in sulphur from the water-soluble fraction of Norton County (thought to be oldhamite sulphur) with a $\delta^{34}S$ value of −5.6‰. The small variations in $\delta^{34}S$ between different compounds were interpreted as mass-dependent isotopic fractionations which occurred during their formation on the meteorite parent bodies. Moreover, the overall constancy in $\delta^{34}S$ was used as evidence for the isotopic homogeneity of sulphur in the solar nebula.

The very restricted range in $\delta^{34}S$ reported for meteorites (Figure 1.3) prompted Hulston and Thode (1965a) to consider the remaining two isotopes of sulphur (^{33}S and ^{36}S) that could be measured. Initial results using sulphur dioxide for mass spectrometric analyses were discouraging because interferences from oxygen isotopes in the mass spectrum led to unacceptable precision of $\delta^{33}S$ and $\delta^{36}S$. This problem was surmounted by using sulphur hexafluoride as the analysis gas (fluorine being monoisotopic thus avoiding any isobaric interferences). The analysis of a number of different carbonaceous, enstatite and iron meteorites yielded $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ values which could be accounted for by chemical and physical fractionation effects alone. Again the most extreme sulphur isotopic compositions were measured in the water-soluble fraction of Norton County ($\delta^{34}S = -5.5‰$, $\delta^{33}S = -2.9‰$, $\delta^{36}S = -4.5‰$) and the weighted means of the components in all meteorites gave $\delta^{34}S$ values close to 0‰.

In a separate study, Hulston and Thode (1965b) searched for spallation sulphur in iron meteorites. Troilite nodules were avoided because detection of spallation sulphur in these areas would not be possible due to the large amount of natural sulphur present. Instead, Hulston and Thode, measured the sulphur in the iron-phase of meteorites and found evidence for spallation ^{36}S in three samples (Clark County, Pinon and Tlactopec) with the possibility of some spallation ^{33}S.

Despite a recommendation by Hulston and Thode (1965b) that techniques should be improved to allow more precise estimation of cosmic-ray-produced ^{33}S and ^{36}S in meteorites, no sulphur isotopic measurements of meteorites were reported between 1965 and 1977. This neglect was probably due to: (a) the narrow range in $\delta^{34}S$ values which had so far been reported for meteoritic sulphur compared to that of terrestrial samples, and (b) the return of the first lunar samples in 1969 diverting attention away from meteorites.

Many investigations of stable sulphur isotopes commenced following provision of lunar material from the Apollo missions which began in 1969. The observations of lunar sulphur isotope systematics may be summarized as follows. The lunar basaltic rocks have slightly positive $\delta^{34}S$ values relative to the meteoritic value ($\delta^{34}S = 0‰$). The heavy isotopes of sulphur, like those of oxygen, silicon and potassium are enriched in lunar soils relative to lunar rocks and the degree of enrichment increases with increasing sample maturity (Kaplan et al., 1970; Petrowski et al., 1974; Rees and Thode, 1975). Various mechanisms have been proposed to explain this heavy isotope enrichment of sulphur which accompanies maturation of the lunar material.

Kaplan and Smith (1970) and Berger (1970) speculated that enrichment in ^{34}S in the soils was due to exposure to the solar wind protons. The ^{32}S removal process is thought to involve conversion to H^{32}S which is subsequently lost from the moon. The greater depletion of ^{32}S in the lunar soils may be due to their larger surface area available for interaction with the solar wind. An alternative ^{34}S enrichment process was proposed by Clayton et al. (1974) who considered that Rayleigh fractionation occurred when material was either vapourised during meteorite impact or sputtered from vapour deposited layers. Isotope effects associated with the former process, the thermal decomposition of troilite due to localized heating from meteorite and micrometeorites impact, has been discussed by McEwing et al. (1980), while the latter, sputtering of the grain surfaces by the solar wind, was considered by Haff et al. (1977). Despite the uncertainty surrounding the nature of the ^{34}S enrichment process, the lunar soils contain the highest δ^{34}S values of all extraterrestrial matter so far measured in the laboratory, with the 0.5μm size fraction of lunar soil 1571 having a δ^{34}S value of +20.2‰ (Thode and Rees, 1976).

Interest in meteorites resumed when Rees and Thode (1977) discovered a 1‰ excess of ^{33}S in the last fraction of sulphur extracted from a bulk Allende sample by progressively stronger HCl leaches. However, using an alternative leaching technique, Thode and Rees (1979), were unable to confirm the previous determination of a ^{33}S excess. More recently, Ueda et al. (1986) have chemically extracted sulphide (troilite) and sulphate sulphur from three type 6 ordinary chondrites (Peace River, Bruderheim and Vulcan). The sulphate in each of these meteorites was found to be enriched in ^{34}S ($\delta^{34}S = +1.9$ to $+3.0$‰) relative to the sulphide ($\delta^{34}S = -1.0$ to -0.2‰), however, Ueda et al. made no comment upon the origin or chemical nature of the sulphate.

1.6 Research objectives

Sulphur is present in terrestrial and extraterrestrial materials in a multitude of forms, both in elemental state and in compounds. Although the concentration of sulphur is routinely measured in chemical assays of meteorites, isotopic measurements are not normally part of this procedure. Indeed, only a few papers concerned with sulphur isotope studies of meteorites have appeared since the middle sixties, after it was shown that the range in δ^{34}S of these materials is very restricted. Even so, our knowledge of sulphur isotope systematics in extraterrestrial materials is still far from complete. An important objective of this research is to re-investigate the abundance speciation and isotopic composition of sulphur in specific types of meteorites. Progress towards this objective requires the application of an analytical method capable of extracting sulphur from different compounds without having to separate them from the host meteorite prior to analysis. It was decided to evaluate the use of a new method that would avoid conventional chemical processing, which is usually undertaken, to extract sulphur and, in so doing, keep sample requirements to a minimal level. The feasibility of using a stepped combustion technique for isotopic measurements of carbon, hydrogen and nitrogen has already been demonstrated (e.g. DesMarais, 1978; Swart et al., 1983; Lewis et al., 1983; Yang and Epstein, 1983), but its application for sulphur has not been previously considered. Thus, an initial undertaking was the development of a stepped combustion technique capable of producing sulphur dioxide gas for sulphur abundance and isotopic measurements. Chapter 2 details this development and demonstrates the success of this method to selectively liberate sulphur dioxide from mixtures of sulphur compounds whose constituent members burn or decompose over discrete temperature intervals.

Before the stepped combustion method could be applied to meteorite samples, the performance of a dynamic mass spectrometer for making sulphur isotope measurements was assessed. During the latter part of this study, the mass spectrometer was adapted so that sulphur isotope analyses using either sulphur dioxide, or sulphur hexafluoride could be performed. In Chapter 2, the ability of the mass spectrometer to routinely measure sulphur isotope ratios using sulphur dioxide (using the conventional and modified instruments) and sulphur hexafluoride (using the modified instrument only) is evaluated using reference gases of known isotopic composition.

The success of stepped combustion to resolve different sulphur components from an artificially produced reference mixture encouraged further studies involving meteorites. Three investigations were undertaken.

C1 and C2 carbonaceous chondrites

There is evidence that C1 and C2 carbonaceous chondrites have undergone parent body aqueous alteration (e.g. DuFresne and Anders, 1962; Bostrom and Fredriksson, 1966; Bunch and Chang, 1980). Sulphur in C1 and C2 carbonaceous chondrites is known to occur in both oxidised (sulphate) and reduced (sulphide) forms, however, the reactions which led to the formation of these compounds, although probably related to the aqueous alteration event, are not fully understood (Monster et al., 1965; Lewis, 1967; Lewis and Krouse, 1969).

Previous sulphur isotope research on meteorites has concentrated on C1 and C2 carbonaceous chondrites. Sulphur isotopic studies were undertaken by Monster et al. (1965), Hulston and Thode (1965a) and Kaplan and Hulston (1966), but were: (a) carried-out on a limited number of meteorites, and (b) made on sulphur extracted from meteorites using chemical reagents whose effects were only poorly understood. Chapter 3 details efforts to measure the concentration and isotopic composition of the various components of C1 and C2 carbonaceous chondrites using stepped combustion. The samples studied include some samples for which sulphur data already exists but include many samples for which sulphur isotope measurements are not available. Also in Chapter 3, the effects of conventional chemical processing of meteorites, to extract sulphur components, are assessed by using the results of stepped combustions of residues and extracts prepared from the Murchison meteorite.

C3-C6 carbonaceous chondrites

Petrographic, mineralogic and chemical studies have revealed that hydrous activity has affected type 3 ordinary and carbonaceous chondrites (Bunch and Chang, 1980; Hutchison et al., 1985; Alexander et al., 1986; Grossman et al., 1986; Tomeoka and Buseck, 1986) . It is usually considered that sulphur in meteorites of higher petrologic types occurs exclusively as sulphide (mainly as troilite). However, if hydrous alteration has been active at some stage in the evolution of these meteorites, this may have led to the formation of a small quantity of oxidised sulphur. Previously, the chemical techniques applied to meteorites, have probably been too complicated and insufficiently sensitive to detect small amounts of oxidised sulphur (Kaplan and Hulston, 1966). Chapter 4 describes use of the stepped combustion method to investigate types C3 to C6 carbonaceous chondrites in an effort to resolve their different sulphur components. This was done in the hope that the distribution of sulphur (as sulphate or sulphide) can be used to confirm that early solar system aqueous alteration affected some of these meteorites, such information would have implications for existing models of carbonaceous chondrite evolution. For comparative purposes, the analyses were extended to include a preliminary investigation of a type 3 ordinary chondrite.

Enstatite chondrites and aubrites

The relationship between enstatite chondrites and the chemically and mineralogically similar aubrites has been the subject of much discussion. Many features (e.g. chemical, textural and isotopic) indicate that these two groups could be cogenetic and derive from the same parent body (e.g. Watters and Prinz, 1979; Biswas et al., 1980; Wolf et al., 1983). However, there is an interruption in the chemical trends between chondrites and aubrites making evidence for a common origin for these two groups inconclusive (e.g.

Wasson and Wai, 1970; Brett and Keil, 1987). Enstatite chondrites and aubrites contain the same sulphide minerals, but the sulphur content of aubrites is significantly lower (Mason, 1966). Stepped combustion analyses of enstatite chondrites and aubrites may provide clues to their relationship and whether the differences in sulphur were influenced by processes active in the nebula or by metamorphism and partial melting on the parent body or bodies. Stepped combustion results for enstatite chondrites and aubrites are discussed in Chapter 5.

Chapter 2

Experimental Methods

The abundance and isotopic composition of sulphur in meteorites has been investigated conventionally either by combustion of the bulk sample to produce sulphur dioxide gas, or by selectively liberating the sulphur from the minerals of interest using chemical reagents and then converting this sulphur to a stable compound (usually barium sulphate or silver sulphide) which can be combusted to form sulphur dioxide (Hulston and Thode, 1965a; Monster et al., 1965; Kaplan and Hulston, 1966; Ueda et al., 1986). As meteorites are among the rarest materials available for study on Earth, it is imperative that destructive analytical techniques should consume minimum quantities of sample and yet maximise the amount of obtainable data at an acceptable level of accuracy and precision. It is also important to ensure that the sample analysed is representative of the bulk meteorite. Sample requirements are dictated by the minimum amount of sulphur measurable in the mass spectrometer, blank levels and chemical extraction procedures. Previous work utilizing rather complicated chemical pathways, necessary to free sulphur from different minerals in meteorites, has meant that in some cases up to several grams of meteorite are required for a good analysis (e.g. Kaplan and Hulston, 1966).

The issue of sample availability was a key factor in determining the current approach to analysing sulphur isotope ratios in meteorites. The coupling of a gas extraction line, to be used for stepped combustion experiments, to a mass spectrometer with maximised sensitivity was undertaken so that sulphur isotope measurements could be obtained from milligram quantities of meteorites. The mass spectrometer used in the latter part of this study was not a commercially available instrument, so it was necessary to fully assess the capablities of this instrument for sulphur isotope ratio measurements. The mass spectrometer was connected to a computer for control of data-acquisition, -handling, and -storage. An initial period was spent developing the software for these procedures.

When a compound containing sulphur is combusted in oxygen, sulphur dioxide is the main sulphur-containing product along with perhaps a little sulphur trioxide. The stepped combustion method (incremental heating of the sample in oxygen) allows relatively involatile species (e.g. sulphides, sulphates) to be converted to a gas. This technique discriminates between sulphur from different compounds on the basis of combustion or decomposition temperature. In the case of sulphides, the sulphur is oxidised to a gas, whereas sulphates decompose to yield sulphur dioxide. The combustion technique has already been applied successfully to studies involving the elements carbon, nitrogen and hydrogen (e.g. DesMarais, 1978; Swart et al., 1983; Lewis et al., 1983; Yang and Epstein, 1983). The main advantages of stepped combustion over chemical separation appear to be:

1. The smaller sample requirements.
2. The reduced risk of sample loss or contamination.
3. The ease of analysis.

Point (3) is particularly important since the use of stepped combustion does not entail time-consuming and intricate chemical and physical separation techniques, which often need to be applied to the sample in order to: (a) isolate the particular sulphur component of interest, and (b) convert this compound into a form suitable for conversion to sulphur dioxide.

2.1 Mass spectrometry

2.1.1 The mass spectrometer

Sulphur, after being converted to sulphur dioxide, is analysed in the mass spectrometer. During the first part of this project the instrument used was a VG Micromass 602E (Vacuum Generators, Cheshire, England). This is a 90° sector, 6.2cm radius double collecting mass spectrometer essentially of the type described by Nier (1940, 1947) and later modified by McKinney et al. (1950). The mass spectrometer operates in the dynamic mode where reference and sample gases are alternately admitted to the ion source via a dual inlet system. Both inlets are fitted with variable volume bellows assemblies to enable balancing or equalisation of reference and sample ion source pressures. Each inlet also has a metal cold finger which allows the sample gas to be cryogenically transferred into a small volume, and thus, measurement of sulphur samples as small as 10μg are possible (this lower limit has been reduced to 1μg sulphur using the modified instrument described below). Twin capillary leaks are connected to an electrically operated changeover valve of the design of Murphey (1947) and improved by McKinney et al. (1950). As

	602E	Modified Instrum.
Radius	6cm	9cm
No. of collectors	2	4
Magnet	Permanent	Electro-
Gases analysed	N_2, CO_2, SO_2	CO_2, SO2, SF_6
Min. sample size	10μg S	1μg S
Precision :		
10μg sulphur	± 0.3‰	± 0.2‰
1μg sulphur	———	± 0.3‰

Table 2.1 Comparison of the 602E with the modified mass spectrometer.

one gas (reference or sample) flows into the ion source the other is diverted to the pumps to ensure that both gas pressures decay at the same rate.

The 602E has a double collector system to allow two ion beams to be collected separately in two Faraday buckets. The ion beam signals are amplified and then digitised via a 16-bit analogue-to-digital (a-to-d) converter before being sent to the computer (BBC microcomputer, Acorn Computers Ltd., Cambridge) for handling and reduction of the raw data. The computer is interfaced via a digital-to-analogue (d-to-a) signal conversion unit (built by Mr A.W. Joines) to the programmable high voltage power supply and allows software-controlled adjustment of the accelerating voltage. The computer can also control the reference-sample-isolate switching facilities of the changeover valve.

During the latter part of this project the mass spectrometer was substantially modified to improve sensitivity and allow measurement of up to four individual ion beam intensities, rather than having two ion beams impinging on one collector. The general features of the original and modified instrument are compared in Table 2.1. For the original instrument, the gases that could be analysed included carbon dioxide and sulphur dioxide by collection of the following ion beams.

1. m/z 44+45 and 46 from CO_2^+.
2. m/z 48+49 and 50 from SO^+.
3. m/z 64+65 and 66 from SO_2^+.

The new instrument has a VG SIRA 24 9cm radius extended geometry flight tube, four collectors and an electromagnet. The main components of this system are shown in Figure 2.1. The positions of the collector slits are fixed

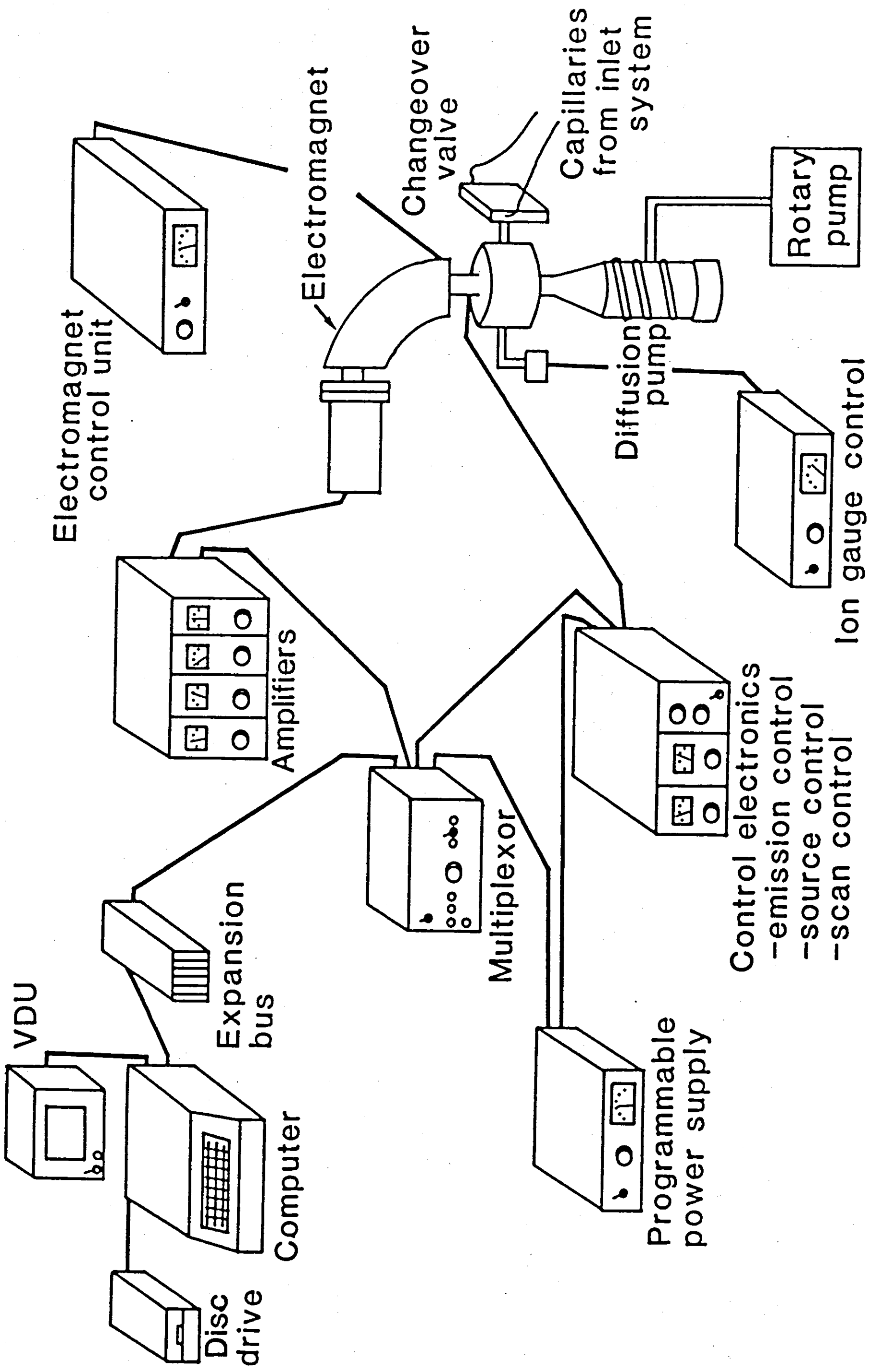


Figure 2.1 Components of the mass spectrometer-computer system.

Half-plate voltage	8V
Ion repellor voltage	+0.5V
Electron energy	65V
Trap current	200μA
Magnet current	2.5A
Accelerating voltage	
(m/z = 66)	2.23KV
(m/z = 50)	2.85KV

Table 2.2 Ion source operating parameters.

but spaced such that detection of ion beams from the following ionic species are all possible:

1. m/z 44, 45 and 46 from CO_2^+.
2. m/z 48 and 50 from SO^+.
3. m/z 64 and 66 from SO_2^+.
4. m/z 127, 128, 129 and 131 from SF_5^+.

An appraisal of the use of sulphur hexafluoride in this mass spectrometer is made in Section 2.6 and Appendix A. (Essentially, because fluorine is monoisotopic, analysis of sulphur hexafluoride allows direct measurement of $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$).

The ion source operating conditions for sulphur dioxide are shown in Table 2.2. During sulphur dioxide analysis it is necessary to alter the accelerating voltage between the measurement sequence for SO_2^+ (m/z 64 and 66) and SO^+ (m/z 48 and 50). The segment of the mass spectrum containing the parent ions (SO_2^+) is shown in Figure 2.2 and all the ionic species of sulphur dioxide produced in the mass spectrometer are given in Table 2.3.

The mass spectra of SO_2^+ and SO^+ are complicated by the presence of ions containing ^{17}O and ^{18}O atoms. The contribution of $^{32}S^{16}O^{18}O$ to mass 66 is much smaller than that from $^{34}S^{16}O^{16}O$ and a suitable correction can be applied. However, $\delta^{36}S$ measurements using sulphur dioxide are impractical because the contribution of $^{32}S^{18}O^{18}O$ to m/z 68 is of the same order as $^{36}S^{16}O^{16}O$. Similarly, the presence at m/z 65 of $^{32}S^{16}O^{17}O$ and $^{33}S^{16}O^{16}O$ means that $\delta^{33}S$ measurements are equally unobtainable. Even for $\delta^{34}S$ measurements the isotopic composition of the oxygen in the reference and sample gases are different and it is necessary to perform isobaric corrections on the raw data obtained from the sulphur dioxide analyses. This is achieved

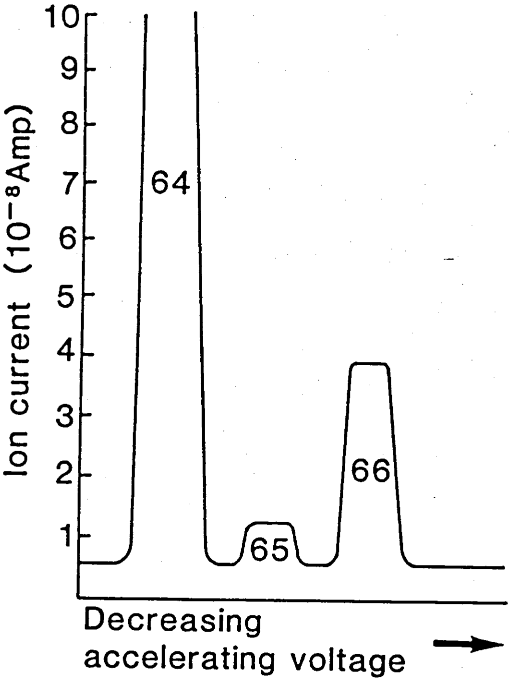


Figure 2.2 The mass spectrum of sulphur dioxide in the region from m/z 64 to 66. The m/z 64 peak is offscale.

64	65	66	67
$^{32}S^{16}O^{16}O$	$^{33}S^{16}O^{16}O$ $^{32}S^{16}O^{17}O$	$^{34}S^{16}O^{16}O$ $^{32}S^{17}O^{18}O$ $^{33}S^{16}O^{17}O$ $^{32}S^{17}O^{17}O$	$^{32}S^{16}O^{18}O$ $^{33}S^{17}O^{17}O$ $^{33}S^{16}O^{18}O$

68	69	70	71 & 72
$^{36}S^{16}O^{16}O$ $^{34}S^{16}O^{18}O$ $^{33}S^{17}O^{18}O$ $^{32}S^{18}O^{18}O$	$^{36}S^{17}O^{16}O$ $^{34}S^{17}O^{18}O$ $^{33}S^{18}O^{18}O$	$^{36}S^{17}O^{17}O$ $^{36}S^{16}O^{18}O$ $^{34}S^{18}O^{18}O$	$^{36}S^{17}O^{18}O$ $^{36}S^{17}O^{18}O$

Table 2.3 The molecular species of sulphur dioxide.

by measuring the isotopic compositions of both SO_2^+ (m/z 66/64) and SO^+ (m/z 50/48) and then applying appropriate corrections to obtain the $\delta^{34}S$ and $\delta^{18}O$ values (in a fashion similar to that of Holt, 1975).

2.1.2 Sulphur dioxide in the mass spectrometer

Sulphur dioxide has some drawbacks for use in mass spectrometry. The most important of these is that it is adsorbed readily onto cold metal surfaces making it difficult to remove from the mass spectrometer and inlet system by pumping. This characteristic of sulphur dioxide necessitates both longer pumping cycles (at least 5 minutes) and increased delay intervals when switching between reference and sample sides of the metal changeover valve of the instrument. This delay is the time between admitting the gas to the ion source and the start of isotope ratio measurements. The delay interval is 5 seconds when using carbon dioxide and sulphur hexafluoride, but must be increased to 30 seconds for sulphur dioxide.

After pumping, sulphur dioxide slowly desorbs from the cold metal surfaces of the inlet manifold, changeover valve and ion source. This is an important problem because mixing of desorbing sample gas with reference gas (and vice versa) in any of these sites will lead to errors in the $\delta^{34}S$ measurements. The error is manifested as a reduction in the true isotopic difference between sample and reference gases. This "memory" effect can be alleviated by heating various components of the mass spectrometer (Rees, 1978) since this causes faster desorption of sulphur dioxide gas from metal surfaces. For the instrument used in this study, most of the mass spectrometer (including the ion source, flight tube, changeover valve, capillaries, metal inlet and collectors, but not the remote head amplifiers) was heated to about 110°C. In order to assess the efficiency of the heating, the m/z 64 ion current was monitored during pumping. Decay rates of the m/z 64 ion current obtained when the mass spectrometer was heated (to 110°C) and unheated, are plotted in Figure 2.3. For comparison, the more favourable pumping rate of sulphur hexafluoride (m/z 127) is also plotted. From Figure 2.3, it can be seen that after 8 seconds the value of the m/z 127 ion current ($^{32}SF_5^+$) is about 1% of the normal operating value, for the m/z 64 ion current ($^{32}SO_2^+$) to reach the same value it takes 80 seconds when the mass spectrometer is unheated, and 44 seconds when it is heated. Even after 300 seconds (5 minutes) the m/z 64 ion current ($^{32}SO_2^+$) for the instrument when unheated, is still 0.6% of the operating value, whereas that of m/z 127 ($^{32}SF_5^+$) for the same time-period is $< 0.1\%$. The effect of temperatures above 110°C was tested but found not to improve pumping efficiency. Moreover, heating to higher temperatures was not desirable because of the adverse effect upon electrical components in the head amplifiers and the accelerated oxidation

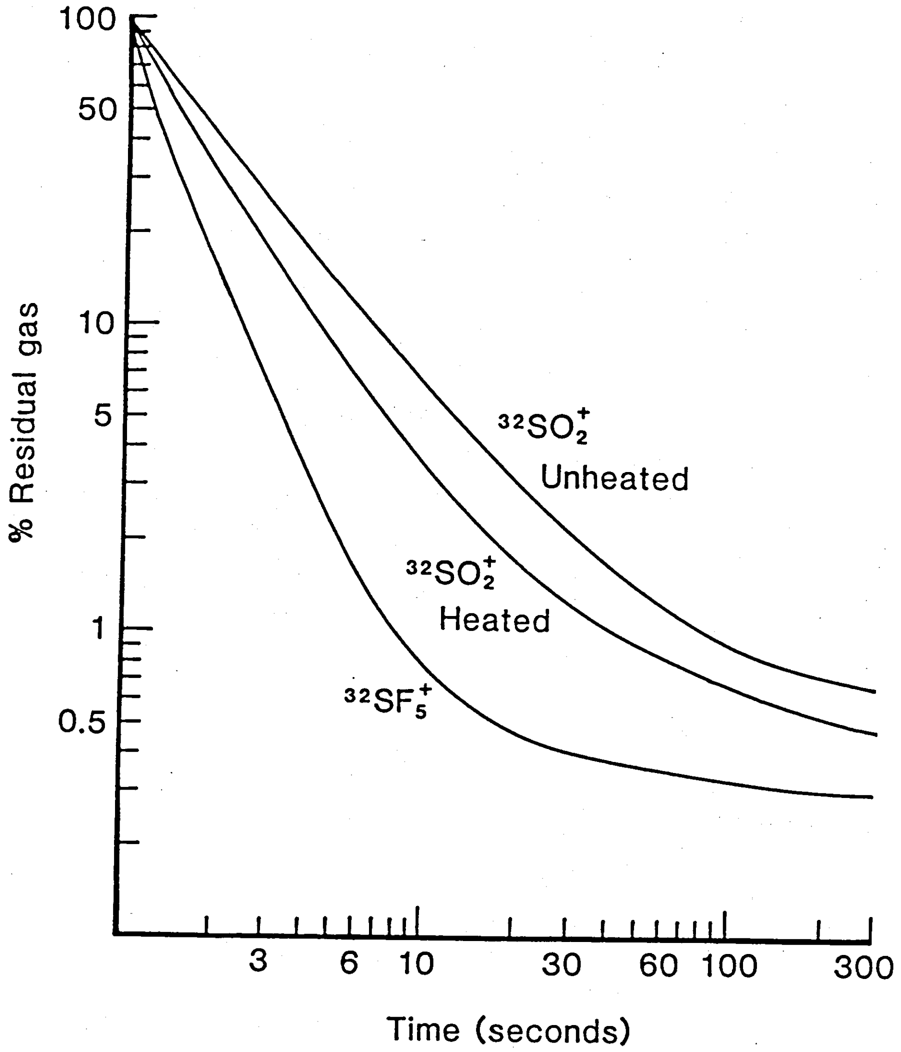


Figure 2.3 Variation with time of the $^{32}SO_2^+$ and $^{32}SF_5^+$ ion currents after termination of sample gas to the ion source.

of the wires connecting the power supply to the electromagnet and those carrying the high voltage signals to the ion source. At a temperature of 110°C, a minimum pumping time of 5 minutes is required before admission of a new gas sample into the mass spectrometer and a 30 second delay is imposed between switching of the changeover valve and proceeding with isotope ratio measurements.

The mass spectrum of sulphur dioxide occurs in a region which can potentially suffer from instrument background. A mass scan of the background in the modified instrument from m/z 20 to 80 is shown in Figure 2.4a. Prior to the background scan the instrument had been pumped for ten minutes to obtain a source pressure of 3×10^{-10} mb. For comparison, Figure 2.4b shows a mass scan of sulphur dioxide gas at a typical working source pressure of 4×10^{-8} mb achieved using a sample of $17\mu g$ of sulphur as sulphur dioxide. It can be seen from the background scan (Figure 2.4a) that there is only a trace of residual sulphur dioxide gas present in the mass spectrometer. The background level of sulphur dioxide is less than 0.007% of the total working pressure, therefore, no correction is required for a background contribution.

2.1.3 Isotopic reference gases

Two isotopic reference gases were prepared and stored in demountable two litre capacity glass bulbs for daily use. These gases are:

SO_2–1 Taken directly from a cylinder of compressed gas (BDH Chemicals, Ltd, England), with an $\delta^{34}S$ value of +10.16‰ relative to CDT.

SO_2–2 Prepared by the thermal decomposition of barium sulphate at temperatures above 1300°C using the apparatus shown in Figure 2.5, this gas has an isotopic composition of +16.11‰ relative to CDT.

Both gases are stored in separate bulbs at a pressure of approximately one atmosphere. The isotopic compositions of the reference gases were checked regularly by comparison with sulphur dioxide obtained by combustion of solid materials with known $\delta^{34}S$ values (e.g. Bella Roca troilite). Removal of about 400 aliquots of SO_2–1 (the reference most frequently used), over a period of two years, only changed the $\delta^{34}S$ value of this gas by 0.1‰.

2.1.4 Operating procedure

The sulphur dioxide samples prepared using the glass extraction line, which will be described in Section 2.2.1, are passed directly to the inlet manifold of the mass spectrometer. Admission of the sample gas to the ion source of the mass spectrometer is followed by equalisation of the major ion beam

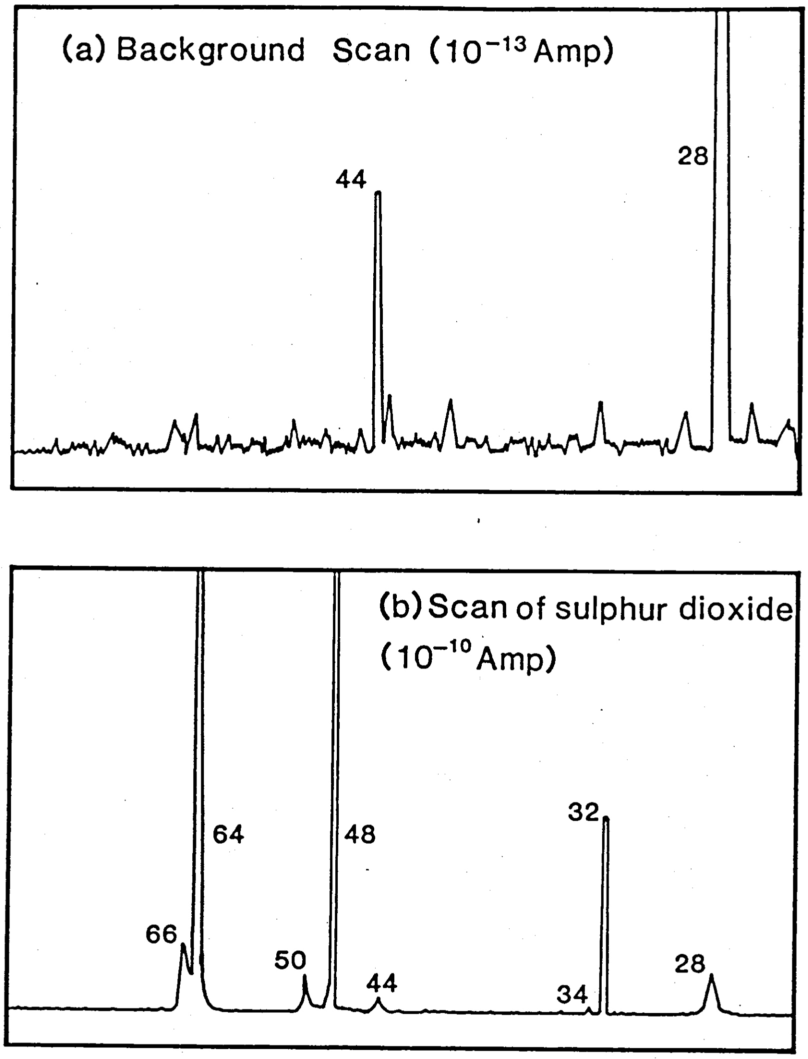


Figure 2.4 Mass scans of: (a) background, and (b) sulphur dioxide in the mass spectrometer.

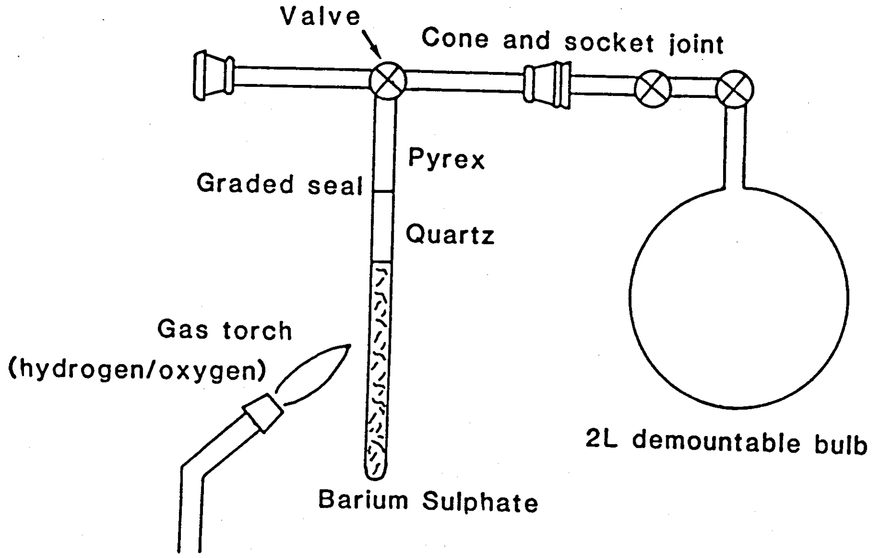


Figure 2.5 Apparatus for the preparation of SO_2–2.

(m/z 64) intensities and ion source pressures of the sample and reference gases. This procedure is more difficult to achieve using sulphur dioxide than for carbon dioxide, because the "sticky" nature of the gas means that there is a significant time delay between manual adjustment of the variable volume and response in ion beam intensity. The procedure is assisted by a graphical display of the ion beam intensities on the computer VDU screen and supplemented by a direct readout of the reference and sample ion beam currents in amps. Pressure balancing is always carried-out using the intensity of the major beam m/z 64, and not m/z 66, 48 or 50, because it is both the most intense and stable of the four beams. Using this method, the reference and sample ion beam currents can be routinely balanced to within 5%. The graph in Figure 2.6 shows that balancing of the ion beams is a critical part of the analysis procedure since an imbalance in the m/z 64 ion currents of 30% leads to an error of ± 0.5‰ on the $\delta^{34}S$ measurement, this is reduced to ± 0.3‰ for a 20% imbalance. Once the beams are matched, they must be allowed to stabilise for at least 30 seconds before isotope ratio measurements commence, to ensure that the gas pressure equilibrates fully in the ion source.

Following pressure balancing, the data acquisition computer program (written in conjunction with Dr I.P. Wright) is initiated by typing the appropriate commands at the keyboard. The computer is programmed to examine the segment of the mass spectrum from m/z 64 to 66. By using the output from a coarse (0–0.2 KV) 8-bit d-to-a converter, the computer

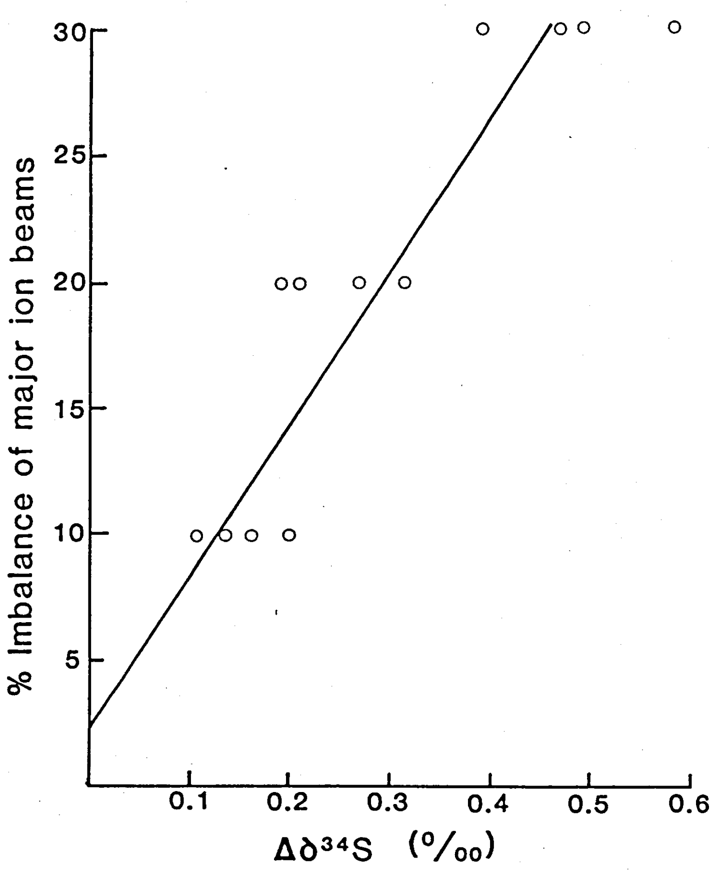


Figure 2.6 The effect of reference/sample ion beam imbalance on the measured δ^{34}S value.

identifies the region of the mass spectrum containing m/z 66 and programs a fine (0–75 V, and varied by a potentiometer) d-to-a to produce a "min-isweep" of 256 data points of the ion current across the minor collector. The computer program then evaluates the accelerating voltage that corresponds to the mid-point of the m/z 66 beam profile and sends the appropriate output code to the d-to-a in order to focus the ion beams on the collectors. The ion beam profiles obtained from both the coarse and fine scans are plotted on the computer VDU screen as a visual guide to peak shape and correct alignment of the ion beams on the collectors. At this point data acquisition commences; a sequence of six comparisons of the reference and sample gases is made. During each comparison a total of 500 ratio measurements (66/64) are made. Each block of 500 ratios is divided into 10 groups of 50 to obtain a real-time ratio display and the average of each of the 10 groups is used in the data reduction part of the program. The average ratio is output, in real-time, to the computer VDU screen which is useful for identifying:

1. The presence of contaminating species.
2. Fluctuations in the apparent ratio due to mechanical vibrations and electrical interference.
3. Ratio drift, i.e. changes that may result from:
    - unbalanced capillaries.
    - incomplete sealing or opening of the tungsten carbide balls of the changeover valve.
    - fluctuations in the magnetic field or source parameters.
    - small atmospheric leaks in the inlet or mass spectrometer.

Some of the ratio traces that can be encountered and the conditions that caused them are presented in Figure 2.7.

A 30 second time delay is required between each comparison (i.e. from switching the changeover valve from the reference to sample sides) to allow the pressure of sulphur dioxide gas to fully equilibrate in the ion source. This is illustrated in Figure 2.8, which is a graph showing the ion current versus time profile for the major beam (m/z 64) just after operation of the changeover valve. At least fifteen seconds elapse until the major ion current reaches its maximum value, i.e. before the gas has fully equilibrated. That it is not an idiosyncrasy of the instrument was established by observing the behaviour of carbon dioxide and sulphur hexafluoride gases, both of which reached equilibrium conditions in about one second.

The first sample versus reference comparison of m/z 64/66 is made to establish an approximate $\delta 66$ value so that the ratio trace, as plotted on the

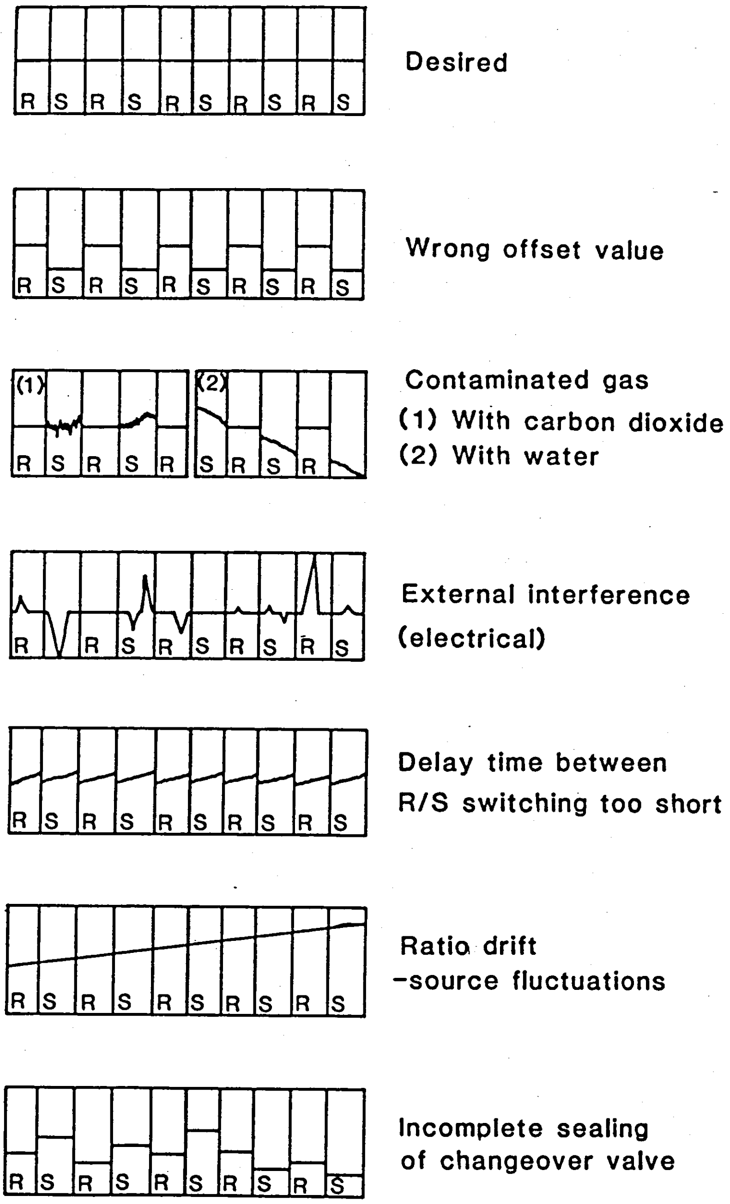


Figure 2.7 A selection of different ratio traces.

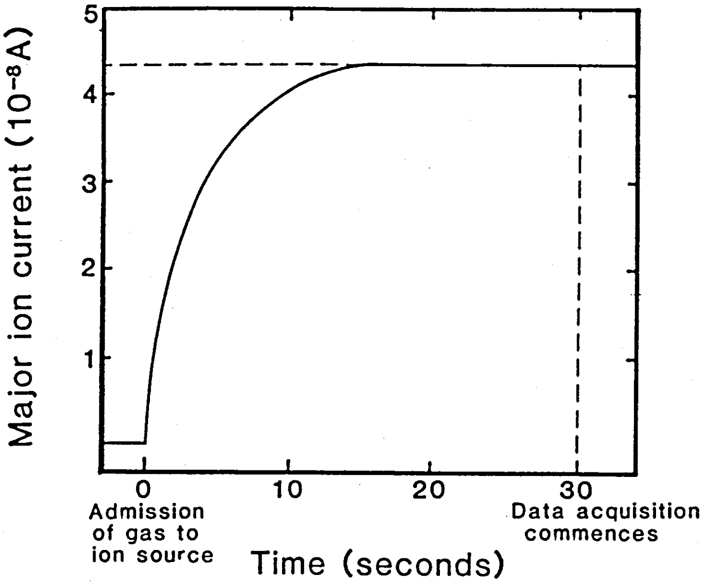


Figure 2.8 Response of the major amplifier monitoring the m/z 64 ion current and illustrating the slow equilibration of sulphur dioxide in the ion source.

VDU screen, occupied the middle of the display. Measurements made during the first comparison are not used in the data reduction procedure. Once all six comparisons between reference and sample gases have been made for δ66, the output of the programmable power supply is adjusted, by means of the coarse d-to-a, by the computer. This is done, in a similar way to the previous ion beam optimisation procedure (for m/z 66), to focus m/z 50 onto the minor collector. The ion beams m/z 48 and 50 are approximately half the intensity those measured for m/z 64 and 66. With the m/z 50 and 48 beams focussed on the minor and major collectors respectively, a sequence of ratio measurements analogous to those of 66/64 commences.

On completion of ratio measurements the δ^{34}S value along with other relevant information (such as δ66 and δ50 values, δ^{18}O values, errors etc.) are displayed on the computer VDU screen and transferred to a floppy disc for storage. The total time taken for each complete δ^{34}S determination is approximately twenty minutes. With five minutes necessary for pumping between consecutive sample analyses there is no possibility of making repeat measurements on individual samples produced from a stepped combustion experiment as fresh sulphur dioxide gas is generated approximately every thirty minutes (Section 2.2).

2.1.5 Data interpretation

The raw mass spectrometric data obtained as 66/64 and 50/48 ratios are converted to δ–values.

$$\delta 66\mathrm{m} = \left[\frac{(66/64)\mathrm{sample}}{(66/64)\mathrm{reference}} - 1\right] \times 1000$$

$$\delta 50\mathrm{m} = \left[\frac{(50/48)\mathrm{sample}}{(50/48)\mathrm{reference}} - 1\right] \times 1000$$

$\delta 66\mathrm{m}$ = measured $\delta 66$ value.
$\delta 50\mathrm{m}$ = measured $\delta 50$ value.

The measured δ–values can then be adjusted by application of valve-mixing (Section 2.1.6) and isobaric corrections. The isobaric corrections are of the form:

$$\delta^{34}\mathrm{S} = (1.0892 \times \delta 66\mathrm{m}) - (0.004 \times \delta^{18}\mathrm{O})$$

$$\delta^{18}\mathrm{O} = (26.8402 \times \delta 66\mathrm{m}) - (25.7413 \times \delta 50\mathrm{m})$$

During each analysis of sulphur dioxide gas a total of 5000 measurements of the 64/66 and 48/50 ratios are determined and stored in the computer memory. At the end of the analysis, the mean ratio and the standard error of the mean ratio are calculated for $\delta 66$ and $\delta 50$.

$$\text{e.g. } E_{\delta 66} = \left\{E^2_{\delta 66\mathrm{sam}} + E^2_{\delta 66\mathrm{ref}}\right\}^{-0.5}$$

The standard error reflects perturbations in isolation and purification procedures applied to the sample as well as fluctuations in instrument parameters. For this reason the errors quoted for samples prepared on the gas extraction system are usually greater than those of the reference gases. The largest errors occur at levels near the detection limit, consecutive analyses of 1μg and 10μg aliquots of sulphur as SO_2–1 reference gas have errors on the 66/64 ratios of ± 0.5‰ and ± 0.2‰ respectively. Similarly, typical errors for 50/48 ratios are ± 0.7‰ and ± 0.3‰ for 1 and 10μg sample sizes respectively.

The precision of the δ^{34}S value can be estimated by combining the errors associated with the $\delta 66$ and $\delta 50$ measurements. The typical error for an isotopic analysis of sample SO_2–1 versus reference SO_2–1 (the so-called zero enrichment test), using sample sizes in the order of 10μg, on the modified instrument, is ± 0.2‰, this value increases to around ± 0.3‰ for zero enrichments involving 1μg of sulphur. For isotopic measurements of real sample gases (prepared on the gas extraction line), where it is impossible to remove all traces of carbon dioxide and water, the errors typically increase to ± 0.3‰ for 10μg of sulphur and ± 0.8‰ for 1μg sulphur samples.

2.1.6 Combined valve-mixing and memory correction

A small amount of gas leakage across the tungsten carbide balls of the changeover valve is inevitable as the seals between the balls and seats are imperfect. This means that some of the gas which is being bled to waste, leaks through the seat and mixes with the gas that is being analysed. In consequence, the true difference in δ^{34}S between sample and reference gases cannot be ascertained. Normally the amount of crossover is insignificant, but if it exceeds 0.1% a valve-mixing correction (VMC) must be applied.

The seat leakage for the valve on the instrument used in this study has previously been determined using carbon dioxide (Grady, 1983) and required the measured δ^{13}C value to be multiplied by 1.001. In other words, there was a 0.1% crossover of gas between the two sides of the valve. Grady (1983) obtained the VMC using the method described by Fallick (1980) and this approach was adopted for an evaluation of the leakage for sulphur dioxide gas with the valve heated to a temperature of 110°C.

The reference reservoir is filled with 4×10^{-8} mb pressure of argon and the m/z 64 ion current (I_{64}) is measured for the reference side with the sample reservoir evacuated. This gives a value for contaminant sulphur dioxide in the argon. The sample reservoir is then filled with 4×10^{-8} mb sulphur dioxide and the increase in I_{64} in the argon-filled side is measured. Subtraction of the contaminant value then gives the true leakage of sulphur dioxide from the sample to reference chambers of the changeover valve. As both seats will have different leakage characteristics, it is necessary to repeat the process to determine the leakage from the reference reservoir. The valve crosstalk is then equal to the sum of the leakages through the reference and samples reservoirs and for the instrument used in this study gave a value of 1.0045. The corrected δ^{34}S value is then calculated as:

$$\delta^{34}\text{Scorr.} = \delta^{34}\text{Smeas.} \times 1.0045$$

Where δ^{34}Smeas. = measured δ^{34}S value.

Thus, there is a 0.45% leakage of sulphur dioxide between the two sides of the valve, this value is larger than that obtained previously (by Grady, 1983), possibly because the valve is heated. However, the VMC determined in this study represents both valve crosstalk and a contribution from the memory effect because gas is constantly desorbing from the metal walls of the valve and ion source. As both effects are additive, i.e. they both tend to reduce the isotopic difference between reference and sample gases, it may explain why the correction is greater than the previous result obtained by Grady (1983). The individual contributions from crosstalk or memory to the overall correction factor are impossible to distinguish, although the contribution from the memory effect will decrease with time as sulphur dioxide desorbs from the metal and is pumped to waste.

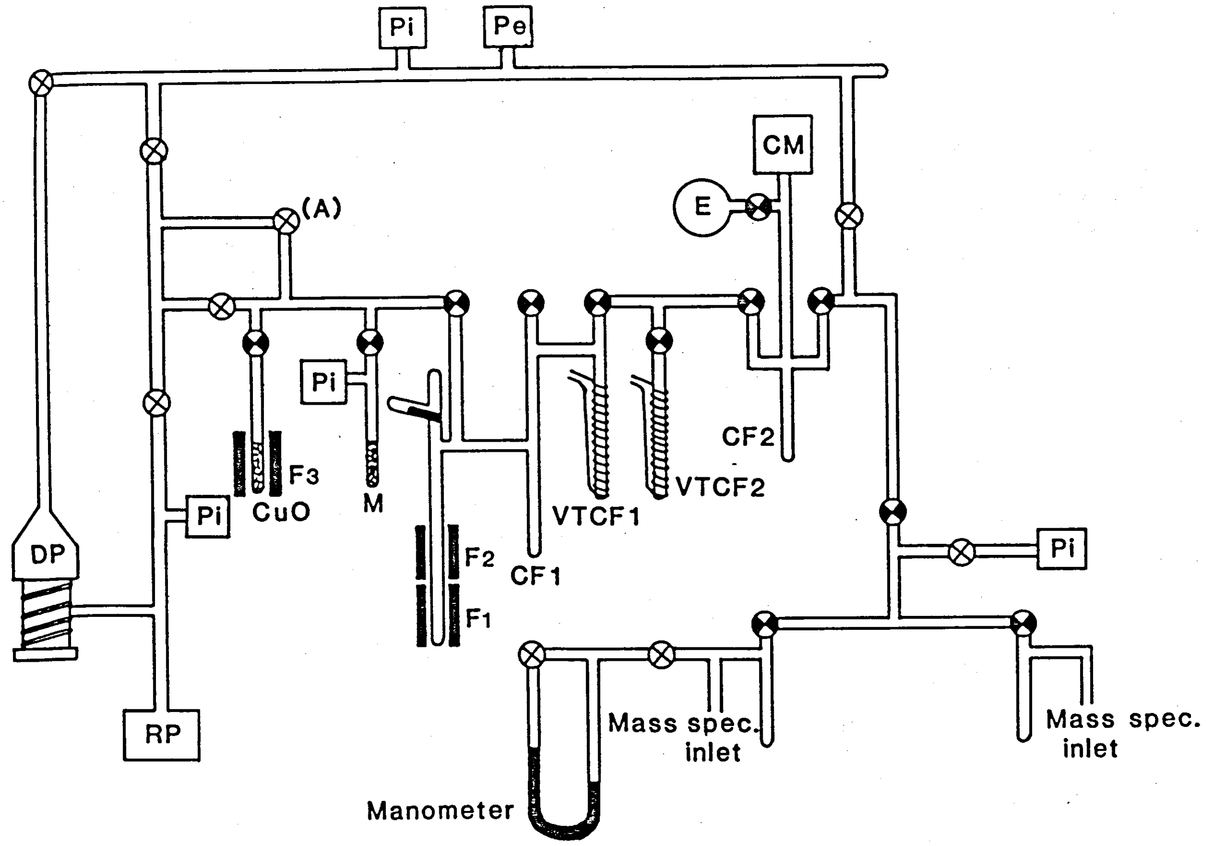
2.2 Stepped combustion analysis

2.2.1 Gas extraction system

The sulphur-bearing components of meteorites (e.g. S^0, S^{2-}, SO_4^{2-} etc.) are converted to sulphur dioxide by combustion in pure oxygen using an extraction system which is shown diagrammatically in Figure 2.9. The extraction system is constructed, predominantly, of Pyrex glass and greaseless vacuum valves (Young's, Acton, England) Prior to the analysis, meteorite samples are weighed and loaded into pre-baked (at 1200°C in air) quartz glass tubes (or "buckets" with dimensions: 15mm length, 3mm o.d. by 2mm i.d.) that have been sealed at one end.

The bucket, containing the sample, is placed in the uppermost region of the combustion tube where it is suspended by means of a magnetic iron slug encased in Pyrex glass. The reaction tube is carefully evacuated to a pressure of less than 10^{-2} torr by slowly opening a needle valve (valve A in Figure 2.9), connected to a rotary pump, while the pressure in the reaction tube is constantly monitored by a Pirani gauge. This procedure has been adopted to prevent sample from being inadvertently displaced from the bucket during removal of air trapped between the grains of the material. Sample loss can occur if the vessel is pumped too rapidly following isolation from atmosphere. At a pressure of less than 10^{-2} torr it is no longer necessary to continue evacuation through the needle valve, the pumping is switched over to an oil diffusion pump, and the entire extraction system is evacuated to a pressure lower than 10^{-6} torr.

The lower section of the combustion tube is constructed of 8mm diameter quartz tubing and is attached to the rest of the extraction system via a quartz/Pyrex graded seal (Cambridge Glass, Cambridge, England). Prior to sample analysis, the quartz tubing is heated under vacuum to 1200°C using a wire-wound resistance furnace (F_1, with dimensions: 16cm length, 7cm o.d. and 1.5cm i.d.) controlled by a variable transformer (Zenith Electric Company, Milton Keynes, England); the section of glass directly above is heated to 1000°C using a second furnace (F_2) of similar design. The furnace temperatures are measured using a chromel-alumel thermocouple, connected to a digital thermometer (KM10000, Kane-May Ltd, Herts, England), positioned between the outside of the reaction vessel and the wall of the furnace. Heating is allowed to continue for at least eight hours before the sample is loaded, in order to remove any sulphur contaminants from this area of the glass. Sulphur-containing contaminant compounds in the



CF = Cold finger

CM = Capacitance manometer

DP = Diffusion pump

E = Expansion volume

F = Furnace

M = Molecular sieve

Pe = Penning gauge

Pi = Pirani head

RP = Rotary pump

VTCF = Variable temperature cryogenic finger

Valves

⊗ Single

● Backed

Figure 2.9 Schematic representation of the gas extraction line used for stepped combustion.

extraction system are not considered to be present at significantly high levels to interfere with the stepped combustion analysis of samples (discussed in Section 2.2.3). However, it is possible that some sulphur may be inadvertently introduced into the system during sample loading (in the form of fingerprints, dust, fibres etc.), hence the reaction tube is always pre-baked. Before sample analysis, the two furnaces (F_1 and F_2), are allowed to cool to room temperature. Oxygen for the sample combustion is prepared by cryogenically trapping, at −196°C, onto 5Å molecular sieve, the gas liberated from heating copper (II) oxide (wire form, BDH Chemicals Ltd, Poole, England) to 950°C using F_3 (the CuO was initially outgassed by repeatedly heating at 1000°C and cooling to 600°C in an isolated volume, followed by pumping the remaining gases to waste). This is continued for fifteen minutes following which the copper (II) oxide is isolated and cooled to 600°C. To provide aliquots of oxygen for each step of the combustion the molecular sieve is warmed to room temperature. The total pressure of oxygen, which always exceeds 200 torr, is measured with a Pirani gauge. The molecular sieve is pre-baked at 300°C, before being used as an oxygen reservoir, in order to remove any contaminant gases (e.g. nitrogen, carbon dioxide, argon, sulphur dioxide) adsorbed onto this material.

The sample is dropped into the cool reaction tube by external manipulation of the iron slug using a hand magnet. An aliquot of oxygen is expanded into the combustion tube, which is then isolated, and F_1 is raised to the temperature of the first step (usually 100°C). All condensible gases formed during heating are frozen onto a cold finger (CF1, at −196°C) as they form. F_2, which is positioned directly above F_1, is kept at 1000°C for two reasons.

1. To reduce as much as possible any sulphur trioxide forming during the combustion to sulphur dioxide. According to the equilibrium:

   $$2SO_2 + O_2 \rightleftharpoons SO_3$$

   Sulphur trioxide is only stable at room temperature or at very high pressures, however, below 1000°C some sulphur trioxide remains undecomposed (Schenk and Steudel, 1968).

2. To allow any subliming elemental sulphur, which would otherwise condense onto cool glass above F_1, the opportunity to react with oxygen at high temperature and thus form sulphur dioxide. A heater tape is wrapped around the remaining exposed glass and kept at a temperature of 110°C for the same purpose and also to prevent water, sulphur dioxide and sulphur trioxide from condensing.

At the end of the combustion step, which is always thirty minutes in duration, any unreacted oxygen is readsorbed onto the molecular sieve finger following immersion in liquid nitrogen. Non-condensible gases released during the combustion step are either, inadvertently adsorbed onto the molecular sieve along with oxygen, or they are pumped away. Following isolation of the molecular sieve finger, the gases produced during the combustion are transferred from CF1 to the first of two variable temperature cryogenic fingers (VTCF1). Meanwhile, a fresh aliquant of oxygen is expanded into the reaction tube and the temperature of F_1 raised to that of the next step.

The VTCF are constructed of resistance wire coiled around a short tube of Pyrex glass (6mm i.d.) with a thermocouple included for temperature measurement, this assembly is enclosed in a sheath of Pyrex glass. The VTCF are immersed in liquid nitrogen and an electrical current, which can be varied by means of a variable transformer, is passed through the wire to give the required temperature. VTCF1 is kept at −90°C and its function is to remove any water liberated during heating/combustion of the sample. This is particularly important for samples of C1 and C2 carbonaceous chondrites which can contain up to 20% silicate-bound water and hydrogen in organic compounds that forms water on combustion. Failure to remove water from the product gases at this stage results in sulphur isotopic measurements of poor quality. Although water and sulphur dioxide will react readily to form sulphurous acid, this process does not occur to a significant extent during the stepped combustion experiments. The reaction of interest is:

$$H_2O + SO_2 \rightarrow H_2SO_3$$

In order to test for the effects of this reaction, known volume aliquots of sulphur dioxide were mixed with, and then cryogenically separated from water. Complete recovery of the original sulphur dioxide was achieved by this method.

VTCF2 facilitates purification of the remaining product gases, which consist mainly of carbon dioxide and sulphur dioxide, by allowing separation according to volatility. During careful calibration experiments, carried out on mixtures of carbon dioxide and sulphur dioxide in varying proportions, a nominal temperature range of −152°C to −135°C was deduced as that suitable to allow carbon dioxide to enter the gas phase while sulphur dioxide remained frozen. The exact temperature necessary for separation was found to vary depending upon the proportions of sulphur dioxide and carbon dioxide in the frozen mixture; high carbon dioxide content relative to sulphur dioxide suppresses the separation temperature and vice versa, a certain amount of practice is necessary to achieve a successful separation. As an aid to cryogenic separation of carbon dioxide from sulphur dioxide, the pressure of gases evolving from VTCF2 is monitored using a capacitance manometer (MKS Baratron type 315, MKS Instruments Inc., Mass., USA).

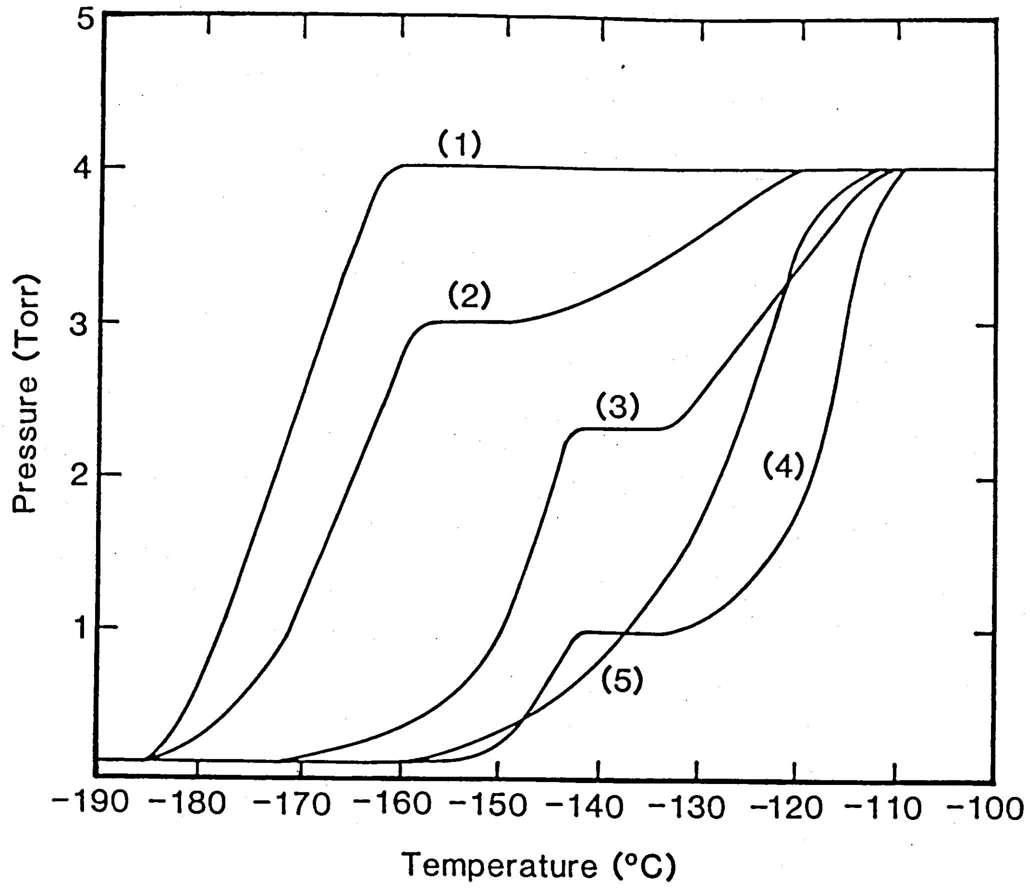


Figure 2.10 Characteristic temperature versus gas pressure profile obtained for CO_2/SO_2 separations. Curves represent the following mixtures: (1) Pure CO_2, (2) 75% CO_2 : 25% SO_2, (3) 50% CO_2 : 50% SO_2, (4) 25% CO_2 : 75% SO_2, (5) Pure SO_2.

The measuring head of this instrument is kept at a temperature of about 110°C to prevent sulphur dioxide from being adsorbed onto the metal surfaces. The baratron is interfaced to a computer so that a graphical display of the gas pressure versus time profile can be obtained. Normally an approximately linear heating program is employed, at +1°C per second from −170°C, and thus the display is essentially gas pressure versus temperature of VTCF2. Typical heating profiles for different mixtures of sulphur dioxide and carbon dioxide are shown in Figure 2.10. There is clearly a plateau in the gas pressure versus time profile for each mixture, which follows the evolution of carbon dioxide, but occurs before the liberation of sulphur dioxide. If the onset of sulphur dioxide evolution is observed prematurely, then the temperature program is stopped, all the gases re-frozen into VTCF2 and the separation procedure is repeated. Following a successful separation, the carbon dioxide is frozen onto a cold finger (CF2) connected to the capacitance manometer and isolated from VTCF2. After measurement of the carbon dioxide pressure, the gas is pumped away. Meanwhile, the temperature of VTCF2 is raised to −110°C to liberate sulphur dioxide, whilst leaving behind any water not already frozen in VTCF1. If some water is found to be present in the sample gas at this stage then the sulphur dioxide and water mixture can be left in contact with VTCF1 at −90°C to ensure complete purification of sulphur dioxide. Water can be detected in the "separated" gases by the instability of the baratron reading, which begins to decrease rapidly as water condenses onto the glass. Pure sulphur dioxide is transferred to CF2. The volume of CF2 is calibrated to facilitate sulphur yield measurement, it can be increased via connection to a 500cm^3 glass bulb (E_1) for measurement of large gas samples. The yield of pure sulphur dioxide is measured using the baratron and then the gas is admitted to the mass spectrometer.

2.2.2 Sample handling

Determination of sulphur in meteorite samples requires the use of procedures which minimise the amount of foreign matter (including both particles and adsorbed gases) added to the sample during weighing and loading into the gas extraction line. The samples have been prepared by crushing 200mg chips of meteorite to a <50μm-sized powder by Dr M.M. Grady. Aliquants of these crushed reservoirs are removed for stepped combustion analyses. Sample weighing is carried-out on a balance in a clean room equipped with a laminar air-flow bench. Fine-pointed stainless steel tweezers are used to manipulate a small "boat" of aluminium foil onto a balance, an aliquant of sample is added, and the boat and sample re-weighed, the sample weight is calculated by subtraction. Each aluminium boat is used for a single weighing operation and then discarded. The aluminium foil and tweezers are cleaned before use by ultrasonification in a 50:50 mixture of toluene and methanol followed by drying in an oven at 100°C. The sample is manipulated into a pre-baked quartz bucket and the aluminium boat is reweighed to check for zero (i.e. to ensure that all the sample has been transferred to the quartz bucket). The bucket, containing the sample is transfered to the gas extraction system where it is loaded into the reaction vessel. This is usually done within five minutes of the sample being weighed.

2.2.3 System blank

A procedural blank of a stepped combustion analyses of an empty quartz bucket gives a total yield of sulphur of about 1μg up to 1200°C. Figure 2.11 shows a stepped combustion profile obtained from an empty bucket and it can be seen that most of the sulphur is released below 500°C. The usual yield per 100°C step is between 0.2 and 0.3μg sulphur, which is about 2% or 3% of the usual sample size (10μg) for a 100°C temperature step of a meteorite stepped combustion. As such, the background level of sulphur is

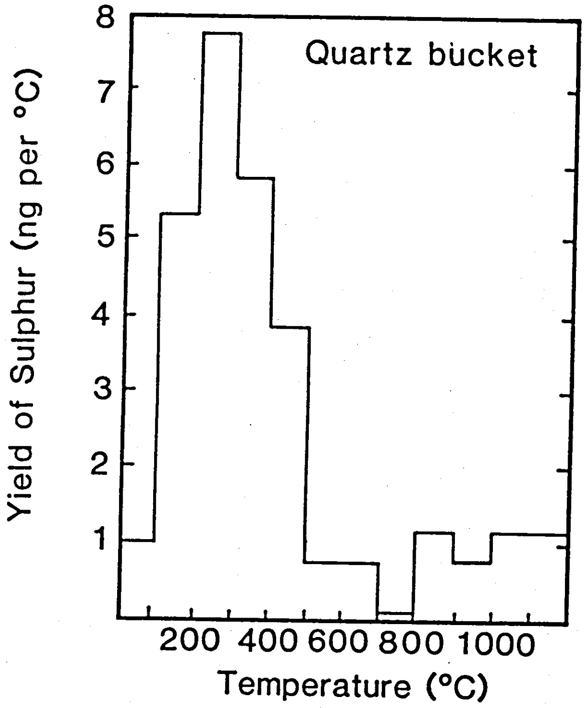


Figure 2.11 Stepped combustion of an empty quartz bucket (ng = nanogram).

deemed insignificant and no correction is applied to the data. The small blank that is present in the system must derive predominantly from the quartz bucket and is probably introduced during sample weighing. This follows because a blank combustion at 1200°C (as a single step) carried out on an empty system, liberates about 100ng of sulphur. This also indicates that there is a negligible amount of sulphur produced by heating either the copper oxide, or the reaction vessel.

2.3 Application of stepped combustion to reference materials

In order to assess whether stepped combustion could resolve the different sulphur compounds expected to be present in meteorites and to test if the sulphur isotope measurements made using this technique would be isotopically fractionated (discussed in Section 2.4), a number of analyses of pure chemical substances were made. These materials (which included sulphides and sulphates) were chosen to be chemically representative of minerals that have been petrographically identified in meteorites. Measurements were made on both the pure compounds and mechanical mixtures composed of several different sulphur compounds.

2.3.1 Elemental sulphur

This substance has been observed in at least one group of meteorites, the C1 carbonaceous chondrites. A stepped combustion profile of elemental sulphur is shown in Figure 2.12; it was found to burn at the lowest temperature of all sulphur species analysed by this technique so far (T<200°C). Unfortunately it proved to be very difficult to obtain 100% yields of elemental sulphur as sulphur dioxide during stepped combustion. This is because elemental sulphur tends to sublime when heated and then recondense onto cooler regions of the reaction tube (the melting point of elemental sulphur at 1 atm is 119°C: Meyer, 1968). The failure of furnace F_2 (at 1000°C) to convert sulphur to sulphur dioxide may be attributed to the large and sudden evolution of sulphur vapour as the temperature of the combustion furnace (F_1) is raised through the sublimation point. Attempts to increase yields of sulphur dioxide by combusting in smaller temperature increments (i.e. lowering the heating rate) over the interval from room temperature to 200°C (using 50°C temperature steps as opposed to 100°C), made only a modest improvement. Presumably, at these low temperatures the reaction rate of sulphur oxidation is so slow that the process of volatilisation predominates. This is clearly a problem for the stepped combustion analysis of

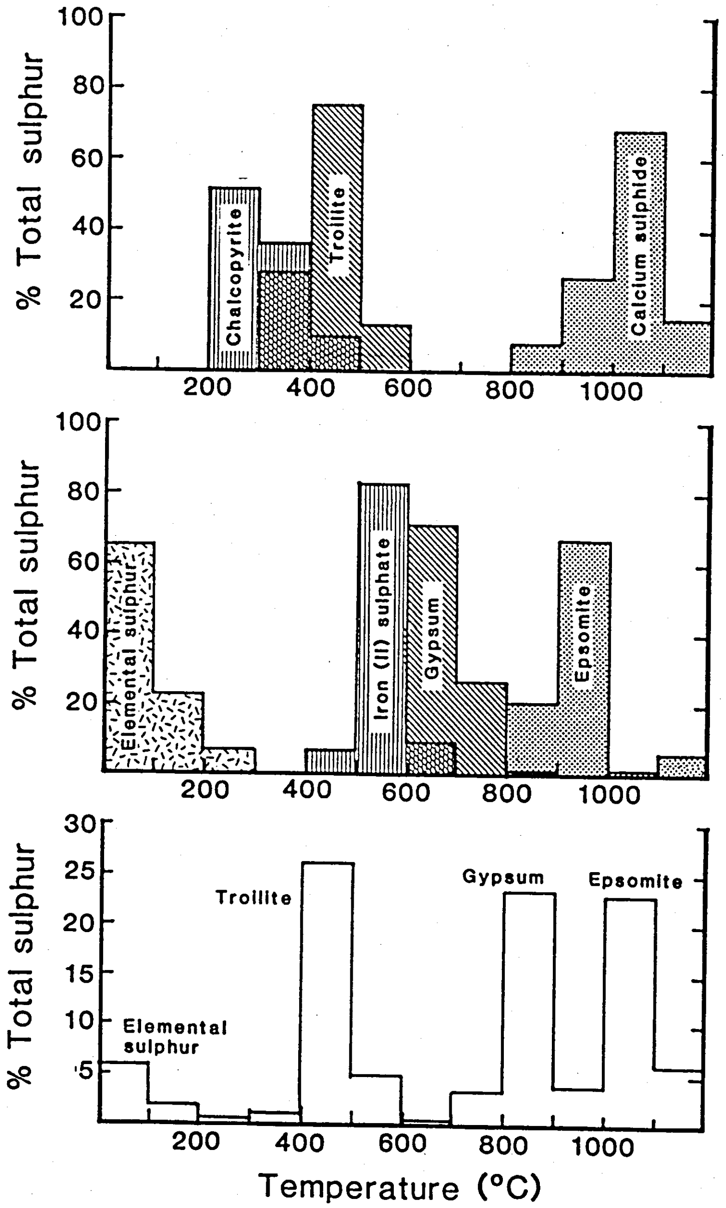


Figure 2.12 Stepped combustion profiles of elemental sulphur, sulphides, sulphates and a reference mixture.

meteorites containing elemental sulphur, because the recondensed material might:

1. Burn later during the experiment under the influence of convected heat from elevated temperatures of the combustion furnace and mix with sulphur liberated from other compounds.

2. Be available for isotopic exchange resulting in erroneous $\delta^{34}S$ measurements.

In an attempt to prevent isotopic exchange reactions from occurring, the sulphur dioxide formed during each combustion step is cryogenically removed from the reaction tube as it forms.

2.3.2 Sulphide

A number of different sulphide minerals have been treated to stepped combustion, including: troilite (FeS), pyrite (FeS_2), chalcopyrite ($FeCuS_2$) and calcium sulphide (CaS). A composite profile of separate stepped combustions for some of these sulphides is given in Figure 2.12. With the exception of calcium sulphide, all the sulphides analysed, burn over a narrow temperature interval, i.e. between 200 and 600°C. Troilite, hand-picked from the Bella Roca iron meteorite, has been analysed by stepped combustion seven times in the course of this work and has a remarkably constant combustion temperature, with a maximum release occurring between 400 and 450°C. The mixture of sulphides shown in Figure 2.12 probably could not be resolved satisfactorily using 100°C temperature steps, but it may be possible to do this using step sizes of 50°C or 25°C. For most of the sulphides studied it is assumed that reaction with oxygen results in the formation of sulphur dioxide and the metal oxide.

$$2MS + 3O_2 \rightarrow 2MO + 2SO_2$$

Where M represents the metal. An idealised metal(M)-sulphur-oxygen stability diagram is shown in Figure 2.13. During the usual conditions of stepped combustion every effort is made to achieve experimental conditions which favour the MO field, thus the the partial pressure of oxygen is greater than log -4 Pa and partial pressure of sulphur dioxide is minimised by immediate cryogenic trapping in a cold finger.

Calcium sulphide was chosen to be the closest terrestrial analogue to the mineral oldhamite which is known to occur in enstatite meteorites (see Chapter 5). Calcium sulphide combusts between 800 and 1100°C (Figure 2.12) which is at significantly higher temperatures than the other sulphides analysed. The high combustion temperature of calcium sulphide may be

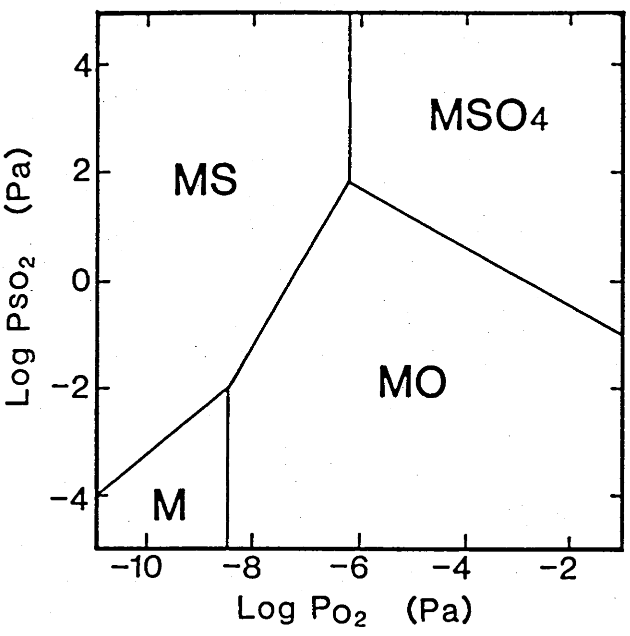


Figure 2.13 Idealised stability diagram for the metal(M)–sulphur–oxygen system (after Greenwood and Earnshaw, 1986).

explicable in terms of an initial reaction of this compound with oxygen occurring below 600°C.

$$CaS + 2O_2 \rightarrow CaSO_4$$

Calcium sulphate would then decompose to calcium oxide and liberate sulphur dioxide at higher temperatures (Section 2.3.3). In order to assess the extent of this process, a weighed sample of CaS was exposed to the atmosphere at 600°C for eight hours. If all the calcium sulphide is converted to calcium sulphate then an 89% weight increase would be expected, however, a weighed gain of only 30% was observed. The calcium sulphide may have undergone only a partial reaction with atmospheric oxygen, or else it may have reacted with water vapour during the following reaction (Mellor, 1925):

$$2H_2O + 2CaS \rightarrow Ca(OH)_2 + Ca(SH)_2$$

The products of this reaction are calcium hydroxide and calcium hydrosulphide. This reaction could only occur at the very surface of the calcium sulphide powder, because water would be driven-out of the material at the relatively high temperatures involved. The reaction between calcium sulphide and water should lead to a 25% weight gain if it goes to completion, although some hydrogen sulphide may be formed by this reaction.

2.3.3 Sulphates

Stepped combustion profiles of three sulphates (iron sulphate, $FeSO_4$; calcium sulphate, $CaSO_4.2H_2O$; magnesium sulphate, $MgSO_4.7H_2O$) are combined in Figure 2.12. Sulphates do not combust, rather they decompose at very precise temperatures to produce an oxide and sulphur dioxide gas (Wilson and Newall, 1966). For example, magnesium sulphate decomposes at 1124°C (Weast et al., 1985).

$$3MgSO_4 \rightarrow 3MgO + 3SO_2 + SO_3$$

Sulphur trioxide is thermally unstable above 1000°C (Schenk and Steudel, 1968) and will be reduced to sulphur dioxide at the decomposition temperature of magnesium sulphate.

$$2SO_3 \rightarrow 2SO_2 + O_2$$

Because of their discrete combustion and decomposition temperatures most sulphates and sulphides should be resolvable by stepped combustion.

2.3.4 Reference mixture

A mixture of four reference compounds was prepared using equal proportions of sulphur as elemental sulphur, troilite (FeS), gypsum ($CaSO_4.2H_2O$) and epsomite ($MgSO_4.7H_2O$). The sulphur release profile is shown in Figure 2.12. The composition of this mixture was chosen to approximate to the sulphur-bearing mineral content of type C1 and C2 carbonaceous chondrites. The plot in Figure 2.12 illustrates some important features:

- There is a fairly close correspondence between the temperature of decomposition/combustion for each pure reference compound and that recorded from the same component as a constituent of the mixture.

- The stepped combustion method is able to resolve the individual constituents of a mixture of different sulphur compounds even when using step sizes of 100°C. Possibly even better resolution may be obtainable using smaller temperature increments such as 50°C or even 25°C. However, it is noted that the reference material is merely a mechanical mixture of four 50μm-sized powders, which may be quite different to a meteorite sample containing fine-grained intergrowths of different mineral components. Mineral intergrowths may promote combustion because exothermic reactions will result in localised heating effects.

- The yields of sulphur as gypsum and epsomite are better than 10% of the predicted amounts, with due allowance for weighing and yield

> measurement errors, this demonstrates that sulphur trioxide formation is of minor importance during stepped combustion at high temperature (however, see Section 2.4 for a discussion of isotope fractionation). The yield of troilite is somewhat lower (82%), but in the case of elemental sulphur the yield is very poor (16%). This can be attributed to sublimation of elemental sulphur during heating, as was explained in Section 2.3.1.

The sulphur release profile of the reference mixture is utilised in Chapter 3 for "calibrating" the sulphur release patterns obtained from meteorites.

2.4 Sulphur isotope measurements of reference materials

Figure 2.14a shows the release and isotopic composition of sulphur versus temperature obtained for a stepped combustion analysis of Bella Roca troilite. It is apparent that there are changes in isotopic composition with varying temperature. In order to assess whether the measured isotopic values obtained by stepped combustion are representative of the true isotopic composition of troilite sulphur, it is necessary to compare the calculated $\delta^{34}S$ value from the stepped combustion data with the $\delta^{34}S$ value obtained by bulk combustion of an identical sample at 1200°C. The cumulative $\delta^{34}S$ value obtained from the stepped combustion of Bella Roca troilite, shown in Figure 2.14a, is −2.5‰ and the total yield of sulphur is 89%, whereas that obtained by bulk combustion is −0.4‰ and the yield is 98%. Shown in Figure 2.14b, are the results for an early analysis of troilite which gave a $\delta^{34}S$ value of −0.1‰, this is in good agreement with the value obtained by bulk combustion and indicates that stepped combustion analyses carried-out at an early stage of this project yielded reliable isotopic data. Thode et al. (1961) have previously reported a $\delta^{34}S$ value of −0.45‰ for Bella Roca troilite.

The reasons for the isotopic differences between the stepped and bulk combustion data could be due to one or a combination of the following:

1. Sample weighing errors.
2. Loss of sample powder during evacuation.
3. Loss of sulphur dioxide during separation of the product gases.
4. Kinetic isotope fractionation (this would have to be an incomplete combustion of the troilite, otherwise, the calculated $\delta^{34}S$ value would equal the bulk $\delta^{34}S$ measurement).

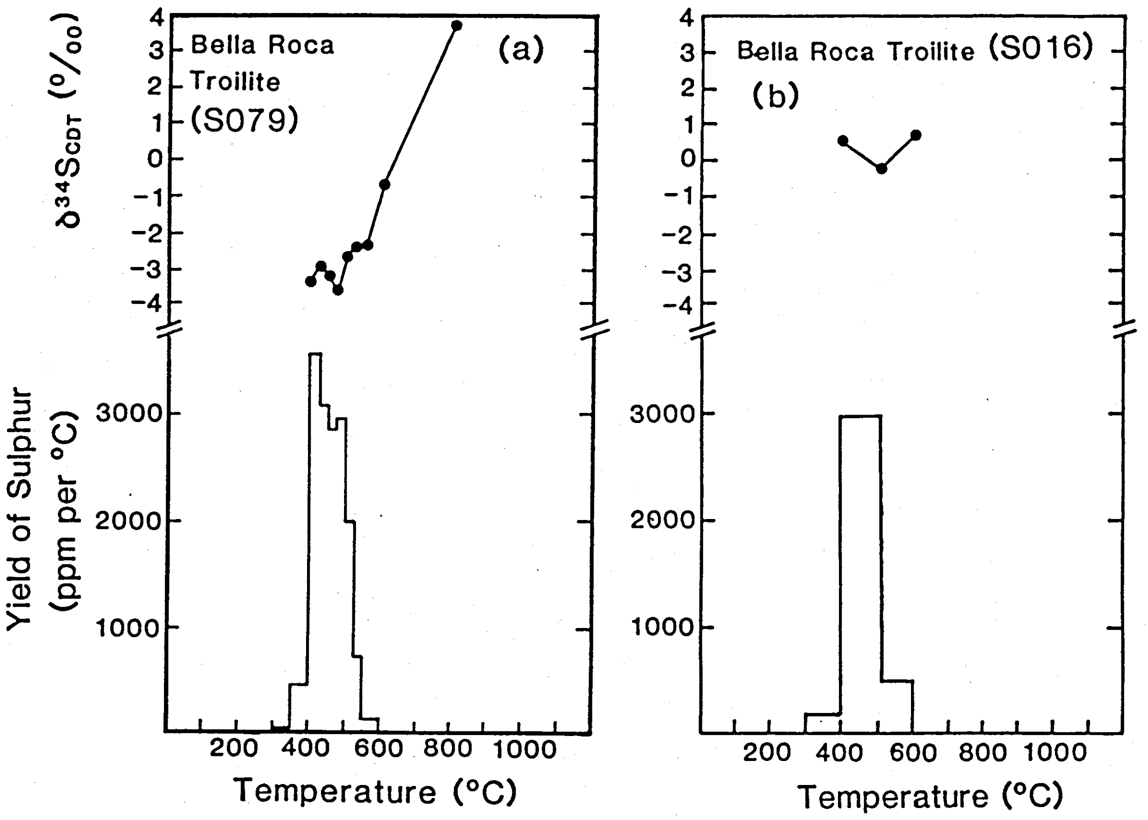


Figure 2.14 The abundance (—) and isotopic composition (-•-) of sulphur in two Bella Roca troilite samples as determined by stepped combustion. (a) Sample S079 (pre-fluorination experiments) and (b) sample S016 (post-fluorination experiments).

5. Sulphur trioxide formation.

Problems 1 and 2 can only account for low yields and moreover, the effects of 1–3 can largely be dismissed for the following reasons. Reasons 1 and 2 are unlikely to be significant because samples analysed by bulk combustion (which were about the same weight as those used for stepped combustion) gave consistently good yields of sulphur of 100 ± 5% of the theoretical value. Moreover, the same method of sample evacuation was applied to samples in both types of experiment. Indeed a considerable effort was made in order to devise a method of evacuating the samples from atmosphere, specifically to avoid losing any sample powder. The effects of reason 3 should be very small, since trial experiments performed in order to cryogenically separate mixtures of known quantities of sulphur dioxide, carbon dioxide and water have shown that the VTCF (Section 2.2.1) achieve an excellent separation of these gases. Moreover, the analysis of a fairly pure sulphide mineral, such as troilite, will produce only very small quantities of carbon dioxide and water making the effects of this problem even more unlikely. This leaves options 4 and 5 as the principal mechanisms accounting for low yields and isotopic fractionation, they are discussed in more detail in Sections 2.4.1 and 2.4.2.

Isotopic measurements made on sulphur dioxide released above 700°C during stepped combustion seem to be free from error. Isotopic measurements for the reference mixture are shown in Figure 2.15 and in Table 2.4 the sulphur isotopic composition of each component in the reference mixture has been calculated by summing the δ^{34}S values measured over each temperature interval corresponding to a separate release in sulphur. When these δ^{34}S values are compared with those obtained by separate bulk combustions of each component (Table 2.4), the isotopic values compare favourably only for gypsum and epsomite, both of which decompose above 700°C. The difference between the two δ^{34}S values obtained for elemental sulphur is probably influenced mainly by the low yields (i.e. a kinetic isotope fractionation).

2.4.1 Kinetic isotope fractionation

The stepped combustion profile of Bella Roca troilite (Figure 2.14a) shows changes in δ^{34}S with varying temperature, these changes may result from the selective and progressive loss of one isotope due to a kinetic isotope fractionation. During the conversion of sulphur as troilite to sulphur dioxide the isotopic changes can be represented by the following equilibrium:

$$\mathrm{Fe^{32}S} + \mathrm{^{34}SO_2} \rightleftharpoons \mathrm{Fe^{34}S} + \mathrm{^{32}SO_2}$$

Where the species on the left of the equation are favoured. The change in the isotopic composition of the sulphide as it is progressively combusted can be described by the Rayleigh distillation equation:

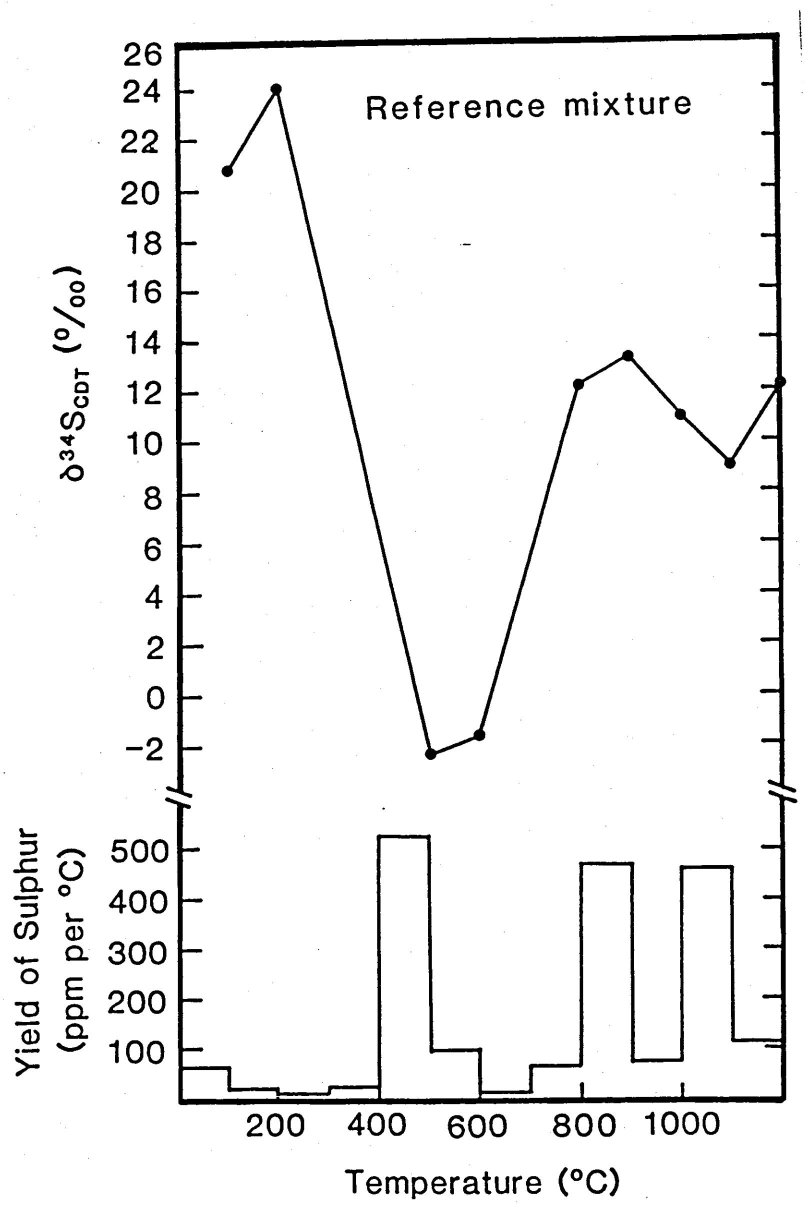


Figure 2.15 The abundance (—) and isotopic composition (–•–) of sulphur in the reference mixture as determined by stepped combustion.

Component	Stepped combustion			Bulk combustion	
	Temperature interval (°C)	% Yield	$\delta^{34}S$ (‰)	% Yield	$\delta^{34}S$ (‰)
Elemental S	0–300	16	+20.85	61	+15.92
Troilite	300–600	82	−2.13	98	−0.40
Gypsum	600–900	92	+12.32	97	+11.87
Epsomite	900–1200	100	+9.61	95	+9.79

Table 2.4 Comparison of sulphur data obtained for the reference mixture by stepped combustion and bulk combustion.

$$\delta^{34}S_r = \delta^{34}S_o + \varepsilon_{(SO_2/FeS)}.\ln f$$

$\delta^{34}S_r$ = isotopic composition of the residual material.

$\delta^{34}S_o$ = isotopic composition of the original material.

$\varepsilon_{(SO_2/FeS)} = 1000(\alpha - 1)$.

$\alpha = R_{SO_2}/R_{FeS}$.

$R = {}^{34}S/{}^{32}S$.

f = fraction of material remaining.

As $\delta^{34}S_o \sim 0‰$ in this instance, then the equation reduces to:

$$\delta^{34}S_r = 1000(\alpha - 1).\ln f$$

Figure 2.16 shows the isotopic composition of material with isotope effects ranging from 1 to 11‰. Figure 2.16 also shows the change in $\delta^{34}S$ of material remaining during progressive combustion of two sulphides; troilite (calculated from the data of Figure 2.14a, sample S079) and chalcopyrite (sample S080). The curves calculated from the stepped combustion data for troilite and chalcopyrite are comparable with the theoretical curves shown in Figure 2.16, particularly with that for the 1‰ effect. The troilite data show that 95% to 97% of the sulphide burns with a relatively constant isotopic composition, but the last 3% to 5% are strongly enriched in ^{34}S. When comparing the results of the troilite combustion with the theoretical curves (Figure 2.16), it must be remembered that the value of α is temperature dependent. Troilite combusts over the temperature range 400 to 600°C (Figure 2.14), the enrichment factors for sulphur dioxide over sulphide are between 11‰ (at 400°C) and 6‰ (at 600°C). In Figure 2.16, kinetic isotope fractionation

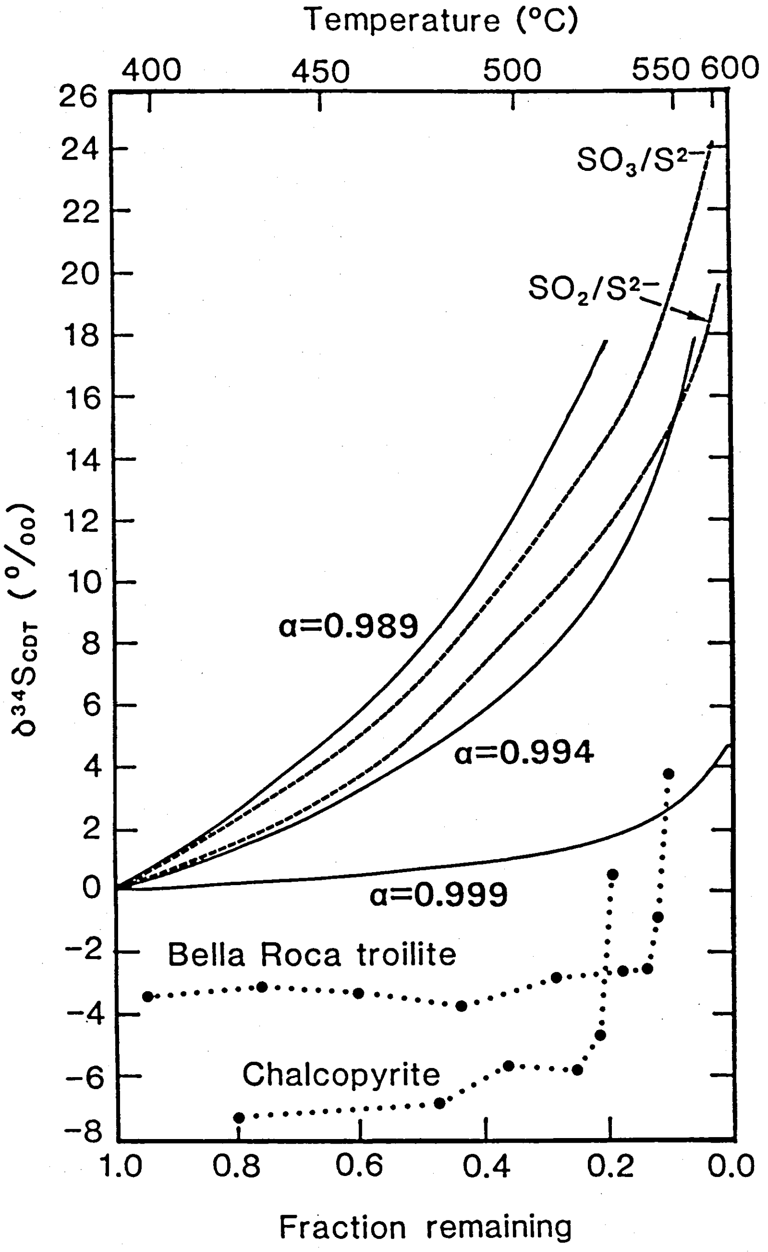


Figure 2.16 Calculated variation in $\delta^{34}S$ of material remaining for different isotopic fractionation between troilite and sulphur dioxide (solid line). Variation in $\delta^{34}S$ of material remaining during stepped combustion of troilite and chalcopyrite (dotted lines). Kinetic isotope fractionation curves for the experimental data of Bella Roca troilite stepped combustions with allowance for the change in the value of the fractionation factor with temperature (dashed line and temperature scale).

curves for sulphur dioxide and sulphur trioxide have been plotted where the effects of temperature on the value of α have been included. These curves are quite different from those of troilite and chalcopyrite (also in Figure 2.16) and suggest that, if a kinetic fractionation is involved during stepped combustion, it is not accompanied by an equilibrium fractionation.

Treatment of data obtained by stepped combustion of systems containing only one component (in this case either troilite, or chalcopyrite) is relatively straightforward. In meteorites, where a mixture of minerals are present, the situation is complicated because the combustion temperatures of different minerals will overlap to some extent. For this reason alone many of the meteorite isotope data will not resemble the curves of Figure 2.16, even though kinetic isotope effects may occur.

2.4.2 Sulphur trioxide

Considerable effort was expended in attempts to characterise the effects of sulphur trioxide production during the combustion experiments. In order to accomplish this, sulphur trioxide was prepared directly by oxidation of sulphur dioxide using platinum (on Triton Kaowool, BDH Chemicals Ltd., Poole, England) as a catalyst at 450°C and about 1 atm pressure of oxygen.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Under the conditions of the experiment sulphur trioxide did not remain in the gaseous phase, but formed fine white ice-like crystals on the reaction vessel walls which were mainly concentrated around the seats of the teflon valves. When these crystals were heated to temperatures just in excess of 100°C they changed from white to bright yellow, the latter being indicative of elemental sulphur. This colour change was accompanied by the formation of a gas, which when scanned in the mass spectrometer, was identified as sulphur dioxide. The reactions involved can be summarised as:

$$2SO_3 \rightarrow 2S + 3O_2$$
$$2SO_3 \rightarrow 2SO_2 + O_2$$

These results led to:

1. The incorporation of a furnace kept at 1000°C, positioned directly above the combustion furnace, to thermally reduce any sulphur trioxide as it formed.

2. Enclosing the entire reaction vessel with heater tape at 110°C, to prevent crystallisation of sulphur trioxide.

At first this arrangement appeared to work quite successfully as the whole-rock $\delta^{34}S$ values, obtained by stepped combustion of the first meteorites to be measured (C1 and C2 carbonaceous chondrites, see Chapter 3), were consistent with published data. Unfortunately, after the extraction line had been used for a series of fluorination experiments (Section 2.5 and Appendix A), it was found that whole-rock $\delta^{34}S$ values obtained by stepped combustion were between 2 and 3‰ lower than those acquired by bulk combustion.

It is known that low temperature (below 1000°C) equilibrium isotope exchange between sulphur dioxide and sulphur trioxide and/or sulphate results in sulphur dioxide with a $\delta^{34}S$ value lower than that of the sulphur in the more oxidised species (Tudge and Thode, 1950). Clearly, if sulphur trioxide had been formed during the stepped combustion then this could explain the anomalously low $\delta^{34}S$ values of sulphur dioxide. Evidence that some sulphur trioxide is formed during stepped combustion comes from comparing the data obtained by bulk combustion of troilite at 1200°C (which gave 100% of the theoretical yield of sulphur with isotopic value of −0.4‰) with the results obtained by stepped combustion of an identical sample, which gave only a 87% yield of sulphur with $\delta^{34}S = -2.5‰$ (Figure 2.14a). Further experiments, carried out using Bella Roca troilite, showed that only between 80 and 90% of the sulphur is liberated in the form of sulphur dioxide. The remaining 10 to 20% sulphur is assumed to be combusted to sulphur trioxide. The $\delta^{34}S$ value of the sulphur trioxide can be calculated using the equation:

$$\delta^{34}S_{SO_3} = (\delta^{34}S_{\mathrm{troilite}} - \delta^{34}S_{SO_2}.Y_m)/1-Y_m$$

Y_m = fractional yield of sulphur dioxide.

$\delta^{34}S_{SO_2}$ = measured isotopic composition of sulphur dioxide.

$\delta^{34}S_{\mathrm{troilite}}$ = true isotopic value of the troilite (−0.4‰).

The $\delta^{34}S$ values of sulphur trioxide formed during successive stepped combustions of troilite were found to vary between 1 and 25‰ (Table 2.5).

The magnitude of the sulphur trioxide problem should decrease as a function of temperature for two reasons. Firstly, sulphur trioxide is unstable at high temperature (T>1000°C), which accounts for the correct $\delta^{34}S$ values of the troilite obtained from bulk combustion analysis (at 1200°C). Secondly, the fractionation factors between sulphur trioxide and sulphur dioxide decrease with increasing temperature. Figure 2.17 shows curves plotted for the change in reduced fractionation factors with temperature for isotopic equilibria involving sulphur dioxide, sulphur trioxide and sulphides. The curves were calculated using the data of Richet et al. (1977). For the SO_3/SO_2

Sample	% Yield	$\delta^{34}S_{SO_2}$	$\delta^{34}S_{SO_3}$
S082	83	−3.02	+12.4
S083	92	−1.97	+17.7
S084	95	−1.45	+19.6
S085	95	−0.79	+7.0
S086	82	−1.00	+2.3
S087	81	−2.18	+7.3
S088	86	−2.59	+13.1
S089	87	−1.17	+4.8
S090	76	−1.28	+2.4
S091	94	−1.99	+24.5
S092	81	−0.81	+1.3

Table 2.5 Sulphur data for eleven consecutive stepped combustion analyses of Bella Roca troilite. The method used to calculate $\delta^{34}S_{SO_3}$ is given in the text.

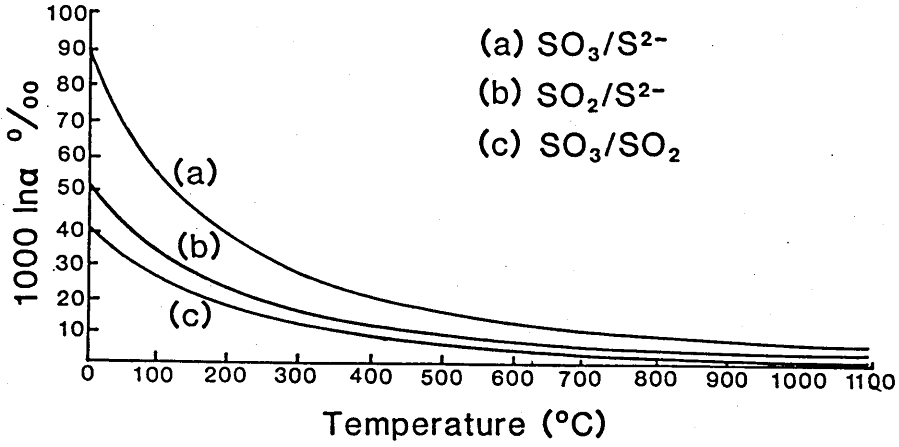


Figure 2.17 Calculated variation with temperature of the reduced sulphur isotope fractionation factors (1000lnα). Calculated from the data of Richet et al. (1977).

system the isotopic exchange process is represented by the following equilibrium:

$$^{32}SO_3 + {}^{34}SO_2 \rightleftharpoons {}^{34}SO_3 + {}^{32}SO_2$$

For which the fractionation factor is defined as:

$$\alpha = R_{SO_3}/R_{SO_2}$$

Where R = $^{34}S/^{32}S$ and the reduced fractionation factor equals $1000\ln\alpha$. For this equilibrium, $1000\ln\alpha$ is between 9‰ at 400°C and 6‰ at 600°C (the temperature interval over which troilite combusts). However, the enrichment in ^{34}S of sulphur trioxide is calculated from the experimental results, to be larger (between 1 and 25‰ heavier than the coexisting sulphur dioxide). Stronger isotopic fractionations are shown by the SO_3/S^{2-} and SO_4^{2-}/S^{2-} systems where enrichment factors at 400°C are 19‰ and 21‰ respectively, and at 600°C they are 9‰ and 13‰ respectively. However, it is unlikely that equilibrium between solids (S^{2-} and SO_4^{2-}) and a gas (SO_3) can be established even at these high temperatures. Moreover, the theoretical curves are not incontrovertible as deviation of experimental results from predicted values has been reported for other systems (Grinenko and Thode, 1970; Robinson, 1973).

Overall, the observations made indicate that there is a significant amount of sulphur trioxide forming along with sulphur dioxide during stepped combustion. The sulphur trioxide is clearly not reduced by the 1000°C furnace and the fate of this compound is problematical. As far as can be assessed it does not remain after the product gases, carbon dioxide and sulphur dioxide, have been cryogenically separated e.g. it is not identified in a mass scan of the sample gas. Presumably, it condenses onto the glass walls of the extraction line, and in particular, on the coolest areas of glass around the seats of the greaseless valves. A fine white film of crystals has been observed to develop around the seats of those valves which regularly came into contact with the product gases (this phenomenon is very similar to the result of the experiment designed to produce sulphur trioxide by direct oxidation of sulphur dioxide using a platinum catalyst). It is noted that sulphur trioxide formation was a more serious problem after fluorination experiments in the glass system.

Sakai and Yamamoto (1966) found that the yield of sulphur dioxide, formed by combustion of silver sulphide at 1200°C, decreased rapidly as the quartz tube, used for the combustion experiment, became devitrified after a number of samples had been analysed. The low yields were thought to be related to the increased capacity of sulphur trioxide to condense onto the rough surfaces of the devitrified glass (Sakai and Yamamoto, 1966). Although, during the present study, a fresh section of glass is used for each combustion experiment, it is possible that the fluorination experiments etched glass surfaces elsewhere in the extraction line which has enhanced the trapping or stabilizing of sulphur trioxide.

A number of different methods were tested in order to eliminate sulphur trioxide formed during stepped combustion, these included both thermal degradation and catalytic reduction. In these experiments, stepped combustions of Bella Roca troilite samples were undertaken and the gases formed during each temperature step were treated in different ways in an attempt to reduce any sulphur trioxide that may have formed. Sulphur trioxide is thermally unstable and will decompose at temperatures above 1000°C to form sulphur dioxide (Schenk and Steudel, 1968). In order to exploit this effect, the condensible reaction gases, obtained from each step of the combustion, were treated for five minutes to a temperature of approximately 1000°C. In another experiment, reduction of sulphur trioxide in the product gases was attempted using platinum as a catalyst at 500°C in the absence of oxygen (Schenk and Steudel, 1968). However, neither of these experiments appeared to have a significant effect in reducing sulphur trioxide, as the formation of this compound was again strongly suggested by the low yield of sulphur obtained as sulphur dioxide (between 80 and 90%) and the low $\delta^{34}S$ values (between -2 and $-3‰$). This result adds further support to the notion that sulphur trioxide condenses directly onto the glass, rather than being cryogenically transferred to the cold finger. This hypothesis was tested by heating the entire combustion tube and carrying out further stepped combustion experiments on Bella Roca troilite samples. The results of these experiments are shown in Figure 2.18. When the reaction vessel was heated to 200°C using heater tapes wrapped around the glass, some improvement in sulphur yield and bulk $\delta^{34}S$ values was noted. The yield of sulphur reaches 97% and the $\delta^{34}S$ value of sulphur dioxide is $-0.74‰$ at 220°C. Extrapolation of both graphs in Figure 2.18 suggests that at temperatures in the region of 250 to 270°C the theoretical yield of sulphur (36.36%, assuming pure FeS) and the true $\delta^{34}S$ value of the troilite ($-0.4‰$) will be attained. Unfortunately, the PTFE constituents of the greaseless valves (e.g. barrels, 'O' rings etc.) can only withstand a maximum temperature of about 200°C. Higher temperatures result in permanent deformation of the valve barrel making it impossible to seal the valve properly with the glass seat. In an attempt to overcome this problem the valve bodies were heated to 200°C while the rest of the reaction vessel was maintained at 400°C, the maximum attainable temperature of the heater tape. Under these conditions the maximum yield of sulphur was 87% and the $\delta^{34}S$ value was $-1.3‰$.

As it is impractical to heat the valves to higher temperatures the only remaining course of action would be to prevent sulphur trioxide forming from the sample during combustion. This may be achieved by careful con-

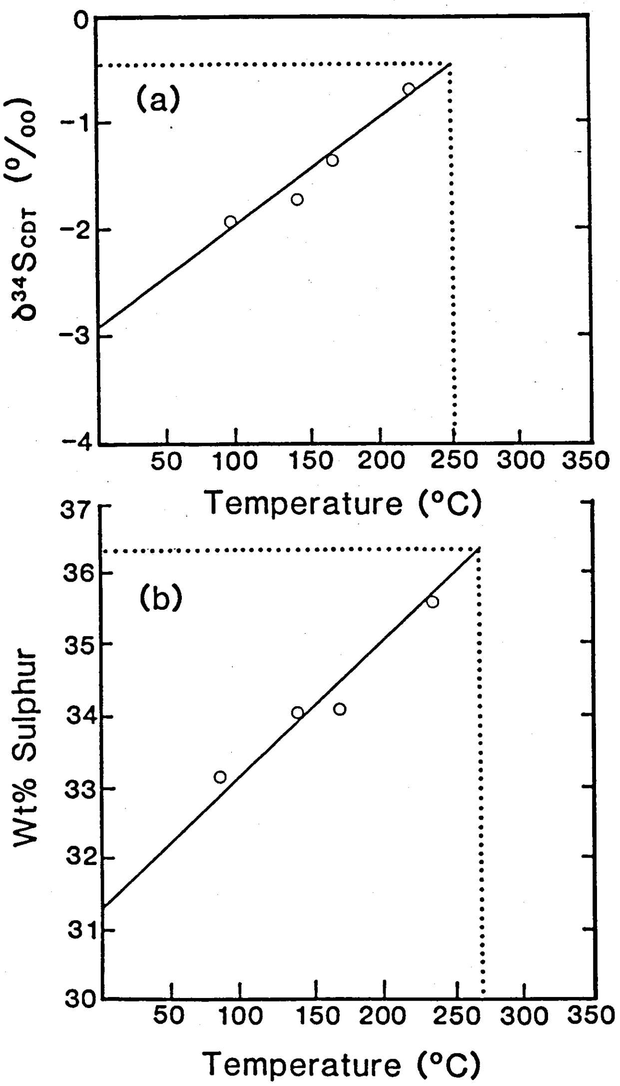


Figure 2.18 The effect of different temperatures on: (a) $\delta^{34}S$ value, and (b) yield of sulphur, for Bella Roca troilite stepped combustion experiments.

trol of the partial pressure of oxygen during combustion as sulphur trioxide formation will be favoured by a high pressure of oxygen. This is the method conventionally chosen to avoid sulphur trioxide formation during combustion. In conventional techniques, the partial pressure of oxygen is controlled by:

1. Using copper (I) oxide (as an oxygen donor) intimately mixed with the sample and combusted at elevated temperatures (above 1000°C) (Fritz et al., 1974; Robinson and Kusakabe, 1975).
2. Using mixtures of nitrogen and oxygen (Sakai and Yamamoto (1966).
3. Using vanadium pentoxide to oxidise the sample (Ricke, 1964).

Unfortunately, during stepped combustion it is almost always impossible to predict the amount of sulphur that will be released at each temperature step, hence, the amount of oxygen required can never be accurately known. However, it may be possible to use a copper (II) oxide finger connected directly to the combustion vessel. This arrangement would ensure that there is always a constant oxygen pressure during combustion.

$$2CuO \rightleftharpoons 2Cu + O_2$$

The extent of this equilibrium, and hence the oxygen pressure, is controlled by the temperature. Several trial experiments have been performed in an attempt to find the optimum conditions for the formation of sulphur dioxide without any sulphur trioxide. Some success has been achieved, with the copper (II) oxide heated to 720°C a 90% yield of sulphur from Bella Roca troilite with $\delta^{34}S$ of −0.84‰ has been attained. It is hoped that further experiments will improve the results.

2.5 Summary

An all-glass extraction system has been constructed to produce pure sulphur dioxide from meteorite samples. The extraction line is connected to a mass spectrometer capable of performing sulphur isotope analyses. Experiments carried-out on pure reference materials and mixtures have demonstrated that stepped combustion is capable of resolving sulphur from different components and this aspect of the technique has significant potential for the study of meteorites. However, isotopic measurements made on sulphur dioxide generated from samples below 600°Care fractionated to lower values by between 1 and 3‰. This fractionation probably results from the production of small quantities of sulphur trioxide. The ^{34}S isotope is preferentially partitioned into sulphur trioxide, which leads to sulphur dioxide with artificially low $\delta^{34}S$ values. Several attempts have been made to reduce the sulphur trioxide to sulphur dioxide including catalysis (using platinum) and thermal decomposition (above 1000°C). However, preliminary experiments have shown that controlling the partial pressure of oxygen during the combustion and hence, preventing sulphur trioxide formation altogether, is potentially the most likely method to overcome this problem.

2.6 Sulphur isotope measurements using sulphur hexafluoride

Sulphur hexafluoride has some favourable characteristics for mass spectrometry. The most important of these is that fluorine is monoisotopic, therefore, there are no isobaric corrections to be applied to the raw mass spectrometric data so $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ measurements are all possible. Measurement of the minor sulphur isotopes of sulphur are particularly relevant for studies of extraterrestrial materials since isotopes can be produced by different nuclear processes (e.g. nucleosynthesis, spallation reactions etc.) in various proportions. These effects have been predicted for sulphur (Clayton and Ramadurai, 1977) and observed for other elements (e.g. for oxygen; Clayton et al., 1973; Clayton and Mayeda, 1977; Clayton et al., 1977) For sulphur, where there are three stable isotopes, enrichments in one or other of the isotopes can be unambiguously identified as anomalous by departures from the mass fractionation relationships (Hulston and Thode, 1965a):

$$\delta^{33}S = \delta^{34}S/1.94$$
$$\delta^{36}S = 1.89 \times \delta^{34}S$$

Hulston and Thode (1965a) determined $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ measurements for separated sulphur compounds for a number of meteorites, but found no anomalous enrichments in any of the isotopes. However, none of the meteorites investigated in that study were of the type likely to have an isotopic anomaly. Some samples that may, potentially, yield unusual isotopic enrichments of sulphur were proposed by Pillinger (1984).

The instrument used in this study has been specially modified to enable either sulphur dioxide or sulphur hexafluoride to be analysed. An extended discussion of the application of sulphur hexafluoride, including experimental details of the methods used in this study for its formation is given in Appendix A. What follows here, is a summary of the results.

An isotopic reference gas, SF_6–1, was obtained (BDH Chemicals Ltd., Poole, England) and stored in a two-litre demountable glass bulb. Zero-enrichment tests performed using this gas showed that the precision of the isotopic measurements, using a sample size in the order of 10μg sulphur,

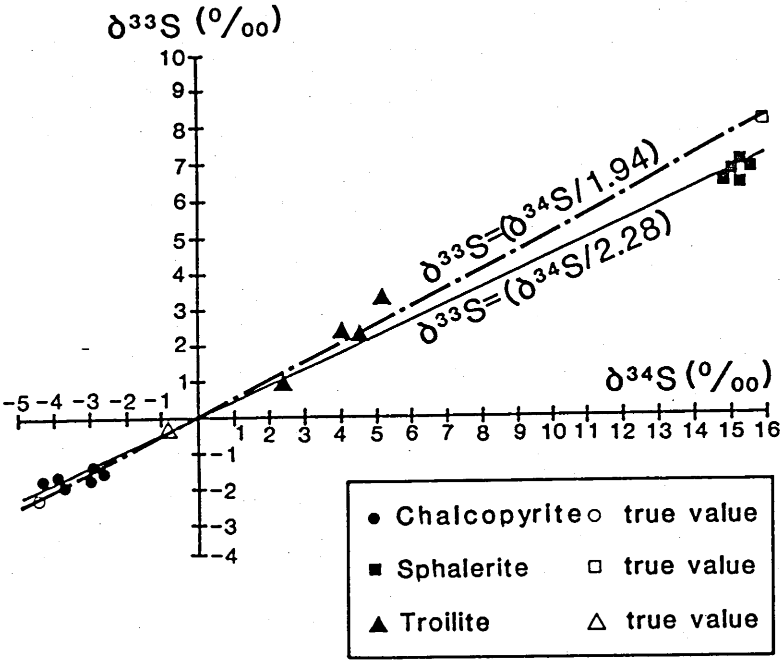


Figure 2.19 A graph of δ^{33}S versus δ^{34}S for three different sulphide minerals. Filled symbols – values obtained by fluorination (SF_6), open symbols – values obtained by bulk combustion (SO_2).

were: ± 0.7‰ for δ^{33}S, ± 0.1‰ for δ^{34}S and ± 3‰ for δ^{36}S. The minimum sample size on which isotopic measurements could be made was about 0.5μg sulphur as sulphur hexafluoride.

The preparation of sulphur hexafluoride was approached in two ways:

1. Using chlorine trifluoride in an all-metal system.
2. Using solid metal fluorides (AuF_3 and CoF_3) in a glass system.

The δ^{33}S and δ^{34}S measurements obtained using method (1) on three different sulphides (chalcopyrite, sphalerite and troilite) are given in Figure 2.19. The δ^{33}S and δ^{34}S values define a straight line,

$$\delta^{33}\mathrm{S} = \delta^{34}\mathrm{S}/2.28$$

With the exception of troilite the δ^{34}S values are close to those obtained by using sulphur dioxide produced from a bulk combustion experiment. δ^{36}S measurements made on sulphur hexafluoride samples were rendered meaningless by the presence of an unidentified contaminant at m/z 131, this is presumably the same as that encountered by Thode and Rees (1965).

Troilite (separated from the Bella Roca iron meteorite) gave consistently low yields of gas, this explains the spread of δ-values obtained for this mineral (Figure 2.19). The consistently low yields obtained using troilite, means that this method will be of only limited use for meteorites, as this mineral is usually the dominant sulphur-bearing component.

The reaction of solid metal fluorides with sulphides and elemental sulphur has been tested in an attempt to overcome the necessity of specialized handling techniques required for the use of chlorine trifluoride. A number of experiments were undertaken using the reactions of gold trifluoride and cobalt trifluoride with elemental sulphur and sulphides. These experiments have been conducted in the glass extraction line described in Section 2.2.1 and shown in Figure 2.9. Unfortunately, neither of the fluorides were successful in synthesising sulphur hexafluoride, mass scans of the product gases showed that they consisted mainly of silicon tetrafluoride, sulphuryl fluoride and thionyl fluoride. Furthermore, the use of fluorine compounds in the gas extraction system is thought to have been indirectly responsible for the problem of isotopic fractionation associated with sulphur trioxide formation during the stepped combustion experiments (Section 2.4.2).

In Appendix A, various methods are proposed in order to overcome the difficulties associated with the synthesis of sulphur hexafluoride (i.e. presence of contaminants, low yields and poor $\delta^{36}S$ measurements). These problems are probably not insurmountable, but they are considered to be beyond the scope of this research.

Chapter 3

The C1 and C2 Carbonaceous Chondrites

Sulphur is a constituent of all C1 and C2 carbonaceous chondrites being present in elemental form, and also as oxidised (e.g. sulphates) and reduced (e.g. sulphides) compounds. The importance of sulphur in these meteorites is demonstrated in Section 3.5.2 where it is is estimated that the sulphur components of Orgueil constitute 14 wt% of the meteorite. This study was directed firstly, at repeating samples for which sulphur isotopic measurements already exist, but thereafter, to explore samples for which the results are not predictable. Another aspect of the investigation was to validate, using stepped combustion, the chemical extractions employed by previous workers to concentrate or isolate specific sulphur-bearing minerals. To place the study in context there follows a brief introduction to the carbonaceous chondrites and a review of their sulphur-bearing components. This introduction is intended to serve also for the investigation of sulphur in C3, C4 and C5/6 meteorites which is discussed separately in Chapter 4.

3.1 General properties and classification

The carbonaceous chondrites, with around 67 members (Graham et al., 1985), constitute only about 1 to 2% of the world meteorite collections, and yet they are among some of the most studied materials of extraterrestrial origin. Really intense study of carbonaceous chondrites did not begin until after the fall of two hitherto rare types, the Pueblito de Allende meteorite (about 2000 Kg of material) in Mexico and the Murchison meteorite in Australia (about 100 Kg of material), both of which came to earth in 1969.

Carbonaceous chondrites are represented by a number of different petrologic types ranging from C1 through to C6. The C1 type, of which there are only five known examples, have special importance because they have bulk chemical compositions which most closely match those of the Sun and as such they are the primary source of information for the solar system abundances of elements and isotopes (Cameron, 1982). The term "carbonaceous chondrite", which was first used by Tschermak (1883), is misleading for two reasons. Firstly, the C1 meteorites do not contain chondrules and secondly, although the carbon contents of the group as a whole can be high (between 0.13 wt% and 3.30 wt%, Grady, 1983), there are comparable and even greater amounts of carbon found in enstatite chondrites (0.15 to 0.70 wt%; Grady et al., 1986), ordinary chondrites (0.01 to 1.77 wt%; Grady, 1983) and ureilites (0.2 to 5.9 wt%; Grady et al., 1985).

The origin of carbonaceous chondrites is uncertain, they may have an asteroidal source, or they may be residues derived from comets (Anders, 1975). This is one of the most fundamental issues of carbonaceous chondrite research as comets and asteroids are stored at vastly different distances from the Sun. Asteroids can be up to 100 km in diameter and are mainly located between the orbits of Mars and Jupiter (between 1.8 and 4.0 AU). Spectral reflectance studies of asteroidal surfaces indicate that C-type asteroids, which are the most abundant class, are probably composed of carbonaceous chondrite-like material (Larson et al., 1979; Feierberg et al., 1985). In contrast, comets are smaller bodies having diameters of between 1 and 10 km and are composed of volatile compounds (containing the elements H, C, N and O) with some refractory material (silicates and metal). Comets are stored in the Oort cloud which extends as far as 10^5 AU. If carbonaceous chondrites come from comets, then they are most likely to be the relatively nonvolatile residue which remains after the active life of the comet has ceased (Wasson and Wetherill, 1979).

The carbonaceous chondrites show a large degree of variation in texture, mineralogy and petrology. They are composed of varying amounts of fine-grained matrix which formed predominantly at low temperature (0.1 to 2μm particle sizes, consisting of hydrated ferromagnesian silicates, organic macromolecular material, magnetite and sulphides), and high temperature condensates (including chondrules, refractory inclusions, metal and Fremdlinge). Evidence from the isotopic composition of oxygen (Clayton et al., 1977) and magnesium (Gray and Compston, 1974; Lee and Papanastassiou, 1974; Lee et al., 1976) indicate that some of the refractory inclusions present in some C3 chondrites (calcium and aluminium-rich inclusions or CAI) may in part have a pre-solar origin. In contrast, many of the low temperature components were probably formed by secondary aqueous alteration of the primary minerals on the parent body (DuFresne and Anders, 1962a; Nagy and Claus, 1962; Bostrom and Fredriksson, 1966; Kerridge, 1964, 1979a,b; Kerridge and Bunch, 1979; McSween, 1979a). McSween (1979a) and Bunch and Chang (1980) have established the order of increasing aqueous alteration as being C1>C2>C3. The higher petrologic types of carbonaceous chondrites have suffered little or no aqueous alteration but have been subjected to static thermal metamorphism.

An initial classification of the carbonaceous chondrites was established by Wiik (1956) who subdivided them into types I, II and III, primarily on the basis of their carbon and water contents. Van Schmus and Wood (1967) later re-classified the carbonaceous chondrites into a single chemical group (C) with the retention of Wiik's numbers as C1, C2 and C3. C3 meteorites were further subdivided into C3(O), Ornans subtype, and C3(V), Vigarano subtype, by Van Schmus (1969) and Van Schmus and Hayes (1974). However, Wasson (1974) argued that chemical differences between different carbonaceous chondrites could not be rationalised in terms of a single chemical group and he classified them into separate chemical groups labelled CI, CM, CV and CO (where I, M, V and O represent the initial letters of the four type-meteorites, viz Ivuna, Mighei, Vigarano and Ornans); these groups correspond to the previous C1, C2, C3(V) and C3(O) classes respectively. Later, McSween (1979a) added a further group, CR, to include two meteorites (Renazzo and Al Rais) which, although having textural affinities to the CV meteorites and chemical similarities to the CM group, were significantly different in their oxygen isotopic compositions (Clayton and Mayeda, 1977) and free metal contents (containing up to 10% metal) to justify a separate grouping. Fitzgerald and Jones (1977) have proposed the inclusion of a further chemical subtype of the carbonaceous chondrites, designated CK, to include three meteorites; Adelaide, Bench Crater and Kakangari, based primarily on their low calcium contents. However, McSween (1977b) has raised the objection that, on petrographic grounds, these meteorites are too dissimilar to be included in the same group. Wilkening (1978) has suggested that Karoonda is the only representative sample of the CK group, however, the chemical data of Fitzgerald (1979) indicate that Karoonda has stronger affinities with the CV group. The inclusion of a CK group of carbonaceous chondrites still awaits universal acceptance. Some carbonaceous chondrites are ungrouped or have uncertain classifications (e.g. Adelaide, Allan Hills A77307). These are either 'unique', or are outlying members of established compositional clusters (Kallemeyn and Wasson, 1982).

The current classification of the carbonaceous chondrites is based upon the schemes of both Van Schmus and Wood (1967) and Wasson (1974), with the following groupings: CI1, CM2, CV3, CV4, CV5/6, CO3; this is illustrated in Figure 3.1. The C3→C1 association represents a progression of increasingly primitive chemical composition rather than a metamorphic series. There is evidence that the C3 chondrites have been affected by aqueous alteration, but to a lesser extent than the C1 and C2 meteorites (Kerridge, 1972; Bunch and Chang, 1980). Many C3 chondrites (e.g. Allende, Mokoia, Vigarano) contain abundant amounts of phyllosilicates and

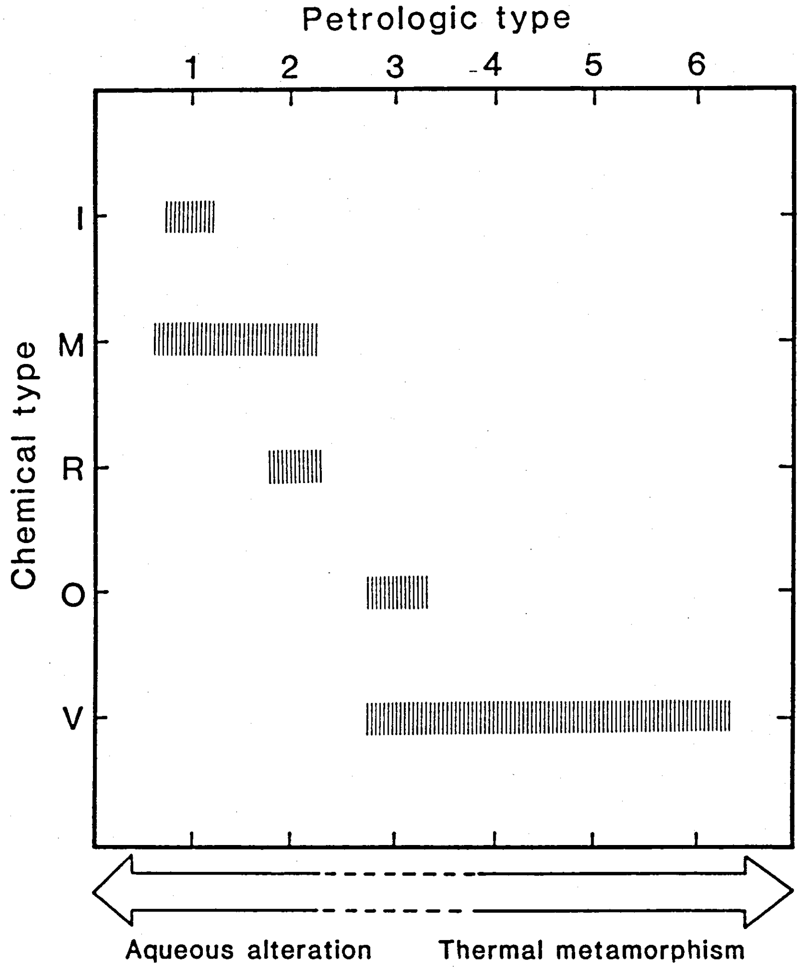


Figure 3.1 The classification of carbonaceous chondrites.

amorphous to poorly crystalline material resulting from the alteration of precursive olivine, metal and sulphides (Bunch and Chang, 1980; Grossman et al., 1986). Furthermore, Kerridge (1972) has identified iron-rich veins invading olivine chondrules in Warrenton (CO3) and has suggested that water may have been present during metamorphism of this meteorite.

Of the five known CI meteorites; Orgueil, Ivuna, Alais, Revelstoke and Tonk, only the first three are available in reasonable quantity for study. The CI meteorites are composed mainly of phyllosilicates and disequilibrium sulphide assemblages which were formed by aqueous alteration of pre-existing minerals (Kerridge et al., 1978a). Recently, Grady et al. (1986) have suggested that an Antarctic achondrite find (Yamato 82042), be classified as a CM1. This classification is based on data for oxygen isotopes and trace elements which indicate CM affinities, and textural/petrologic data (including the lack of chondrules) which suggests a C1 relationship. McSween (1979a), has previously considered the possibility of re-classifying Nogoya from its current CM2 status to a CM1, due to its exceptionally altered nature. Bunch and Chang (1980) report that 95% of the precursor minerals in Nogoya are altered.

A diagnostic feature of aqueous alteration appears to be the presence of phyllosilicates. In some cases the exact nature of these minerals is not well constrained and, as such, they are referred to collectively, as the "poorly characterised phases" (PCP), a term originally introduced by Fuchs et al. (1973), to describe a single phase of unknown identity in Murchison. Using the transmission electron microscope (TEM), the components of PCP are begining to be unravelled (Mackinnon and Zolensky, 1979; McKee and Moore, 1979; Bunch and Chang, 1980; Barber, 1981; Tomeoka and Buseck, 1982a,b, 1983a,b, 1985; Mackinnon and Zolensky, 1984). Despite this work, there is still uncertainty surrounding the mineralogical identity of some of the components of PCP. Tomeoka and Buseck (1985) have identified the following minerals in PCP: cronstedtite, chromite, magnetite, a Fe-Ni-Cr-P bearing mineral and a phase known as FESON (named after its predominant components, i.e. Fe, S, O and Ni). As such, the term PCP has been re-defined as "partly characterised phases" (Tomeoka and Buseck, 1985). FESON (the sulphur-bearing phase) is especially relevant to sulphur isotope studies since this component is known to contain much of the sulphur in the matrices of C2 chondrites (Fuchs et al., 1973; Bunch and Chang, 1980; Tomeoka and Buseck, 1985). Mackinnon and Zolensky (1984) have suggested that this phase has a structure and chemical composition similar to that of the terrestrial iron-rich form of tochilinite.

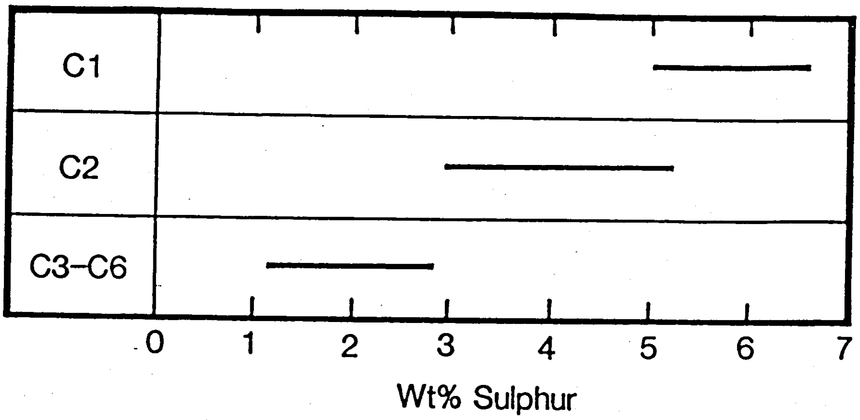


Figure 3.2 The sulphur content of carbonaceous chondrites. Data from Mason (1963).

3.2 The sulphur components of carbonaceous chondrites

The total sulphur concentrations of each subgroup of carbonaceous chondrites is shown in Figure 3.2 (due to their rarity, sulphur contents for C4-6 chondrites are included in with C3 data in this diagram). It can be seen that there is a decrease in sulphur content with increasing petrologic grade, the mean sulphur contents of C1, C2, and C3 chondrites are 5.9 wt%, 3.4 wt% and 2.2 wt% respectively (Mason, 1963). The major forms of sulphur in the C1 and C2 chondrites are elemental sulphur, sulphides, sulphates and organic sulphur (DuFresne and Anders, 1962a; Hayes, 1967); the C3, 4 and 5/6 chondrites contain predominantly sulphides. The major sulphur-bearing minerals of the carbonaceous chondrites are listed in Table 3.1 along with accessory sulphur minerals, the identity of some of the latter awaits confirmation. The most important sulphur compounds are now discussed in turn.

3.2.1 Elemental sulphur

Elemental sulphur is not a common constituent of carbonaceous chondrites. Organic solvents used to extract carbon compounds in CI chondrites inevitably yield elemental sulphur upon evaporation (Kaplan and Hulston, 1966). DuFresne and Anders (1962a) noted the presence of elemental sulphur in ether extracts of the following carbonaceous chondrites: Ivuna (CI1), Murray (CM2), Lancé (CO3) and Mokoia (CV3). Bostrom and Fredriksson (1966) measured a concentration of 1.7% elemental sulphur in Orgueil and

Mineral	Formula	C1	C2	C3	C4	C5/6
Chalcopyrite	$CuFeS_2$				•	
Cubanite	$CuFe_2S_3$	•				
Molybdenite	MoS_2			•		
Pentlandite	$(Fe,Ni)_9S_8$	•	•	•	•	•
Pyrite	FeS_2				•	
Pyrrhotite	$Fe_{1-x}S$	•	•		•	
Troilite	FeS	•	•	•	•	
Anhydrite	$CaSO_4$	•				
Bloedite	$MgSO_4.Na_2SO_4.4H_2O$	•				
Boussingaultite	$(NH_4)_2SO_4.MgSO_4.6H_2O$		(•)			
Epsomite	$MgSO_4.7H_2O$	•	•			
Gypsum	$CaSO_4.2H_2O$	•	•	(•)		
Elemental	S	•	•	•		
FESON	$Fe_{1.4}Ni_{0.1}SO_{1.4}$	(•)	•			
Organic	?	•	•			

Table 3.1 Known sulphur constituents of carbonaceous chondrites. After Nagy (1975) with modifications. • = present; (•) = presence suspected.

observed sulphur in the form of globules associated with corroded pyrrhotite grains. They also noted that some sulphur occurs as finely disseminated particles which are not easily identifiable by petrographic methods. Bass (1970) found sulphur crystals along the surfaces of cracks that cut carbonate- and sulphate-bearing veins in CI chondrites.

3.2.2 Sulphides

Troilite and pyrrhotite, FeS and $Fe_{1-x}S$

Troilite (FeS) is claimed to be a common constituent of nearly all carbonaceous chondrites. It is considered to be an end-member of the pyrrhotite series. Pyrrhotite ($Fe_{1-x}S$), which is a common terrestrial mineral, occurs in carbonaceous chondrites as a nickel-rich form.

There is confusion surrounding the exact nature of the iron sulphide in carbonaceous chondrites. DuFresne and Anders (1962a) consider that troilite is a rare mineral in CI chondrites, while Fitch et al. (1962) described both euhedral and corroded troilite crystals in Orgueil. Mason and Wiik (1962a) have described troilite in Renazzo and furthermore, "pure" troilite has been identified in Allende (Clarke et al. 1971), Coolidge (Scott and Taylor, 1985) and in other CV3 chondrites by McSween (1977a). A detailed study of 35 sulphide grains in Murray (Fredriksson and Keil, 1964) revealed nickel contents of between 0.95 wt% and 21.5 wt%; the Ni-rich grains were considered to be pentlandite and the Ni-poor grains attributed to troilite. It is clear therefore that the glib use of the term troilite to describe sulphides, which have not been analysed by the electron microprobe, in carbonaceous chondrites is perhaps somewhat erroneous. Ramdohr (1973), Folinsbee et al. (1967) and Kerridge (1976) have all pointed out that pyrrhotite is a more appropriate name for most of the "troilite" hitherto reported in carbonaceous chondrites. Both troilite and pyrrhotite are probably present in carbonaceous chondrites, with some or all of the pyrrhotite having a secondary low temperature origin (Kerridge, 1976).

Pentlandite, $(FeNi)_9S_8$

Pentlandite is often found intimately associated with troilite and/or pyrrhotite in carbonaceous chondrites. It is considered to be a secondary mineral which has formed by exsolution from troilite (Kerridge et al., 1979a). Kerridge et al. (1979a) observed pentlandite completely enclosed by pyrrhotite in Alais and determined that the compositions of the two minerals were not in equilibrium and therefore, unlikely to have formed during condensation from a gas of solar composition. Although troilite (or pyrrhotite) is usually considered to be the dominant sulphide mineral in carbonaceous chondrites, pentlandite is more abundant in some CV chondrites (McSween, 1977a) such as Allende (Clarke et al. 1971), Karoonda and PCA 82500 (Scott and Taylor 1985).

Patches of pentlandite (20μm diameter) were identified in Revelstoke (Folinsbee et al., 1967) and intergrowths of pentlandite and troilite were found in the matrix of Murchison (Fuchs et al., 1973). Bunch and Chang (1980) reported the presence of altered pentlandite in the matrices of two other CM2 chondrites, Nogoya and Murray. The nickel content of pentlandite in a number of different carbonaceous chondrites has been determined (Clarke et al., 1971; Kerridge et al., 1979; Bunch and Chang, 1980) and found to vary between 16.5 wt% to 39.0 wt%, these values compare with the normal nickel content of terrestrial pentlandite of 32.6 wt% nickel (assuming Fe/Ni=1; Hurlbut and Klein, 1977).

Minor sulphide minerals

Other sulphides have been found as accessory minerals in carbonaceous chondrites. Cubanite ($CuFe_2S_3$) was first identified by Macdougal and Kerridge (1977) in Orgueil and Alais and later in Ivuna (Kerridge et al., 1978). Cubanite appears to be restricted to CI meteorites where it has a secondary, low temperature origin. Ramdohr (1973) and Scott and Taylor (1985) have noted the presence of chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) in Karoonda and Scott and Taylor have also identified chalcopyrite in PCA 82500.

Molybdenite (MoS_2) has so far only been found in the CAI of Allende where it was discovered by Fuchs and Blander (1977). It occurs as elongated blades (16–24μm long) embedded in iron-nickel metal. Fuchs and Blander (1977) have proposed that during condensation of the nebular gas, molybdenum formed an alloy with iron and nickel and then, at lower temperature the molybdenum reacted with hydrogen sulphide gas in the nebula to form molybdenite.

3.2.3 Sulphates

Epsomite, $MgSO_4.7H_2O$

Epsomite was first identified in a carbonaceous chondrite (Orgueil) by Calvin (1961). It occurs in veins in CI chondrites along with gypsum and some carbonate minerals. Epsomite has been studied extensively in Orgueil where the exact concentration appears to be highly variable due to the heterogeneous distribution of this mineral. Estimates vary from 6.7% (Bostrom and Fredriksson, 1966) to 17% (DuFresne and Anders, 1962a) and 19% (Kaplan and Hulston, 1966). Epsomite occurring in veins has also been observed in Ivuna and Alais (Richardson, 1978).

Kerridge (1967) considers that sulphates are late-stage minerals in the carbonaceous chondrites, and were contemporaneous with brecciation. Furthermore, Kerridge (1964, 1967) has proposed that epsomite formed in the parent body regolith environment by the reaction of oxygen with sulphur dioxide or sulphur trioxide.

Gypsum, $CaSO_4.2H_2O$

DuFresne and Anders (1962a) isolated one large grain (100μg) of gypsum from Mighei. Nagy and Andersen (1964) identified gypsum in Orgueil and were able to perform a very detailed chemical analysis using the electron microprobe (19.1 wt% Ca, 3.1 wt% Fe, 15.5 wt% S and trace amounts of Si, Al and Mg), while Fuchs et al. (1970) found gypsum in the matrix of Murchison. Bass (1970) confirmed the presence of gypsum in all the C1 and C2 meteorites which he studied, even so, this mineral is not reckoned to be an important constituent of carbonaceous chondrites.

Nagy and Andersen (1964) considered that all the gypsum in carbonaceous chondrites was formed by the hydration of anhydrite in the earth's atmosphere. Anhydrite ($CaSO_4$) was tentatively identified in Orgueil by Bass (1970).

Other minor sulphates

Bostrom and Fredriksson (1966) proposed that sulphates containing other cations, notably Fe, Na, and Ni, may occur in carbonaceous chondrites. They found evidence for sodium sulphate (bloedite: $MgSO_4.Na_2SO_4.4H_2O$) near to the margins of veins. Boussingaultite ($(NH_4)_2SO_4.MgSO_4.6H_2O$) was was reported from Cold Bokkeveld and Haripura by Bass (1970) but its presence has not been corroborated by any later study.

3.2.4 Organic sulphur compounds

In a study unrelated to carbonaceous chondrites, Bryce and Hinshelwood (1949) have shown that, when sulphur is heated with alkanes, the products are thiols and sulphides. Thus, if both elemental sulphur and hydrocarbons were present in carbonaceous chondrites under conditions favourable for reaction, organic sulphur compounds would be the expected products (Murphy and Nagy, 1966).

Early studies revealed that organic compounds in carbonaceous chondrites (Mighei and Grosnaja) contain sulphur (Vdovykin, 1963). The identity of these compounds was later elucidated by Studier et al. (1965) who solvent-extracted Orgueil to reveal sulphonic acid esters ($R{-}SO_3{-}CH_3$). Murphy and Nagy (1966) found evidence for sulphur in heterocyclic aromatic compounds in Orgueil, but no evidence for open chain thiols (RSH) or open chain sulphides (R–S–R). Furthermore, Hayes and Biemann (1968) found sulphur in the inextractable polymeric material of Murray and Simmonds et al. (1969) pyrolysed Murray at 500°C to give a range of thiosphene related compounds.

3.3 Previous sulphur isotopic studies and the proposed origins of the sulphur compounds in carbonaceous chondrites

The first attempts to measure the sulphur isotopic composition of components in carbonaceous chondrites, were made by Briggs (1963) who reported the $\delta^{34}S$ value of organic matter in four carbonaceous chondrites to vary between +2.0‰ and +4.0‰). Unfortunately the use of organic solvents by Briggs (a benzene and methanol mixture) to extract the organic material would undoubtedly have also removed some of the elemental sulphur as well.

Sulphur isotope analyses of carbonaceous chondrites have also been undertaken in the past by Monster et al. (1965), and Kaplan and Hulston (1966), the results of the latter study were initially reported by Hulston and Thode (1965a). Monster et al. (1965) have conducted an investigation of Orgueil and attempted to make sulphur isotope measurements on the different sulphur species which were extracted, or concentrated, by means of chemical reagents. Troilite and elemental sulphur were found to be enriched in ^{34}S ($\delta^{34}S = +2.6$‰ and +1.5‰ for troilite and elemental sulphur respectively) relative to epsomite ($\delta^{34}S = -1.3$‰). A similar pattern of $\delta^{34}S$ values was obtained for the same three minerals by Kaplan and Hulston (1966), who extended the range of measurements to include three CM2 meteorites (Cold Bokkeveld, Mighei and Murray) in addition to Orgueil. In all cases the isotopic values averaged out to give bulk meteorite $\delta^{34}S$ values between 0‰ (Murray) and +0.5‰ (Cold Bokkeveld). Kaplan and Hulston obtained a whole rock $\delta^{34}S$ value for Orgueil of +0.35‰ which was almost identical to that obtained previously by Monster et al. (1965).

The nature of the primary sulphur bearing components in C1 and C2 meteorites remains unresolved. On the basis of sulphur isotope studies Monster et al. (1965) have suggested that elemental sulphur is the precursor mineral. However, elemental sulphur is not expected to be a primary condensation product from a gas of solar composition, nor has it been identified in any other class of meteorite. Alternatively, DuFresne and Anders (1962a) and Lewis (1967) proposed that the primary sulphur component of C1 and C2 meteorites was troilite.

Several possible chemical reactions which could involve sulphur components on the parent bodies have been considered.

1. Elemental sulphur with forsterite at high temperature followed by disproportionation reactions of the products to form sulphates (DuFresne and Anders, 1962a).
2. Sulphur with water, at temperatures less than 100°C, in neutral reducing conditions (Monster et al. 1965).
3. Troilite with water (Bostrom and Fredriksson, 1966).
4. The oxidation of troilite to form sulphates in a unidirectional reaction with hydrogen peroxide in an alkaline environment (Lewis, 1967).

Reaction (1) suffers from several disadvantages as was pointed out by Lewis and Krouse (1969). As already noted, elemental sulphur is not predicted to be a direct condensation product of the solar nebula. Pure forsterite is not a component of these meteorites, and the reaction of forsterite with elemental sulphur is thermodynamically unfavourable (Lewis and Krouse, 1969). The reaction proposed by Monster et al. (1965) (reaction 2) is:

$$4S + 3H_2O \rightarrow 2H_2S + S_2O_3^{2-} + 2H^+$$

This reaction was found to produce very similar sulphur isotopic fractionations to those which had been measured during their study of the sulphur components in Orgueil (i.e. an enrichment of ^{34}S in elemental sulphur and sulphate compared to sulphide). However three broad assumptions were made during the experiments.

1. That the hydrogen sulphide formed during the reaction is the precursor of all the troilite.
2. The sulphur oxyanions are the precursor of all the sulphates.
3. The effects on equilibrium by the presence of hydrogen sulphide were not considered, since this gas was removed from the reacting mixture as it formed.

The reaction of water with troilite (reaction 3) was proposed by Bostrom and Fredriksson (1966).

$$FeS + 2H_2O \rightarrow FeOOH + H_2S + \tfrac{1}{2}H_2$$
$$FeS + 2H_2O \rightarrow FeOOH + 1\tfrac{1}{2}H_2 + S$$

Both reactions produce limonite (FeOOH) which, together with sulphates and elemental sulphur, have been observed in close association with corroded pyrrhotite grains (Mueller, 1962; Nagy and Claus, 1962; Bostrom and Fredriksson, 1966; Bass, 1970). Indeed, Mueller (1962) has found limonite pseudomorphs of troilite in Ivuna and Orgueil where some 10μm-sized troilite crystals in Orgueil have been completely converted to limonite.

Lewis (1967) has suggested that troilite was the precursor of all the sulphur minerals in Orgueil. Using an initial suggestion of Bostrom and Fredriksson (1966), Lewis (1967) advocates the oxidation of troilite in a unidirectional reaction with hydrogen peroxide in an alkaline environment (reaction 4). Hydrogen peroxide could have formed by ultra-violet reactions occurring in a wet environment, possibly on a large asteroid capable of maintaining a trace of an atmosphere (Lewis, 1967).

The exact nature of the aqueous alteration event seems to have been complex. Veins of carbonate and sulphate have been identified in CI1 chondrites (Nagy and Claus, 1962; Nagy and Andersen, 1964; Richardson, 1978). Richardson (1978) has found evidence for three episodes of vein mineralisation, with calcite precipitation followed by anhydrite and then epsomite. Kerridge and Bunch (1979) suggested that vein formation in CI chondrites was contemporaneous with brecciation, since some of the veins are undisturbed by the brecciation event. This raises the possibility of impact heating as an important process for generating the aqueous fluids from which the sulphates and carbonates were deposited (Lange et al., 1985). An alternative fluid-generating process was proposed by DuFresne and Anders (1962a) who showed that internal heating, possibly by radionuclide decay, of an object containing chemically-bound water, could produce a narrow zone of liquid water within the object. This zone would slowly migrate towards the surface until it was immediately below an icy surface-layer. Whether this ice layer can remain intact during constant meteoroid bombardment was not considered by DuFresne and Anders, but thought to be likely by Kerridge and Bunch (1979). Constraints upon the fluid-generating processes can be eased if the alteration occurred at temperatures below the melting point of ice, due to the presence of an interfacial water layer along grain boundaries (Rietmeijer, 1985). Nevertheless, it is still necessary to invoke an active aqueous medium to account for vein mineralisation in C1 meteorites. Clayton and Mayeda (1984) have placed temperature constraints on the hydrothermal alteration episode, by using $^{18}O/^{16}O$ thermometry they propose that C1 material was altered at higher temperatures (100 to 150°C) than C2 material (<40°C). Therefore, the absence of veins in C2 chondrites may be explained by the lower temperature (than C1) of aqueous alteration.

3.4 Sulphur abundance and isotopic measurements determined by stepped combustion

An investigation of the isotopic composition of sulphur in carbonaceous chondrites was undertaken for a number of reasons. Primarily, since the work of Monster et al. (1965), Hulston and Thode (1965a) and Kaplan and Hulston (1966) a wealth of data has accumulated concerning the petrology and chemistry of the carbonaceous chondrites (McSween, 1979a; provides a review). These data have been used as a basis for many theories about the nature of the hydrothermal activity which played an important role in the early evolution of at least some of these meteorites. In light of recent developments in this field, it was considered that reappraisal of the sulphur isotopic composition of carbonaceous chondrites would be worthwhile. Since the 1965/1966 studies covered only a minimal number of meteorites, it was considered vital to include a number of additional samples for which no previous sulphur isotope measurements exist. The major differences between the sulphur abundance and isotopic data of this study with those determined previously, are discussed in Section 3.5.

In the following sections the stepped combustion profiles of sulphur obtained for the meteorites will be referred to the mixture of reference compounds which was described in Section 2.3.4, and which is reproduced in Figure 3.3. The composition of this mixture was chosen to be analogous to the sulphur mineral content of C1 and C2 chondrites in that it contains the four most common minerals; elemental sulphur, troilite, gypsum and epsomite.

3.4.1 Pre-analytical treatment

Between 5 and 20 mg of meteorite samples were taken for stepped combustion analysis from a "reservoir" of about 200mg of bulk sample which had been crushed to a fine powder (<50μm). Larger aliquants of Orgueil and Murchison were taken for treatment with hydrochloric and hydrofluoric acids for the preparation of residues OHF and MHF. These residues were prepared by Dr M.M. Grady in the following way: after extraction with organic solvents, samples of Orgueil and Murchison were reacted with 12M HCl for 12 hours at 18°C and then with HF acid for 48 hours at 18°C. The material which remained was re-treated with 12M HCl and the resulting residues washed until neutrality with distilled water. During preparation, OHF and MHF underwent weight losses of 95.5% and 97.7% respectively.

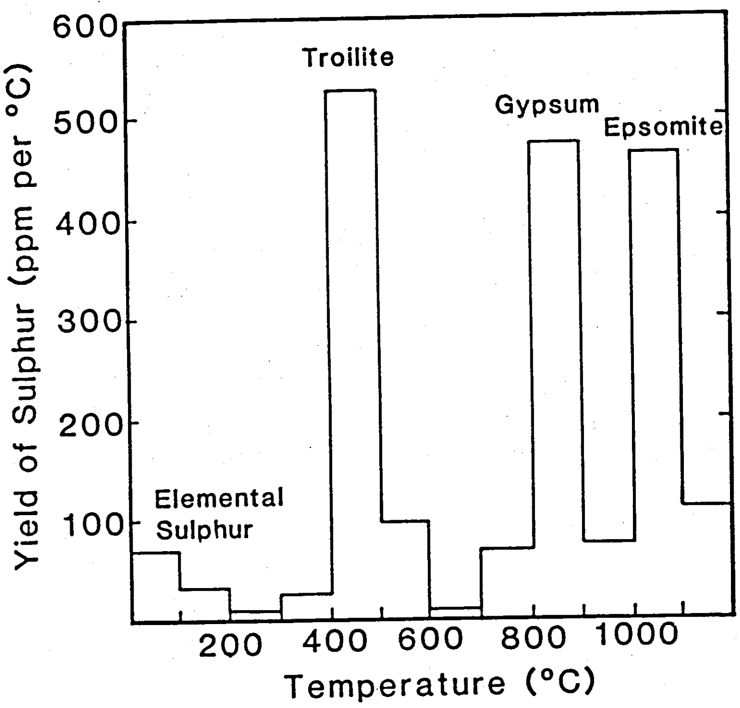


Figure 3.3 Sulphur released upon stepped combustion of the reference mixture.

Sample	Yield of sulphur Wt%	Lit. value sulphur Wt%	$\delta^{34}S$ (‰)	Lit. value $\delta^{34}S$ (‰)
Ivuna	2.94	6.70 (a)	+0.25	
Orgueil-a	2.83	5.49 (a)	+0.38	+0.35 (b)
Orgueil	4.38	5.96 (b)		0.00 (b)
Orgueil	3.72	4.08 (b)		+0.41 (c)
Y 82042	2.55	2.50 (d)	+0.37	–

Table 3.2 A summary of sulphur data obtained for C1 meteorites and comparison with previous measurements. References: (a) Mason (1963); (b) Kaplan and Hulston (1966); (c) Monster et al. (1965); (d) Graham and Yanai (1985).

3.4.2 C1 meteorites

The distribution and isotopic composition of sulphur was determined in two CI1 meteorites, Orgueil and Ivuna, and Yamato 82042 which is probably a CM1 chondrite (Graham et al., 1985; Grady et al., 1986). Four samples of Orgueil have been analysed, but only stepped combustion data for two of these, labelled Orgueil-a and Orgueil-b, will be discussed. The remaining two Orgueil samples are not considered further because poor isotopic measurements were obtained from these samples. Orgueil-a was analysed by stepped combustion from room temperature to 1200°C, whilst Orgueil-b was only stepped combusted up to 600°C. Orgueil-b was analysed in this way in order to assess the reproducibility of the method in the temperature region over which most of the carbon and water are released in this meteorite (the presence of small amounts of these compounds along with sulphur dioxide in the mass spectrometer have an adverse effect upon the sulphur isotope measurements and as such it is imperative that only pure sulphur dioxide is admitted to the instrument).

The stepped combustion profiles of the C1 meteorites are shown in Figure 3.4. The total sulphur contents and whole-rock $\delta^{34}S$ values obtained by summation of the stepped combustion data are compared with published values in Table 3.2. The total sulphur contents of Orgueil-a, Ivuna and Yamato 82042 are between 2.55 wt% and 2.94 wt%. There is good agreement for the sulphur content of Yamato 82042 obtained in this study with that determined previously by Graham and Yanai (1985), but the values obtained for Ivuna and Orgueil are significantly lower (by 56% in the case of Ivuna) than previous estimates (Table 3.2). The sulphur contents of the four

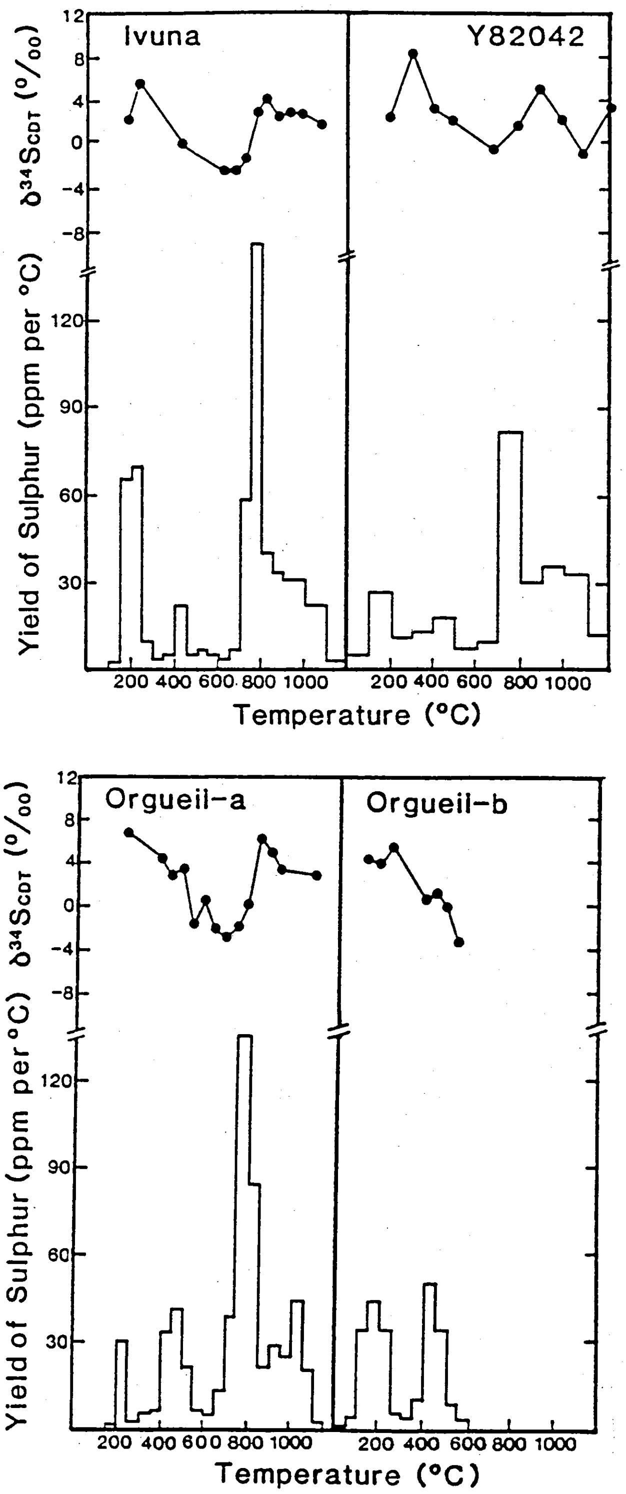


Figure 3.4 The abundance (—) and isotopic composition (-•-) of sulphur in C1 meteorites as determined by stepped combustion.

Orgueil samples vary between 2.83 and 4.38 wt% (Table 3.2), which suggests that this meteorite has a very heterogeneous distribution of sulphur. This is not surprising as most of the sulphur in Orgueil (and Ivuna) is concentrated in sulphate-bearing veins and it is possible that the quantity of material available for study (200mg), was not representative of the bulk meteorite. This argument is strengthened by the good agreement that was obtained between the sulphur abundances measured in this study for Yamato 82042 and C2 chondrites (Section 3.4.3, Table 3.6) with published analyses, since vein mineralisation is uncommon or absent in these samples.

The whole-rock $\delta^{34}S$ values are slightly positive (between +0.25‰ and +0.38‰), and are within the characteristic range for meteorites of ± 1‰ of CDT (Table 3.2). The whole-rock $\delta^{34}S$ value for Orgueil–a (+0.38‰), obtained by stepped combustion, is identical to that reported by Kaplan and Hulston (1966) for this meteorite (Table 3.2). It is apparent that the multi-release profiles of the C1 meteorites, shown in Figure 3.4, are qualitatively similar to each other and reminiscent of the stepped combustion profile obtained for the reference mixture (Figure 3.3). For the meteorites, the four releases of sulphur seen in the profiles can be tentatively assigned, in order of increasing temperature, to the following minerals.

1. Elemental and/or organic sulphur.
2. Sulphides. Probably troilite or pyrrhotite although possibly pentlandite as well.
3. Gypsum.
4. Epsomite.

Halbout et al. (1986) have previously reported results for a stepped combustion of sulphur in Orgueil, however, the yields of sulphur obtained were too low (a total yield of only 0.25 wt% sulphur) to permit a quantitative interpretation of the release profile. Halbout et al. did identify four main liberations of sulphur which occurred at similar temperatures to those observed from the stepped combustion data of Orgueil–a.

The abundance and $\delta^{34}S$ values for each of the sulphur-bearing components in these meteorites, are given in Table 3.3. A discussion of the methods used to calculate the values given in Table 3.3 now follows.

Organic, elemental and troilite sulphur

It is generally accepted that the carbonaceous material remaining after extraction with organic solvents and demineralisation with hydrochloric and

		Ivuna	Orgueil–a	Orgueil—b	Y 82042
Organic S	Yield (wt%)	0.12	0.16		0.04
	$\delta^{34}S$ (‰)	ND	+2.70		ND
Elemental	Yield (wt%)	0.65	0.10	0.55	0.36
	$\delta^{34}S$ (‰)	+1.91	+4.20	+1.35	+1.53
Sulphide	Yield (wt%)	0.15	0.48	0.47	0.39
	$\delta^{34}S$ (‰)	−2.75	−1.78	−2.34	−1.40
FESON	Yield (wt%)	0.41	0.78	–	0.88
	$\delta^{34}S$ (‰)	ND	ND	–	ND
Gypsum	Yield (wt%)	0.97	0.66	–	0.23
	$\delta^{34}S$ (‰)	ND	ND	–	ND
Epsomite	Yield (wt%)	0.63	0.66	–	0.97
	$\delta^{34}S$ (‰)	+0.23	+1.55		−0.43

Table 3.3 Summary of sulphur data for the constituents of C1 meteorites. ND = not determinable.

hydrofluoric acids, is representative of the carbon in the form of macromolecular organic material indigenous to the meteorite. Therefore, in order to assess what proportions of the material released at low temperature is due to sulphur in either elemental or organic forms, residue OHF was treated to a stepped combustion (Figure 3.5).

The stepped combustion profile of OHF shows that there is a bimodal release of sulphur, with maxima between 250 to 350°C and 400 to 500°C. The two releases suggest that the macromolecular material material in Orgueil is inhomogeneous. For instance, the low temperature sulphur may represent the combustion of side-chain material, with the more stable (core) material burning at higher temperature (Gilmour et al. 1985).

In OHF, 44% of the organic sulphur combusts (equivalent to 0.07 wt% sulphur in the bulk meteorite) between room temperature and 300°C. The first peak in the sulphur release of bulk Orgueil (Figure 3.4), occurs between room temperature and 300°C, for which the measured sulphur contents are 0.17 wt% for Orgueil–a and 0.62 wt% for Orgueil–b. Thus, a more realistic appraisal of the elemental sulphur contents can be calculated as being 0.10 wt% and 0.55 wt% in Orgueil–a and Orgueil–b respectively. The difference in elemental sulphur contents between the two Orgueil samples may be due to:

1. Sample inhomogeneity.

2. Problems associated with combusting elemental sulphur (this was dis-

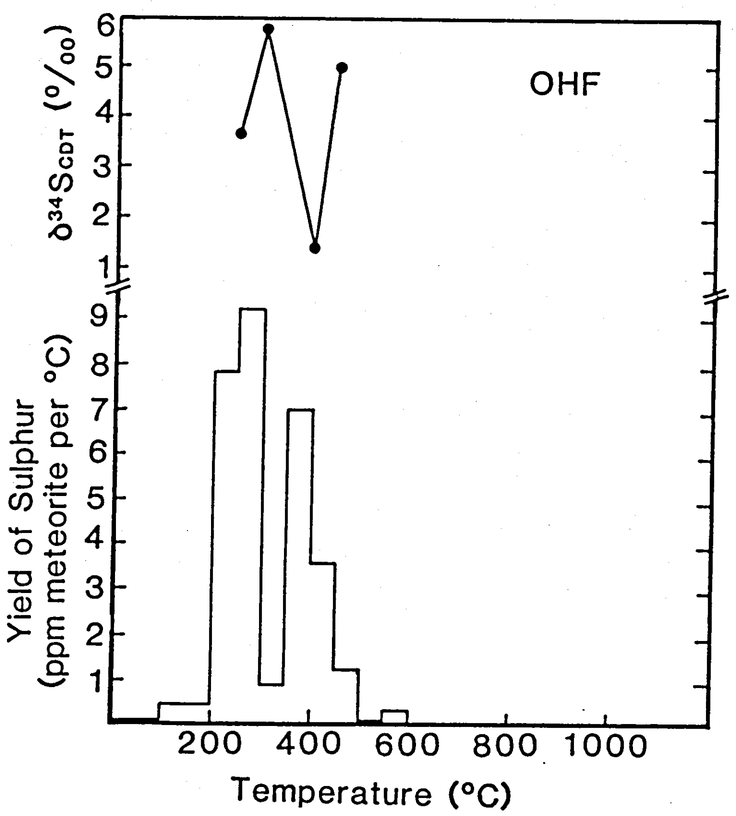


Figure 3.5 The abundance (—) and isotopic composition (-•-) of sulphur in Orgueil HF/HCl residue (OHF) as determined by stepped combustion.

cussed in Section 2.3.1).

3. A poor separation of sulphur dioxide from other product gases (notably carbon dioxide and water).

If any of these explanations are correct, then the higher value of 0.55 wt% elemental sulphur would seem more appropriate. Previous determinations for the elemental sulphur content of Orgueil include: 0.67 wt% (DuFresne and Anders, 1962a), 1.76 wt% (Hayatsu et al., 1963, quoted in Monster et al., 1965), 1.7 wt% (Bostrom and Fredriksson, 1966) and 1.8 wt% (Kaplan and Hulston, 1966).

The troilite sulphur content of Orgueil has not previously been defined with any firm conviction. Values of 0.8 wt% (Monster et al., 1965), 0.04 wt% (Kaplan and Hulston, 1966) and 1.65 wt% (Bostrom and Fredriksson, 1966) have all been reported. In the present study, it was not possible to determine troilite sulphur contents directly from the stepped combustion data because of interference from organic sulphur. An estimate of the troilite sulphur can be made, however, because between 300 and 600°C (the temperature range over which troilite burns), 56% (0.09 wt%) of the total organic sulphur (0.16 wt%) in OHF will combust (Figure 3.5). The quantities measured for the second peak in the sulphur release (300 to 600°C) are 0.57 wt% and 0.56 wt% for Orgueil–a and Orgueil–b respectively (Figure 3.4). Thus by difference, the amounts of troilite sulphur are calculated as being 0.48 wt% and 0.47 wt% for Orgueil–a and –b respectively.

The elemental and troilite sulphur contents of Ivuna (given in Table 3.3) can be estimated using the data from OHF by assuming that:

1. The C:S ratio of the acid- and solvent-insoluble macromolecular material in Ivuna, is identical to that of Orgueil.

2. The organic sulphur in Ivuna has a similar combustion pattern to that of Orgueil.

Smith and Kaplan (1970) determined a value of 2.15 wt% carbon for the acid- and solvent-insoluble macromolecular material in Orgueil, this can be used to obtain a C:S ratio of 13.44. Furthermore, Smith and Kaplan (1970) obtained a value of 1.57 wt% for the inextractable carbon of Ivuna. Using this information, the organic sulphur content of Ivuna is estimated to be 0.12 wt%.

In Ivuna, the sulphur released over the two temperature intervals, from room temperature to 300°C, and from 300 to 600°C, amounts to 0.70 wt% and 0.22 wt% respectively (Figure 3.4). Applying a correction for the amounts of organic sulphur liberated over these two temperature intervals gives values of 0.65 wt% elemental sulphur and 0.15 wt% troilite sulphur in

Ivuna. There are no published values for the contents of elemental sulphur and troilite in this meteorite. Since elemental and troilite sulphur appear to be genetically related in C1 meteorites (e.g. Bass, 1970), the relative proportions of these two minerals may be used as indication of the relative extent of aqueous alteration. The ratio of elemental to troilite sulphur is higher in Ivuna (4.33) than in Orgueil (0.96), which seems to indicate that Ivuna is more altered than Orgueil.

For Yamato-82042, carbon has been determined using stepped combustion of a whole-rock sample to be 1.05 wt% (Grady et al., 1986) which is low for a C1 chondrite. The carbon released below 600°C (i.e. from macromolecular organic material) amounts to 0.56 wt%, which is significantly less than that in Orgueil. Using similar reasoning as was applied to Ivuna, the organic sulphur content of Yamato 82042 is estimated to be 0.024 wt%. Assuming 13% (0.018 wt%) of the organic sulphur combusts below 300°C, then there is 0.37 wt% elemental sulphur in Yamato 82042. For sulphur liberated from between 300 and 600°C, there is estimated to be 0.024 wt% organic sulphur and thus 0.39 wt% sulphur as troilite. This gives a elemental to sulphide sulphur ratio in Yamato 82042 of 0.94, which suggests that Yamato 82042 is less altered than either Ivuna or Orgueil and this is consistent with its CM1 classification.

The $\delta^{34}S$ value for sulphur released below 600°C in OHF (Figure 3.5) is +2.7‰. Briggs (1963) has determined the stable isotopic composition of the organic sulphur in Orgueil to be +3.14‰. The isotopic value reported by Briggs is relative to the isotopic standard used by Thode et al. (1954). When this value is converted to the CDT scale, this transforms to +4.04‰. However, the $\delta^{34}S$ values obtained by Briggs must be considered with caution since the extraction technique involved the use of organic solvents which may have also removed some of the elemental sulphur.

Isotopic data obtained for temperature steps below 300°C in OHF ($\delta^{34}S$ = +4.1‰), can be employed to calculate the $\delta^{34}S$ value of the elemental sulphur in the Orgueil samples (Table 3.3). The values so obtained, are +4.20‰ in Orgueil–a and +1.35‰ in Orgueil–b. These compare with values of +1.4 to +3.0‰ from Monster et al. (1965) and +1.0 to +3.3‰ from Kaplan and Hulston (1966). Since Yamato 82042 is so depleted in organic sulphur, then the $\delta^{34}S$ value of +1.53‰ recorded from steps below 300°C, is probably the best direct estimate of the isotopic composition of elemental sulphur. There are no previous isotopic measurements available for the organic sulphur in Ivuna, but the $\delta^{34}S$ value of +1.91‰, recorded for steps below 300°C, probably represents an upper limit for the $\delta^{34}S$ of elemental sulphur in this meteorite.

As the quantity of organic sulphur liberated between 300 and 600°C in Yamato 82042 is estimated to be only 0.02 wt%, the $\delta^{34}S$ value recorded

Sample	Yield (600–900°C) wt%	Calc. gypsum wt%	Calc. Ca wt%	Lit. Ca wt%
Ivuna	1.38	7.42	1.73	1.34 (a)
Orgueil–a	1.44	7.74	1.80	0.87 (a)
Y 82042	1.11	5.97	1.39	1.21 (b)

Table 3.4 Contents of calcium as gypsum in C1 meteorites calculated from sulphur released between 600–900°C. References: (a) Mason (1963); (b) Graham and Yanai (1985).

in this temperature interval of +1.49‰ is probably representative of the isotopic compostion of troilite sulphur (Figure 3.4). Using the $\delta^{34}S$ value of +3.11‰ obtained for sulphur released between 300 and 600°C in OHF (Figure 3.5), to correct the summed $\delta^{34}S$ values for the 300 to 600°C sulphur in bulk Orgueil samples, gives values for sulphide of −1.78‰ and −2.34‰ for Orgueil–a and Orgueil–b respectively. Unfortunately, the quantities of sulphur released from Ivuna for temperature steps between 300 and 600°C, were generally too small for isotopic analysis and as such only a single measurement ($\delta^{34}S = -2.0$‰) was obtained. This undoubtedly represents a mixture of organic sulphur and troilite sulphur. The negative $\delta^{34}S$ values recorded for Orgueil and Ivuna troilite differ from that obtained for Yamato 82042 (+1.49‰) and previous $\delta^{34}S$ measurements reported for Orgueil troilite which include +3‰ (Kaplan and Hulston, 1966) and +2.6‰ (Monster et al., 1965). However, the results of this study agree with the overall sulphur isotopic fractionation that would be predicted for kinetic isotope effects associated with the aqueous alteration of troilite to elemental sulphur. Alteration of troilite should lead to a preferential transfer of ^{34}S into the oxidised sulphur component (elemental sulphur).

Sulphates and FESON

The concentrations of sulphur released between 600 and 900°C by stepped combustion of Ivuna, Orgueil–a and Yamato 82042 are given in Table 3.3. Assuming, in the first instance, that all the sulphur liberated over this temperature interval is from gypsum (as it is in the reference mixture, Figure 3.3), then the data can be used to calculate the contents of this mineral in the meteorites. The gypsum contents so derived, are given in Table 3.4 together with the equivalent amounts of calcium which are compared with literature values for the bulk calcium contents of the meteorites. From the data in Table 3.4, it can be seen that the calcium contents obtained from the "gypsum" values are consistently higher than the published bulk Ca contents. Although most of the Ca in C1 chondrites is probably in the form of gypsum, some of this element will also occur as carbonates (calcite and dolomite) and a smaller amount will be in pyroxene. These results indicate that in addition to gypsum, there is another major sulphur-bearing phase in the meteorites which combusts between 600 and 900°C. There is evidence that this sulphur-bearing phase could be the component of PCP known as FESON (Tomeoka and Buseck, 1985), or meteoritic tochilinite (Mackinnon and Zolensky, 1984). The matrices of CM2 chondrites and Orgueil are known to contain sulphur in greater amounts than can be explained by visible sulphides on an optical microscope scale (Bostrom and Fredriksson, 1966). For the CM2 chondrites, this has been explained by the presence of FESON in the matrix, formed by aqueous alteration of pre-existing kamacite and sulphides (Tomeoka and Buseck, 1985). The matrix of Orgueil and other C1 meteorites is mineralogically similar to that of the C2 chondrites and as such it has been proposed that FESON is also an important constituent of the C1 matrix (Tomeoka and Buseck, 1985). The proposed chemical formula of FESON is $Fe_{1.4}Ni_{0.1}SO_{1.4}$ (Tomeoka and Buseck, 1985) and is similar to that of a sulphate, which would be consistent with the relatively high combustion temperature (above 600°C) predicted for this component.

In an attempt to define the combustion temperature of FESON, a sample of tochilinite (from the Jacupiranga mine, Sao Paulo, Brazil and provided by Dr M.E. Zolensky) which is considered to be the terrestrial analogue to the sulphur-bearing component of PCP (Mackinnon and Zolensky, 1984), was treated to stepped combustion (Figure 3.6). Tochilinite releases 87% of its total sulphur (27.23 wt%) between 400 and 700°C. This is between 100 and 200°C lower than the suspected combustion temperature of FESON in C1 chondrites, however, this difference may be due to mineralogical and textural dissimilarities between FESON in the meteorite matrix and the pure terrestrial analogue.

If the interpretation that the 600 to 900°C sulphur represents a mixture of gypsum and FESON is valid, then it is possible to calculate the amounts of sulphur present in these two minerals (Table 3.5). Gypsum and FESON sulphur contents can be calculated as follows: firstly a small correction is applied to the bulk meteorite calcium data (of McSween and Richardson, 1977) to account for the amount of this element present as carbonate. The carbonate contents for Orgueil and Ivuna were determined by Dr M. M. Grady (unpublished data) and for the purposes of these calculations it is assumed that all the carbonate is present as calcite, although it is noted that other carbonate minerals are probably present including dolomite. After the correction for calcium as calcite, the remaining calcium is attributed

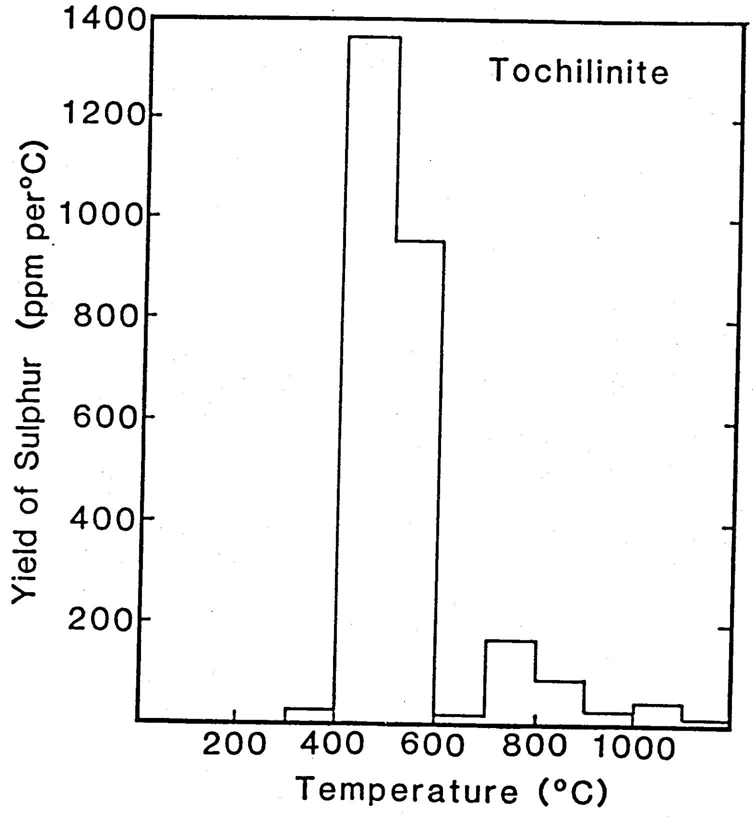


Figure 3.6 The abundance (—) of sulphur in terrestrial tochilinite as determined by stepped combustion.

Sample	Total Ca content wt%	Ca as carbonate wt%	S as gypsum wt%	Gypsum content wt%	S as FESON wt%	FESON content wt%
Ivuna	1.34 (a)	0.13 (c)	0.97	5.20	0.41	1.71
Orgueil-a	0.87 (a)	0.05 (d)	0.66	3.53	0.78	3.24
Y 82042	1.21 (b)	0.92 (d)	0.23	1.25	0.88	3.66

Table 3.5 Calculated gypsum and FESON contents of C1 meteorites. References: (a) and (b) as Table 3.4; (c) Smith and Kaplan (1970); (d) Dr M.M. Grady, unpublished data.

to gypsum. Quantities of sulphur as gypsum are calculated and subtracted from the total sulphur released between 600 and 900°C in the meteorite. The remainder of the sulphur was attributed to FESON. The calculated sulphur contents as gypsum are 0.97 wt% (equivalent to 5.20 wt% gypsum) in Ivuna, 0.66 wt% (or 3.53 wt% gypsum) in Orgueil-a and 0.23 wt% (or 1.25 wt% gypsum) in Yamato 82042 (Table 3.5). For Orgueil, the values for gypsum content calculated in this way, are all higher than previous determinations of 0.7 wt% by Kaplan and Hulston (1965) and 2.9 wt% by Bostrom and Fredriksson (1966).

The sulphur in FESON amounts to 0.41 wt%, 0.78 wt% and 0.88 wt% in Ivuna, Orgueil-a and Yamato 82042 respectively (Table 3.5). Therefore, the calculated concentrations of FESON are: 1.71 wt% in Ivuna, 3.24 wt% in Orgueil-a and 3.66 wt% in Yamato 82042. These data indicate that a significant amount of sulphur in C1 meteorites may occur as FESON, indeed, 30% of the total sulphur in Yamato 82042 can be attributed to this component. No previous study has determined the abundance of sulphur as FESON in C1 meteorites. The significance of the FESON data will be discussed in more detail in relation to the C2 chondrites in Section 3.5.3.

For data above 900°C (thought to be sulphur mainly as epsomite, as it is in the reference mixture, Figure 3.3) a sulphur content of 0.63 wt% is obtained for Ivuna, 0.66 wt% for Orgueil-a and 0.97 wt% for Yamato 82042 (Table 3.3). The calculated concentration of epsomite is thus, 4.84 wt% in Ivuna, 5.07 wt% in Orgueil and 7.46 wt% in Yamato 82042. As there is a certain amount of overlap in the combustion/decomposition temperatures of FESON/gypsum and epsomite, the epsomite contents are considered to be approximations. Most previous measurements of the epsomite content of Orgueil are much higher and include 16.96% (DuFresne and Anders, 1962a), 16 ± 1% (Monster et al., 1965), 18.99% (Kaplan and Hulston, 1966) and 6.7% (Bostrom and Fredriksson, 1966).

The total concentrations of sulphur as sulphate (gypsum and epsomite sulphur) for the data acquired by stepped combustion, are; 1.32 wt% (equivalent to 46% of the total sulphur) for Orgueil, 1.70 wt% (54% of the total sulphur) for Ivuna and 1.20 wt% for Yamato 82042 (42% of the total sulphur. These figures are somewhat lower than is suggested by previous determinations for Orgueil of 2.21 wt% (DuFresne and Anders, 1962a), 2.08 wt% (Monster et al., 1965) and 2.47 wt% (Bostrom and Fredriksson, 1966).

An indication of the relative extent of aqueous alteration of the C1 meteorites considered in this study, can be gained by considering the ratio of oxidised sulphur (i.e. elemental, sulphate and FESON) to reduced sulphur (i.e. sulphide) in each of the samples. The ratios so obtained show that the alteration sequence is Ivuna (17.7)>Yamato 82042 (6.3)>Orgueil (4.6). Thus, it seems that, while Yamato 82042 and Orgueil have been subjected to about the same degree of alteration, Ivuna has experienced considerably more hydrothermal processing.

It has been suggested that, in addition to gypsum and epsomite, there may be minor sulphate minerals present in C1 chondrites (Table 3.1). These include hydrated sulphates of sodium and calcium, and sodium and magnesium (Bostrom and Fredriksson, 1966; Richardson, 1978). DuFresne and Anders (1962a), isolated a single crystal of bloedite ($MgSO_4.Na_2SO_4.4H_2O$) from Ivuna. Sodium sulphate appears-to be present in Orgueil at concentrations up to 0.6 wt% (Bostrom and Fredriksson, 1966) this corresponds to a sulphur content of 0.01 wt% (assuming merabilite, $Na_2SO_4.10H_2O$). It is not surprising that the exact nature and chemical composition of sulphate is poorly known, as sulphates are finely disseminated within the matrices of C1 chondrites (Bostrom and Fredriksson, 1966; Richardson, 1978). Even the exact form of magnesium sulphate is not well known, it occurs both as epsomite ($MgSO_4.7H_2O$) and hexahydrite ($MgSO_4.6H_2O$); it is also possible that kieserite ($MgSO_4.H_2O$) may have been a pre-terrestrial form (Richardson, 1978).

From the stepped combustion data obtained for the reference mixture (Figure 3.3) it is considered that most of the sulphur liberated above 900°C is from epsomite. Assuming that the same is true for sulphur in the C1 meteorites, then it is possible to say that the $\delta^{34}S$ value of epsomite is +1.55‰ in Orgueil–a, +0.23‰ in Ivuna, and −0.43‰ in Yamato 82042 (Table 3.3). As with the isotopic data for sulphide sulphur, there is a clear discrepancy between the $\delta^{34}S$ values for epsomite of this study with those reported previously (discussed in Section 3.5) which for Orgueil include $\delta^{34}S$ values of −1.6‰ and −1.7‰ from Kaplan and Hulston (1966) and −1.3‰ reported by Monster et al. (1965).

The gases liberated from 600 to 900°C are probably a mixture of sulphur from gypsum and FESON. Inspection of the stepped combustion profile (Figure 3.4) shows that the $\delta^{34}S$ values vary markedly between 600 and 900°C (from −4.5‰ to +1.9‰ in Ivuna, −4.8‰ to +4.5‰ in Orgueil, and −2.3‰ to +3.1‰ in Yamato 82042) which is strong evidence that sulphur is being liberated from at least two components with quite different $\delta^{34}S$ values. Kaplan and Hulston (1966) suggested that gypsum sulphur has $\delta^{34}S$ = 0‰ in Orgueil. Because of the disagreement in $\delta^{34}S$ values, for sulphur in troilite and epsomite, between the present study and that of Kaplan and Hulston (1966), it is unjustifiable to use the $\delta^{34}S$ value for gypsum sulphur, determined by Kaplan and Hulston, to estimate the sulphur isotopic composition of FESON.

Sample	Yield wt%	Literature wt%	δ^{34}S (‰)	Literature δ^{34}S (‰)
Kivesvaara	1.74	3.00 (a)	+1.10	-
Mighei	2.65	2.99 (b) 3.66 (c)	−0.76	+0.30 (b)
Murchison	3.38	2.99 (d) 3.24 (e)	+0.40	-
Murray	3.07	2.26 (b) 2.80 (c)	+1.27	−0.01 (b)
Nogoya	2.84	3.27 (c)	+1.18	-
Al Rais	1.82	2.66 (c)	−1.09	-
Renazzo	1.05	1.31 (c)	−0.65	-

Table 3.6 Summary of whole-rock sulphur data for C2 chondrites and comparison with published values. References: (a) Kinnunen and Saikkonen (1983); (b) Kaplan and Hulston (1966); (c) Mason (1963); (d) Jarosewich (1971); (e) Fuchs et al. (1973). Note: Kaplan and Hulston (1966) also measured δ^{34}S = +0.52‰ for Cold Bokkeveld (CM2).

3.4.3 C2 chondrites

The stepped combustion profiles of five CM2 chondrites (Kivesvaara, Mighei, Murchison, Murray and Nogoya) are given in Figure 3.7 and those for two CR2 meteorites (Al Rais and Renazzo) are shown in Figure 3.8. As the sulphur chemistry of CR2 meteorites is similar to that of the CM2 meteorites, the results from both types will be discussed together. In Table 3.6 the whole-rock δ^{34}S values and sulphur contents of the C2 chondrites, analysed in this study, are compared with published values. For the CM2 chondrites the total sulphur contents fall within the range 1.74 wt% (Kivesvaara) to 3.38 wt% (Murchison) and all measurements except for Kivesvaara are in reasonable agreement with previously reported values (Table 3.6). The sulphur contents measured during this study for the CR2 meteorites are generally lower than those of the CM chondrites; Al Rais contains 1.82 wt% and Renazzo 1.05 wt% sulphur (Table 3.6). It is noteworthy that the sample of Kivesvaara analysed in this study contains significantly less sulphur than other CM2 chondrites. However, the value of 1.74 wt% sulphur for this meteorite is at variance with the whole-rock data of Kinnunen and Saikkonen (1983) who determined the sulphur content of Kivesvaara to be 3.00 wt%. Perhaps the sample analysed herein contains a relatively higher proportion

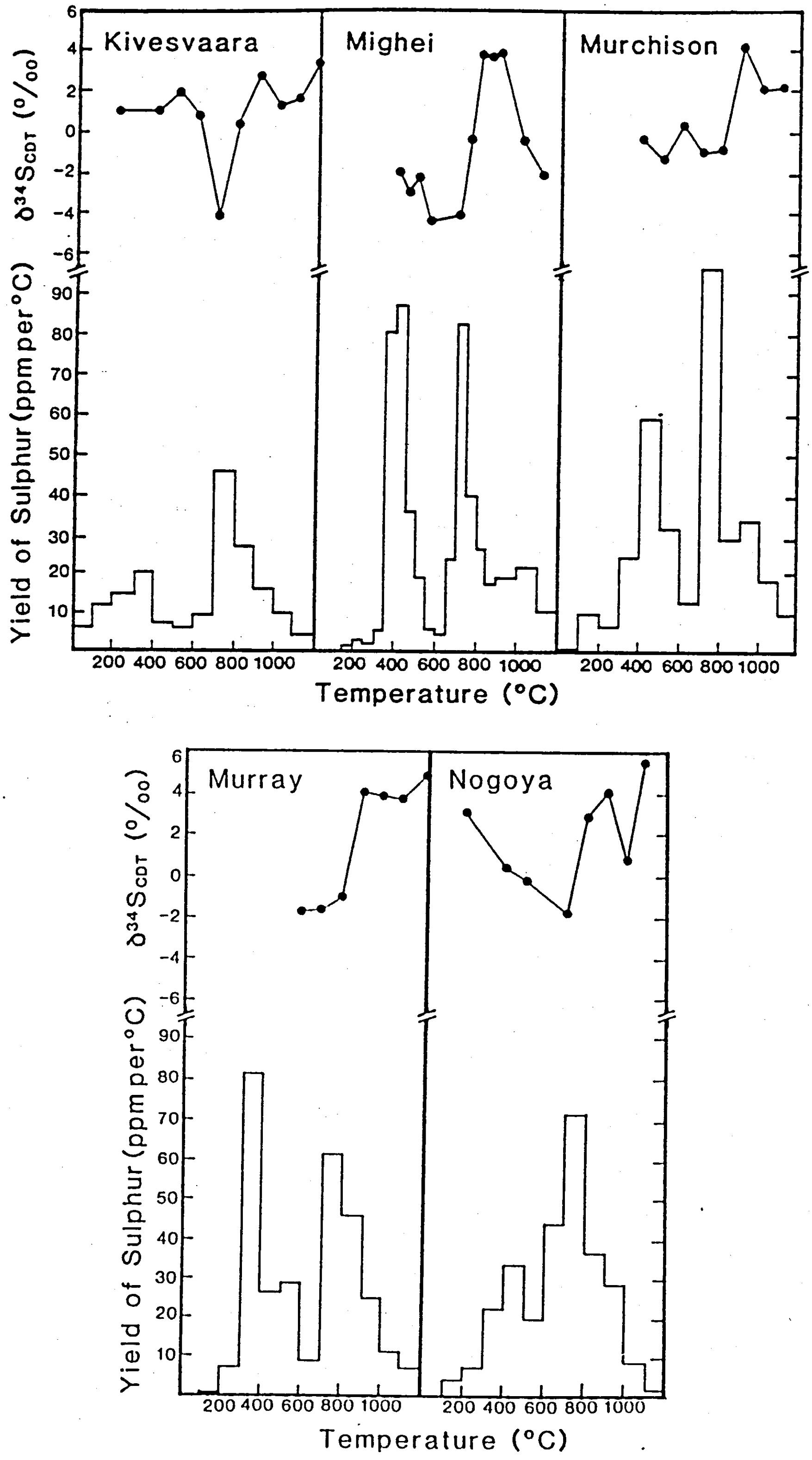


Figure 3.7 The abundance (—) and isotopic composition (-•-) of sulphur in CM2 chondrites as determined by stepped combustion.

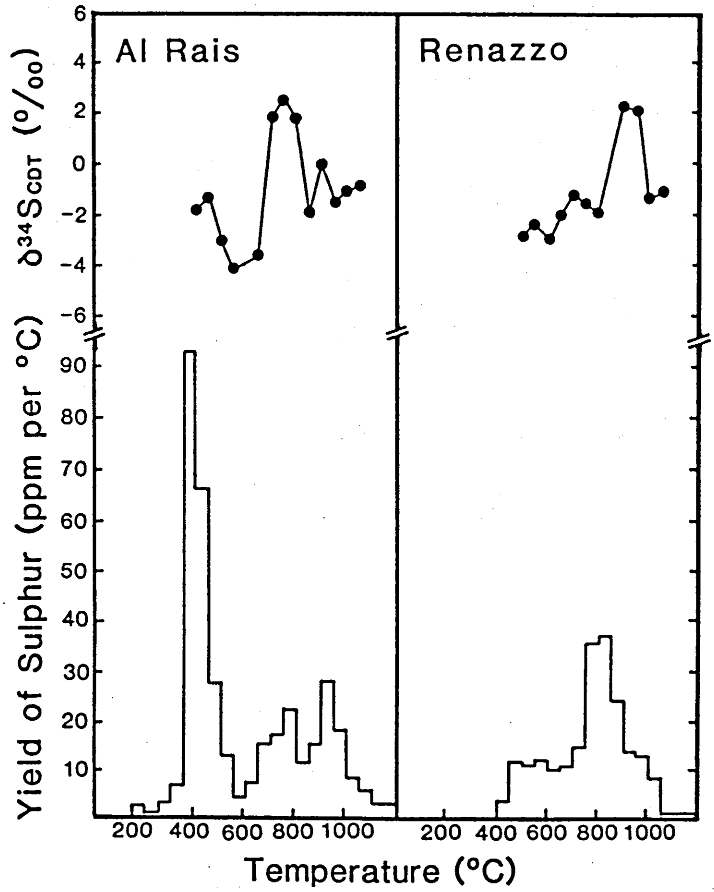


Figure 3.8 The abundance (—) and isotopic composition (-•-) of sulphur in CR2 chondrites as determined by stepped combustion.

	Kivesvaara	Mighei	Murchison	Murray	Nogoya	Al Rais	Renazzo
Organic S							
Yield (wt%)	0.25	0.17	0.25	0.32	ND	ND	0.09
δ^{34}S (‰)	ND	ND	−0.11	ND	ND	ND	ND
Elemental							
Yield (wt%)	0.11	ND	0.07	ND	ND	ND	ND
δ^{34}S (‰)	ND	ND	ND	ND	ND	ND	ND
Sulphide							
Yield (wt%)	0.21	1.04	0.87	1.04	ND	1.04	0.16
δ^{34}S (‰)	+2.60	−2.47	−0.56	−0.05	ND	−1.80	−2.20
FESON							
Yield (wt%)	0.51	0.90	1.00	–	1.17	0.22	0.46
δ^{34}S (‰)	ND	ND	ND	ND	ND	ND	ND
Gypsum							
Yield (wt%)	0.21	0.05	0.41	–	0.28	0.20	0.15
δ^{34}S (‰)	ND	ND	ND	ND	ND	ND	ND
Epsomite							
Yield (wt%)	0.44	0.50	0.79	0.68	0.59	0.34	0.25
δ^{34}S (‰)	+2.17	−0.52	+2.37	+4.05	+2.54	−0.75	+0.69

Table 3.7 Summary of sulphur data for C2 chondrites. ND = not determinable.

of matrix (which is known to be sulphur-deficient in CM2 meteorites; McSween and Richardson, 1977).

The main liberations of sulphur during stepped combustion of C2 meteorites occur at similar temperatures in all the samples. It can be seen from Figures 3.6 and 3.7 that there are two main releases of sulphur in the case of Kivesvaara, Nogoya and Renazzo, three for Mighei, Murray and Al Rais and four distinct releases in Murchison. As in the previous section for C1 meteorites, the results can again be interpreted on the basis of the profiles obtained for the reference mixture. The δ^{34}S values and sulphur contents for different sulphur-bearing components of C2 chondrites are given in Table 3.7. Stepped combustion analyses for sulphur in CM2 chondrites have been undertaken previously by Halbout et al. (1986), for Murchison, Murray and Cold Bokkeveld. The sulphur release profiles were similar to those obtained during the present study for Murchison and Murray. However, as with their analysis of Orgueil, Halbout et al. (1986) obtained very low yields of sulphur for the CM meteorites analysed.

Organic, elemental and troilite sulphur

The presence of elemental sulphur in CM2 chondrites is poorly constrained. Kaplan and Hulston (1966) detected small amounts of elemental sulphur in some CM2 meteorites (e.g. Cold Bokkeveld, Murray) but found it to be absent from other samples (e.g. Mighei). Jarosewich (1971) found no evidence for elemental sulphur in Murchison but Fuchs et al. (1973), during a detailed study of this meteorite, suggested a value of 0.49 wt%, although it is possible that this value may be an overestimate because the analytical technique, involving the use of solvents, may have extracted some organic sulphur. For C2 samples, concentrations of sulphur burning below 300°C (Table 3.7) range from 0.003 wt% (Renazzo) to 0.20 wt% (Kivesvaara). Only Murchison and Kivesvaara show any real evidence for a release of sulphur below 200°C which is in contradistinction to the results obtained from the C1 meteorites. The stepped combustion profile for MHF (i.e. an HF/HCl residue of Murchison) is given in Figure 3.9. It is noted that MHF has a bimodal release of sulphur occurring at similar temperatures to the two sulphur releases identified in OHF. As with OHF, the bimodal release in MHF may be an indication of the structure of the macromolecular material present in Murchison. The sulphur combusting below 600°C in MHF is equivalent to 0.25 wt% sulphur in the bulk meteorite, which is significantly more than was obtained for the organic sulphur content of Orgueil (0.16 wt%). Using the value of 1.48 wt% carbon reported for the HF/HCl residue of Murchison (Swart et al., 1983; Wright et al., 1984) the C:S ratio is calculated as 5.9, which compares with a ratio of 13.44 in Orgueil. In Figure 3.9, 29% (or 0.08 wt%) of the organic sulphur in Murchison is released between room temperature and 300°C which can be used to correct the amount of sulphur released between room temperature and 300°C in Murchison (0.15 wt%), which gives an elemental sulphur content for this meteorite of 0.07 wt%. It is possible to estimate the proportions of elemental and troilite sulphur in other C2 chondrites (Table 3.7) by assuming that the acid- and solvent-insoluble material in these meteorites has:

1. An identical C:S ratio to that in Murchison.
2. The same combustion characteristics as that in MHF.

Carbon contents for the organic fractions have been determined for Murchison and three other samples considered in this study; 1.88 wt% in Murray (Grady, 1982), 1.50 wt% in Kivesvaara (Dr D.W. McGarvie, unpublished data) and 1.00 wt% in Mighei (Dr M.M. Grady, unpublished data). From these data the elemental sulphur content of Kivesvaara is estimated to be 0.11 wt%. However, for Mighei and Murray the concentrations of organic sulphur calculated to be released between room temperature and 300°C are greater than those measured directly from the stepped combustion data. It is apparent that in Murray and Mighei, either the organic fraction has a different C:S ratio (i.e. higher), or the organic sulphur has different combustion characteristics compared to that in Murchison (i.e. relatively less

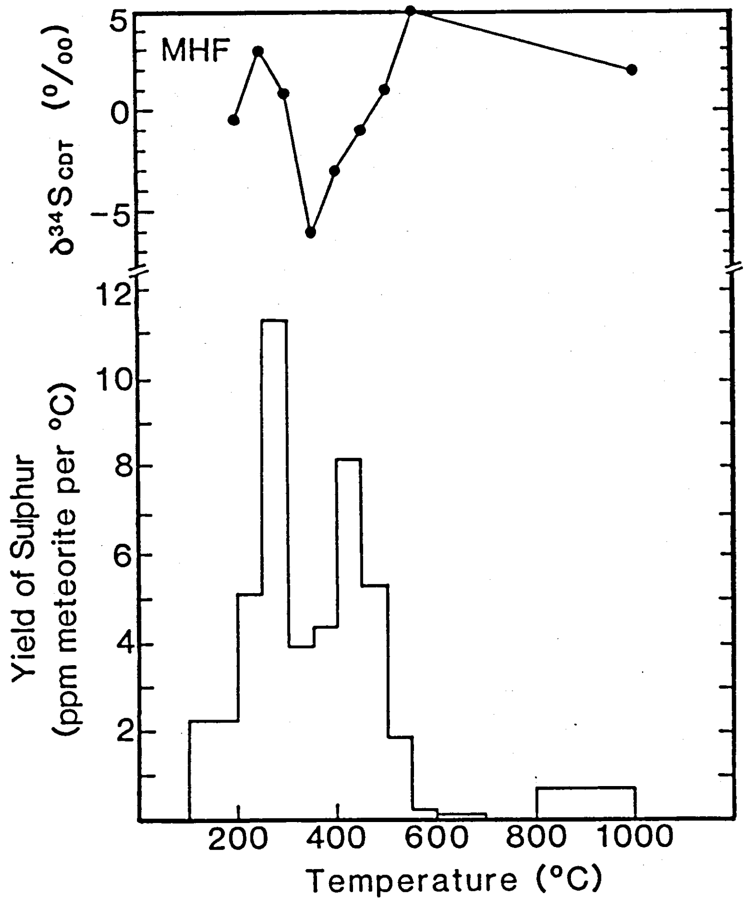


Figure 3.9 The abundance (—) and isotopic composition (-•-) of sulphur in Murchison HF/HCl residue (MHF) as determined by stepped combustion.

sulphur is liberated below 300°C). As for the C1 stepped combustion data, it is stressed that the contents of elemental sulphur determined for Murchison and Kivesvaara could be lower limits due to the difficulties associated with combusting this mineral. Unfortunately Nogoya has not been analysed for carbon by stepped combustion but it would seem likely to be low in elemental sulphur because a high organic sulphur content would be expected to accompany the relatively large amounts of carbon (up to 5.21 wt%) suggested to be present (Bunch and Chang, 1980).

Comparing the data acquired by stepped combustion with published measurements it is noted that:

1. Kaplan and Hulston (1966) have determined elemental sulphur to be present in Cold Bokkeveld at a level of 0.03 wt% with a δ^{34}S value of −0.6‰.
2. Briggs (1963) has reported that the δ^{34}S of the organic fraction of Murray is +2.86‰ (although this is subject to uncertainty as this value may represent a mixture of organic and elemental sulphur).

The δ^{34}S value for sulphur released below 600°C in MHF is −0.12‰ (Figure 3.9), which is again different from that recorded in OHF of +2.70‰. The quantities of sulphur released from temperature steps below 300°C were usually too small for isotopic analysis, so data are only available for Kivesvaara (+1.0‰) and Nogoya (+3.0‰), these values are broadly similar to measurements for the C1 meteorites. As in the case of C1 meteorites, the δ^{34}S values of the sulphur burning below 300°C, presumably represent a mixture of elemental and organic sulphur.

In MHF (Figure 3.9), 69% (or 0.71 wt%) of the organic sulphur is released between 300 and 600°C. For the sulphur liberated between 300 and 600°C in the bulk C2 meteorites, considered to be a mixture of organic sulphur and troilite sulphur, the concentrations vary between 0.16 wt% (Renazzo) and 1.26 wt% (Murray). The amounts of organic sulphur considered to be liberated over this temperature interval (Table 3.7) are between 0.12 wt% (Mighei) and 0.22 wt% (Murray). Applying a correction for organic sulphur liberated between 300 and 600°C, as done for C1 data, reveals that meteorites like Kivesvaara contain only small amounts of sulphides (0.21 wt% sulphur, equivalent to 0.58 wt% troilite), whereas there is 0.87 wt% (2.39 wt% troilite) in Murchison and 1.04 wt% (2.86 wt% troilite) in both Mighei and Murray. Similar determinations of the troilite sulphur contents for Nogoya, Al Rais and Renazzo are not possible because the carbon contents of the organic fractions in these meteorites have not been measured. In Nogoya the amount of sulphur released between 300 to 600°C is 0.71 wt% and it is considered that this is predominantly organic sulphur because:

1. Nogoya contains a high abundance of carbon (5.21%; Bunch and Chang, 1980) and by inference a high organic sulphur content.
2. This meteorite is highly altered (Bunch and Chang, 1980) so much of the original troilite sulphur will have been oxidised.

In Al Rais the sulphur liberated between 300 and 600°C represents the largest peak in the release profile (Figure 3.8), so it is considered that the sulphur released between 300 and 600°C in this meteorite (and Renazzo) is representative of troilite sulphur (1.04 wt% in Al Rais and 0.16 wt% in Renazzo). Thus, the contents of troilite could be as high as 2.86 wt% in Al Rais and 0.44 wt% in Renazzo (Table 3.7). These data compare with previous determinations of sulphide sulphur made by Kaplan and Hulston (1966), of 0.18 wt% in Mighei and 0.06 wt% in Murray. Clearly sulphide is more abundant than has been suggested in previous studies and moreover, is more prevalent in the C2 chondrites than it is in C1 meteorites.

The stepped combustion profiles of Kivesvaara, Nogoya, Mighei and Murchison (Figure 3.7), show evidence for only one release of sulphur between 300 and 600°C with little variability in the $\delta^{34}S$ values over this temperature interval (with a maximum variation of 2.5‰ in Mighei). Thus it is impossible to distinguish different sulphide components from the stepped combustion data. The integrated $\delta^{34}S$ values obtained for the 300 to 600°C steps are +1.00‰, −0.06‰, −2.30‰ and −0.61‰ for Kivesvaara, Nogoya, Mighei and Murchison respectively. If a correction is applied for the presence of organic material (with a $\delta^{34}S$ value of −0.87‰ obtained from steps between 300 and 600°C in MHF) then $\delta^{34}S$ values for the sulphides (Table 3.7) are between +2.5‰ (Kivesvaara) and −2.47‰ (Mighei). These values are similar to those obtained for the C1 meteorites but are in marked contrast with the $\delta^{34}S$ values for FeS quoted by Kaplan and Hulston (1966) of between +1.7‰ and +2.5‰ for C2 meteorites.

Murray differs from other C2 meteorites in having a bimodal release of sulphur below 600°C, with maxima occurring at 300 to 400°C and 500 to 600°C (Figure 3.7). The 500 to 600°C peak is not as distinct as other releases in Murray and may be an artefact of the experiment. However, both troilite and pentlandite have been petrographically identified in Murray (Bunch and Chang, 1980), and it is tempting to suggest that the two releases of sulphur below 600°C possibly come from two different sulphide minerals. Troilite is known to combust between 300 and 600°C, however, a sample of pure pentlandite has not been treated to stepped combustion, although it is possible that this mineral may have a similar combustion temperature to that of troilite, since these two minerals are chemically alike. If pentlandite sulphur is responsible for the 500 to 600°C release in Murray, then it is curious that a release at similar temperatures is not clearly observed for other meteorites in which pentlandite has been found, viz Renazzo (Mason and Wiik, 1962), Nogoya (Bunch and Chang, 1980) and Murchison (Fuchs et al., 1973). The $\delta^{34}S$ value of the putative pentlandite component in Murray is −1.7‰.

Sulphates and FESON

Upon stepped combustion, the CM2 meteorites release between 55% (Mighei) and 72% (Nogoya) of their total sulphur above 600°C (Figure 3.7). In the case of CR2 meteorites, Al Rais and Renazzo, sulphur liberated above 600°C constitutes 42% and 84% of the total amount respectively (Figure 3.8). The stepped combustion profiles show that, for all samples, there are distinct releases of sulphur combusting between 600 and 900°C (from 0.42 wt% in Al Rais and 1.45 wt% in Nogoya). Furthermore, distinct releases of sulphur above 900°C (i.e. from epsomite) are obvious in Al Rais, Murchison and Mighei. The presence of epsomite in other C2 chondrites can be inferred because:

1. There is a broad release of sulphur over the high temperature section of the release profile (above 900°C).
2. There is a distinct change in isotopic composition above 900°C (e.g. for Murray, $\delta^{34}S$ changes from −1.0‰ at 800°C to +4.0‰ at 900°C).

During the petrographic investigation of Murchison by Fuchs et al. (1973), gypsum was the only sulphate to be positively identified, although the presence of sodium and magnesium sulphates was inferred. Kaplan and Hulston (1966) were noncommittal about the exact nature of the sulphates in C2 meteorites and alluded to $(Mg,Ca)SO_4$, although they detected 0.1 wt% sulphur as gypsum in Murray.

It is assumed that the sulphur dioxide released between 600 and 900°C represents a mixture of sulphur from FESON and gypsum as was invoked to account for sulphur released over this temperature interval in C1 meteorites. If all the sulphur liberated between 600 and 900°C in CM2 and CR2 chondrites is calculated as gypsum, then the required calcium contents exceed the known contents of this element in the matrices in all cases, and in three instances (Mighei, Murchison and Nogoya), they exceed the total calcium contents of the meteorites (Table 3.8). The relative proportions of sulphur as gypsum and FESON have, therefore, been assessed (Table 3.9) according to the method described in Section 3.4.2 for the C1 meteorites. For the purpose of these calculations it is assumed that all of the gypsum in C2 chondrites resides in the matrix (as there are no distinct mineral veins present in these meteorites) so only the matrix Ca contents (McSween and Richardson, 1977) are considered. The matrix Ca contents have been

Sample	Yield S (600–900°C) wt%	Calc. gypsum wt%	Ca required wt%	Lit. Ca (wt%)	
				matrix	bulk
Kivesvaara	0.72	3.87	0.90	0.52 (a)	1.39 (a)
Mighei	0.95	5.11	1.19	0.33 (b)	1.18 (c)
Murchison	1.41	7.58	1.76	0.61 (b)	1.25 (d) 1.35 (e)
Murray	1.08	5.81	1.35	0.54 (b)	1.36 (c)
Nogoya	1.45	7.79	1.81	0.41 (b)	1.79 (c)
Al Rais	0.42	2.26	0.53	0.95 (b)	1.43 (c)
Renazzo	0.62	3.33	0.77	0.62 (b)	1.27 (c)

Table 3.8 Contents of calcium as gypsum in C2 chondrites calculated from sulphur released between 600–900°C. References: (a) Kinnunen and Saikkonen (1983); (b) McSween and Richardson (1977); (c) Mason (1963); (d) Fuchs et al. (1973); (e) Jarosewich (1973).

Sample	Matrix Ca content wt%	Ca as carbonate wt%	Gypsum content wt%	FESON content wt%
Kivesvaara	0.40 (a)	0.05 (b)	1.51	1.83
Mighei	0.20 (c)	0.14 (c)	0.26	3.74
Murchison	0.39 (c)	0.09 (b)	1.29	4.87
Murray	0.32 (c)	0.32 (b)	ND	ND
Nogoya	0.35 (c)	–	1.51	4.87
Al Rais	0.26 (c)	0.01 (b)	1.08	0.92
Renazzo	0.35 (c)	0.16 (b)	0.82	1.95

Table 3.9 Calculation of gypsum and FESON contents in C2 chondrites. The matrix calcium contents reported in the table have been normalised to whole-rock values using the proportions of matrix reported for these meteorites by McSween (1979b). References: (a) Kinnunen and Saikkonen (1983); (b) Dr M.M. Grady, unpublished data; (c) Smith and Kaplan (1970). ND = not determinable.

normalised to bulk meteorite values using the matrix volumes for each meteorite determined by McSween (1979b). A correction was also applied for the amount of Ca in carbonate (assumed to be calcite only for these calculations). This correction could not be applied to Nogoya for which the carbonate content has not been determined. Without exception, the C2 chondrites contain more sulphur as FESON (0.22 wt% to 1.17 wt%) than as gypsum (0.05 wt% to 0.41 wt%) (Table 3.7). It is significant that Nogoya has the highest FESON content (4.87 wt%) indicating that the extent of alteration is greatest in this meteorite, this observation is in agreement with the conclusion of Bunch and Chang (1980). The FESON and gypsum contents derived for the meteorites in Table 3.7 are plotted in Figure 2.10 where they are compared with the matrix proportions (McSween, 1979b, Kinnunen and Saikkonen, 1983) which can be used as a measure of aqueous alteration.

Both McSween and Richardson (1977) and Tomeoka and Buseck (1985) have independently calculated that about 30% of the matrix iron content of Murchison is in the form of FESON. However, this estimate is in error, because it is based on the assumption that all the sulphur in the matrix can be attributed to either troilite or FESON. The stepped combustion data for Murchison indicates that sulphur in the matrix is present in at least six different forms, namely: elemental state, organic macromolecular material, troilite, FESON, gypsum and epsomite (Table 3.7). Using this information, and the value of matrix iron determined by McSween and Richardson (1977), the amount of matrix iron that can be attributed to FESON is recalculated as being only about 10%.

The formation and alteration sequence of PCP has been studied in detail by Tomeoka and Buseck (1985), and much of the following discussion is based upon their work. The formation of FESON (or type I PCP) is attributed to a reaction between kamacite and a sulphur-rich fluid. Tomeoka and Buseck (1985) did not propose a mechanism for producing the fluid, but it is plausible that an initial reaction occurred between troilite and water (Bostrom and Fredriksson, 1965) that led to the formation of limonite and elemental sulphur, both of which are often found in close association in C1 chondrites (Bass, 1970). However, if this is correct, it is difficult to account for the very low abundances of elemental sulphur in the C2 chondrites. It is possible that much of the original elemental sulphur formed during alteration of troilite underwent further reactions with organic material on the parent body, especially as it seems that C2 chondrites have higher organic sulphur contents than C1 meteorites (as can be discerned by the results for OHF and MHF).

The alteration process is not a straightforward transformation of troilite to FESON. Indeed, it has been observed (Tomeoka and Buseck, 1985) that,

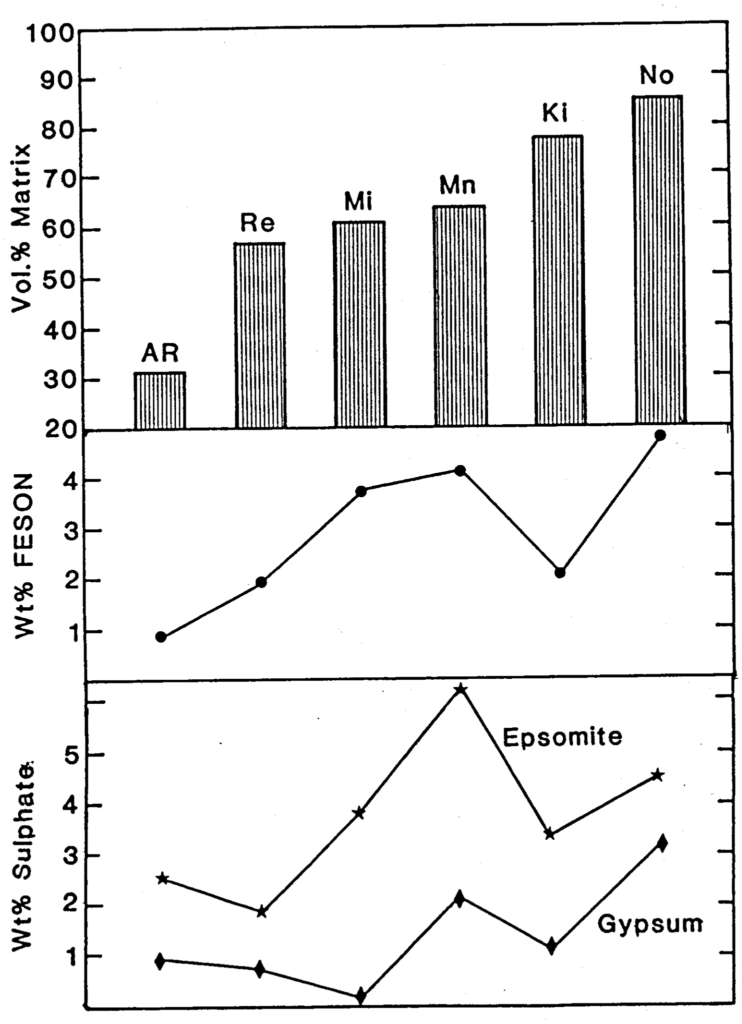


Figure 3.10 Variations in the amounts of matrix, FESON and sulphate in some C2 chondrites. The proportions of matrix are from McSween (1979b) and Kinnunen and Saikkonen (1982). AR=Al Rais; Ki=Kivesvaara; Mi=Mighei; Mn=Murchison; No=Nogoya; Re=Renazzo.

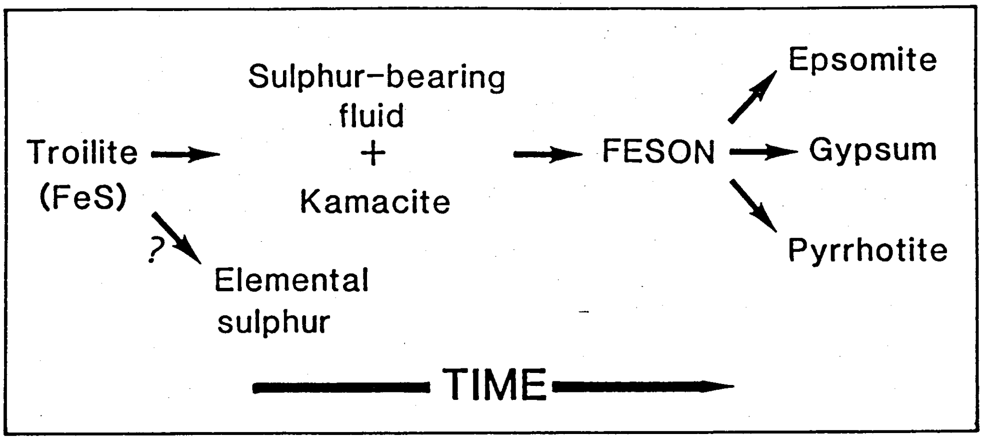


Figure 3.11 The succession of sulphur-bearing minerals in C1 and C2 meteorites. The precursive sulphur mineral is troilite formed in the solar nebula. Aqueous alteration of troilite forms elemental sulphur (in C1 meteorites) and a sulphur-rich fluid which reacts with kamacite to form FESON. During advanced stages of alteration FESON is consumed to form cronstedtite, the FESON sulphur forms pyrrhotite and sulphates.

during the second stage of alteration, cronstedtite (type II PCP) is formed by the reaction of FESON (type I PCP) and silicon which is released by the decomposition of olivine and pyroxene. At this stage Fe, S, Ni, Cr and P are leached out of type I PCP and dispersed throughout the matrix, via an aqueous medium, leading to the formation of pentlandite and pyrrhotite (Tomeoka and Buseck, 1985). Concurrently, Mg and Ca are removed from pyroxene and olivine, these ions probably combine with sulphur (SO_4^{2-}) in the fluid phase, to form gypsum and epsomite. During advanced stages of alteration, or where there has been more extensive aqueous activity (as in the C1 chondrites), much of the original FESON is consumed to form cronstedtite (Tomeoka and Buseck, 1985). The proposed scheme for the progressive formation of sulphur constituents in C1 and C2 meteorites is shown in Figure 3.11.

The amounts of sulphur as gypsum, estimated from the data for combustion steps between 600 and 900°C (Table 3.9), range between 0.05 wt% (Murray) and 0.28 wt% (Kivesvaara and Nogoya). This translates to a variation in gypsum concentration of between 0.26 wt% (Murray) and 1.51 wt% (Kivesvaara and Nogoya). The putative epsomite contents (i.e. that sulphur released above 900°C, Table 3.7) are relatively low compared to C1 meteorites. Sulphur as epsomite accounts for between 0.25 wt% (Renazzo) and

0.64 wt% (Murchison). The total amount of sulphur as sulphate is estimated to be between 0.40 wt% (Renazzo) and 1.03 wt% (Murchison). These results compare favourably with previously determined values, Kaplan and Hulston (1966) established a range in sulphate sulphur content for CM2 meteorites of between 0.46 wt% and 1.05 wt%, while Jarosewich (1971) and Fuchs et al. (1973) obtained concentrations of sulphur as sulphate in Murchison of 0.36 wt% and 0.95 wt% respectively.

It is obvious that there is a wide range in sulphate content in the C2 meteorites. If sulphides are the primary constituents of carbonaceous chondrites then the degree of aqueous alteration will be reflected by the relative amounts of sulphates present. Considering the CM2 meteorites only, the ratio of sulphur as FESON and sulphates to sulphur as sulphides, decreases in the order: Kivesvaara (5.5)>Murchison (2.1)>Mighei (1.6)> Murray (1.4). Unfortunately, the sulphide content of Nogoya cannot be determined (since the contribution of organic sulphur liberated between 300 and 600°C is not known), so an alteration index for this meteorite cannot be established. However, Bunch and Chang (1980) reported that Nogoya is the most highly altered CM2 chondrite, and reclassification to a CM1 has been considered (McSween, 1979a). Kinnunen and Saikkonen (1983) also found that Kivesvaara is highly altered and this is supported by the results from the present study which suggest that this meteorite may have suffered alteration, comparable in extent, to that of C1 meteorites (e.g. the alteration index of Orgueil was calculated to be 5.5).

The integrated $\delta^{34}S$ values for the sulphur released between 600 and 900°C in the C2 chondrites (Table 3.6) are between $-0.75‰$ (Renazzo) and $+1.16‰$ (Nogoya) and the average value is $+0.32‰$. It is difficult to define the individual $\delta^{34}S$ values for sulphur from FESON and gypsum as these components both seem to liberate their sulphur over this temperature interval. Kaplan and Hulston (1966) determined the $\delta^{34}S$ of $CaSO_4$ in Murray to be $+0.1‰$. There is a notable variation of $\delta^{34}S$ values between 700 and 900°C in the isotopic profiles of the C2 chondrites (e.g. in Mighei the isotopic composition of sulphur changes from $-3.9‰$ at 700°C to $+4.2‰$ at 900°C). A similar phenomenon was noted for $\delta^{34}S$ values measured for sulphur released over the same temperature interval in C1 meteorites (Section 3.4.2), where it was interpreted to represent the burning of two discrete sulphur-bearing components having different isotopic compositions.

The results of the calculations in Table 3.9, suggest that all the sulphur liberated above 600°C in Al Rais can be attributed to sulphates. Thus the $\delta^{34}S$ value of $-0.75‰$ obtained for the sulphur released between 600 and 900°C in Al Rais, may provide a more reasonable indication of the $\delta^{34}S$ value of gypsum in carbonaceous chondrites.

The $\delta^{34}S$ values of the sulphur released above 900°C (thought to derive from epsomite) during stepped combustion of C2 meteorites (Table 3.6), are between −0.75‰ and +4.05‰ (average $\delta^{34}S$ value is +1.5‰). Vein mineralisation of sulphates in C2 chondrites is not as extensive as that in C1 meteorites and yet, the $\delta^{34}S$ values of epsomite sulphur in both types, are similar (between +1.60‰ and −0.43‰ in C1's and +4.05‰ and −0.75‰ in C2's). This suggests that hydrothermal processes were similar in C1 and C2 carbonaceous chondrites. Previously, Kaplan and Hulston (1966) have determined the isotopic composition of sulphur in (Mg,Ca)SO_4 for CM chondrites to be between −1.7 and +0.7‰.

3.5 Comparison with previous studies

The sulphur data, obtained by stepped combustion, for constituents in C1 and C2 meteorites are often at variance with those determined in previous studies. In Figure 3.12, the results obtained in this study are compared with available literature values for four meteorites (Orgueil, Mighei, Murchison and Murray). The most important differences in the data of this study compared with those obtained previously, seems to be:

1. The lower estimates of elemental and epsomite sulphur.
2. The higher contents of troilite and gypsum sulphur.
3. The higher $\delta^{34}S$ values of epsomite and lower $\delta^{34}S$ values of troilite.

Kaplan and Hulston (1966) and Monster et al. (1965) made sulphur isotope measurements on different constituents of meteorite samples using an analytical procedure summarised in Table 3.10. Unfortunately, these investigators did not undertake any experiments to confirm the integrity of the chemical procedures (in terms of their ability to completely remove all the sulphur from the component of interest, and the effect on other sulphur-bearing components). In an attempt to assess the effects of chemical reagents on sulphur minerals in carbonaceous chondrites, a number of analytical treatments were applied to the Murchison meteorite (Figure 3.13). Murchison was selected for a detailed study because stepped combustion of the whole-rock sample has provided evidence for six components of sulphur (discussed in Section 3.4.3). Where possible, techniques were chosen to be fairly comparable to those used by Kaplan and Hulston (1966). The distribution of sulphur in each of the residues and extracts obtained, was characterised using stepped combustion (Figure 3.13). However, interpretation of the stepped combustion data is at best semi-quantitative, as some experiments necessary for the full assessment of the observations made herein, have yet to be carried out. Nevertheless, the objective of these experiments

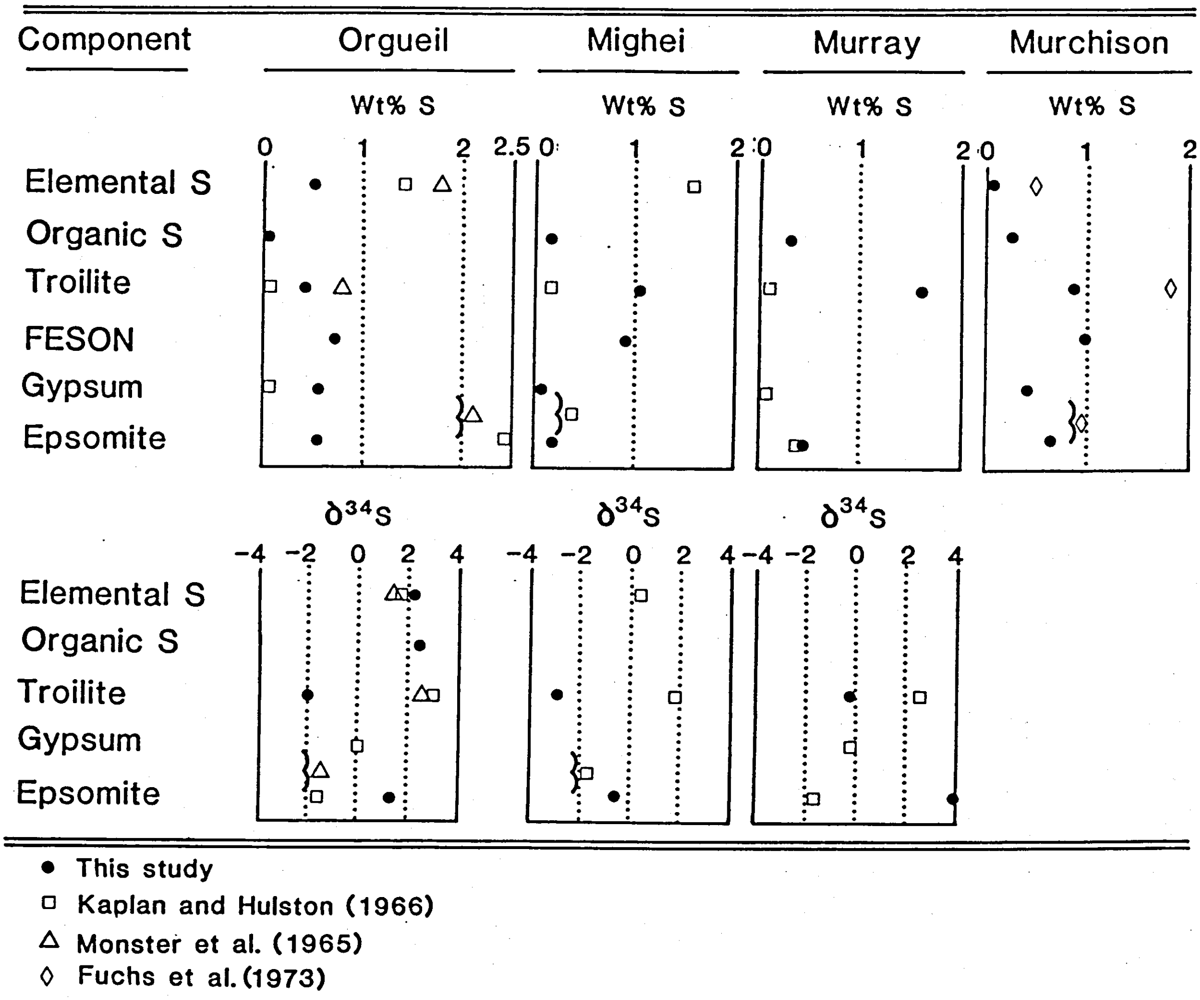


Figure 3.12 A comparison of the sulphur data obtained in this study with published values for four carbonaceous chondrites.

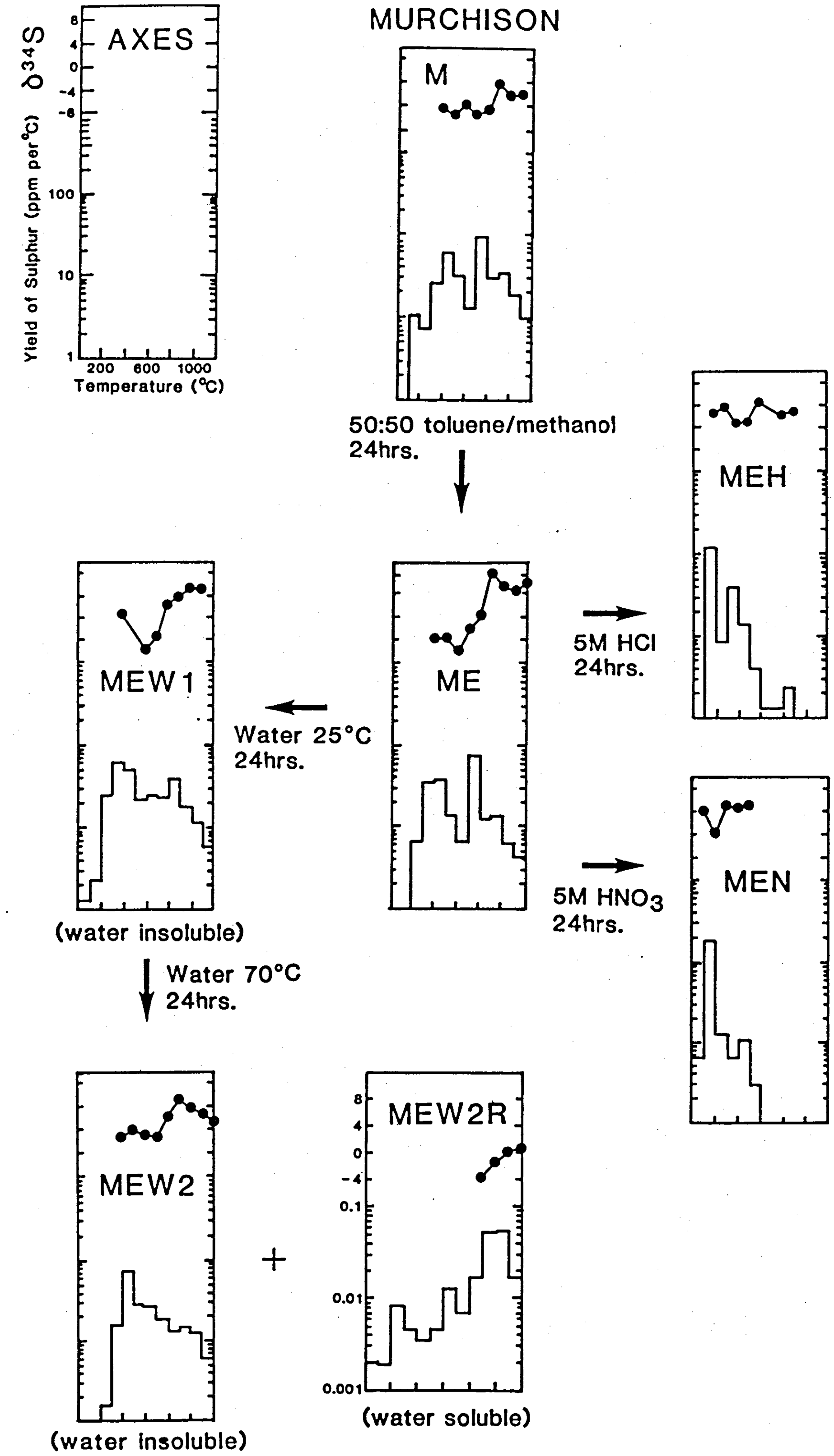


Figure 3.13 The chemical preparation scheme applied to Murchison and the abundance (—) and isotopic composition (-•-) of sulphur in the resulting residues and extracts.

Kaplan & Hulston (1966)			This study	
Step	Phase	Extraction method	Extraction method	Residue
1	S^0	Acetone–benzene	Toluene–methanol	ME
2	SO_4^{2-}	Refluxing with water	Cold water Hot water	MEW1 MEW2
3	S^{2-}	Refluxing with 5M HCl	5M HCl at 18°C 5M HNO_3 at 18°C	MEH MEN
4	SO_4^{2-}	Acid soluble		
5	S^0	Benzene		
6	S^0	Acetone–benzene		
7	S?	Aqua regia		

Table 3.10 The analytical procedures applied to carbonaceous chondrites by Kaplan and Hulston (1966) compared with the methods used in this study.

was simply to demonstrate that chemicals act on meteoritic components in a complicated and unpredictable way. During the preparation of the meteorite residues no measurements of weight-loss were recorded. Thus, the apparent increases in total sulphur content that occur going from ME to MEW1 and MEN can be accounted for by the removal of water and nitric acid soluble components from Murchison respectively. Experiments considered to be a worthwhile part of future studies are mentioned.

ME

Previous determinations of elemental sulphur in carbonaceous chondrites have involved measurement of the solvent-extractable material (Table 3.10). During the present study, parent Murchison (designated M) was extracted with a 50:50 toluene-methanol mixture to give ME. Stepped combustion of ME revealed that a total of 1.22 wt% sulphur has been removed by the organic solvents. Most of the sulphur which burns between room temperature and 300°C (0.15 wt%) and attributed to elemental and organic sulphur in M, has been extracted in ME (the corresponding sulphur content for this temperature interval in the residue is 0.04 wt%). In Section 3.4.3 the elemental sulphur content of Murchison was estimated to be 0.07 wt%, so it appears that organic solvents could also have removed some of the organic sulphur. However, it was noted in Section 3.4.3 that the elemental sulphur content determined using stepped combustion represents a minimum value, due to the problems associated with burning this component. Nevertheless,

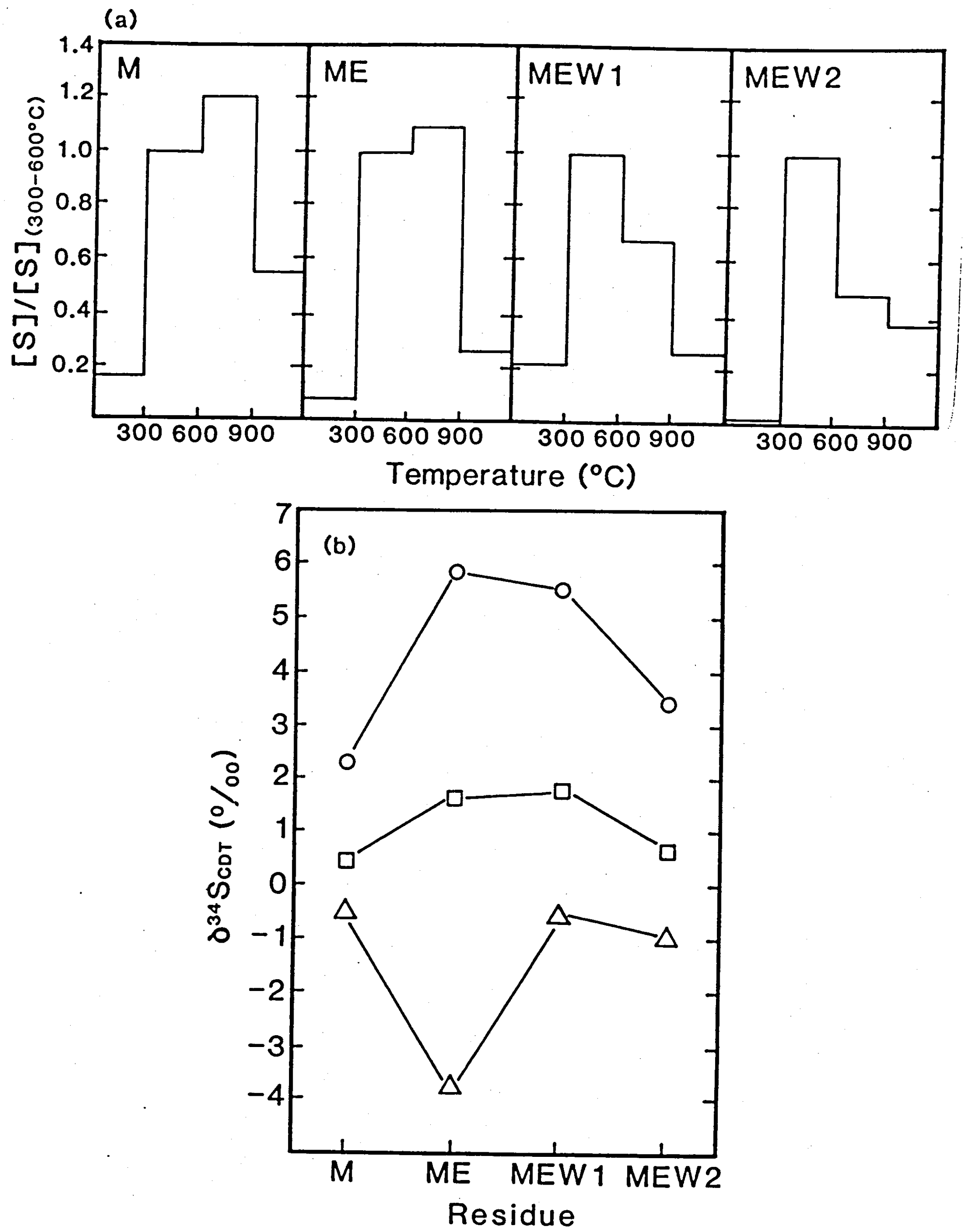


Figure 3.14 Sulphur in bulk Murchison compared to three residues. (a) Sulphur abundances of solvent- (ME) and water-extracted (MEW1 and MEW2) residues of Murchison, normalised to sulphur combusting between 300–600°C in bulk Murchison. (b) The isotopic composition of sulphur liberated over three temperature intervals during stepped combustion of M, ME, MEW1 and MEW2. ○ = 900–1200°C; □ = 600–900°C; △ = 300–600°C.

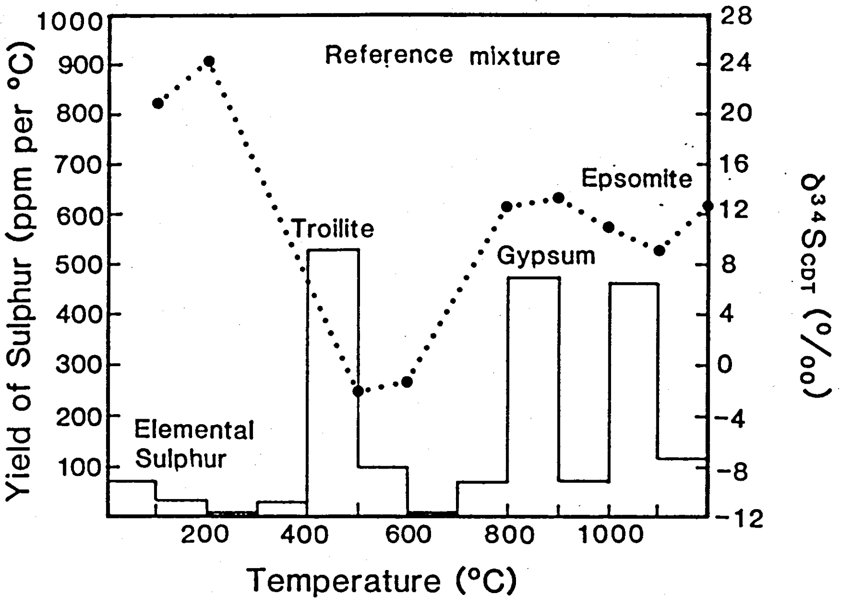
Kaplan and Hulston (1966) and Fuchs et al. (1973) suspected that the organic solvents they used for removing elemental sulphur would also have extracted some soluble organic sulphur, so this may also explain the higher elemental sulphur contents reported by these workers (Figure 3.12). This appears to be confirmed by the results for sulphur burning between 300 and 600°C in ME (attributed to a mixture of organic and troilite sulphur in M), which is reduced from 1.04 wt% in M to 0.85 wt% in ME.

A significant amount of sulphur lost by treatment with toluene-methanol cannot be wholly attributed to the removal of elemental sulphur and organic sulphur, because in Section 3.4.3 it was demonstrated that these components constitute only 0.32 wt% of the sulphur in the meteorite. Significant amounts of sulphur have also been removed from the 600 to 900°C (gypsum and FESON sulphur) and 900 to 1200°C (epsomite sulphur) temperature intervals (Figure 3.14a). Most of the loss occurs between 600 and 900°C with ME containing 0.44 wt% less sulphur than that in M (Figure 3.14a). Unfortunately, methanol was a poor choice as an organic solvent, since its polarity may have caused partial dissolution of sulphate (gypsum and epsomite). In order to determine the true elemental sulphur content it will be necessary to treat samples with non-polar solvents only (e.g. toluene).

In Figure 3.14b, it is apparent that the $\delta^{34}S$ value of the sulphur released from 900 to 1200°C changes by about 4‰ the corresponding amount of sulphur removed (0.48 wt%) has a $\delta^{34}S$ value of -0.26‰. Concomittantly the $\delta^{34}S$ value of the 600 to 900°C sulphur increases by about 1‰ suggesting removal of some isotopically light sulphur (ca. -1.19‰). The isotopic composition of the sulphur released from 300 to 600°C decreases ($\delta^{34}S = -3.3$‰) and is notably different from that determined for troilite in M ($\delta^{34}S = -0.56$‰).

MEW1

Sulphur reclaimed from water extracts of Murchison and other carbonaceous chondrites has previously been attributed wholly to sulphates (Table 3.10). Extraction of the residue ME with water at 25°C was undertaken to remove soluble sulphates. The material was mixed with water for 24 hours and agitated several times using ultrasound. The residue so-produced, MEW1 (Figure 3.13), has evidently lost some of the gypsum and FESON (about 19% of the sulphur liberated between 600 and 900°C in ME has been removed) but appears to contain about the same amount of epsomite (Figure 3.14a). The cold water treatment was also applied to the reference mixture, the stepped combustion data of which show that both of the sulphate components are almost completely removed (Figure 3.15), although small amounts of gypsum remained. It is not clear why cold water does not dis-



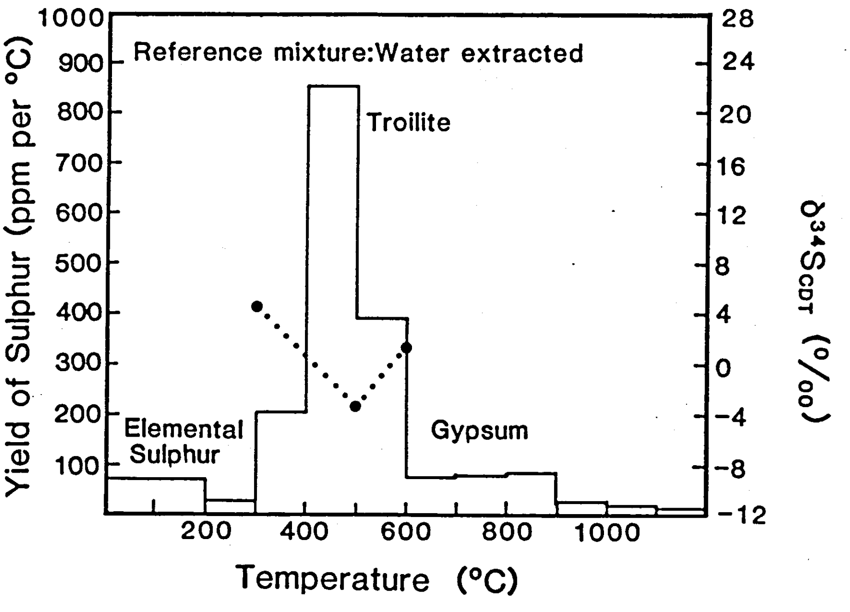


Figure 3.15 The abundance (—) and isotopic composition (-•-) of sulphur in the reference mixture and a water extracted residue of the mixture as determined by stepped combustion.

solve epsomite in the meteorite, particularly as magnesium sulphate is more soluble than calcium sulphate and should be more readily removed. Perhaps the epsomite in the meteorite is 'protected' by a mantle of a less soluble mineral such as magnesium carbonate, calcium carbonate or some other mineral which does not dissolve in cold water. However, it is notable that Fuchs et al. (1973) reported that hot water treatment could not completely remove all of the sulphate (gypsum) in Murchison.

The δ^{34}S values of the 600 to 900°C and 900 to 1200°C sulphur in MEW1 are very similar to those in ME but the δ^{34}S value of the 300 to 600°C sulphur fraction is about 3‰ heavier (Figure 3.14b).

MEW2

The residue MEW1 was extracted with water at 70°C to ensure complete removal of soluble sulphates. After 24 hours the residue was reclaimed and evaporated to dryness (MEW2). In an attempt to recover the material taken into solution (MEW2R), the supernatant liquid was evaporated and analysed separately (Figure 3.13). It can be seen from Figure 3.14a, that progressively more of the sulphur released between 600 and 900°C is removed in MEW2 (equal to 0.13 wt% sulphur with a δ^{34}S value of −0.43‰), while that liberated above 900°C has remained unaffected. However, on the basis of δ^{34}S values (Figure 3.14b) it appears that some of the epsomite has been removed, this is calculated as being equivalent to 0.13 wt% sulphur with $\delta^{34}S = +6.27$‰. That the residue still contains some sulphates may reflect the experimental procedure in which the very last fraction of water could not be removed by means of a pipette and is evaporated to dryness. However, this should be considered a minor problem as clearly a large amount of water-soluble sulphates were recovered in MEW2R (Figure 3.13).

The δ^{34}S value of the water-soluble sulphur of −0.5‰ is distinctly different from that of the epsomite in MEW2 ($\delta^{34}S = +6.27$‰). This would seem to suggest that MEW2R is largely composed of gypsum and FESON ($\delta^{34}S = +0.04$‰) or an, as yet, unidentified sulphate. This suggestion is strengthened by the fact that the sulphur which combusts between 600 to 900°C in MEW1 has a similar δ^{34}S value to the sulphur measured over the same temperature interval in MEW2R (i.e. $\delta^{34}S = -0.4$ and −0.5‰ for MEW1 and MEW2R respectively). It is considered that the hot water treatment does not cause leaching of troilite because, as can be seen from Figure 3.14a, the troilite sulphur/epsomite sulphur ratio does not change in going from MEW1 to MEW2; it would seem unreasonably coincidental for troilite and epsomite to dissolve in water to the same degree. Of particular interest for isotopic studies, is the presence of isotopic minima in meteorite residues MEW etc., due to unidentified sulphur burning at 600 to 700°C with a δ^{34}S value of −6‰.

MEH and MEN

HCl-volatile sulphur in C1 and C2 chondrites was attributed to sulphide (troilite) by Kaplan and Hulston (1966). Two residues were prepared by reaction of 5M HCl (to produce MEH) and 5M HNO_3 (to form MEN) with ME at room temperature for 24 hours (the mixture was agitated by ultrasonics at frequent intervals). Following digestion with acid, the mixtures were centrifuged, the supernatant liquids removed and the residues washed to neutrality before being evaporated to dryness at 40°C.

The effects of hydrochloric (MEH) and nitric acids (MEN) on the solvent-extracted residue of Murchison (ME) are fairly similar in that they both appear to convert a large fraction of the sulphur components (i.e. sulphides and sulphates) to elemental sulphur. This accounts for the large release of sulphur occurring between 100 to 200°C in the stepped combustion data for both MEH and MEN (Figure 3.13). This result calls into question the elemental sulphur contents of C2 chondrites reported by Kaplan and Hulston (1966). These workers noted that toluene-benzene extracts of C2 meteorites yielded significantly more sulphur following HCl treatment, which is understandable, if the effects of their acid treatments are the same as those recorded in the present study.

HCl reacts readily with FeS but curiously, neither epsomite nor gypsum, on their own, are decomposed by hydrochloric or nitric acids. As both components disappear from the meteorite (Figure 3.13) some alternative mechanism must be operative. A proposed reaction scheme is as follows, initially hydrochloric acid will react with troilite:

$$2HCl + FeS \rightarrow H_2S + FeCl_2$$

Hydrogen sulphide, being soluble in hydrochloric and nitric acids, will then reduce both gypsum and epsomite:

$$MgSO_4 + H_2S \rightarrow MgO + S + SO_2 + H_2O$$

The SO_2 formed will react further with hydrogen sulphide:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

Consequently, both the oxidised and reduced forms of sulphur will be converted to elemental sulphur (although presumably there are some losses of sulphur due to the evolution of SO_2 and H_2S). Sulphur in the macromolecular organic material should remain unaffected by the HCl acid treatment, but will be oxidised by HNO_3. Thus the release of sulphur in MEH between

300 and 500°C could be due to burning of sulphur from organic macromolecular material (being poorly resolved due to the large amounts of elemental sulphur present) and/or possibly pentlandite which is known to be fairly insoluble in hydrochloric acid. Close inspection of the data for MEN also shows a release of sulphur from 400 to 500°C. This cannot be due to pentlandite, which is soluble in nitric acid, but it is possible that this sulphur arises largely from undissolved troilite. A slight isotopic enrichment of sulphur which accompanies a slight depletion in total sulphur content in MEH ($\delta^{34}S = +2.27$‰, 1.96 wt% S) and MEN ($\delta^{34}S = +0.88$‰, 2.35 wt% S) compared to bulk Murchison, is thought to result from the small loss of sulphur from the acid mixture.

It is not known how FESON responds to any of the reagents mentioned above. However, it does appear to dissolve in nitric and hydrochloric acids (Figure 3.13). Fuchs et al. (1973) reported that this mineral is highly magnetic. A magnetic fraction of Murchison would probably contain some sulphides (troilite and pentlandite), but the isotopic composition of these components could be distinguished using stepped combustion.

3.6 Conclusions

The sulphur components of the C1 and C2 carbonaceous chondrites are predominantly the result of secondary, low temperature, aqueous alteration processes which occurred on the parent bodies. The C1 and C2 meteorites contain sulphur in the form of organic macromolecular material, elemental sulphur, sulphides, sulphates and FESON. Most of the sulphur seems to be present as sulphates (gypsum and epsomite). The ratio of oxidised/reduced sulphur is highest in the C1's indicating that they are more extensively altered than the C2 chondrites. The similarities in distribution and isotopic compostion of sulphur in C1 and C2 chondrites implies that hydrothermal evolution of these two groups has followed a common pathway.

The isotopic compositions of each of the main sulphur components of C1 and C2 chondrites seems to be distinct; elemental and epsomite sulphur are relatively enriched in ^{34}S compared to sulphur in gypsum, FESON and troilite. The isotopic compositions of gypsum and FESON cannot be distinguished since these two minerals appear to combust over similar temperature intervals. The precursive mineral is considered to be troilite from which sulphur was leached during aqueous alteration to form FESON, sulphates and elemental sulphur. The FESON produced in this way was subsequently decomposed to liberate sulphur which formed secondary sulphides (pyrrhotite) and sulphates.

The results show that stepped combustion is a valuable technique for resolving the individual sulphur-bearing phases and their isotopic compositions in carbonaceous chondrites. It is more informative than conventional 'wet' chemical techniques used to separate indigenous components of meteorites, it has been shown that some of these are not as specific to particular minerals as considered by previous investigators (Kaplan and Hulston 1966, Thode et al. 1965). Kaplan and Hulston (1966) assigned all water-soluble sulphate in carbonaceous chondrites to epsomite; it has been shown herein that gypsum appears to be a major constituent of many of these meteorites. Moreover, the effect of acid hydrolysis on Murchison was not merely the decomposition of troilite but has converted all the sulphur-bearing components to elemental sulphur. Kaplan and Hulston (1966) considered all the sulphur extracted by organic solvents after acid treatment to be elemental sulphur indigenous to the meteorite. Nevertheless, appropriate chemical extractions coupled with stepped combustion techniques could be used to reveal minor sulphur components and important isotopic deviations from zero within meteorites as is evidenced by the detailed study of Murchison.

Chapter 4

The C3 to C6 Carbonaceous Chondrites

4.1 Introduction

The carbonaceous chondrites, as a group, have been subjected to intense scientific study. With the exception of the Allende (CV3) meteorite, the bias has been in favour of the C1 and C2 meteorites, with significantly less investigation of the C3 to C6 chondrites. Sulphur isotope studies are a good example of the veracity of this statement. Previous sulphur isotope studies of C3 to C6 chondrites are limited to those reported by Hulston and Thode (1965a), which were discussed in Kaplan and Hulston (1966). Kaplan and Hulston (1966) measured δ^{34}S values of whole-rocks and separated minerals for one CV3 chondrite (Mokoia), three CO3 chondrites (Felix, Lancé and Warrenton) and one C4 chondrite (Karoonda).

During the current study, eight carbonaceous chondrites of petrologic types 3 to 6 have been investigated for their sulphur abundance and isotopic composition by stepped combustion. The relevant meteorites are listed in Table 4.1 along with their Van Schmus-Wood classifications and a list of the sulphide minerals identified in each sample. Allende and Vigarano are CV3 chondrites (McSween, 1977a) and Ornans and Felix are CO3 chondrites (McSween, 1977b). The classification of the remaining meteorites is less certain. Kallemeyn and Wasson (1982) examined the non-volatile element abundances of Coolidge and agreed with Van Schmus (1969) that a CV4 classification is appropriate. Similarly, consensus suggests that Yamato 6903 is also a CV4 chondrite (Okada et al., 1975; Clayton et al., 1979), although McSween (1977a) determined it to be a CV3. The classification of Karoonda is controversial; originally Mason (1971) assigned it to the CO group whereas Van Schmus and Hayes (1974) were unable to place it in any group but thought that Karoonda was a type 4 or 5. McSween (1977b) originally placed Karoonda in the CO group, but later McSween (1979a) agreed with Takahashi et al. (1978a) and Fitzgerald (1978) that it was better placed in the CV group as a type 5. Wilkening (1978) has assigned Karoonda to a

Sample	Class	Type	FeS	$Fe_{1-x}S$	FeS_2	$(Fe,Ni)_9S_8$	$FeCuS_2$
Ornans	CO	3	•				
Felix	CO	3	•				
Vigarano	CV	3				•	
Allende	CV	3	•			•	
Coolidge	CV	4	•				
Y 6903	CV	4	(•)			•	
Karoonda	C	4		(•)	•	•	•
Mulga West	CV	5/6				•	

Table 4.1 The classification and sulphide minerals of the carbonaceous chondrites analysed in this study. • = present; (•) = presence uncertain. (Data from McSween, 1977a,b; Scott and Taylor, 1985; Binns et al., 1977).

separate group (CK) on its own. On the basis of refractory lithophile element abundances, Kallemeyn and Wasson (1982) have classified Karoonda as intermediate between the CM-CO and CV clans.

Mulga West is the most highly metamorphosed carbonaceous chondrite known and has been classified by Binns et al. (1977) as a type 5 or 6 member of the Vigarano group. There are no known highly metamorphosed CO chondrites (i.e. none of higher petrologic grade than type 3), Fitzgerald and Jacques (1982) have suggested several reasons to account for this:

1. Poor statistical sampling.
2. The greater size of the CV parent body with more intense metamorphism at depth.
3. The CO parent body being so large that the inner regions have yet to be sampled.

The C3 chondrites have suffered only modest levels of metamorphism and are petrologically the most primitive carbonaceous chondrites (McSween, 1979a). Only 3% of carbonaceous chondrite falls are represented by highly metamorphosed types (4–6), this compares with 93% of the ordinary chondrites (Wasson, 1974; Scott and Taylor, 1985). CO3 and CV3 chondrites have not been subjected to temperatures much in excess of 500°C (McSween 1977a,b) and Green et al. (1971) reports that Allende (CV3) has probably not been heated above 230°C. Using the $^{18}O/^{16}O$ thermometer, it has been established that Karoonda was heated to 590°C (Clayton et al., 1977) and Yamato 6903 attained a temperature of 600°C (Clayton et al., 1979). There are no quantitative data available for the metamorphic temperature reached by Coolidge, however petrographic observations indicate that metamorphic features in this meteorite are akin to those of other C4 chondrites (Scott and Taylor, 1985). It is thought that Mulga West may have been heated to a temperature of 800°C (Binns et al., 1977).

The differences in sulphide mineralogy between the C3 to C6 chondrites have been attributed to metamorphism, rather than to processes active in the nebula (McSween, 1977a; Scott and Taylor, 1985). Nickel is a siderophile element and will transfer from the sulphide to the metal phase of the meteorite during metamorphism. However, if metamorphism is accompanied by highly oxidising conditions, most of the iron will be in magnetite and nickel will be forced to remain in the sulphide. Therefore, the meteorites which are considered to have been metamorphosed in an oxidising environment, including Allende, Karoonda and Yamato 6903 (McSween, 1977a; Scott and Taylor, 1985), will contain predominantly nickel-rich sulphide (pentlandite). Alternatively, those meteorites that were metamorphosed under reduced conditions, which include Felix, Ornans and Vigarano, contain troilite as their dominant sulphide mineral (McSween, 1977a,b).

In addition to static metamorphism, there is some evidence to suggest that the matrices of C3 chondrites have been aqueously altered, albeit to a much lesser extent than those of C1 and C2 meteorites (Bunch and Chang, 1980; Grossman et al., 1986; Keck and Sears, 1986; Tomeoka and Buseck, 1986). Sulphates and carbonates that are prominent in C1 and C2 meteorites have been found in C3 chondrites. Kaplan and Hulston (1966) extracted 0.14 wt% water-soluble sulphur from Mokoia, which they attributed to calcium sulphate and the presence of carbonates in Felix and Lancé was indicated by carbon stable isotope studies undertaken by Krouse and Modzeleski (1970). Phyllosilicates have been found in Allende (Grossman et al., 1986) and Mokoia (Tomeoka and Buseck, 1986) and water may have been the agent responsible for veins of iron enrichment in Warrenton (CO3) olivine chondrules (Kerridge, 1972). Cathodoluminescence studies indicate that Colony (CO3) has also undergone hydrous alteration (Keck and Sears, 1986), although this may be of terrestrial origin (Dr A.L. Graham, personal communication).

The parent body relationships of the C3 to C6 chondrites are poorly constrained. The CO and CV chondrites are chemically and petrographically distinct (McSween, 1977a), and by using non-volatile element abundances, Kallemeyn and Wasson (1979, 1982) have found evidence to suggest that CO and CV chondrites accreted separately in the solar nebula and that there is evidence for a relationship between the CO and CM chondrites (termed the CO-CM clan). On a plot of $\delta^{18}O$ against $\delta^{17}O$ the whole-rocks and anhydrous minerals from CM, CO and CV chondrites plot along an ^{16}O mixing line (Clayton and Mayeda, 1977; Clayton et al., 1977; Clayton and Mayeda, 1982). The higher petrologic types have lower $\delta^{18}O$ values suggesting a loss of carbon monoxide during metamorphism, thus CV4-CV6 chondrites might all have formed from CV3-like precursors (Scott and Taylor, 1985).

The present study considers eight carbonaceous chondrites of higher petrologic type (3–6). Investigation of this petrologic sequence has revealed the probable presence of an oxidised form of sulphur in C3 chondrites. This discovery has generated new insight into the aqueous alteration that is so pervasive among CI1 and CM2 meteorites. Stepped combustion analyses were carried-out after the use of fluorine compounds in the extraction system.

4.2 Results and discussion

4.2.1 The concentration and distribution of sulphur in C3 to C6 chondrites

The total sulphur contents of the C3 to C6 meteorites were determined by two methods:

1. Summation of the sulphur liberated between room temperature and 1200°C during stepped combustion.
2. By a single combustion step carried out at 1200°C (bulk combustion).

The results are presented in Table 4.2 and Figure 4.1. The single-step bulk combustion analyses were made to confirm the validity of the stepped combustion results. Sample sizes for both methods were chosen to be approximately equivalent in order to highlight any potential problems associated with the stepped combustion technique.

The C3 to C6 samples range in sulphur content from 800 ppm (Mulga West) to 2.34 wt% (Allende) which is between about 2 and 3 wt% less sulphur than C1 and C2 chondrites. The sulphur content of Mulga West has not previously been determined, however, the low value obtained in this study supports the contention of a C5/6 classification for this meteorite. The results in Table 4.2 and Figure 4.1 show that the agreement for total sulphur abundance between stepped and bulk combustion is best for Vigarano and Yamato 6903 where the two values differ by only 8% in each case. For most other samples (except Coolidge), agreement between the two methods is fairly good and no worse than the differences reported in the literature for replicate analyses (e.g. Felix and Karoonda in Table 4.2). No model of carbonaceous chondrite formation has been specifically invoked to account for either, the decrease of up to 60% sulphur between the C1/C2

Sample	δ^{34}S (‰) Step.	δ^{34}S (‰) Bulk	δ^{34}S (‰) Lit.	Wt% S Step.	Wt% S Bulk	Wt% S Lit.
Ornans	−1.51	+0.72	–	2.13	1.79	2.23 (1)
Felix	−2.45	+0.22 −0.13	+0.3 (2)	1.78	1.61 2.05	2.00 (1) 1.83 (2)
Vigarano	−1.74	+0.17	–	1.30	1.42	2.32 (1)
Allende* Allende–1	−1.89 −0.18	+0.22 +0.15	–	2.03 2.34	1.96 1.77	2.06 (3)
Coolidge	−2.72	+0.88	–	0.33	0.37	2.06 (4)
Y 6903	−2.99	−0.30	–	1.30	1.42	1.32 (5)
Karoonda	−1.77 −2.66	+0.12	−0.2 (2)	1.39 1.28	1.53	1.38 (2) 1.58 (6)
Mulga West	+7.33	ND	–	0.06	0.008	–

Table 4.2 A summary of sulphur data obtained by stepped and bulk combustion of C3 to C6 chondrites. *Allende–1 was analysed prior to the fluorination experiments. References:(1) Mason (1963); (2) Kaplan and Hulston (1966); (3) Clarke et al. (1970); (4) Jarosewich (1966); (5) Shima (1974); (6) Mason and Wiik (1962b). Note: Kaplan and Hulston (1966) also reported whole-rock δ^{34}S values for the following: Lancé (CO3) = +0.5‰, Warrenton (CO3) = +0.4‰ and Mokoia (CV3) = 0.0‰. Bulk = Bulk combustion; Step. = Stepped combustion; Lit. =Literature value; ND = not determinable.

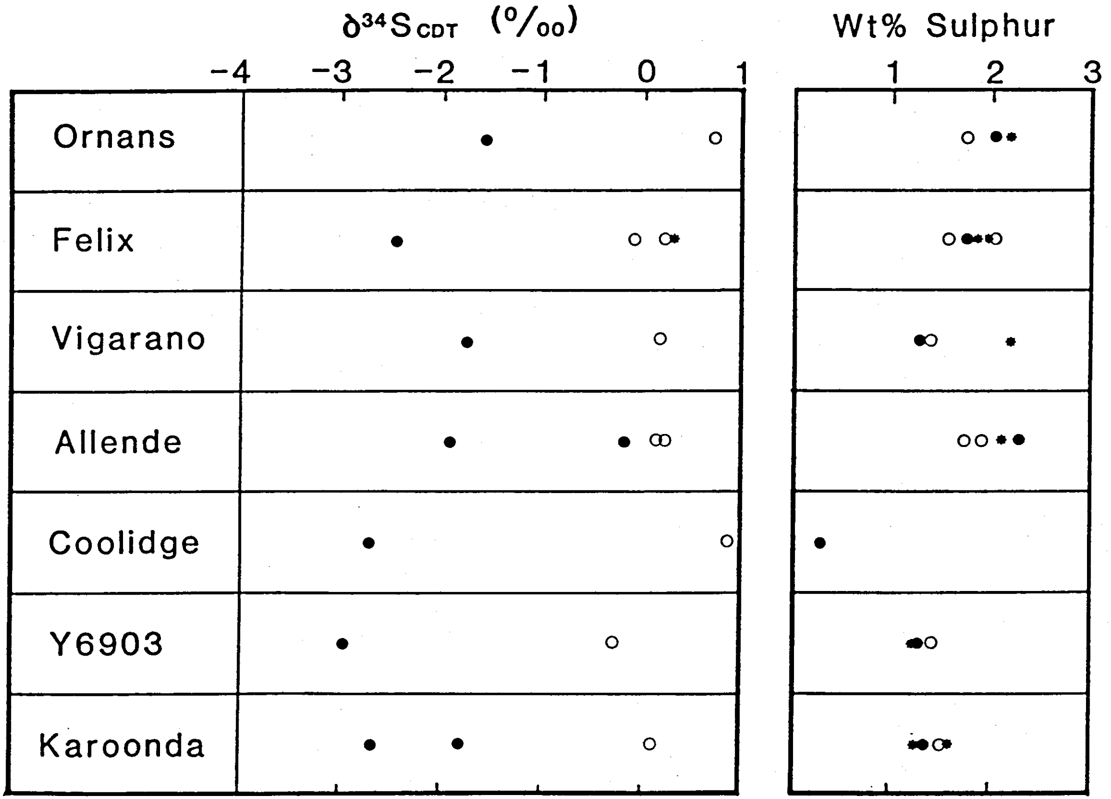


Figure 4.1 Comparison of sulphur data obtained by stepped and bulk combustion with literature values for C3 to C6 chondrites. • = stepped combustion; ∘ = bulk combustion; * = literature values (refer to Table 4.1 for data sources)

and C3 chondrites, or the decreasing sulphur content associated with increasing petrologic type in the C3 to C6 sequence. Changes in total sulphur content may reflect condensation processes in the solar nebula, this has been suggested to explain the volatile element abundance patterns of C3 to C6 chondrites (e.g. Anders et al., 1976; Grossman and Larimer, 1974; Takahashi et al., 1978a,b). Alternatively, the same volatile element variations have also been attributed to open system metamorphism (e.g. Ikramuddin and Lipschutz, 1975, Matza and Lipschutz, 1977). It is also possible that sulphur was lost during thermal metamorphism particularly if temperatures were high enough to cause melting and separation of sulphide minerals. However, this seems unlikely, because the temperature attained by, even the most severely metamorphosed carbonaceous chondrite, Mulga West, did not exceed 800°C (Binns et al., 1977) which is below the Fe-Ni-S eutectic temperature of 950°C (Kullerud, 1963). Feierberg et al. (1985) have proposed that the carbonaceous chondrite parent bodies were originally composed of material with C1- and C2-like compositions and that subsequent internal heating of these bodies by radionuclide decay (e.g. ^{26}Al), leaves cores with C3-like compositions mantled by layers of hydrated and altered C1 and C2 material.

The stepped combustion profiles obtained for C3 and C4 chondrites are shown in Figure 4.2. All the samples show similar sulphur release patterns which are notably different from those obtained for C1 and C2 chondrites. The sulphur data of Coolidge and Mulga West are different from those of any other meteorites considered in this Section so the results for these samples will be largely treated separately below. Between 92% (Vigarano) and 98% (Allende) of the total sulphur is liberated between 400 and 900°C. This includes the temperature interval which is the characteristic range determined for the combustion of many common sulphide minerals (400 to 600°C: Section 2.3.2). Karoonda and Yamato 6903 have two sulphur releases, one between 400-600°C, and another between 600-900°C. Felix, Ornans, Allende and Vigarano show a single dominant sulphur release. This occurs from 450 to 500°C in Felix and Allende, 500 to 550°C in Vigarano and 600 to 650°C in Ornans. The sulphur in these meteorites is released over a wide temperature range, between 50% (Ornans) and 24% (Allende) of the total sulphur is liberated above 600°C. For comparative purposes the data for all the samples can be subdivided into two temperature intervals which approximately coincide with the two releases in Karoonda and Yamato 6903, and are analogous to those used in the discussion of the C1 and C2 meteorite sulphur data (Chapter 3).

1. A 300 to 600°C release accounting for 50% or more of the sulphur in each meteorite. The amounts of sulphur are given in Table 4.3 and

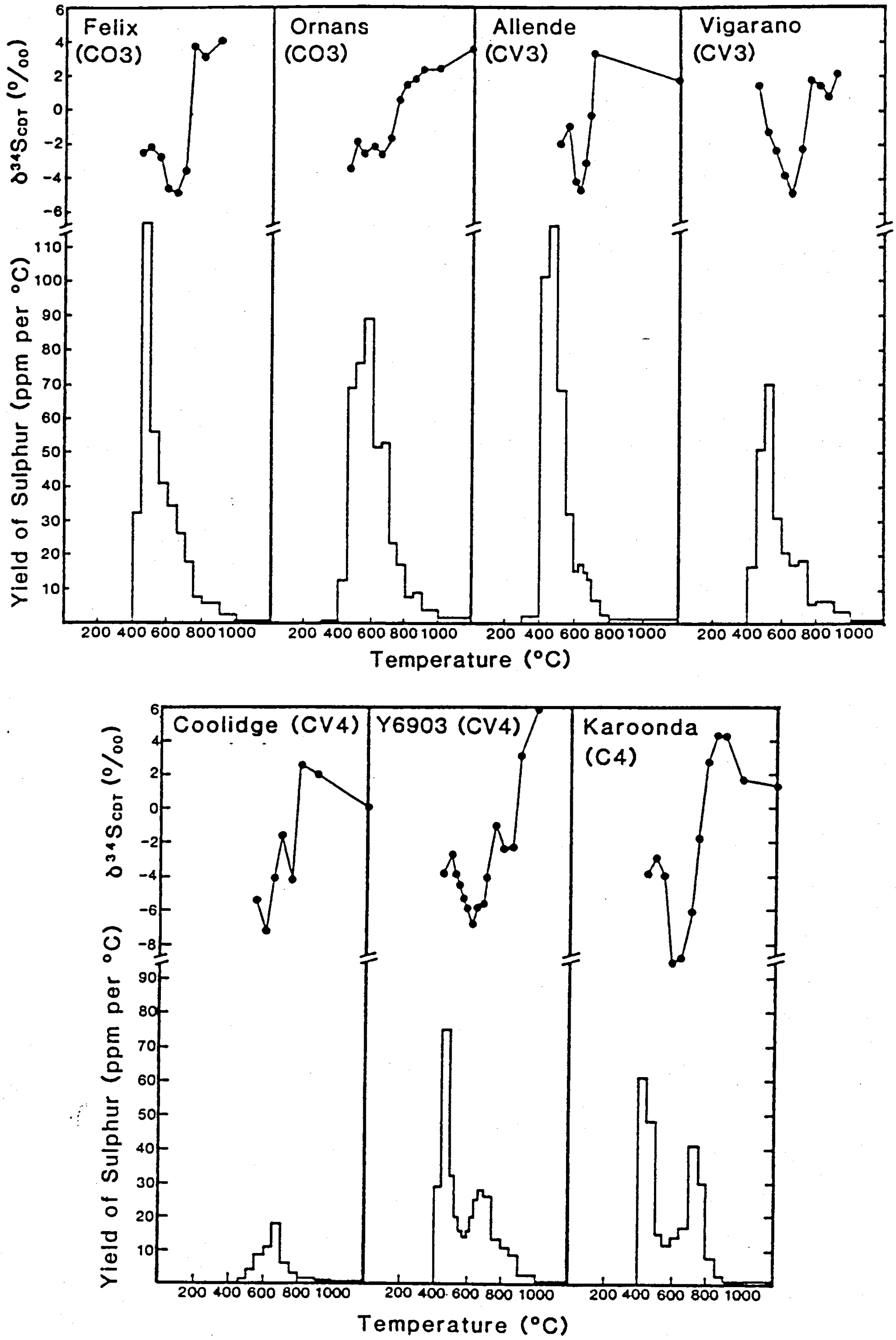


Figure 4.2 The abundance (—) and isotopic composition (-•-) of sulphur in C3 and C4 chondrites as determined by stepped combustion.

are between 0.65 wt% (Karoonda) and 1.54 wt% (Allende).

2. A 600 to 900°C release, accounting for between 0.42 wt% (Vigarano) and 1.02 wt% (Ornans) sulphur (Table 4.3).

Troilite and pentlandite

In Chapter 3, the sulphur released between 300 and 600°C in C1 and C2 chondrites was considered to be a mixture from the combustion of troilite and sulphur-bearing macromolecular organic material. The latter constituent has not previously been recognised in carbonaceous chondrites of type 3 and above, so the sulphur liberated between 300 and 600°C can be wholly attributed to sulphide combustion. However, it is not possible to make a distinction between sulphur from either troilite or pentlandite using the stepped combustion results shown in Figure 4.2 (as was the same for most of the C2 and C1 meteorites). In the case of the CO3 chondrites, McSween (1977b) reports that the sulphide is almost exclusively stoichiometric troilite. Using the 300 to 600°C sulphur release to calculate the abundance of troilite gives 3.11 wt% and 2.81 wt% of this mineral in Felix and Ornans respectively. Kaplan and Hulston (1966) extracted 1.83 wt% sulphur from Felix by HCl treatment, which they attributed to FeS (equivalent to 5.03 wt% troilite). There are no comparative data for the troilite content of Ornans.

Petrographic studies of Vigarano, Allende, Yamato 6903 and Karoonda suggest that pentlandite is normally dominant over troilite (Clarke et al., 1970; Fuchs and Olsen, 1973; McSween, 1977a; Scott and Taylor, 1985). Karoonda contains the following sulphide minerals in order of decreasing abundance: pentlandite, pyrite, chalcopyrite and pyrrhotite (Scott and Taylor, 1985). The amounts of sulphur released between 300 and 600°C in the CV chondrites and Karoonda represent between 42% (Karoonda) and 76% (Allende) of the total sulphur which, based on petrographic evidence, seems too high to be accounted for by troilite combustion alone. A previous analysis of sulphur in Karoonda by Kaplan and Hulston (1966) gave an acid-soluble sulphur (troilite?) content of 0.02 wt% which is a small proportion of the 0.65 wt% sulphur released between 300 and 600°C during stepped combustion. A probable explanation for the difference is that the sulphur liberated between 300 and 600°C during stepped combustion is a mixture from pentlandite and other sulphides including troilite. Although an authentic sample of pentlandite has not been analysed by stepped combustion, it is conceivable that troilite and pentlandite may combust at similar temperatures, as these minerals are chemically alike and indeed, much of the troilite probably contains some nickel. Using the value of 0.02 wt% troilite sulphur obtained

Sample	Yield S Wt% (300–600°C)	δ^{34}S (‰) (300–600°C)	Yield S Wt% (600–900°C)	δ^{34}S (‰) (600–900°C)
Felix	1.13	−2.64	0.56	−2.33
Ornans	1.02	−2.20	1.02	−1.20
Allende	1.54	−1.97	0.49	−1.70
Allende–1	1.28	−0.94	0.84	+0.50
Vigarano	0.77	−1.90	0.42	−1.94
Y 6903	0.71	−3.41	0.51	−3.14
Coolidge	0.05	−3.62	0.22	−1.83
Karoonda	0.65	−5.02	0.5	−2.54

Sample	Calc. anhydrite Wt%	Calc. Ca Wt%	Matrix Ca Wt% (1)	Calc. FESON Wt%
Felix	2.38	0.70	0.92	2.33
Ornans	4.34	1.28	0.29	4.24
Allende	1.87	0.60	1.27	2.00
Allende–1	3.57	1.05	1.27	3.49
Vigarano	1.79	0.53	0.74	1.75
Y 6903	2.17	0.64	–	2.12
Coolidge	0.94	0.28	0.14	0.92
Karoonda	2.51	0.74	1.37	2.45

Table 4.3 Summary of the sulphur concentration and δ^{34}S values obtained over temperature intervals during stepped combustion. Calculated anhydrite and FESON contents represent maximum estimates. References: (1) Matrix determinations of Ca from McSween and Richardson (1977) normalised to whole-rock values using the vol.% matrix determinations of McSween (1977a,b).

for Karoonda by Kaplan and Hulston, then from the stepped combustion data, the amount of sulphur as pentlandite in this meteorite could be as high as 0.57 wt% (equivalent to 1.72 wt% pentlandite). This value is much lower than that of 1.25 wt% sulphur as pentlandite obtained for Karoonda by Kaplan and Hulston (1966). However, Kaplan and Hulston attributed all the acid-insoluble and acid non-volatile sulphur in Karoonda to pentlandite (i.e. the residual sulphur after HCl treatment). It has been shown from the stepped combustion results of Murchison residue MEH (Section 3.5.4) that HCl acid is not specific in its effect upon sulphur-bearing minerals. Despite this, it may be possible to gain some indication of the pentlandite/troilite abundances in these meteorites (including Karoonda) from stepped combustion analyses of HCl residues.

Oxidised sulphur compounds

The sulphur liberated in the temperature interval 600 to 900°C, represents between 32% (Vigarano) and 50% (Ornans) of the total amount of sulphur in the C3-C4 chondrites. Elucidation of the sulphur-bearing component which releases its sulphur above 600°C is not straightforward.

In Chapter 3, the effects of parent body aqueous alteration in the C1 and C2 carbonaceous chondrites was discussed. It was suggested that, during aqueous alteration, sulphur was removed from pre-existing sulphides (i.e. represented by sulphur released between 300 and 600°C in C1 and C2 meteorites) to form FESON, gypsum and epsomite (i.e. sulphur released above 600°C in C1 and C2 meteorites). Figure 4.3 is a plot of 300–600°C sulphur versus 600–900°C sulphur for the C3 and C4 chondrites considered in this study. There is a suggestion of a relationship ($r = 0.662$) which becomes significant ($r = 0.875$) when the data from Ornans is excluded. This correlation indicates that pre-existing sulphide(s) has been altered to a mineral(s) that combusts or decomposes at higher temperatures. The amount of sulphur released between 600 and 900°C is normally higher in C3 compared to C4 chondrites. The proportions of sulphur released over each temperature range should provide a superior indication of alteration than the absolute amounts. The ratio of sulphur liberated between 300 and 600°C to that released between 600 and 900°C decreases in the following order: Allende>Felix>Vigarano>Yamato 6903>Karoonda>Coolidge (i.e. C3>C4). This sequence suggests that, firstly, the C3 chondrites did not escape aqueous alteration on parent bodies and secondly, they have suffered more intense alteration than the C4 chondrites. This observation is consistent with the proposed "onion-skin" model of carbonaceous chondrite evolution (e.g. Feierberg et al., 1985) in which extent of metamorphism increases and the magnitude of aqueous alteration decreases towards the centre of the

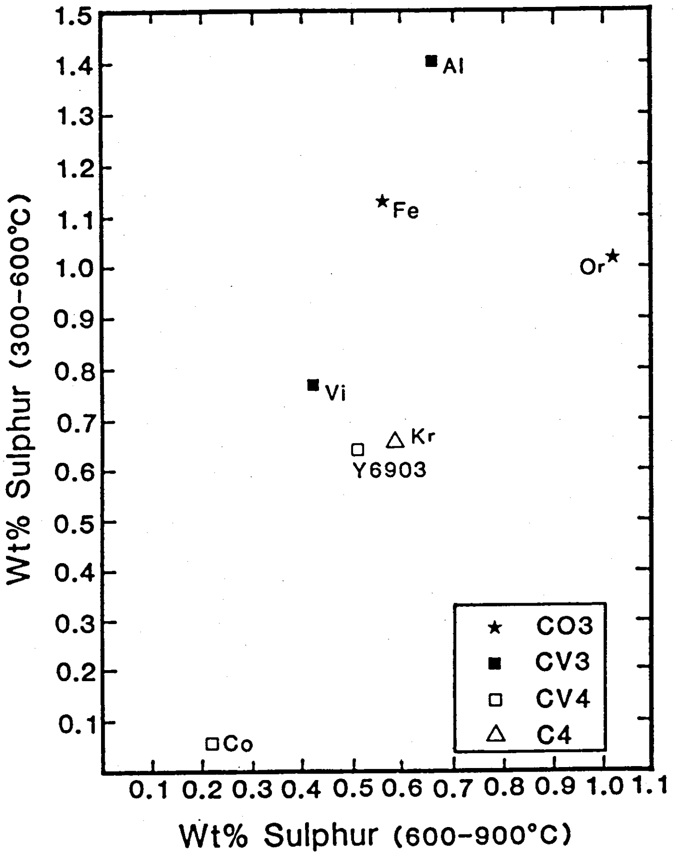


Figure 4.3 A plot of sulphur (300–600°C) versus sulphur (600–900°C) released during stepped combustion of C3 and C4 chondrites. Al=Allende, Co=Coolidge, Fe=Felix, Kr=Karoonda, Or=Ornans, Vi=Vigarano, Y6903=Yamato 6903.

parent body.

In an effort to determine the identity of the sulphur released between 600 and 900°C it is instructive to determine which elements in C3 and C4 chondrites are correlated with sulphur. McSween and Richardson (1977) found correlations between nickel and sulphur and iron and sulphur using the matrix abundances of these elements in C2 and some C3 carbonaceous chondrites. This led them to conclude that a Ni-bearing Fe-S-O phase is present in greater or lesser amounts in the matrices of C2's and some C3 chondrites. McSween and Richardson considered that this sulphur-bearing phase was the same as that first identified in the matrix of the Murchison (CM2) meteorite by Fuchs et al. (1977). Subsequent detailed petrographic studies using transmitted electron microscopy have revealed that the Fe-S-O phase is widespread in CM2 chondrites where it is now known as meteoritic tochilinite or FESON (Chapter 3).

It is known that aqueous alteration in CI1 and CM2 carbonaceous chondrites has led to the formation of significant amounts of gypsum and epsomite (e.g. Bostrom and Fredriksson, 1966). Therefore, plots of calcium against sulphur and magnesium against sulphur have been constructed to investigate whether these elements are associated in the matrices of C3 and C4 chondrites. These graphs are given in Figure 4.4 and use the matrix determinations of sulphur, calcium and magnesium (all normalised to silicon) reported by McSween and Richardson (1977). It can be seen from Figure 4.4 that there is a suggestion of a relationship between calcium and sulphur ($r = 0.667$) in some of the meteorites. Figure 4.4b indicates that there is less of a correlation between magnesium and sulphur ($r = 0.0078$). The mineral in the matrices of these meteorites most likely to contain calcium and sulphur is anhydrite ($CaSO_4$), as temperatures experienced by all these meteorites must, at some point, have exceeded the dehydration temperature of gypsum ($CaSO_4.2H_2O$) which is 95°C (Hurlbut and Klein, 1977). Based on Figure 4.4a, the concentration of anhydrite is expected to be highest in Mokoia with Allende next; it would seem to be low in most other C3 and C4 chondrites. This is supported by:

1. The extraction of 0.14 wt% water-soluble sulphur from Mokoia attributed to $CaSO_4$ (Kaplan and Hulston, 1966).
2. A stepped combustion analysis of Mokoia undertaken by Halbout et al. (1986) which gave a dominant release of sulphur between 740 and 1040°C. This is the characteristic release temperature for gypsum (Chapter 2).

It is tempting to attribute the calcium sulphate contents, derived from the stepped combustion data, to anhydrite or gypsum formed in the meteorite parent body. However, it is also possible that some of this mineral

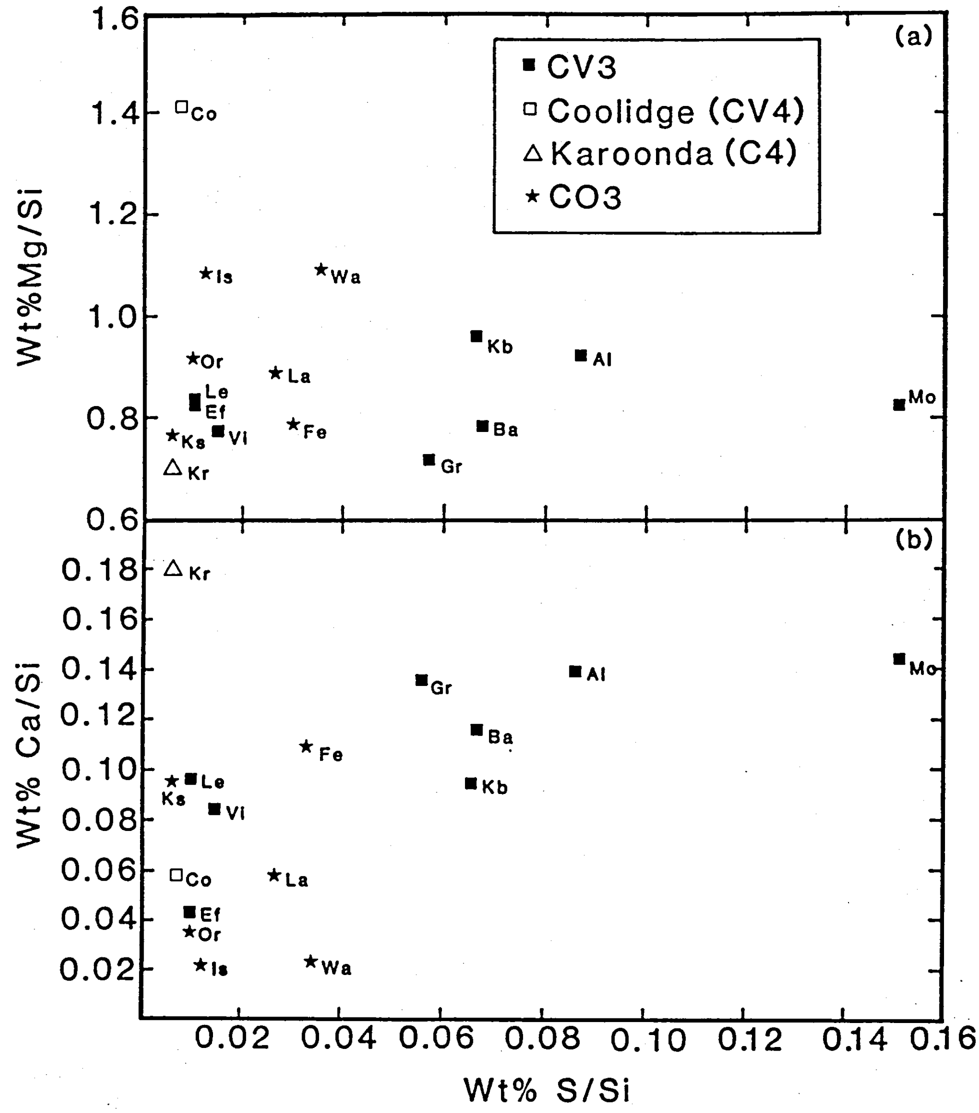


Figure 4.4 Silicon normalised, (a) Mg vs. Si, and (b) Ca vs. S values in C3 and C4 chondrite matrices (data from McSween and Richardson, 1977). Al=Allende, Ba=Bali, Ef=Efremovka, Gr=Grosnaja, Kb=Kaba, Le=Leoville, Mo=Mokoia, Vi=Vigarano, Co=Coolidge, Fe=Felix, Is=Isna, Ks=Kainsaz, La=Lancé, Or=Ornans, Kr=Karoonda, Wa=Warrenton.

formed by weathering of the meteorite on Earth. Sulphates, carbonates and iron oxides are common chemical weathering products identified in Antarctic meteorites (Gibson and Andrawes, 1980; Marvin, 1980; Gooding, 1981; Grady, 1982; Gooding, 1986). However, an origin by weathering processes is unlikely to account for the relatively high concentrations of calcium sulphate indicated to be present from the results of this study, because:

1. Most of the C3 meteorites and Karoonda are falls (only Coolidge and Yamato 6903 are finds).
2. Any terrestrially-formed gypsum will tend to be concentrated in the outer regions of the meteorites, whereas the samples used in this study were interior fragments.

The less striking correlation between magnesium and sulphur is also of interest as it suggests that the C3 and C4 chondrites probably contain negligible quantities of epsomite. According to Richardson (1978), epsomite mineralisation in C1 meteorites occurred after that of gypsum and calcite. The presence of gypsum in Mokoia (Kaplan and Hulston, 1966) and calcite in Felix and Lancé (Krouse and Modzeleski, 1970) suggests that alteration ceased after precipitation of these two minerals but before that of epsomite. Assuming that the C3 chondrites sample material from the inner regions of parent bodies (e.g. Feierberg et al., 1985), then it is probable that hydrothermal alteration occurred during a period of increasing temperature. As the temperature increased, dehydration of the precursive C3 material will have occurred as the water migrated towards the surface of the parent body.

The aqueous alteration of type 3 carbonaceous chondrites is not well-documented. However, recent petrologic, microprobe and cathodoluminescence studies have provided evidence for widespread hydrous activity in type 3 unequilibrated ordinary chondrites (Hutchison et al., 1985; Alexander et al., 1986; Guimon et al., 1986). In particular, Hutchison et al. (1986) have proposed that Semarkona (LL3) is borderline between types 2 and 3. Alexander et al. (1986) reports that aqueous alteration of Semarkona has led to the formation of the following minerals:

1. Phyllosilicates (smectite).
2. Altered olivine associated with a Zn-rich, Fe-Si-S phase.
3. Abundant calcite.

A stepped combustion analysis of Semarkona (Figure 4.5) gives a sulphur release profile which strongly resembles those obtained for C3 carbonaceous chondrites. The sulphur release in Semarkona is bimodal and dominated by a peak between 300 and 600°C which accounts for 1.27 wt% sulphur

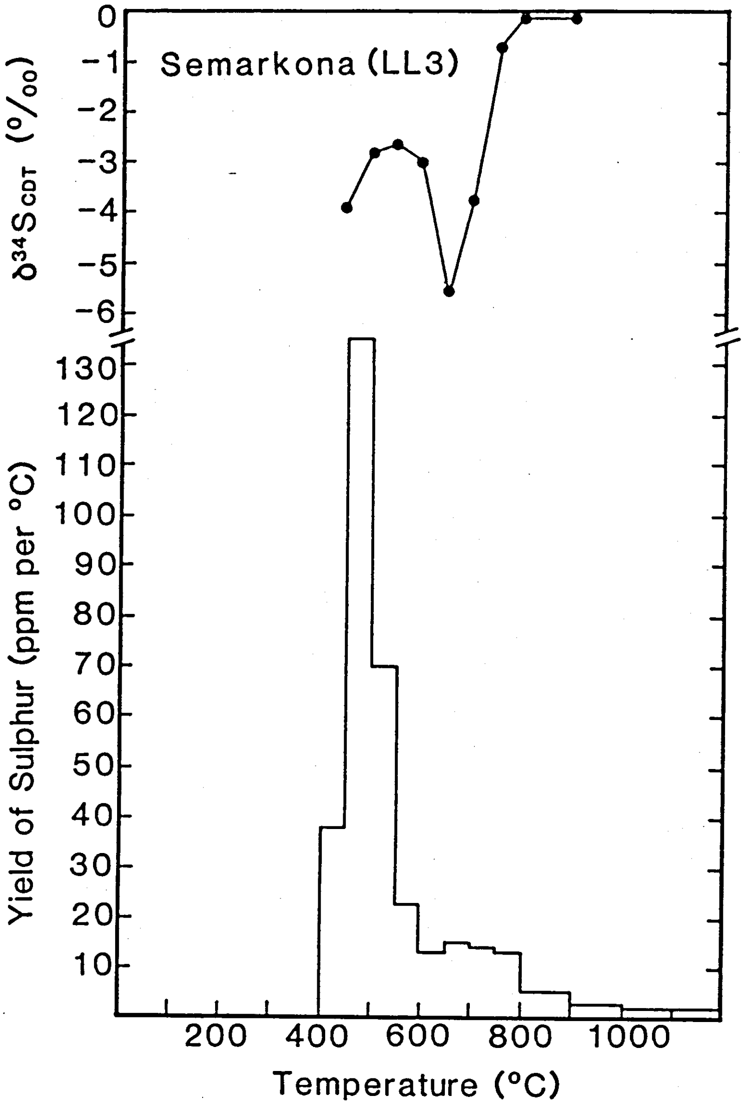


Figure 4.5 The abundance (—) and isotopic composition (-•-) of sulphur in Semarkona as determined by stepped combustion.

(equivalent to 74% of the total sulphur). The second release, at higher temperatures, amounts to 0.36 wt% sulphur (Figure 4.5). The proportions of sulphur released over the two temperature intervals, 300 to 600°C and 600 to 900°C, are similar to those determined for Felix and Allende (Table 4.3). The matrix of Semarkona contains abundant pentlandite (Alexander et al., 1986) and the combustion of this mineral probably accounts for the large peak in the sulphur release profile (400 to 600°C). The identity of the sulphur compound that burns above 600°C cannot be defined with certainty, since neither gypsum nor FESON have been reported as constituent matrix components of Semarkona. The stepped combustion results show that Semarkona, in which the effects of aqueous alteration have been relatively well-studied, is similar to C3 carbonaceous chondrites for which the possibility of hydrous activity had, until recently, been largely discounted.

From the stepped combustion data for C3 and C4 chondrites, it is difficult to predict the relative amounts of sulphur that may be present in either FESON or anhydrite. If all the sulphur liberated between 600 and 900°C is attributed to anhydrite then the maximum amounts of this mineral possible in any of the C3 or C4 meteorites is 4.34 wt% in Ornans (Table 4.3). The quantities of calcium determined from the anhydrite contents are between 0.48 (Coolidge) and 1.28 wt% (Ornans). In Table 4.3, it can be seen that the amounts of calcium as anhydrite can, with the exception of Ornans and Coolidge, be accommodated by the matrix calcium contents determined for these meteorites by McSween and Richardson (1977). Other calcium-bearing minerals in C3 and C4 chondrites include pyroxenes (augite, ferroaugite, diopside), anorthite, grossular, and melilite. However, most of these minerals are present mainly in aggregates (e.g. CAI) and chondrules which were avoided during the microprobe analyses made by McSween and Richardson (1977). Therefore, the relatively high calcium contents of the matrices are not easily explained in terms of the known mineralogy (unless the calcium is accommodated in extremely small CAI or perhaps mineral fragments). Thus, on chemical grounds it is plausible that significant quantities of anhydrite are present in the matrices of C3 and C4 meteorites. Against such a hypothesis, it is difficult to understand why a mineral present at 2 and 4 wt% concentration has remained undetected during petrographic studies, unless it is very fine-grained. It may be significant that these meteorites have yet to be treated to the same extensive TEM studies that have been applied to many CM2 chondrites.

Turning now to consider the possibility of FESON in C3 and C4 chondrites; if all the sulphur liberated between 600 and 900°C is attributed to this phase then the maximum amounts of FESON in the matrices can be determined. Calculated FESON contents are given in Table 4.3 and vary between 0.92 (Coolidge) and 4.24 wt% (Ornans). These results suggest that

FESON and other PCP, which are important constituents of CM2 matrices, may also be a component of the matrices of C4 chondrites. This suggestion awaits confirmation by petrographic studies.

With the present data it is not possible to differentiate between the amounts of anhydrite and FESON constituting the sulphur which burns between 600 and 900°C in the meteorites. However, a relatively straightforward chemical/physical separation could be envisaged to resolve between anhydrite and FESON. The Fe-S-O phase (FESON) described by Fuchs et al. (1977) is highly magnetic, so a stepped combustion analysis of the magnetic fraction of the matrix (carried-out after washing with distilled water to remove any associated sulphates) could reveal the quantity of FESON sulphur in a C3/C4 meteorite. Similarly a stepped combustion of water extracted sulphur from the meteorites should yield similar information about anhydrite.

Coolidge and Mulga West

Mulga West and Coolidge are both meteorite finds and have suffered extensive terrestrial alteration (Binns et al., 1977; Jarosewich, 1966), which may explain the low total sulphur contents of these meteorites. Compared to the other C4 chondrites studied (Karoonda and Yamato 6903), Coolidge is depleted in sulphur by 1 wt%, which is probably an illustration of the extent of terrestrial weathering suffered by this sample.

Coolidge has a broad release of sulphur between 400 and 900°C, with a maximum release between 600 and 700°C (Figure 4.2). Petrographic examination of this meteorite by Scott and Taylor (1985) and McSween (1977b), revealed that troilite is the only sulphide mineral present. However, the main release of sulphur in the stepped combustion profile of Coolidge, seems to occur at too high a temperature to be accounted for by the combustion of troilite alone (it was shown in Chapter 2 that troilite separated from the Bella Roca iron meteorite has a peak release of sulphur between 400 and 450°C).

The Mulga West meteorite was recovered from the Nullarbor Plain of Western Australia. Weckwerth et al. (1985) suggest that this meteorite has lost some of its original nickel-rich sulphide, possibly by weathering. Calcite in Mulga West has a $\delta^{13}C$ of +3.8‰ relative to PDB (PeeDee Belemnite, the carbon isotope standard), which is consistent with derivation of this mineral from the limestone upon which the meteorite landed (Binns et al, 1977). A stepped combustion analysis of the sulphur in Mulga West is shown in Figure 4.6. The sample has a whole-rock $\delta^{34}S$ value of +7.3‰ and the main release of sulphur occurs between 800 and 1000°C which corresponds to 0.04 wt% sulphur. The sulphide content of the meteorite is very low

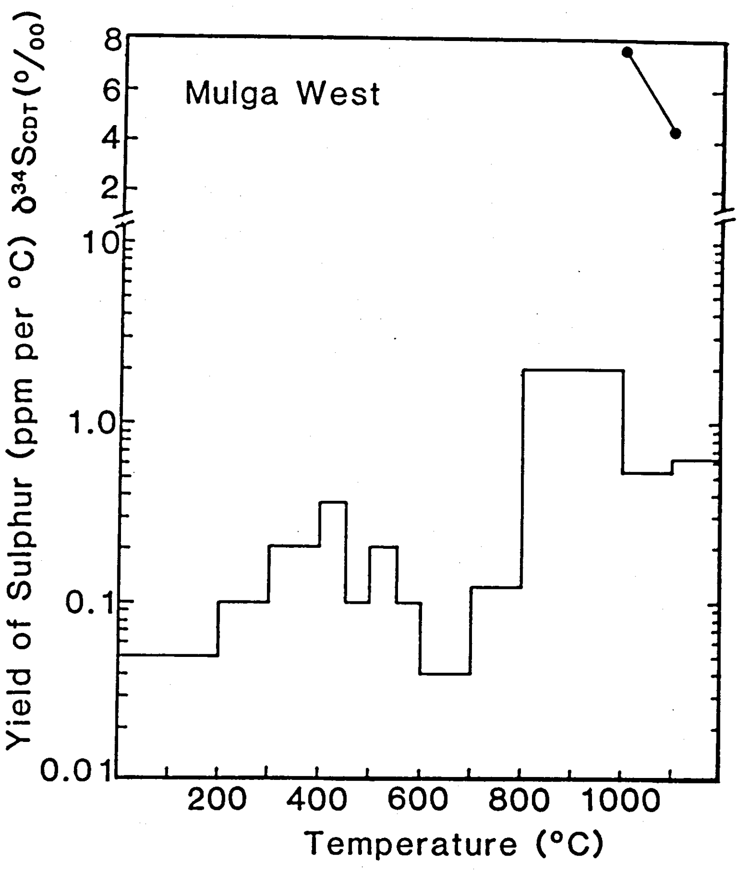


Figure 4.6 The abundance (—) and isotopic composition (-•-) of sulphur in Mulga West as determined by stepped combustion.

since the sulphur combusting between 300 and 600°C amounts to only 700 ppm. The temperature of the dominant release of sulphur in Mulga West is characteristic of that for a sulphate and in particular, it is similar to the decomposition/combustion temperature of gypsum. The presence of gypsum in this meteorite can be attributed to either terrestrial weathering of the meteoritic sulphides, or by the addition of gypsum to the meteorite from the underlying limestone. It is considered unlikely that the sulphate is of extraterrestrial origin.

4.2.2 Sulphur isotope measurements of C3 to C6 chondrites

The whole-rock meteorite $\delta^{34}S$ values obtained by stepped combustion and single-step combustion are compared in Figure 4.1 (and listed in Table 4.1), along with previously reported values. In Figure 4.1, the single-step combustion $\delta^{34}S$ values are in the range -0.33 (Yamato 6903) to $+0.88‰$ (Coolidge), with the majority very close to 0‰. The values obtained by stepped combustion are lower by between about 2 and 3‰. The only exception is for a sample of Allende (designated Allende–1) which was analysed during the same time period as the C1 and C2 meteorites. Allende–1 gave a whole-rock $\delta^{34}S$ value of $-0.18‰$. It is considered that the $\delta^{34}S$ values obtained for sulphides in C3 and C4 chondrites may be erroneous due to the problems detailed in Section 2.4.2. The artificially low $\delta^{34}S$ values are probably the result of isotopic fractionation associated with the formation of a small amount of sulphur trioxide during the low temperature region of the stepped combustion experiment. Due to the high temperatures at which the single-step combustion experiments were carried out, any isotopic fractionation processes are negligible and so the $\delta^{34}S$ values obtained by this method are considered to be reliable.

Overall, the bulk $\delta^{34}S$ values for C3 and C4 meteorites show a slight enrichment in ^{34}S (mean $\delta^{34}S = +0.28‰$). Coolidge has the highest $\delta^{34}S$ ($+0.88‰$) value measured (apart from the anomalous Mulga West) which is probably related to the extensive amount of terrestrial weathering undergone by this meteorite. There appears to be no systematic variation in $\delta^{34}S$ with petrologic type, however the meteorites are generally depleted in ^{34}S with respect to the majority of the C1 and C2 samples. This is illustrated in Figure 4.7 where sulphur content and $\delta^{34}S$ values are plotted for all the C3 and C4 chondrites and all the C1 and C2 meteorites considered in Chapter 3. It was noted in Chapter 3 that the enrichment in ^{34}S of the C1 and C2 meteorites is probably related to minor isotopic exchange reactions occurring during formation of the different sulphur minerals on the C1-C2 parent bodies. The C3 and C4 chondrites have undergone substantially less aqueous alteration and have, therefore, maintained their primitive sulphur isotopic

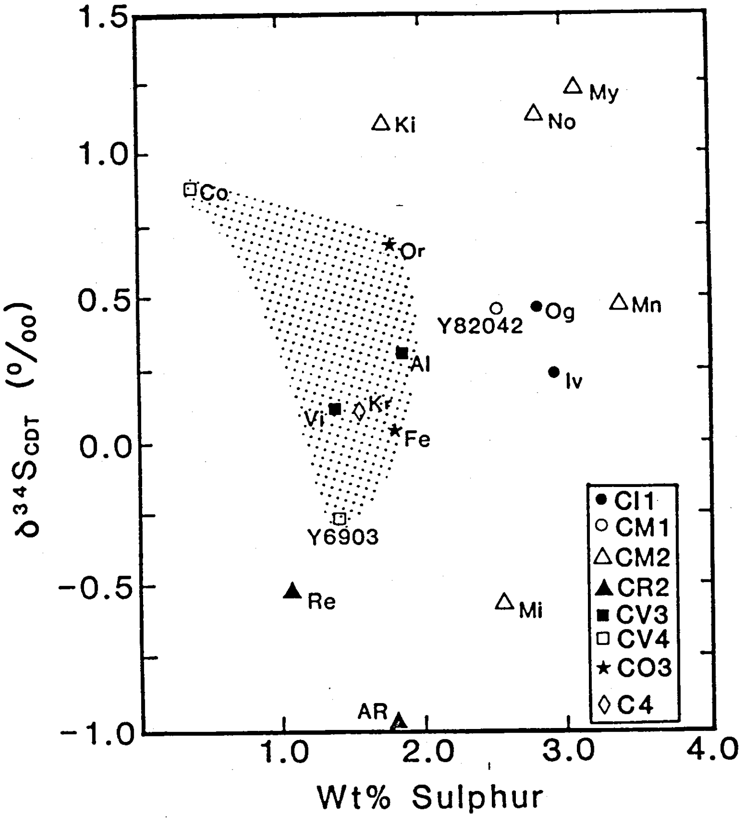


Figure 4.7 Whole-rock δ^{34}S vs. total sulphur abundance for C1 to C4 carbonaceous chondrites. The shaded area represents data for C3 and C4 chondrites. Data for C3 and C4 chondrites were obtained by bulk combustion all other values were determined by stepped combustion. AR=Al Rais, Al=Allende, Co=Coolidge, Fe=Felix, Iv=Ivuna, Ki=Kivesvaara, Kr=Karoonda, Mi=Mighei, Mn=Murchison, My=Murray, No=Nogoya, Og=Orgueil, Or=Ornans, Re=Renazzo, Vi=Vigarano, Y6903= Yamato 6903, Y82042=Yamato 82042.

compositions.

The sulphur isotopic profiles of the C3-C6 meteorites obtained by stepped combustion are shown in Figure 4.2. Despite the problems associated with these isotopic measurements, the profiles can be discussed qualitatively and are useful for comparative purposes. The isotopic profiles for all samples have some features in common. Most of the meteorites display a characteristic minimum $\delta^{34}S$ value between 600 and 650°C, which is coincident with a minimum in sulphur dioxide release. In Figure 4.2, very low $\delta^{34}S$ of $-6.8‰$, $-9.1‰$ and $-7.1‰$ correspond with low sulphur concentrations of 0.06 wt%, 0.04 wt% and 0.04 wt% in Coolidge, Karoonda and Yamato 6903 respectively. It is noteworthy that sulphur burning at 650°C in Semarkona (Figure 4.5) also has a low $\delta^{34}S$ value of $-5.6‰$. The low $\delta^{34}S$ values can be explained by:

1. An artefact of the stepped combustion experiment.
2. The burning of very small amounts of isotopically light sulphur.

It is unlikely that low $\delta^{34}S$ values can be achieved by kinetic isotope fractionation during the progressive combustion of an individual sulphur-bearing component as this would normally lead to a gradual enrichment in ^{34}S in the uncombusted part (this was discussed in Section 2.4.1). A decrease in $\delta^{34}S$ was not obtained at 600°C during the stepped combustion of Bella Roca troilite, although it is possible that at this temperature something in the meteorite (perhaps metal?) may catalyse the production of sulphur trioxide, resulting in a large isotopic fractionation in the remaining sulphur dioxide. This is speculative, but it is apparent that Ornans, which contains troilite as its only sulphide mineral (McSween, 1977b), shows the smallest isotopic deviation ($-2.1‰$) at 600°C. The thermally-metamorphosed C4 chondrites, which are relatively rich in pentlandite, have the lowest $\delta^{34}S$ values. A replicate analysis of Karoonda revealed an isotopic minimum at 600°C of $-8.3‰$, indicating that the result is at least reproducible.

The origin of the isotopically light sulphur is an unresolved problem, it may be an artefact of the experiment, but if it does represent the burning of a discrete sulphur compound or mineral in the meteorites then it is a ubiquitous substance in C3 and C4 chondrites present at low concentration. Minor sulphides with complex and unusual evolutionary histories have recently been described from within the CAI of Allende. Both molybdenite (MoS_2) and iron-nickel sulphide have been identified as common minerals in the unusual aggregates known as "Fremdlinge" in C3 chondrites (Fuchs and Blander, 1977; El Gorsey et al., 1978 ; Armstrong et al., 1985). Most of the minerals in Fremdlinge are thought to have condensed early in the history of the solar nebula (Armstrong et al. 1985). It is tempting to attribute the sulphide minerals in these inclusions with $\delta^{34}S$ values distinct from the normal meteoritic value of 0‰. It is thought that some of the material in CAI could have a pre-solar origin (e.g. Clayton et al., 1973; Clayton and Mayeda, 1977). Survival of a pre-existing minor sulphide through the solar nebula environment is difficult to imagine, but protection by enclosure in a refractory mineral is an obvious possible explanation. Indeed, Fremdlinge are often found within refractory minerals, e.g. the Fremdlinge called "Willy" is included in melilite in Allende (Armstrong et al., 1985). These speculations cannot be substantiated until such times as either the sulphide minerals are separated from the host phases for isotopic analysis, or a stepped combustion of a separated CAI is made. Unlike previous investigations, the mass spectrometer used in this study may be sufficiently sensitive to deal with analysis of separated minor sulphur-bearing components.

As was stated earlier the $\delta^{34}S$ data for the C3-C6 chondrites have been strongly affected by sulphur trioxide formation during stepped combustion. The sulphur released between 300 and 600°C thought to be from the burning of sulphide (troilite and pentlandite) shows a range in $\delta^{34}S$ values from −5.02 (Coolidge) to −1.90‰ (Vigarano). The 300 to 600°C sulphur in Allende–1 has a $\delta^{34}S$ value of −0.94‰. Previous $\delta^{34}S$ values for C3 chondrites reported by Kaplan and Hulston (1966) are between −1.4 (Mokoia) and +0.5‰ (Lancé). The $\delta^{34}S$ values of sulphide in Allende–1 and Mokoia are similar to troilite values determined for C1 and C2 chondrites in Chapter 3. Kaplan and Hulston found that in Karoonda, troilite ($\delta^{34}S = +0.4‰$) is enriched in ^{34}S relative to pentlandite ($\delta^{34}S = -0.2‰$).

For the sulphur released between 600 and 900°C the $\delta^{34}S$ values obtained are between −3.14 (Yamato 6903) and −1.20‰ (Ornans). These values are lower than that obtained from Allende–1 which gave a $\delta^{34}S= +0.5‰$ for sulphur released between 600 and 900°C. It is notable that the value for Allende–1 is quite similar to the isotopic composition of putative gypsum and FESON in C1 and C2 meteorites.

The $\delta^{34}S$ values of sulphur liberated from 300 to 600°C and 600 to 900°C during stepped combustion are probably artificially low by 2 and 3‰. The reason for this, isotopic fractionation resulting from the concurrent formation of sulphur dioxide and sulphur trioxide during combustion, was discussed in Chapter 2. The bulk combustion data and the results of the analysis of Allende–1 suggest that most of the sulphur in C3 and C4 chondrites has a $\delta^{34}S$ value of close to 0‰.

4.3 Conclusions

Based on the results described above, the following additional clues have emerged concerning the origin of types 3 to 6 carbonaceous chondrites.

1. Most of the sulphur in C3 and C4 chondrites occurs as sulphide.
2. C3 and C4 chondrites contain oxidised sulphur most likely to be of preterrestrial origin.
3. The C6 chondrite (Mulga West) contains a very low concentration of sulphur the majority of which is oxidised and has originated from either contamination by terrestrial sulphur, or in situ alteration of pre-existing pentlandite.
4. The meteorite whole-rock δ^{34}S values are within ± 1‰ and do not correlate with extent of metamorphism.
5. Despite the serious problems associated with the isotopic data there are indications that a minor amount of sulphur has an unusually low isotopic composition in most C3 and C4 chondrites.

The sulphur data of this study give evidence that C3 and C4 chondrites have undergone aqueous alteration similar in extent to that experienced by type 3 unequilibrated ordinary chondrites (e.g. Semarkona). The oxidised sulphur in C3 and C4 chondrites seems to occur as anhydrite (or gypsum) and FESON, these are the same compounds which were identified from the stepped combustion data for C1 and C2 meteorites. The absence of elemental sulphur and epsomite from C3 and C4 chondrites indicates that aqueous alteration was less extensive than in C1 and C2 meteorites. Evidence for aqueous alteration in C3 chondrites has been found (e.g. Bunch and Chang, 1980; Tomeoka and Buseck, 1986) but the occurrence of anhydrite and FESON in these meteorites has not been detected previously during petrographic studies. Moreover, no previous study has suggested that C4 chondrites are hydrothermally altered. This observation is in conflict with existing models of carbonaceous chondrite evolution that involve C4-like material forming deep within the parent bodies, and thereby escaping aqueous alteration.

Chapter 5

The Enstatite Meteorites

Current meteorite classification makes a distinction between the enstatite chondrites and aubrites (or enstatite achondrites). There are correlated textural, chemical and mineralogical variations among enstatite chondrites indicating that they are cogenetic and derive from a single parent body. The aubrites are mineralogically and isotopically similar to enstatite chondrites suggesting that these two groups are also related. However, a textural and compositional hiatus exists between chondrites and aubrites making a direct genetic link between them inconclusive. Much of the current research concerning enstatite meteorites has been directed towards understanding which of their properties reflect nebular processes and which were established during metamorphism and/or partial melting of the parent body or bodies.

In this chapter the enstatite chondrites and aubrites are discussed together because of their many similarities. A suite of thirteen samples, including nine chondrites and three aubrites, have been analysed by stepped combustion. The results are used to describe the distribution and isotopic composition of sulphur in the meteorites and to examine the nature of the relationship between chondrites and aubrites. This has not previously been possible because the sulphur isotopic composition of enstatite meteorites has not been studied in enough detail to justify extended discussion. Sulphur isotopic measurements have been reported previously for the chondrites Hvittis, Indarch and Abee, and the aubrite Norton County (Thode et al., 1961; Hulston and Thode, 1965a; Kaplan and Hulston, 1966).

5.1 Definition, classification and origin

The enstatite meteorites are a group of 35 highly reduced stones; they are composed of 24 enstatite chondrites and 11 aubrites (Graham et al., 1985). Known members of the enstatite meteorite clan are listed in Table 5.1 along

Class	Meteorites		
EH3	_Kota-Kota_	Quingzhen*	Yamato 6901
EH4	_Abee_*	Adhi Kot	_Indarch_
	Parsa*	St. Sauveur	_South Oman_*
	Bethune (E4–E5)		
EH5	_St. Mark's_*	_Yilmia_	
EL5	Reckling Peak A80259 -		
EL6	Allan Hills A81021	_Atlanta_	Blithfield
	Daniel's Kuil	Hvittis*	_Khairpur_*
	Jajh deh Kot Lalu*	Pillitsfer*	Ufana*
	North West Forrest		
E7	Happy Canyon		
Aubrites	Allan Hills A78113	Aubres*	Bishopville*
	_Bustee_*	Cumberland Falls*	Khor Temiki*
	Mayo Belwa*	_Norton County_*	Pesyanoe*
	Shallowater	Pena Blanca Spring	

Table 5.1 Known enstatite chondrites and aubrites. From Graham et al. (1985). Samples analysed in the present study are in italics. * Meteorite fall.

with their current petrologic classification (samples analysed in this study are emphasised). Enstatite chondrites have textures comparable with ordinary and carbonaceous chondrites although not all contain clearly defined chondrules (e.g. Happy Canyon which is an E7). The aubrites are coarser-grained than the chondrites, they are achondritic meteorites and, with the exception of Shallowater, they are all breccias.

The mineralogy of enstatite meteorites is dominated by iron-free, low calcium pyroxene (enstatite, $MgSiO_3$, hence the generic name) which accounts for between 60 to 80 vol.% of the meteorites. Other major mineral components present include iron-nickel metal (13–28%) and troilite (FeS, 5–17%) (Dodd, 1981). Numerous accessory phases are known and many are not normally encountered in terrestrial rocks. Perhaps the most important of these are a multitude of unusual sulphides (discussed in Section 5.2) and two nitrogen-bearing minerals, sinoite (Si_2N_2O) and osbornite (TiN). Most of the minerals identified in enstatite chondrites have also been found in aubrites (although sinoite is an exception).

The classification of enstatite meteorites is based mainly upon their major and minor element concentrations. The enstatite chondrites were subdivided into two groups (types I and II) on the basis of variation in Fe/Si and S/Si ratios (Figure 5.1) and extent of recrystallisation (Yavnel', 1963; Anders, 1964). In detailed studies of the mineralogical and chemical properties of enstatite chondrites, Mason (1966) and Keil (1968a) corroborated the subdivisions made by Anders, but the occurrence of two meteorites—St. Sauveur and St. Mark's—with intermediate properties, prompted Keil to introduce a third type. Van Schmus and Wood (1967) re-cast the enstatite chondrites into a single compositional group (E) and assigned petrologic numbers ranging from 4 (least recrystallised) to 6 (most recrystallised). The equalities between the Anders-Keil and Van Schmus-Wood classifications are as follows: E4=type I, E5=intermediate and E6=type II. Baedecker and Wasson (1975) have found evidence for a compositional gap between the E4,5 and the E6 chondrites indicating derivation from two separate, but similar, parent bodies. By analogy with the high-iron and low-iron groups of ordinary chondrites, the E4 and E5 chondrites were placed into an 'EH' group and the E6 chondrites into an 'EL' group (Sears et al., 1982). However, a recent analysis of the iron content of enstatite chondrites by Easton (1985) indicates no clear distinction between types I and II based on the concentration of this element.

The range of enstatite meteorite properties has been extended by the discovery of an E7 chondrite (Happy Canyon: Olsen et al., 1977), two E3 unequilibrated enstatite chondrites or UEC's (Prinz et al., 1984; Weeks and Sears, 1985) and an Antarctic EL5 chondrite (Sears et al., 1984). The discovery of an EL5 chondrite is most significant as this provides evidence for a genetic difference between EH and EL chondrites.

The meteorites analysed for sulphur in this study include some samples which have been subject to re-classification. Kota-Kota was originally classified as an E4 chondrite (Keil, 1968a; Mason, 1966) but is now thought to be an EH3 (Prinz et al., 1984) and Yilmia was originally classified as a type 6 by Buseck and Holdsworth (1968) but is now classified as an E5 (Graham et al., 1985). The Abee sample analysed in this study is consortium sample number 1,1 (Marti, 1983), a large typical clast whose mineralogy has been described in detail by Rubin and Keil (1983).

It is considered that the enstatite chondrites condensed from a gas with a C/O ratio of 0.8 (versus the normal solar ratio of 0.6: Larimer, 1968; Larimer and Bartholomay, 1976) and at a pressure of about 1 atm (versus the normally accepted value of 10^{-4} to 10^{-6} atm for other meteorite classes: Blander, 1971; Herndon and Suess, 1976; Sears, 1980). All enstatite chondrites are relatively rich in volatile elements and EH4's have similar abundances of the highly volatile elements (e.g. Se, Ag, Zn, In, Cd, Br etc.) to CI1 meteorites (Hertogen et al., 1983). The relative depletion of volatiles in EL6 chondrites has been explained by either a higher accretion temperature than E4 material (Larimer, 1973; Alaerts and Anders, 1979), or volatile

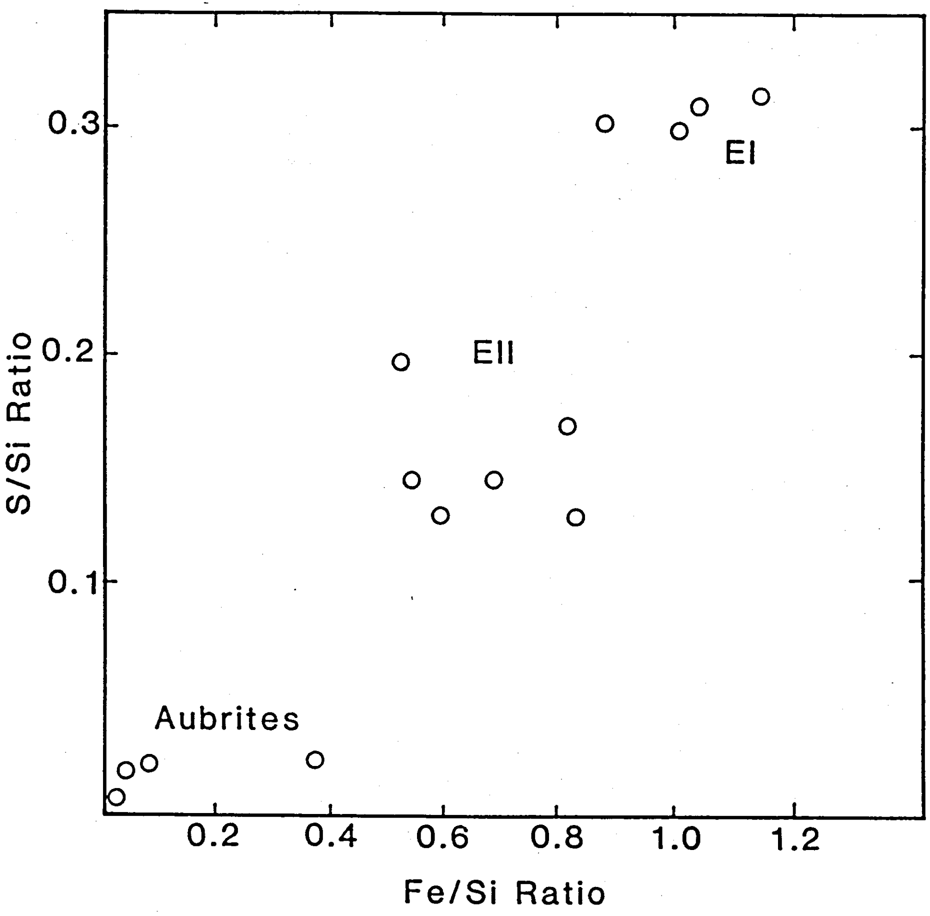


Figure 5.1 Siderophile and chalcophile element fractionation in enstatite chondrites. (After Sears, 1980).

loss due to progressive thermal metamorphism (Binz et al., 1974; Ikramuddin et al., 1976; Biswas et al., 1980), since it has been estimated that E6 material has been heated above 870°C (Keil, 1968a; Skinner and Luce, 1971; Larimer and Buseck, 1974). The evidence for both these arguments has been considered to be about equal (Hertogen et al., 1983) and neither seems to be strongly compelling.

Aubrites could have formed as: (i) igneous differentiates of EL6 material (Watters and Prinz, 1979; Biswas et al., 1980; Wolf et al., 1983), or (ii) nebula condensates (Wasson and Wai, 1970; Sears, 1980). If the aubrites are nebula condensates then the higher temperatures experienced by these meteorites may be attributed to either deep burial within the parent body (Sears, 1980), or surficial heating of the parent body (Wasson and Wai, 1970). Alternatively, Brett and Keil (1985, 1987) have suggested that the aubrites sample a separate parent body from the enstatite chondrites because: (i) there is a hiatus in metal and troilite composition between chondrites and aubrites, (ii) chondrites and aubrites are brecciated and yet clasts of one type within another have not been found, and (iii) they have different cosmic-ray exposure ages.

Oxygen isotope compositions of enstatite meteorites are all very similar and on a graph of $\delta^{18}O$ versus $\delta^{17}O$ they plot close to the bulk Earth and Moon (Clayton and Mayeda, 1978; Mayeda and Clayton, 1980; Clayton et al., 1984). This indicates that enstatite meteorites formed within 1 AU of the proto-Sun (Clayton et al., 1984), which is supported by their extreme state of reduction and high pressure (1 atm) of formation. In contrast, Hertogen et al. (1983), have suggested enstatite chondrites formed in the asteroid belt. This suggestion was made following the earth-based optical studies, carried out by Zellner et al. (1977), which showed that three asteroids are type E (i.e. have a surficial "enstatitic" composition).

5.2 Sulphur content and sulphide mineralogy

The enstatite chondrites can contain relatively high sulphur contents of up to 6.67 wt% (in Abee: Kaplan and Hulston, 1966) and the abundance of this element decreases in the order EH4 > EH5 > EL6 (Mason, 1966). Aubrites contain lower sulphur contents that are normally below 1 wt% (Watters and Prinz, 1979; Easton, 1985b; Gibson et al., 1985), although a value of 3.32 wt% sulphur has been reported for Shallowater (Watters and Prinz, 1979). Troilite is a major mineral in enstatite meteorites and attains a maximum concentration of 16.7 wt% in Blithfield (Keil, 1968a). All other sulphides (Table 5.2) are accessory minerals and of these oldhamite is the most abundant and widespread in all petrologic types (Mason, 1966;

Mineral	Composition	Petrologic type			
		3,4	5	6	A
Troilite	FeS	+	+	+	+
Oldhamite	CaS	+	+	+	+
Alabandite	(Mn,Fe)S	−	−	+	±
Niningerite	(Fe,Mg,Mn)S	+	+	−	−
Daubréelite	$K_3(Na,Ca)(Fe,Ni)_{12}S_{14}$	+	+	−	±
Sphalerite	ZnS	±	±	±	−

Table 5.2 Known sulphur minerals of enstatite meteorites. After Dodd (1981), with modifications. + = present; − = absent; ± = variable. A = Aubrites.

Ramdohr, 1973).

5.2.1 Troilite, FeS

Troilite is the most abundant sulphide in enstatite meteorites. Keil (1968a) reports troilite contents for 13 enstatite chondrites which vary between 4.6 (Hvittis, EL6) and 16.7 wt% (Blithfield, EL6). Troilite contents of aubrites are generally lower but reach a maximum value of 7.1 vol.% in Shallowater (Watters and Prinz, 1979). Titanium, which is a lithophile element on the earth, is chalcophilic in enstatite chondrites and aubrites (Keil, 1968b) and is present in troilite at high concentrations of between 0.2 to 1.0 wt% (Keil, 1968a; Mason, 1966). Some Cr, Mn and Zn are also present in troilite.

Troilite forms in a nebula gas at approximately 700 K by the reaction of hydrogen sulphide and iron metal (Grossman, 1972; Kerridge, 1976).

$$Fe + H_2S \rightarrow FeS + H_2$$

Most of the troilite in enstatite meteorites has a nebula origin, but it is clear that some of this mineral also occurs as an exsolution product in other iron-rich sulphide phases. Exsolved troilite has been identified in lamellae of daubréelite (which itself is exsolved from troilite), sphalerite and djerfisherite (Fuchs, 1966; Ramdohr, 1973).

5.2.2 Oldhamite, CaS

Oldhamite was discovered in the Bustee aubrite by Maskelyne (1870). It has since been identified in most other aubrites and enstatite chondrites (Ramdohr, 1973). Oldhamite contents of between 0.19 and 1.0 wt% have been determined for enstatite chondrites (Keil, 1968a). Ramdohr (1973) attributes the absence of oldhamite from Atlanta (EL6) to terrestrial weathering processes because oldhamite is very susceptible to attack by water.

$$2CaS + 2H_2O \rightarrow Ca(OH)_2 + Ca(SH)_2$$

Besides Ca and S, oldhamite also contains minor amounts of Mg, Mn and Fe (Keil and Andersen, 1965; Keil, 1968a). Oldhamite composition undergoes progressive elemental exchange during metamorphism, losing magnesium and gaining manganese with increasing petrologic grade (Keil, 1968a).

The formation of oldhamite is thought to be related to the highly reducing conditions that prevailed during condensation of the enstatite meteorites. It should be one of the first minerals to condense from a nebular gas, but under any conditions, it has a very narrow stability field. Larimer (1968) found the following equilibrium favours $CaSiO_3$:

$$CaSiO_3(c) + H_2S(g) \rightarrow CaS(c) + SiO_2(c) + H_2O(g)$$

Larimer (1968) argued that oldhamite could only form in a nebular environment with a higher H_2S/H_2O and lower H_2O/H_2 ratio than are normally accepted.

Herndon and Suess (1976) considered the coexistence of osbornite (TiN) and oldhamite in a nebula with a total pressure of 1 atm. They found that these two minerals probably condensed at similar temperatures in such an environment and used evidence of their close association in Bustee, where osbornite is embedded in oldhamite (Bannister, 1941), to support their argument. According to Sears (1980) oldhamite is unstable at any temperature and pressure in a gas of solar composition. By adjustment of the Ca/Si, Al/Si, Ti/Si and Mg/Si ratios to enstatite chondrite values (the so-called lithophile element fractionation) and by increasing the H/O ratio (by removal of 20% of the nebula oxygen), Sears calculated that the condensation of oldhamite occurs at about 2000 K in preference to gehlenite ($Ca_2Al_2SiO_7$). Both Herndon and Suess (1976) and Sears (1980) recognised the instability of oldhamite and attributed its preservation at lower temperatures in the nebular to entrapment within other early condensates at near-formation temperatures.

5.2.3 Minor sulphide minerals

Daubréelite, $FeCr_2S_4$

Daubréelite is an exsolution product from troilite (Mason, 1966; Keil, 1968a; Ramdohr; 1973) and is a common accessory sulphide in enstatite chondrites. Daubréelite reaches a maximum concentration of 1.6 wt% in Blithfield (Keil, 1968a). In enstatite chondrites, this mineral has been referred to as ferroan daubréelite because of its high manganese content and in two meteorites, Kota-Kota and St. Mark's, zincian daubréelite was found (Keil 1968a, 1968c).

Niningerite, (Fe,Mg,Mn)S.

Niningerite was first identified in type I (E4) and intermediate type (E5) enstatite chondrites by Keil and Snetsinger (1967), but it is also present in aubrites (Ramdohr, 1973). The Abee chondrite (EH4) is particularly rich in niningerite which constitutes 11.2 wt% of this meteorite (Keil, 1968a).

It is noteworthy that niningerite is never found co-existing with ferroan alabandite (Keil, 1968a). The chemical and mineralogical properties of niningerite preclude pure MgS (Keil and Snetsinger 1967; Keil, 1968a; Ramdohr, 1973), which had previously been identified by DuFresne and Anders (1962b) in the Pesyanoe aubrite. Keil (1968a) notes that there is considerable variability in the abundances of Fe, Mn, Ca and Cr in niningerite with petrologic grade.

Larimer (1968) has calculated that MgS is a possible condensation product under conditions similar to those favouring the formation of oldhamite (i.e. high H_2S/H_2O ratio and high temperatures). However in the Adhi-Kot (EH4) chondrite, Ramdohr (1973) has found reaction rims of niningerite between troilite and oldhamite grains suggesting the former existence of a complex mixed crystal (Ca,Mg,Mn,Fe)S.

Ferroan alabandite, (Fe,Mn)S

Although alabandite was first reported by Dawson et al. (1960) in Abee (EH4), according to Ramdohr (1973) this was a misidentification. Keil (1968a) has noted that the occurrence of ferroan alabandite is restricted to type II (E6) chondrites where abundances are between 0.25 and 0.94 wt%. The composition of ferroan alabandite shows little variation between different petrologic types of enstatite chondrites (Keil, 1968a).

Sphalerite, ZnS

Sphalerite is a relatively uncommon mineral in most groups of chondrites. However, iron-rich sphalerite occurs at low abundance in enstatite chondrites (Keil, 1968a; Okada, 1975; Ramdohr; 1973). The high temperature polymorph, wurtzite, has been found in Khairpur (Ramdohr, 1977).

Chemical treatment	Component extracted	Abee		Hvittis		Norton County	
		S (Wt%)	δ^{34}S (‰)	S (Wt%)	δ^{34}S (‰)	S (wt%)	δ^{34}S (‰)
Water soluble fraction	CaS	0.07	+1.6	0.10	+1.2	0.13	−5.6
S volatile in HCl	FeS	4.62	−0.2	3.12	+0.1	0.34	0.0
S soluble in acetic acid	MnS	1.92	−0.2	–	–	–	–
HNO_3/HCl insoluble S	$FeCr_2S_4$ $(Fe,Ni)_9S_8$	–	–	0.24	+0.2	0.18	+1.4
Totals	–	6.67	0.0	3.46	−0.1	0.65	−0.7

Table 5.3 Summary of the extraction procedure and sulphur isotopic measurements reported by Kaplan and Hulston (1966).

Djerfisherite, $[K_3(Na,Cu)(Fe,Ni)_{12}S_{14}]$

Djerfisherite is probably the most peculiar sulphide mineral in enstatite meteorites. Essentially a potassium-copper-iron sulphide, this mineral was discovered in Kota-Kota (0.1 to 0.5 wt% djerfisherite) and St. Mark's (abundance less than 0.1 wt%) by Fuchs (1966). The chalcophile behaviour of K and Na in djerfisherite testifies to the highly reducing conditions that must have prevailed during the formation of the enstatite meteorites.

5.3 Previous sulphur isotope studies

The first sulphur isotope measurement of an enstatite chondrite was made by Thode et al. (1961), who carried-out a single analysis of Indarch (EH4) and obtained a δ^{34}S value of −0.36‰. Hulston and Thode (1965a) and Kaplan and Hulston (1966) attempted to measure the isotopic composition of the constituent sulphides in three enstatite meteorites; Abee (EH4), Hvittis (EL6) and Norton County (aubrite). The experiments performed by Kaplan and Hulston (1966) involved isolation, or concentration, of the sulphide minerals using a series of chemical procedures. These experiments, together with the isotopic data, are summarized in Table 5.3. The whole-rock δ^{34}S values of the three meteorites studied are in the range −0.7 to 0.0‰. Kaplan and Hulston found that oldhamite sulphur was enriched in ^{34}S in Abee (δ^{34}S = +0.08‰) and Hvittis (δ^{34}S = +1.5‰) but not in Norton County (δ^{34}S = −5.6‰). Kaplan and Hulston attributed the very low δ^{34}S value of oldhamite in Norton County to isotopic fractionation resulting from terrestrial oxidation of oldhamite.

5.4 Results and discussion

5.4.1 Total sulphur and bulk δ^{34}S measurements of enstatite meteorites

Sulphur abundance and isotopic measurements acquired from thirteen enstatite meteorites during the course of this work, are shown in Figure 5.2 and listed in Table 5.4. The stepped combustion experiments were carried-out following the use of fluorine compounds in the extraction system.

Sample sizes used for stepped combustion were comparable for chondrites but larger for aubrites (2–5mg for enstatite chondrites and 10–14mg for aubrites) than those used for bulk combustion (2–6mg for chondrites; 5–8mg for aubrites). Samples were taken from crushed (<50μm) interior fragments (about 0.20g) of meteorite.

Two values for sulphur concentration are given in Table 5.4 for each meteorite:

1. Calculated as the sum of the sulphur liberated during stepped combustion from room temperature to 1200°C.
2. The total sulphur recorded from a single-step combustion at 1200°C.

With two exceptions (Daniel's Kuil and St. Mark's) the agreement in total sulphur between the two methods is better than 15% (Table 5.4). Minor differences in the sulphur abundance values can be explained by the heterogeneous distribution of sulphur in these samples. This observation is supported by the relatively large variations in sulphur content reported for individual meteorites in the literature (e.g. published values for Indarch include 3.98 wt% and 5.18 wt%, Figure 5.2). Thus, the measurements reported in the present study are as trustworthy as any others currently available.

Sulphur contents in enstatite meteorites decrease in a systematic fashion, in order of EH4 > EH5 > EL6 > aubrites (Figure 5.2). However, the EH3 chondrite (Kota-Kota) cannot be distinguished from EH4 chondrites in terms of its sulphur content (4.74 wt%). The average abundance of sulphur in EH4's is 5.11 wt% and the concentration ranges from 3.32 wt% (South Oman) to 6.79 wt% (Abee) which extends the known scale for this group in both lower and upper limits respectively (Figure 5.2). Abee clast (1,1) contains a higher total sulphur content (up to 7.08 wt%) than the previously reported whole-rock values of 6.67 wt% (Kaplan and Hulston, 1966), 6.12 wt% (Dawson et al., 1960) and 5.50 wt% (Mason, 1966) (see Figure 5.2). For EL6's, the samples analysed have sulphur abundances between 0.88 (North West Forrest) and 3.23 wt% (Atlanta) with an average of 2.18 wt%. North West Forrest is a weathered find from which some of the original sulphur may have been removed. The sulphur contents of the two EH5 chondrites

Meteorite	Class.	Yield S Wt% (Step.)	Yield S Wt% (Bulk)	Lit. Wt%	δ^{34}S (‰) (Step.)	δ^{34}S (‰) (Bulk)	Lit. δ^{34}S (‰)
Kota-Kota	EH3	4.66	4.81	3.46 (1)	−2.51	−0.82	–
Abee	EH4	7.08	6.49	6.67 (2)	−2.86	−0.70	−0.06 (2)
				5.50 (3)			
				6.12 (4)			
Indarch	EH4	5.61	4.87	3.98 (1)	−2.48	−0.20	− 0.36 (5)
				5.18 (6)			
South Oman	EH4	3.60	3.03	4.50 (1)	−3.08	−0.28	–
St. Mark's	EH5	3.42	5.54	4.18 (1)	−2.36	+0.10	–
				5.50 (7)			
Yilmia	EH5	2.13	1.79	2.83 (8)	−2.52	+0.42	–
Atlanta	EL6	2.99	3.46	2.62 (3)	−3.24	−0.80	–
Daniel' Kuil	EL6	3.13	1.36	2.33 (1)	−3.71	−0.53	–
				3.46 (3)			
				2.94 (9)			
Khairpur	EL6	2.67	2.11	3.95 (1)	−2.50	−0.29	–
				2.84 (3)			
				2.71 (9)			
N.W. Forrest	EL6	0.70	1.05	–	−1.38	+0.52	–
Bustee	AUB.	1.72	1.73	0.63 (10)	−2.28	−0.96	–
				0.32 (11)			
				0.40 (12)			
Norton Co.	AUB.	0.36	0.42	0.50 (2)	−2.86	−1.50	
			0.47	0.70 (6)		−1.93	
				0.89 (10)			
				0.44 (11)			
				0.32 (12)			
				0.00 (13)			
Shallowater	AUB.	0.69	0.95	0.55 (10)	−1.92	−0.12	
				3.32 (11)			
				0.32 (12)			
				0.45 (14)			

Table 5.4 Summary of sulphur data obtained for enstatite meteorites. References: (1) Easton (1985a); (2) Kaplan and Hulston (1966); (3) Mason (1966); (4) Dawson et al. (1964); (5) Thode et al. (1961); (6) Wiik (1956); (7) Wiik (1969); (8) Buseck and Holdsworth (1972); (9) Prior (1916); (10) Gibson et al. (1985); (11) Watters and Prinz (1979); (12) Easton (1985b); (13) Beck and LaPaz (1951); (14) Foshag (1940).

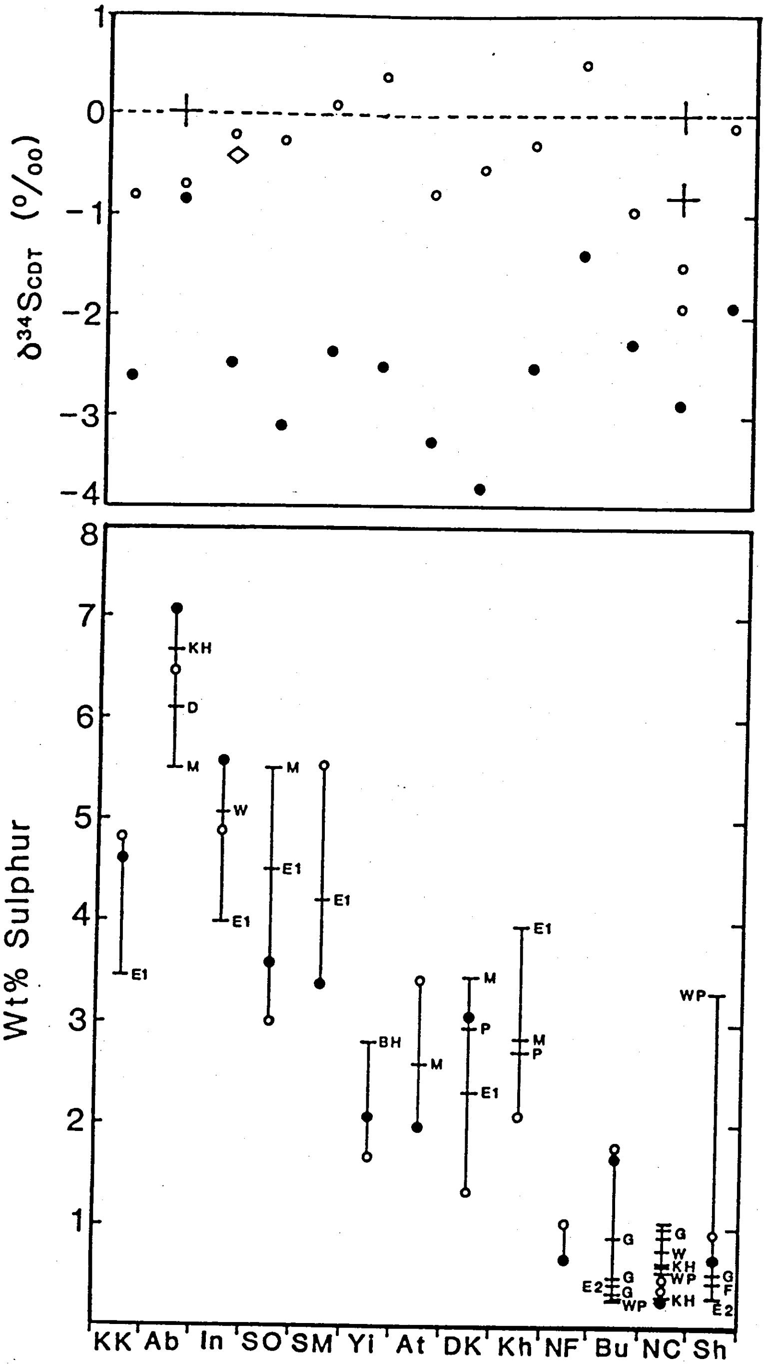


Figure 5.2 Comparison of sulphur data determined by bulk and stepped combustion with published values for enstatite meteorites. References: BH=Buseck and Holdsworth (1972); D=Dawson et al. (1960); E_1=Easton (1985a); E_2=Easton (1985b); F=Foshag (1940); G=Gibson et al. (1985); KH=Kaplan and Hulston (1966); M=Mason (1966); P=Prior (1916); W=Wiik (1956); WP=Watters and Prinz (1979). Symbols: + = Kaplan and Hulston (1966); ◇ = Thode et al. (1961); • = Stepped combustion; ○ = Bulk combustion. Abbreviations: KK=Kota-Kota; Ab=Abee; In=Indarch; SO=South Oman; SM=St. Mark's; Yi=Yilmia; At=Atlanta; DK=Daniel's Kuil; Kh=Khairpur; NWF=N. W. Forest; Bu=Bustee; NC= Norton County; Sh=Shallowater.

differ from each other by 2.52 wt% (Table 5.4); the sulphur value of St. Mark's (4.48 wt%) is similar to the EH4's whereas that of Yilmia (1.96 wt%) is closer to sulphur abundances measured for EL6 chondrites (Figure 5.2).

The aubrites have the lowest sulphur contents of the enstatite meteorites, with values between 0.42 (Norton County) and 1.73 wt% (Bustee) and an average of 0.98 wt% (Table 5.4). Previous determinations for the sulphur content of Bustee are lower than the values obtained in this study. Indeed, Gibson et al. (1985) have made three measurements of Bustee which range between 0.38 and 0.91 wt%; all of these determinations were lower than the value of 1.73 wt% reported herein. The sulphur contents of 0.69 wt% and 0.95 wt% for Shallowater conflict with the estimate of 3.32 wt% reported by Watters and Prinz (1979), but are in better agreement with other published determinations (Table 5.4). The distribution of sulphur in Norton County must be very heterogeneous; during the investigation of this meteorite by Beck and LaPaz (1951) sulphur was not detected, however, Gibson et al. (1985) reports values of between 0.59 and 1.02 wt% which are somewhat higher than those determined in this study (0.42 and 0.47 wt%).

The whole-rock δ^{34}S values obtained by bulk combustion are between -1.72 (the average of two analyses of Norton County) and +0.52‰ (North West Forrest). There is an overall depletion in ^{34}S and the average δ^{34}S value of the enstatite chondrites is -0.41‰ and there seems to be an overall depletion in ^{34}S in enstatite meteorites. Despite showing no systematic trend in isotopic composition (Figure 5.2), sulphur in EH5 meteorites is enriched in ^{34}S ($\delta^{34}S = +0.10$‰ in St. Mark's and +0.42‰ in Yilmia) and depleted in aubrites (Norton County $\delta^{34}S = -1.50$ and -1.93‰; Bustee $\delta^{34}S = -0.96$‰ and Shallowater $\delta^{34}S = -0.12$‰). If sulphur was lost from E4 chondrites to form E6 and aubritic material by metamorphic processes, then a change in δ^{34}S may have been expected to accompany this event. However, such a fractionation is not evident from Figure 5.2, except for the aubrites which are the most intensely metamorphosed and have the lowest δ^{34}S values.

Thode et al. (1961) report a δ^{34}S value of -0.36‰ for Indarch which compares with -0.20‰ obtained in this study. Where comparable data exist, the whole-rock δ^{34}S values determined in the present study are only slightly different from those reported by Kaplan and Hulston (1966) (Figure 5.2 and Table 5.4). Kaplan and Hulston (1966) reported δ^{34}S values of -0.06‰ for Abee (compared to -0.70‰ and -0.86‰ in this study) and for Norton County +0.0‰ and -0.76‰ (compared with -1.50‰ and -1.93‰ from the present study).

5.4.2 The distribution of sulphur components based upon stepped combustion analyses

In Chapter 3 it was demonstrated that, in order to be able to interpret the stepped combustion profiles of C1 and C2 carbonaceous chondrites, it was necessary to obtain a knowledge of the combustion temperatures of their common sulphur-bearing components. It was noted previously in Section 5.2 that the most abundant sulphur components of enstatite meteorites are troilite and oldhamite. Stepped combustion profiles for troilite (separated from the Bella Roca iron meteorite) and calcium sulphide (analytical grade, BDH Chemicals, Poole, England) as the most suitable analogue to oldhamite, are shown in Figure 5.3. The two minerals combust to release sulphur at different temperatures; troilite between 400 and 600°C and calcium sulphide between 800 and 1100°C. The relatively high temperature recorded for the combustion of calcium sulphide (compared to other sulphides) has been explained by the initial formation of calcium sulphate which then decomposes at higher temperatures (discussed in Section 2.3.2).

The sulphur release profiles of the enstatite meteorites analysed in this study are shown in Figures 5.4 and 5.5. In most enstatite meteorites (e.g. St. Mark's, Khairpur, Norton County, Bustee, etc.) there are two clear releases of sulphur occurring at temperatures similar to those of the reference materials troilite and oldhamite (Figure 5.3). In Atlanta, however, there appears to be only a single well-defined peak in the sulphur release. The EH3 and EH4 chondrites show an approximately bimodal release of sulphur except for South Oman where a single broad release is observed occurring between 400 and 1200°C (Figure 5.4).

Troilite

Troilite is the major sulphur species identified petrographically in these meteorites and all EH3,4 samples show evidence for a sulphur release from this mineral, with the possible exception of South Oman. However, only St. Mark's, Indarch and Kota-Kota have a dominant release of sulphur at a temperature coincident with that of the reference troilite material (Figure 5.4). Mostly, the maximum amount of sulphur burns between 400 and 700°C, which is up to 200°C higher than reference troilite (Figure 5.6). Variation in the peak combustion temperature of a mineral is a poorly constrained parameter, but it can be used to gain an indication of a minerals' resistance to oxidation. In enstatite meteorites, there are several characteristics which could cause the combustion temperature of troilite to vary.

1. Chemical composition of the troilite. The transition from E4 to E6 is accompanied by an increase in Ti and decreases in Cr and Mn content

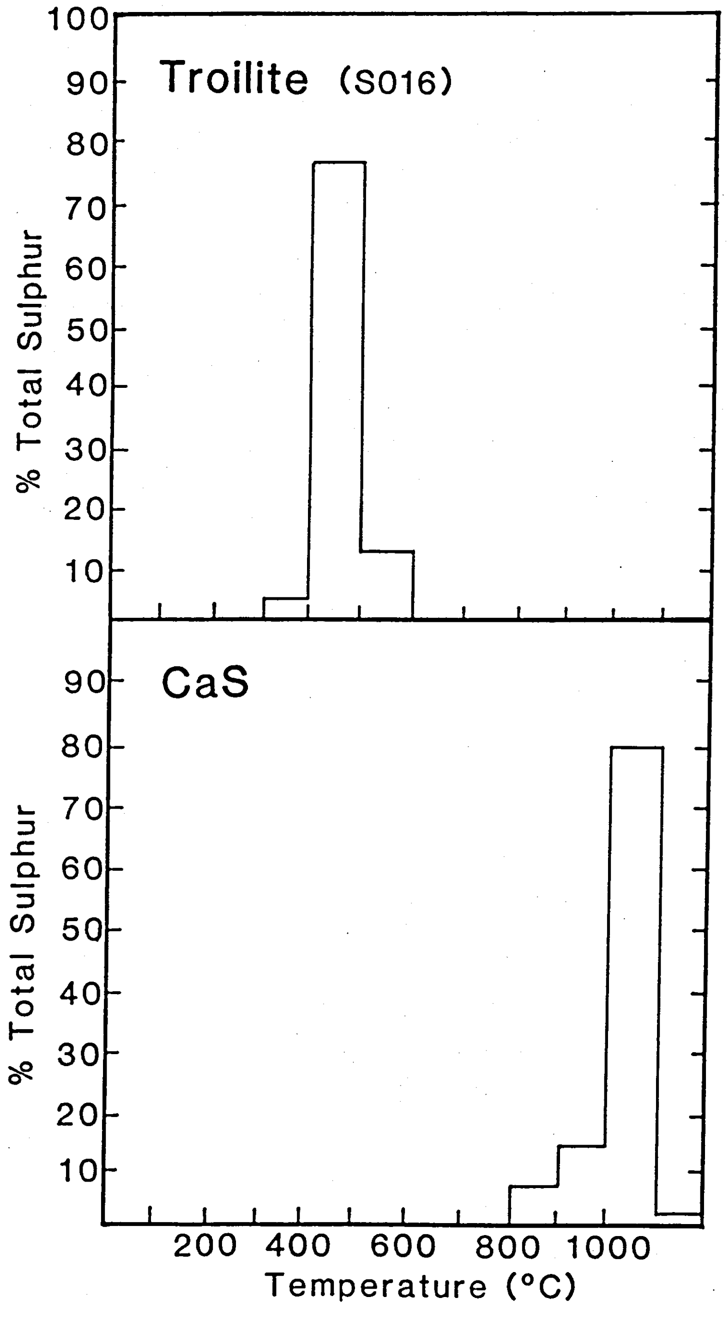
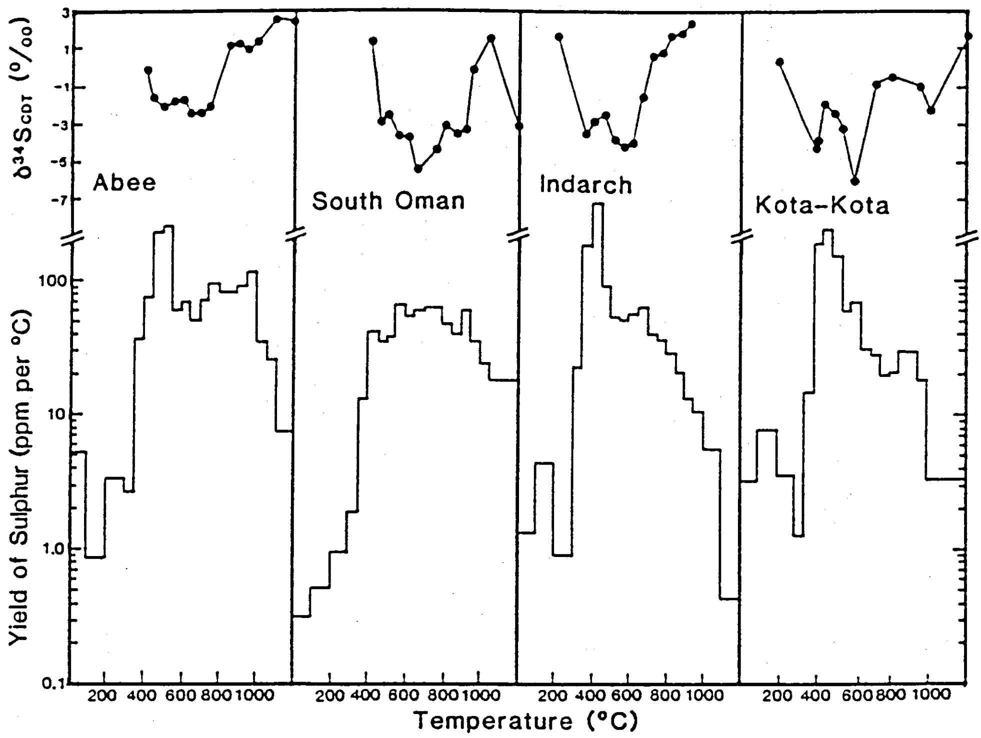


Figure 5.3 The abundance (—) of sulphur in troilite and calcium sulphide as determined by stepped combustion.



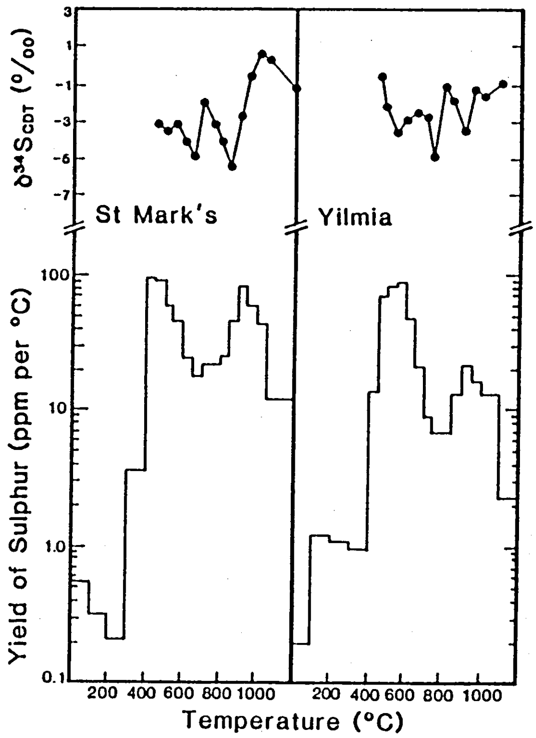


Figure 5.4 The abundance (—) and isotopic composition (-•-) of sulphur in EH3, EH4 and EH5 enstatite chondrites as determined by stepped combustion.

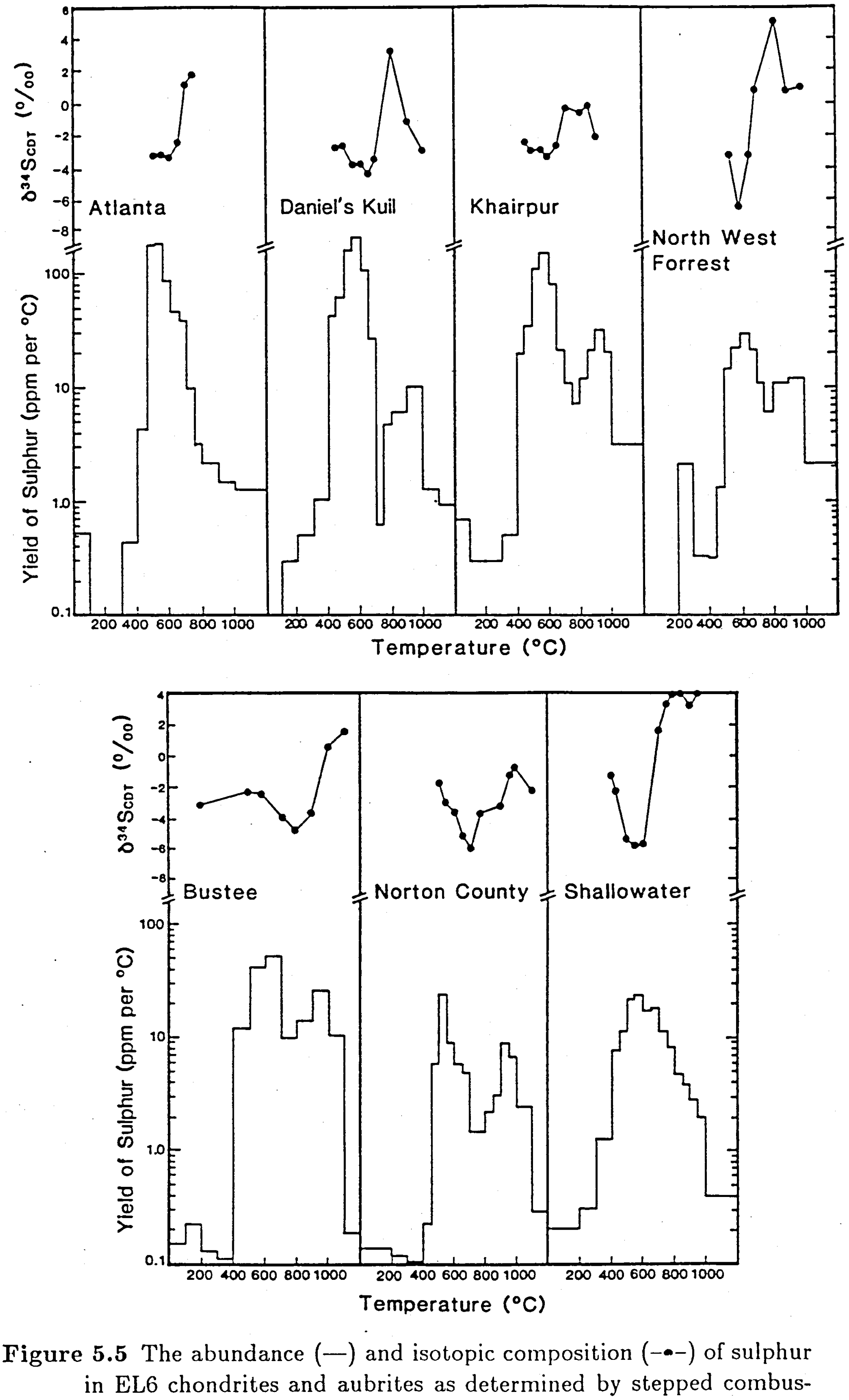


Figure 5.5 The abundance (—) and isotopic composition (-•-) of sulphur in EL6 chondrites and aubrites as determined by stepped combustion.

of the troilite (Keil, 1968a).

2. Grain size. Increasing grain size or a higher degree of crystallinity of the troilite would probably result in a higher combustion temperature due to a concomittant reduction in reaction rate. It is noted that grain size and crystallinity is related to the extent of metamorphism and increases from the E4's to the aubrites.
3. Competing oxidation reactions. During the combustion experiments of enstatite meteorites oxygen will be used up during the oxidation of carbon and carbides in addition to sulphides. However, competition for available oxygen is not considered to be a major contributing factor determining the combustion temperature of troilite during these experiments, because a relatively large pressure of oxygen is used. There is also the possibility that sulphate forms during the experiment and then decomposes at higher temperatures, however, this is unlikely because the same effect is not noted during the combustion of pure troilite.
4. Protecting minerals. If a sulphide is mantled by a mineral phase which decomposes at high temperature then the combustion temperature of the sulphide will effectively be increased because oxygen will be prevented access to the sulphide until the enclosing mineral has been decomposed. This may be important in retarding the combustion of sulphides where they occur as isolated blebs in silicates, but since a fine powder is used (<50μm), this will only effect the finest sulphide grains.

Appraisal of all the stepped combustion data (Figures 5.4 and 5.5) suggests that perhaps troilite combustion temperature is related to petrologic grade. The maximum combustion temperature is plotted in Figure 5.6 and shows that troilite burns more easily in E3–E5 types than in E6 chondrites or aubrites. It is considered that the change in troilite combustion temperature between the E3–5 and E6/aubrites is most likely to be related to changes in chemical composition and the following features associated with metamorphism:

1. Grain size.
2. Extent of crystallinity.

Grady et al. (1986) have noted similar effects for the combustion temperature of graphite in enstatite chondrites, which increases from between 600 and 700°C (the usual combustion temperature of standard graphite) to between 800 and 900°C. This has been attributed to decreasing grain size of the graphite and its enclosure in other minerals more resistant to oxidation.

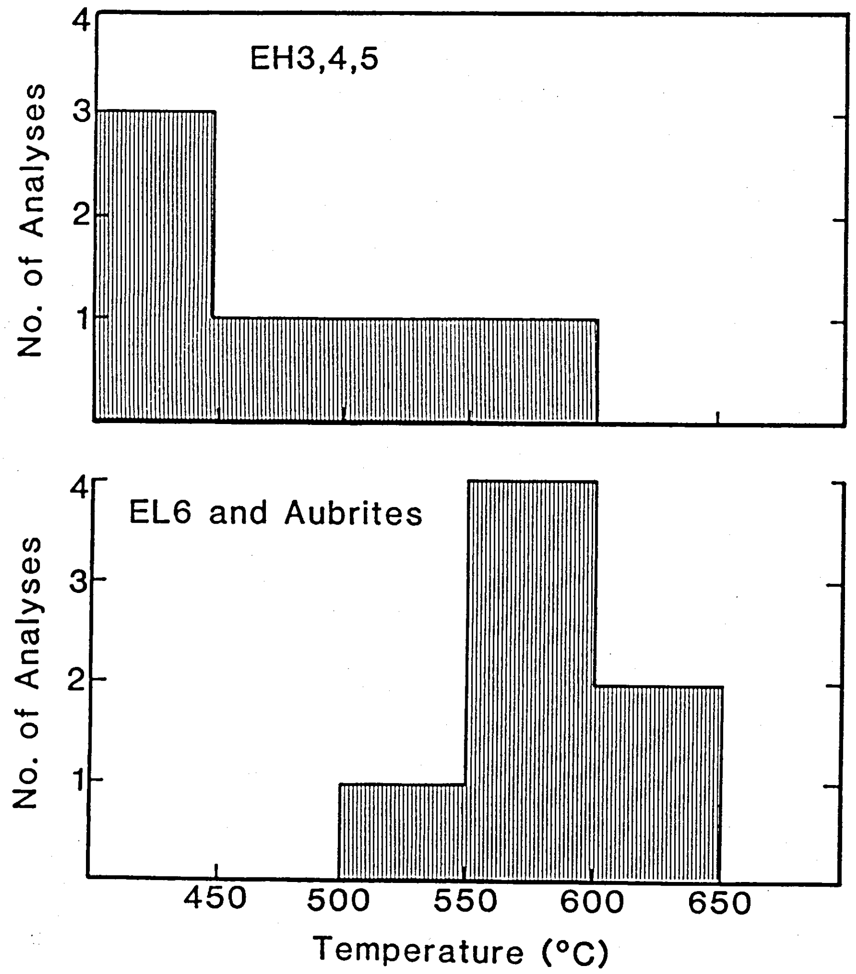


Figure 5.6 Variation in the maximum release of sulphur from troilite with petrologic grade.

Meteorite	Yield S wt% (300–700°C)	Troilite wt%	1	2	3
Kota-Kota	3.65	9.76	–	6.02	–
Abee	3.73	10.14	5.8	–	7 (a)
Indarch	4.56	12.19	7.3	7.7	–
South Oman	1.45	3.92	–	10.43	–
St. Mark's	1.68	4.61	9.7	8.3	–
Yilmia	1.60	4.30	–	–	–
Atlanta	2.79	7.50	–	–	–
Daniel's Kuil	2.83	7.65	5.4	6.14	–
Khairpur	2.05	5.53	9.5	9.6	–
N.W. Forrest	0.41	1.11	–	–	–
Bustee	0.81	1.34	–	–	0.68 (b)
Norton Co.	0.19	0.33	–	–	1.34 (b) 0.94 (c)
Shallowater	0.53	0.88	–	–	6.3 (d)

Table 5.5 The troilite contents of enstatite chondrites as determined by stepped combustion. References: (1) Keil (1968a); (2) Easton (1985a); (3) Others: (a) Rubin and Keil (1983); (b) Kaplan and Hulston (1966); (c) Watters and Prinz (1979); (d) Foshag (1940).

With the possible exception of South Oman, all the meteorites show a peak in the sulphur release between 300 and 700°C (Figures 5.4 and 5.5), which hereafter will be referred to as troilite sulphur. Summing the sulphur liberated between 300 and 700°C gives troilite sulphur contents of between 0.19 (Norton County) and 4.57 wt% (Indarch). Microprobe analyses of troilite in enstatite chondrites have been reported by Keil (1968a) and Buseck and Holdsworth (1972), and in aubrites by Watters and Prinz (1979). The results from these analyses can be combined with the sulphur contents of troilite, determined by stepped combustion, to calculate the abundance of troilite in the meteorites. The troilite contents determined in this way vary from 0.33 (Norton County) to 12.19 wt% (Indarch); the values are listed in Table 5.5 where they are compared with estimates made using planimetry (Keil, 1968a) and wet chemical analyses (Easton, 1985a).

The troilite contents determined by stepped combustion for Kota-Kota, Abee and Indarch are all higher (by up to nearly 5 wt%) than previous data. This is most likely to be the result of sulphur combusting between 300 and 700°C which does not arise from troilite alone. In contrast, the troilite content of South Oman determined by stepped combustion (3.92 wt%) is notably lower than the value of 10.4 wt% obtained by Easton (1985). The troilite content of Abee clast (1,1) is estimated to be 10.14 wt% which seems to be higher than that of the bulk meteorite troilite sulphur value of 5.8 wt% obtained by Keil (1968a). During a detailed study of this clast, Rubin and Keil (1983) identified three sulphides; troilite (7 wt%), niningerite (13 wt%) and oldhamite (0.4 wt%). From the electron probe analyses of these minerals made by Rubin and Keil, the distribution of sulphur in clast (1,1) is calculated as 0.18, 5.45 and 2.58 wt% for oldhamite, niningerite and troilite respectively. Clearly most of the sulphur in Abee clast (1,1) is in the form of niningerite. Unfortunately the combustion temperature of niningerite is unknown, but the high troilite sulphur content reported in the present study compared to previous estimates could represent an admixture of sulphur from the combustion of troilite and niningerite (this is considered in more detail below).

For EH5 and EL6 chondrites there is better agreement between the troilite contents reported in the literature with those calculated from the stepped combustion data (Table 5.5). Considering the differences in troilite abundances determined previously (e.g. compare the troilite values of Keil, 1968a and Easton, 1985 in Table 5.5), then minor deviations from the values obtained in this study can be attributed to the inhomogeneous distribution of this mineral in the meteorites.

If the troilite contents calculated from the stepped combustion data (Table 5.5) are considered to be approximately correct, then there is a decrease in troilite content with increasing petrologic grade (Figure 5.7). The average troilite contents for each of the groups are: 9.0 wt% for EH3,4; 4.5 wt% for EH5; 5.4 wt% for EL6 and 0.9 wt% for aubrites. Previously the variation in troilite content has been explained by partial melting on the meteorite parent bodies. Keil (1968a) calculated that 6 wt% FeS and 4wt% kamacite must be lost by partial melting of type I (E4) material to produce type II (E6) material. As troilite and kamacite are closely associated in the enstatite chondrites, melting temperatures can be estimated using the Fe–Ni–S system, which gives a minimum temperature of 975°C to form a liquid. Mineral assemblages in E4–6 chondrites indicate that equilibrium temperatures were in the 600–975°C range, and thus may have approached the Fe–Ni–S eutectic (Keil, 1968a; Skinner and Luce, 1971; Larimer and Buseck, 1974).

Oldhamite

In many of the samples (e.g. Khairpur, St. Mark's, Kota-Kota and Norton County) there is a second release of sulphur above 700°C, while in others

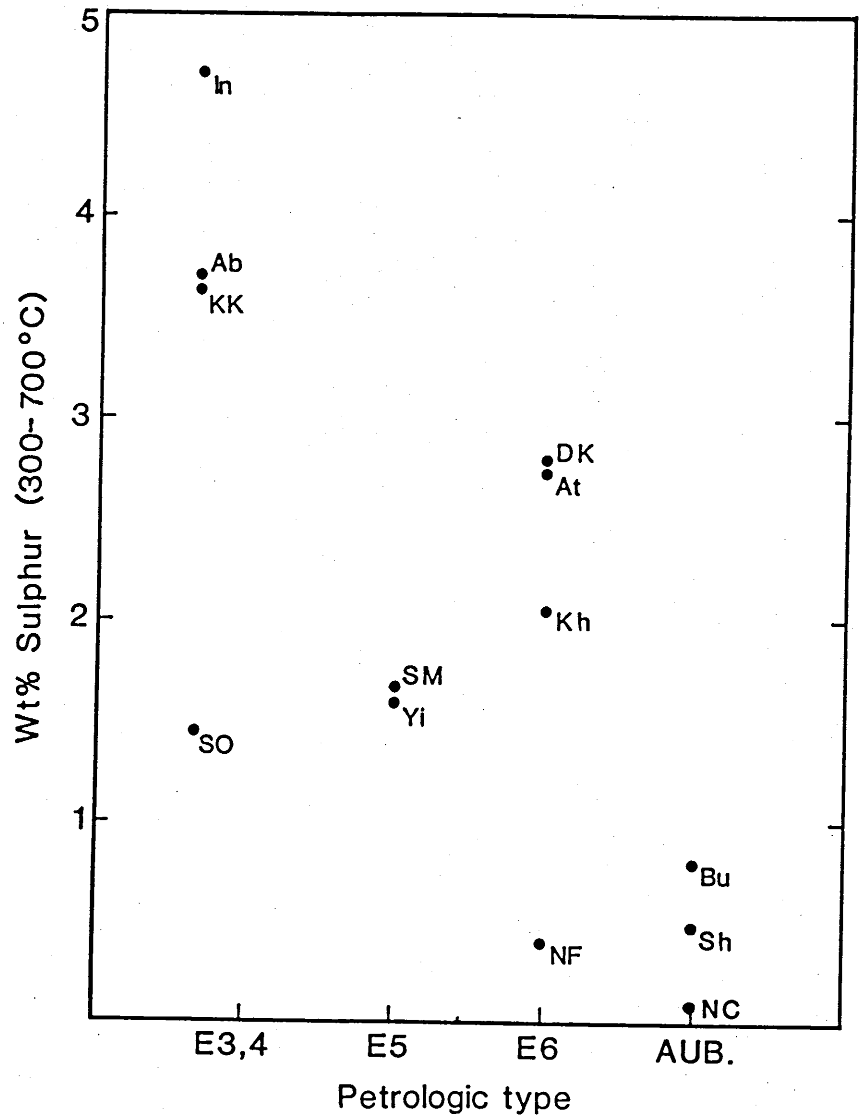


Figure 5.7 Variation with petrologic grade of the sulphur released between 300 to 700°C during stepped combustion of enstatite meteorites. Abbreviations as in Figure 5.2.

(especially South Oman) the pattern of sulphur released at high temperature is more confused. Inspection of the stepped combustion data reveals that only two meteorites, Shallowater and Atlanta, show no clear evidence of a sulphur component above 700°C (Figure 5.6). During petrographic examination of Atlanta, Ramdohr (1973) suggested that prexisting oldhamite had been removed from this meteorite by terrestrial weathering processes. Watters and Prinz (1979) have also noted the absence of oldhamite from Shallowater. A stepped combustion analysis of reference calcium sulphide (Figure 5.3) reveals that most of the sulphur is burned between 800 and 1100°C. Using this evidence, it is considered that the sulphur released at high temperature (above 700°C) in the meteorites is mainly from the combustion of oldhamite. In order to validate this conclusion an experiment was undertaken to selectively remove oldhamite from the meteorite before stepped combustion analysis. During partial dissolution experiments of chondrites, Shima and Honda (1967) used dilute acetic acid to attack oldhamite. So a sample of Khairpur (which shows a clear release of the high temperature sulphur component) was reacted with dilute acetic acid (pH 5) at 21°C for twelve hours. Figure 5.8 shows the stepped combustion profiles of the acetic acid residue compared to bulk Khairpur. The meteorite underwent a 26% weight loss during extraction. As predicted most (95%) of sulphur released above 700°C in the bulk material has been removed by the acid, however it seems that the acid has also removed about 70% of the sulphur originally liberated below 700°C (attributed to troilite) in the bulk meteorite. The lower troilite content of the residue may partly be accounted for by the heterogeneous distribution of troilite in Khairpur, but is mainly due to a partial reaction between acetic acid and troilite.

Assuming that all the sulphur dioxide liberated above 700°C in the meteorites is from the combustion of oldhamite, then there is between 0.16 (Norton County) and 3.27 wt% (Abee) sulphur as oldhamite present (Table 5.6). Combining these oldhamite sulphur contents with the microprobe analyses of oldhamite reported by Keil (1968a) and Watters and Prinz (1979) then the concentrations of this mineral in enstatite meteorites can be calculated (Table 5.6).

The oldhamite abundances determined in this way are between 0.37 (Norton County) and 7.4 wt% (Abee). The oldhamite contents of EH4 chondrites quoted here are higher than those reported previously (Table 5.6).

Rubin and Keil (1983) reported an oldhamite content of 0.4 wt% in Abee clast (1,1) which compares with a value of 7.46 wt% determined in this study. Rubin and Keil also found 13 wt% niningerite and 7 wt% troilite. From these values the amounts of sulphur calculated to be in the form of troilite and oldhamite are 2.58 and 0.18 wt% respectively. The concentration of

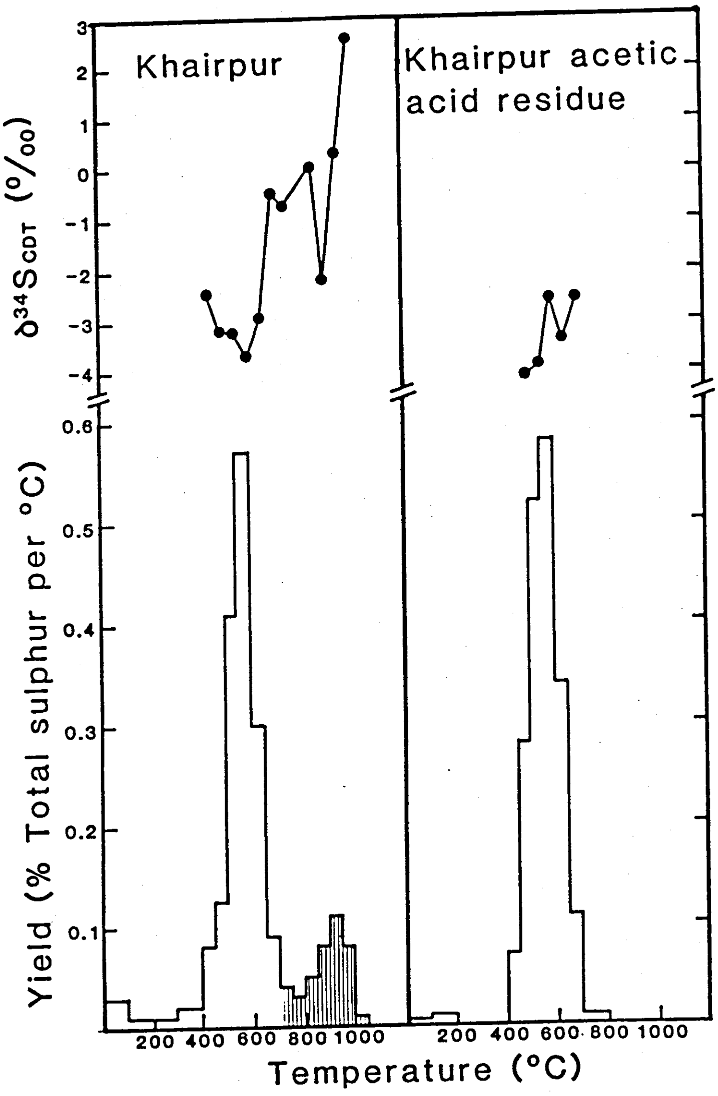


Figure 5.8 The abundance (—) and isotopic composition (-•-) of sulphur in bulk and an acetic acid residue of Khairpur as determined by stepped combustion.

Meteorite	Yield S Wt% (>700°C)	Oldhamite Wt%	1	2	3
Kota-Kota	0.87	2.02	–	1.10	–
Abee	3.27	7.46	0.2	–	0.4 (a) 0.29 (b)
Indarch	0.98	2.28	0.4	1.01	–
South Oman	2.14	4.94	–	0.4	–
St. Mark' s	1.73	3.90	1.0	1.41	–
Yilmia	0.52	1.31	–	–	0.07 (c)
Atlanta	0.20	0.46	–	–	–
Daniel's Kuil	0.29	0.66	0.55	0.64	–
Khairpur	0.61	1.38	0.50	0.59	–
N.W. Forrest	0.28	0.64	–	–	–
Bustee	0.90	2.05	–	–	–
Norton Co.	0.16	0.37	–	–	0.29 (b)
Shallowater	0.20	0.46	–	–	–

Table 5.6 The concentration of oldhamite in enstatite chondrites as determined by stepped combustion. References: (1) Keil (1968a); (2) Easton (1985a); (3) Others: (a) Rubin and Keil (1983); (b) Kaplan and Hulston (1966); (c) Buseck and Holdsworth (1972).

sulphur recorded from extraction steps between 400 and 700°C is 3.73 wt% (troilite) and from between 700 and 1200°C it is 3.27 wt% (oldhamite). By subtraction, this leaves 4.24 wt% sulphur which can be attributed to niningerite. Using the stepped combustion results, it can be calculated that 27% (1.15 wt%) of the sulphur from niningerite combusts between 400 and 700°C and the remaining 73% (3.09 wt%) from 700 to 1200°C. If this interpretation of the sulphur data is correct, then it appears that niningerite has a similar combustion temperature to that of oldhamite which is not unexpected since these components are mineralogically very similar (they are both cubic sulphides).

For the remaining EH chondrites considered in this study, the high oldhamite sulphur contents are difficult to reconcile in terms of sulphide mineralogy. Keil (1968a) has investigated Indarch and reports a niningerite content of 1.0 wt% while that of daubréelite is only 0.05 wt%. That the putative oldhamite contents calculated from stepped combustion data are unrealistically high for EH chondrites can be seen from Table 5.7, where the calculated quantity of calcium in oldhamite exceeds the whole-rock calcium contents reported in the literature. However, the amounts of calcium as oldhamite estimated for EL6 chondrites and aubrites can be accommodated by published whole-rock calcium measurements (Table 5.7) and the agreement in oldhamite contents between the present and previous studies is significantly better for these meteorites (Table 5.6).

Very little quantitative data exists for oldhamite abundances in aubrites apart from a single estimate of 0.13 wt% sulphur as oldhamite (equivalent to 0.29 wt% oldhamite) in Norton County by Kaplan and Hulston (1966). Watters and Prinz (1979) identified only occasional grains of oldhamite in aubrites which is in accord with the relatively low concentrations obtained for Norton County in the present study. The oldhamite content of Bustee (2.05 wt%) is higher than that of other aubrites and is similar to those of EL6 chondrites (Table 5.6).

A plot of oldhamite concentration against petrologic type (Figure 5.9) shows that there is a general decrease with petrologic grade. The EH4,5 chondrites contain a higher concentration of oldhamite (average 3.3 wt%) compared to EL6's (average 0.9 wt%) and aubrites (average 0.4 wt%). However, some of the sulphur liberated above 700°C in EH chondrites probably originates from additional sulphur components (e.g. niningerite), so the oldhamite contents reported here should be regarded as maximum estimates. Previously there has been no report of a decreasing oldhamite content with petrologic grade, which occurs in a similar, but less conspicuous, fashion than that of troilite. This observation is supportive for a nebular origin for the sulphur variations seen in enstatite meteorites, because parent body metamorphic processes cannot be invoked to account for such a variation in

Meteorite	Ca as Oldhamite Wt%	Literature bulk Ca content (wt%)
Kota-Kota	1.06	0.76 (1)
Abee	3.89	0.74 (2)
Indarch	1.20	–
South Oman	2.60	0.27 (1)
St. Mark's	2.10	0.87 (1)
		0.15 (2)
Yilmia	0.70	–
Atlanta	0.24	0.27 (2)
Daniel's Kuil	0.36	0.48 (1)
		1.21 (2)
Khairpur	0.75	0.56 (1)
		1.24 (2)
N.W. Forrest	0.34	–
Bustee	1.10	1.64 (3)
		1.23 (4)
Norton Co.	0.20	0.60 (3)
		0.83 (4)
		0.85 (4)
Shallowater	0.25	0.11 (3)
		0.15 (4)

Table 5.7 Calculated concentrations of calcium as oldhamite in enstatite meteorites compared to published bulk meteorite values. References: (1) Keil (1968a); (2) Easton (1985a); (3) Watters and Prinz (1979); (4) Easton (1985b).

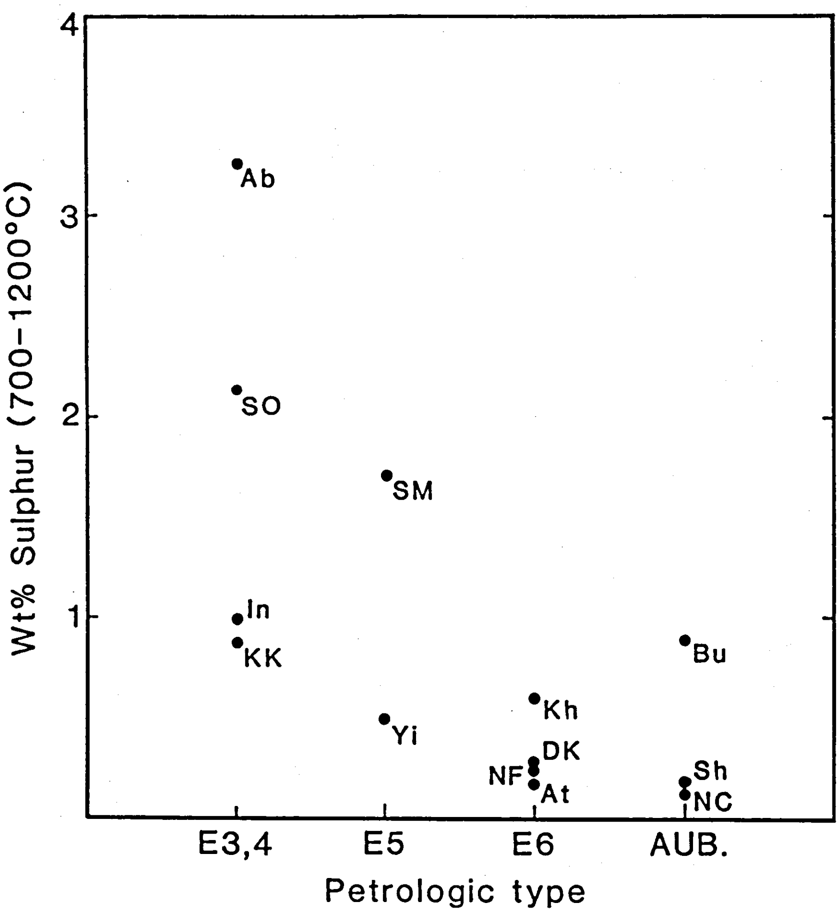


Figure 5.9 Variation with petrologic grade of the sulphur released between 700 and 1200°C during stepped combustion of enstatite meteorites. Abbreviations as in Figure 5.2.

oldhamite content. Oldhamite is a refractory mineral, Chase et al. (1974) has estimated the 1 atm melting point of oldhamite to be about 2673 K. Such high temperatures are inconsistent with partial melting, as silicates are liquid at approximately 1800 K. The higher abundance of oldhamite in EH3,4,5 material would seem to favour its accretion at higher temperatures and before that of E6 and aubritic material, which supports the conclusion of Baedecker and Wasson (1975).

Elemental sulphur

In many of the enstatite chondrites and one of the aubrites (Bustee) studied in this investigation, there is evidence for a minor release of sulphur occurring below 300°C (Figures 5.4 and 5.5). This is similar to the combustion temperature found for elemental sulphur. Summing the sulphur for temperature steps below 300°C gives a range in sulphur concentration of between 0.002 (Shallowater) and 0.13 wt% (Kota-Kota) with an average of 0.029 wt%. Figure 5.10 shows that the EH4 chondrites have the largest range and highest concentrations of this component of sulphur (averages: EH3–5 0.07 wt%; EL6 0.009 wt% and aubrites 0.008 wt%). Assuming that this is elemental sulphur, then it is unlikely that it formed in the solar nebula because this mineral is not a predicted condensation product. Elemental sulphur probably formed by terrestrial weathering of indigenous sulphide components. In this respect it is notable that Keil (1968a) reports the presence of highly weathered oldhamite in Kota-Kota (a find, and, on the basis of the stepped combustion results, the sample with the highest elemental sulphur content). However, other meteorite finds, which include South Oman, Atlanta, Yilmia and North West Forrest, do not have higher contents of elemental sulphur than meteorite falls. Elemental sulphur has not been reported from petrographic studies of enstatite meteorites, however, this is probably due to the very low abundance of this component. Kaplan and Hulston (1965) measured 0.06 wt% elemental sulphur in Abee (compared with 0.08 wt% obtained in this study) which they attributed to a terrestrial oxidation product of oldhamite.

5.4.3 $\delta^{34}S$ values of sulphur components based upon stepped combustion analyses

The whole-rock $\delta^{34}S$ values obtained by stepped combustion are consistently lower than those obtained by bulk combustion (Table 5.4 and Figure 5.2) Those obtained by stepped combustion lie in the range −3.7.1 (Daniel's Kuil) to −1.92‰ (Shallowater) and are between 1.5 and 3‰ lower than those obtained by bulk combustion. The difference in $\delta^{34}S$ values is probably due

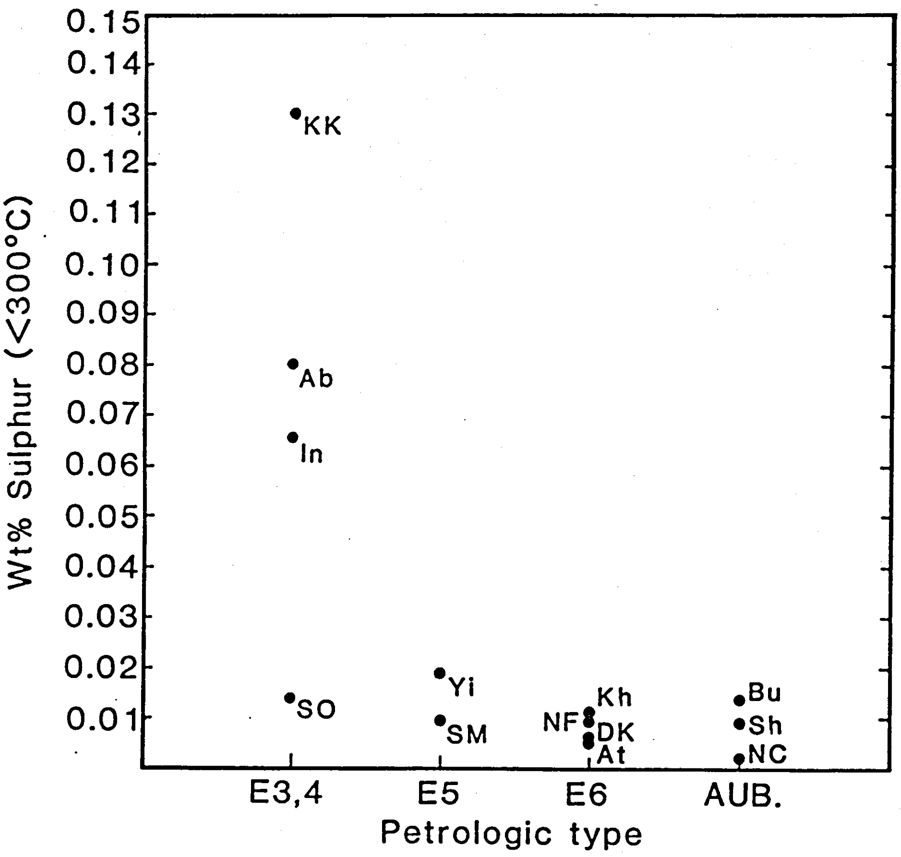


Figure 5.10 Variation with petrologic grade of sulphur released below 300°C during stepped combustion of enstatite meteorites. Abbreviations as in Figure 5.2

to a kinetic isotope fractionation associated with the concurrent formation of sulphur trioxide along with sulphur dioxide at low temperature (below 700°C) during stepped combustion. Therefore, it is necessary to distinguish whether:

1. Sulphur is isotopically fractionated in a consistent manner at all temperatures.
2. Isotopic fractionation is greatest for sulphur burning at low temperature.

If (1) is correct then any variations in δ^{34}S observed between different components would be real; intuitively however, option (2) would seem more plausible. In Section 2.4 the kinetic isotope fractionation between sulphur dioxide and sulphur trioxide was considered with reference to the stepped combustion results for separated troilite. The δ^{34}S values obtained for this mineral were about 3‰ lower than the quoted value. The putative troilite sulphur release in enstatite meteorites gives very similar δ^{34}S values to those obtained for the separated troilite.

Inspection of the isotopic profiles shown in Figure 5.4 and 5.5 for the enstatite meteorites, reveals that the EH chondrites exhibit 'W'-shaped isotopic patterns. The two minimum δ^{34}S values occur at 400°C and 600°C respectively, the lowest δ^{34}S value measured is −6‰ for the sulphur released in Kota-Kota at 600°C. The aubrites and EL6 chondrites show less complicated isotopic traces but contain a minimum value at either 400°C or 600°C. The δ^{34}S values for the sulphur released at 600°C in North West Forrest and at 450°C in Atlanta are both −6.7‰. At present it is not possible to speculate on the significance of the isotopic minima due to the problems associated with the δ^{34}S measurements over this temperature interval. The highest δ^{34}Svalue (+7.0‰) was recorded for sulphur released at 800°C in North West Forrest, this enrichment in ^{34}S may be related to the high degree of terrestrial weathering suffered by this sample (as is suggested by the low total sulphur content of this meteorite).

Figure 5.11 shows the isotopic composition of the sulphur liberated over the three temperature intervals considered in the preceeding discussion, namely:

1. Room temperature to 300°C.
2. 300 to 700°C.
3. 700 to 1200°C.

These temperature intervals are considered to represent sulphur combusting from elemental sulphur (1), troilite (2) and oldhamite (3). No data are plotted for South Oman or Shallowater as the thermal release profiles of

Meteorite	δ^{34}S (‰) (<300°C)	δ^{34}S (‰) (300–700°C)	δ^{34}S* (‰) troilite	Bulk δ^{34}S (‰) (calc.)	δ^{34}S (‰) (>700°C)
Kota-Kota	+0.3	−2.67	+0.69	−0.82	−1.21
Abee	–	−3.69	−0.33	−0.20	−1.27
Indarch	+1.5	−3.18	+0.18	−0.28	–
South Oman	–	−3.78	−0.42	−0.28	–
St. Mark's	–	−3.41	−0.05	+0.30	−1.35
Yilmia	–	−2.78	+0.58	+0.42	−1.77
Atlanta	–	−3.40	−0.04	−0.80	–
Daniel's Kuil	–	−3.84	−0.48	−0.53	−2.04
Khairpur	–	−3.21	+0.15	−0.29	+0.02
N.W. Forrest	–	−3.58	−0.22	+0.52	+1.89
Bustee	−2.9	−2.82	+0.54	−0.96	−1.81
Norton Co.	–	−3.38	−0.02	−1.50	−1.97
Average	–	−3.36	–	−0.27	−0.67

Table 5.8 δ^{34}S values for three sulphur components identified from the stepped combustion profiles of enstatite meteorites. *Corrected values.

these two meteorites cannot easily be subdivided into two, or more, separate releases. The δ^{34}S value of oldhamite in Atlanta could not be measured because the concentration of sulphur released above 700°C was too low to permit isotopic analysis.

Elemental sulphur

In Figure 5.11, δ^{34}S values for sulphur released below 300°C in three meteorites only are included (represented by one isotopic measurement in each case) because of the paucity of this component in the enstatite meteorites. Elemental sulphur has positive δ^{34}S values in Abee (+0.3‰) and Indarch (+1.5‰) but in Norton County a δ^{34}S value of −2.9‰ was obtained. Previously, Kaplan and Hulston (1965) reported a δ^{34}S value of −1.2‰ for the small quantity of elemental sulphur extracted from Abee which was thought to have formed by terrestrial weathering of oldhamite.

Troilite

The calculated δ^{34}S values for sulphur burning between 300 and 700°C (troilite sulphur) are between −3.84 and −2.67‰ (Table 5.8) and the average is −3.36‰. However, it is considered that these values are in error

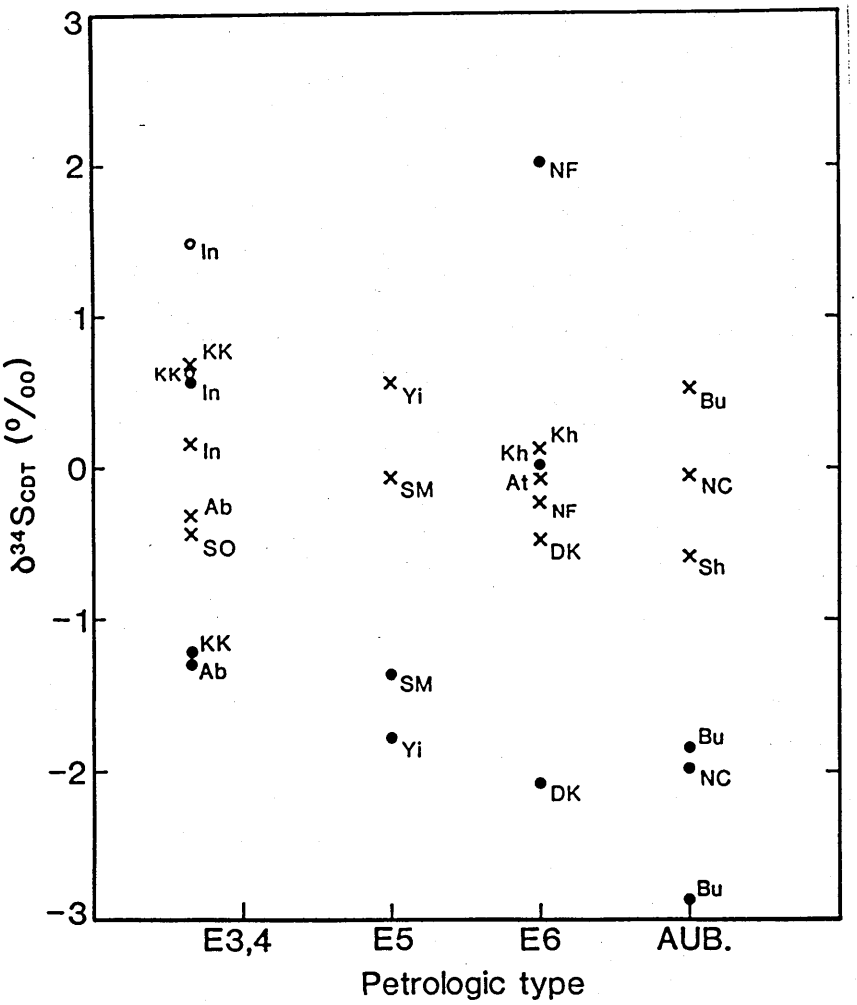


Figure 5.11 Variation with petrologic grade of δ^{34}S values obtained from sulphur combusting over three different temperature intervals during stepped combustion of enstatite meteorites. ○ = <300°C; • = 300–700°C; × = >700°C. Abbreviations as in Figure 5.2. Note: values plotted for sulphur released between 300–700°C have been "corrected" using the method described in the text.

by about 3‰. In order to assess the true value of troilite sulphur, the $\delta^{34}S$ measurements for each meteorite have been corrected by addition of 3.36‰ (i.e. the average troilite sulphur $\delta^{34}S$ value of enstatite chondrites measured in this study has been corrected to that of the average meteoritic troilite value of 0.0‰ reported in the literature). This gives a range in $\delta^{34}S$ from −0.59 to +0.69‰ (Table 5.8 and Figure 5.11). The corrected troilite sulphur $\delta^{34}S$ values can be tested for their validity by using them to recalculate the whole-rock $\delta^{34}S$ values for each meteorite, these can then be compared with the $\delta^{34}S$ value obtained for whole-rock samples by single-step combustion. The "corrected" whole-rock $\delta^{34}S$ values for meteorites are between −1.70 and +0.44‰ (Table 5.8) with an average value of −0.27‰. These values are in reasonable agreement with the results for single-step combustion analyses, which gave an average of −0.44‰ (Table 5.4). It was shown in Chapter 2 that the isotopic composition of the sulphur released above 700°C during stepped combustion of the reference mixture was not appreciably fractionated. Furthermore, the results from enstatite meteorite stepped combustions suggests that sulphur released above 700°C is largely unaffected by isotopic fractionation effects associated with the experimental technique.

If it is assumed that the variations in $\delta^{34}S$ between troilite sulphur in different enstatite meteorites are valid (Table 5.8), then the isotopic values show little variability with petrologic grade. Kaplan and Hulston (1966) extracted the HCl-volatile sulphur from Abee, Hvittis and Norton County to obtain $\delta^{34}S$ values for troilite sulphur of −0.2‰, +0.1‰ and 0.0‰ respectively.

Oldhamite

The $\delta^{34}S$ values of oldhamite sulphur are variable (Table 5.8 and Figure 5.11) and are between −2.08 (Daniel's Kuil) and +2.06‰ (North West Forrest) with an average of −0.67‰. This variability may be caused by:

1. Isotopic fractionation as a result of the combustion experiment (although this is believed to be minimal at temperatures above 700°C).
2. Changes in the original $\delta^{34}S$ value of oldhamite associated with terrestrial weathering of the sample.

If (2) is the correct explanation, then the largest isotopic effects may be expected in the meteorite finds, however, this is not substantiated by the $\delta^{34}S$ values calculated for the oldhamite sulphur of these samples given in Table 5.8 (although oldhamite in North West Forrest has the highest recorded $\delta^{34}S$ value). Nevertheless, it was noted earlier the oldhamite is very susceptible to terrestrial alteration (Ramdohr, 1973) and it is possible that this mineral may be significantly altered even in relatively pristine meteorite samples.

Kaplan and Hulston (1966) extracted oldhamite sulphur from meteorites using distilled water and reported the $\delta^{34}S$ of this sulphur in Abee and Hvittis to be +1.6‰ and +2.5‰ respectively. Moreover, these workers extracted sulphate ions from Hvittis and Norton County (again using distilled water) which were attributed to terrestrial oxidation of oldhamite, the $\delta^{34}S$ values obtained for this sulphur were −0.8‰ in Hvittis and −5.6‰ in Norton County. Thus the negative $\delta^{34}S$ values reported for sulphur liberated above 700°C in this study (Table 5.8) may record that of an admixture of sulphur from oldhamite (enriched in ^{34}S) and a sulphate (depleted in ^{34}S), the latter formed by terrestrial alteration. If this interpretation is correct then the alteration of oldhamite in enstatite meteorites is widespread and only the $\delta^{34}S$ values measured for Indarch, Khairpur and possibly North West Forrest are representative of the true value of oldhamite sulphur.

5.5 Conclusions

The content and isotopic composition of sulphur in enstatite meteorites has been investigated by analysis of representative samples of enstatite chondrites and aubrites. The whole-rock sulphur contents show a decrease with increasing petrologic type i.e. EH3,4 > EH5 > EL6 > aubrite. This systematic decrease in sulphur content has been previously observed by Mason (1966) and used as a means of classifying the enstatite meteorites (Yavnel', 1963, Anders, 1964). Whole-rock $\delta^{34}S$ values obtained by bulk combustion do not show a systematic change with petrologic type and the mean value is −0.44‰. Significantly, the $\delta^{34}S$ values obtained for aubrites are unusually low with Norton County having the lowest $\delta^{34}S$ value measured of −1.72‰. The sulphur isotopic compositions of enstatite meteorites attest to the sulphur isotopic uniformity of the solar nebula because aubrites and enstatite chondrites are thought to have accreted at much closer heliocentric distances (i.e. within 1 AU) than other meteorite groups.

Stepped combustion analysis reveals that there are several components of indigenous sulphur in enstatite meteorites. The most abundant is that which combusts between 400 and 700°C, primarily from troilite. The concentration and isotopic composition of the troilite is variable, but generally higher in EH3–5 (3.92 to 12.19 wt%; corrected $\delta^{34}S = -0.42$ to +0.69‰) than EL6 (1.11 to 7.65 wt%; corrected $\delta^{34}S = -0.48$ to +0.15‰), or aubrites (0.33 to 1.34 wt%; corrected $\delta^{34}S = -0.59$ to +0.54‰). Another sulphur component, which combusts at elevated temperatures (above 700°C), is thought to be oldhamite and has a varied isotopic composition that may result from terrestrial alteration of this mineral. Oldhamite concentrations of EH chondrites are difficult to establish because sulphur from at least one other minor sulphide mineral (niningerite) combusts at a similar temperatures. Nevertheless, the abundance of sulphur as oldhamite, like troilite, appears to decrease with petrologic type and this trend is continued into the aubrites. Oldhamite is more abundant in the EH3–5 (1.31 to 3.90 wt%, $\delta^{34}S = -1.27$ to $+0.66$‰) chondrites relative to the EL6's (0.46 to 1.38 wt%, $\delta^{34}S = -1.41$ to $+2.73$‰) and aubrites (0.33 to 1.34 wt%, $\delta^{34}S = -1.30$ to -1.14‰). Mason (1966) has noted a decrease in troilite concentration with petrologic type, but an analogous trend for oldhamite content has not been previously reported. If the aubrites formed as igneous differentiates of enstatite chondrite material then it is difficult to account for their lower oldhamite contents by such parent body processes since the melting temperature of this mineral is higher that of silicates.

There is also a minor constituent of sulphur that burns below 300°C. From its combustion temperature this component is considered to be elemental sulphur. The concentration of elemental sulphur in enstatite meteorites is low (between 200 and 1300 ppm) and not correlated with petrologic type. Elemental sulphur could be an indigenous component of the meteorites, but it is also a possiblity that it formed by terrestrial alteration of pre-existing sulphide minerals which are unstable in the terrestrial environment (e.g. oldhamite). The isotopic composition of elemental sulphur is not well-defined due to its low abundance, but seems to vary between $+1.6$ and -1.5‰.

Combustion results show that the distribution of sulphur in enstatite meteorites (particularly the EH4 chondrites) is complex. The combustion temperatures of different sulphides in the meteorites appear to be quite similar and this makes unambiguous interpretation of the stepped combustion profiles difficult to accomplish. Even when small temperature steps are used (e.g. 50°C), it is particularly difficult to establish sulphur abundances and isotopic compositions of minor sulphide minerals, including daubréelite, niningerite, alabandite, djerfisherite and sphalerite. An additional problem is that isotopic fractionation effects associated with sulphur dioxide and sulphur trioxide released at low temperatures (below 700°C) has rendered the $\delta^{34}S$ values largely meaningless.

It has been shown that the effects of chemical reagents used to isolate sulphur from constituent minerals of enstatite meteorite are not specific (e.g. dilute acetic acid reacts with both oldhamite and troilite in Khairpur). So, to obtain reliable $\delta^{34}S$ measurements of constituent sulphide minerals in enstatite meteorites, it will be necessary to separate, physically, the minerals from the meteorites and then use single-step combustions (1200°C) to obtain sulphur for mass spectrometric analysis.

Chapter 6

Conclusions

6.1 Conclusions

A stepped combustion technique has been developed to distinguish sulphur components in meteorites on the basis of their combustion temperature and isotopic signature. The method was evaluated using both standard materials and by comparing whole-rock meteorite $\delta^{34}S$ values obtained by stepped combustion with those obtained by single-step combustion of samples at 1200°C. It was found that the sulphur abundance measurements obtained by stepped combustion were reliable and this aspect of the method has been successfully used as a means of determining the concentrations of sulphur components in different meteorites.

Sulphur dioxide was analysed by a mass spectrometer, with optimised sensitivity, coupled directly to a gas preparation line. The mass spectrometer was capable of analysing samples in the order of $1\mu g$ of sulphur with a reproducibility of ± 0.4‰ for $\delta^{34}S$. The use of sulphur hexafluoride was also assessed using this instrument, and it was found that this gas has some excellent properties for mass spectrometry and allows determination of $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$. The reproducibilities of $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$, on a sample of $10\mu g$ of sulphur as sulphur hexafluoride, are ± 0.7‰, ± 0.1‰ and ± 3‰. However, the difficulties associated with preparing sulphur hexafluoride gas from meteorites were beyond the scope of this work. Following the use of fluorine compounds in the extraction system, during the latter part of the study, it was found that isotopic measurements made on sulphur dioxide produced from extraction steps below 700°C were isotopically fractionated to lower $\delta^{34}S$ values by between about 2 and 3‰. The samples analysed prior to the fluorine experiments were the C1 and C2 carbonaceous chondrites, whereas the C3–C6 chondrites and enstatite chondrites were analysed following the use of fluorine compounds. The isotopic fractionation results from the partitioning of the ^{34}S isotope into sulphur trioxide which is produced in small quantities along with sulphur dioxide during combustion.

Isotopic data from sulphur dioxide formed above 600°C have been shown to be free from isotopic fractionation for two reasons:

1. A negligible amount of sulphur trioxide is formed above this temperature.
2. The fractionation of ^{34}S between sulphur dioxide and trioxide decreases with increasing temperature.

The stepped combustion technique was found to be a valuable method for investigating the sulphur compounds of meteorites. Three applications of this technique have been described.

1. The C1 and C2 carbonaceous chondrites have suffered post-agglomeration changes involving brecciation, oxidation and hydration which took place on a sizeable parent body. The sulphur data obtained from stepped combustion of C1 and C2 meteorites provides evidence for extensive oxidation of sulphur and the presence of secondary sulphur minerals. The presence of six different sulphur components have been invoked in these meteorites to explain the data obtained by stepped combustion (elemental and organic sulphur, troilite, FESON, gypsum and epsomite). Oxidised forms of sulphur (elemental sulphur, sulphates and FESON) dominate over reduced forms (sulphides). The relative abundance of oxidised sulphur is highest in the C1 chondrites, which is consistent with their having suffered more intense aqueous alteration. The similarities in the nature of the sulphur compounds in C1 and C2 chondrites indicate that hydrothermal evolution of these meteorites probably followed a common pathway. Changes in the sulphur isotopic composition associated with hydrous alteration have led to enrichment of ^{34}S in elemental sulphur and sulphates compared to the sulphide starting material. Overall, bulk δ^{34}S values of C2 chondrites show a slight enrichment in ^{34}S by about 1‰. This has probably resulted from the loss of volatile sulphur species (e.g. hydrogen sulphide gas) formed as intermediate compounds during aqueous alteration; loss of sulphur is also confirmed by the sub-cosmic abundances of this element in C2 chondrites.
2. Most of the sulphur in C3, C4 and C5/6 meteorites is present as sulphide, but the stepped combustion data indicate that there is also a component of preterrestrial oxidised sulphur in C3 and C4 chondrites. The identity of this sulphur is not known with certainty, but there is chemical evidence to suggest that it could be anhydrite or FESON. Although aqueous alteration in C3 chondrites has not previously been reported in detail, the sulphur data of C3 and C4 chondrites are very similar to those obtained for a type 3 ordinary chondrite (Semarkona)

in which the effects of hydrous alteration have been relatively well-studied. Thus, the C3 and C4 carbonaceous chondrites have undergone a relatively small amount of aqueous alteration on the meteorite parent body and this provides an important evolutionary link between meteorites of higher petrologic type and C1 and C2 meteorites. Bulk $\delta^{34}S$ values of C3 and C4 carbonaceous chondrites do not correlate with petrologic type and are within ± 1‰ of CDT. The original distribution of sulphur in two meteorites, Mulga West and Coolidge, has been significantly affected by terrestrial weathering processes. Pre-existing sulphides in these meteorites seems to have largely been oxidised to sulphates.

3. The sulphur isotopic composition of different sulphide minerals in enstatite chondrites and aubrites is an area of meteoritics that has received little attention. Stepped combustion was used in an attempt to reveal the abundance, distribution and isotopic composition of sulphur in representative samples. Troilite is the main component present in all the samples. The combustion temperature of troilite is controlled by textural and chemical changes of this mineral associated with petrologic type and is highest in the EL6's and aubrites. The sulphur isotopic composition of troilite could not be calculated directly from the stepped combustion data because of the formation of sulphur trioxide and associated isotopic fractionation problems, but it was estimated to be close the usual meteoritic $\delta^{34}S$ value of 0‰.

   Oldhamite was found to be the second most important sulphide. The isotopic composition of oldhamite is variable which probably reflects terrestrial oxidation of this mineral. The $\delta^{34}S$ value of unaltered oldhamite seems to be close to that of troilite (i.e. 0‰), although, these two minerals probably formed at significantly different temperatures in the solar nebula. It was found that elemental sulphur, enriched in ^{34}S, is a minor constituent of many enstatite meteorites and is probably a terrestrial alteration product of oldhamite.

   Total sulphur, troilite and oldhamite abundances show a systematic decrease with petrologic grade in the chondrites and this trend continues into the aubrites. The similarities in the sulphur data suggests that enstatite chondrites and aubrites must have formed in the same region of the solar nebula. The systematic decrease in troilite content with petrologic grade may be accounted for by thermal processes on the meteorite parent bodies; but this process cannot satisfactorily explain the analogous changes in oldhamite content since this mineral is highly refractory.

   Bulk $\delta^{34}S$ values of the enstatite chondrites are close to 0‰, but the aubrites are depleted in ^{34}S by up to about 2‰. The lower $\delta^{34}S$ values of the aubrites may be related to loss of isotopically heavy sulphur during igneous differentiation.

An important feature of this work is the recognition that two meteorite groups (carbonaceous and enstatite chondrites), considered to have formed at separate locations in the solar nebula, have very similar bulk $\delta^{34}S$ values of close to 0‰. However, this does not rule-out the application of sulphur isotopes for establishing genetic relationships among meteorites, but would require precise $\delta^{33}S$ (and $\delta^{36}S$) measurements to be obtained since the isotopic variations are of a very small magnitude. The constancy of bulk $\delta^{34}S$ values measured during this study and of those reported previously, indicates that the reservoir from which meteorites and planets formed must have had a uniform sulphur isotopic composition. Bulk meteorite $\delta^{34}S$ variations which have been measured are in the order of ± 2‰ and do not provide evidence in support of isotopic anomalies in sulphur. Unlike some other major elements, (e.g. oxygen, magnesium), sulphur isotopic variations in meteorites do not appear to retain a record of sulphur formed by different nuclear processes with distinct isotopic compositions. If there were multiple sources of sulphur then the isotopes could have been homogenized by physical processes active in the nebula (e.g. mixing, melting or diffusion).

6.2 Future research

6.2.1 Improvement of techniques

Some suggestions for the improvement of the stepped combustion method and mass spectrometry follow.

1. The most important objective of continued research is to overcome the isotopic fractionation problems associated with the formation of sulphur trioxide in gas samples prepared below 600°C during combustion. Some suggestions have already been detailed in Chapter 2 and those under current investigation include the use of platinum as a catalyst to reduce sulphur trioxide and the incorporation of a copper oxide finger to control the partial pressure of oxygen in the reaction vessel. The latter method has already yielded encouraging results, during a stepped combustion analysis of Bella Roca troilite a bulk $\delta^{34}S$ value of −0.84‰ was obtained (compared to the accepted value of −0.4‰) along with 90% of the theoretical yield of sulphur.
2. The separation of sulphur dioxide from carbon dioxide and water is carried-out cryogenically and is assisted by a computer display of the gas pressure evolving from the variable cryogenic finger. This method

works well most of the time, but problems are encountered when significant quantities of water are present, or where very small sulphur dioxide samples are being separated. Furthermore, this procedure can require the use of the computer for relatively long time periods and sometimes can delay isotopic measurement of gas samples. To obtain good cryogenic separations also demands a relatively high level of skill and experience from the operator. In order to make this part of the stepped combustion technique more routine and methodical a simple gas chromatograph could be incorporated into the extraction line and, by using the different retention times of the product gases, sulphur dioxide could be purified. Such a system has been described by Hirner et al. (1984).

3. Mass spectrometry. The mass spectrometer used in this study was specifically adapted to:

   - Maximized sensitivity.
   - Capable of measuring sulphur isotope ratios using both sulphur dioxide and sulphur hexafluoride.

   There are many potential applications in meteoritics where it is desirable to measure very small amounts of gases. Such studies include the analysis of valuable meteorite residues that are usually produced in small quantity, and for investigating minor components of meteorites, e.g. individual minerals, chondrules, inclusions or matrix. Using conventional dynamic mass spectrometry maximum sample gas consumption is only 10% during analysis (Hallas and Krouse, 1983). There are two departures from conventional dynamic mass spectrometry which can be used to achieve near-total gas consumption and hence, allow measurement of smaller samples.

   (a) Gas mixing or isotope dilution. Mixing the sample with a measured amount of reference gas of known isotopic composition. This method has been applied to carbon isotope studies of meteorites to reveal large isotopic enrichments in ^{13}C (Swart et al., 1983) but the errors are large, ± 10‰ for 100ng of carbon, so this method can only be applied to samples in which large isotopic enrichments are anticipated.

   (b) Static mass spectrometry. Static mass spectrometry is widely used in isotope ratio determinations of rare gases. This approach has been used successfully for obtaining isotope measurements on a few nanograms of nitrogen (Frick and Pepin, 1981; Boyd et al., 1987) and carbon (Carr et al., 1986). This method will probably be of no use for sulphur isotopic measurements using sulphur dioxide because of its poor desorption characteristics and degradation on the hot filament. It has been found that sulphur hexafluoride has some favourable characteristics for mass spectrometry (e.g. no isobaric interferences, better gas desorption characteristics than sulphur dioxide and the main ion, SF_5^+, occurs in a region of the mass spectrum free from instrumental background). Sulphur hexafluoride may prove to be an exceptionally well-suited gas for static mass spectrometry and it has the added advantage of enabling $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ values to be determined for samples.

6.2.2 Application to meteorites

Stepped combustion analyses of carbonaceous chondrites, enstatite chondrites and aubrites has successfully demonstrated the presence of a number of sulphur components. Further research involving these and other meteorite types will enable a more complete picture of sulphur isotopic and abundance variations to be assembled.

1. Meteorite residues: Most stepped combustion analyses have been carried-out on powdered bulk meteorite samples. A preliminary investigation of chemical residues prepared from Murchison (CM2) has shown that these materials need to be well-characterised before any firm conclusions can be drawn from the results. The preparation of new residues from bulk meteorites using combinations of physical and chemical techniques could be undertaken to provide a better understanding of internal sulphur isotope variations. Ideally, to enable unambiguous interpretation, the analysis of individual or a few separated grains of sulphide or sulphate minerals is desirable. However, meteorite residues prepared by chemical methods could be characterised using both stepped combustion and petrographic methods.

2. Carbonaceous chondrites: Only a few samples from each class of carbonaceous chondrites have been analysed by stepped combustion. As there is always a danger of drawing conclusions from analyses of a statistically unrepresentative suite of samples, future work should attempt to include more samples from each petrologic type.

   Since the relative amounts of reduced and oxidised sulphur in each sample seems to accurately reflect the extent of aqueous alteration, a complete dataset could be used to construct a scale of aqueous alteration extending from the C1 (most altered) to the C3 and C4 chondrites (least altered). It is particularly important to establish the nature of the oxidised sulphur component in C3 chondrites. Combined petrographic and stepped combustion studies of Mokoia (CV3), which is known to contain significant quantities of sulphate, could help to achieve this and provide evidence for a genetic link between CM2 and CV3 chondrites.

3. Enstatite meteorites. Stepped combustion analysis of enstatite meteorites has yielded information about the two dominant sulphur minerals, troilite and oldhamite. Many other minor sulphide minerals are known to be present in these meteorites including alabandite, niningerite, sphalerite, djerfisherite etc. (Chapter 5). In order to reveal the sulphur isotopic abundances of these minor components it will be necessary to either, remove them from the meteorite by selective physical and/or chemical separation methods, or remove the two dominant minerals troilite and oldhamite. If the latter course is pursued, then the distribution of sulphur in the minor components can be revealed by stepped combustion of the material remaining after troilite and oldhamite have been removed.
4. Other meteorite groups.
   (a) Ordinary chondrites: The ordinary chondrites are the largest meteorite group but have been mostly neglected in sulphur isotope studies. Ueda et al. (1986) have chemically extracted sulphide (troilite) and sulphate sulphur from three type 6 chondrites (Peace River, Bruderheim and Vulcan). The sulphate in each of these meteorites was found to be enriched in ^{34}S (δ^{34}S = +1.9 to +3.0‰) relative to the sulphide (δ^{34}S = −1.0 to −0.2‰).
   (b) Iron meteorites. Sulphur in iron meteorites is concentrated mainly in troilite-rich nodules making it a relatively simple task to separate them from the metal phase. A study is currently being undertaken (in collaboration with Dr J. Arden) to measure the δ^{34}S value of the sulphide and δ^{13}C of associated carbide from well-characterised fractions of the Toluca and Cape York iron meteorites. These measurements may give clues as to the history of the sulphide in these two types of irons.
   (c) Achondrites. The sulphur contents of achondritic meteorites are very low and as such only a single sample (Norton County) has been analysed for its sulphur isotopic composition. Nevertheless, some samples are appealing for study.

   The SNC meteorites reputedly contain martian weathering products. Carr et al. (1985) found evidence for carbonate in Nakhla and Gooding and Muenow (1986) found oxidised sulphur and

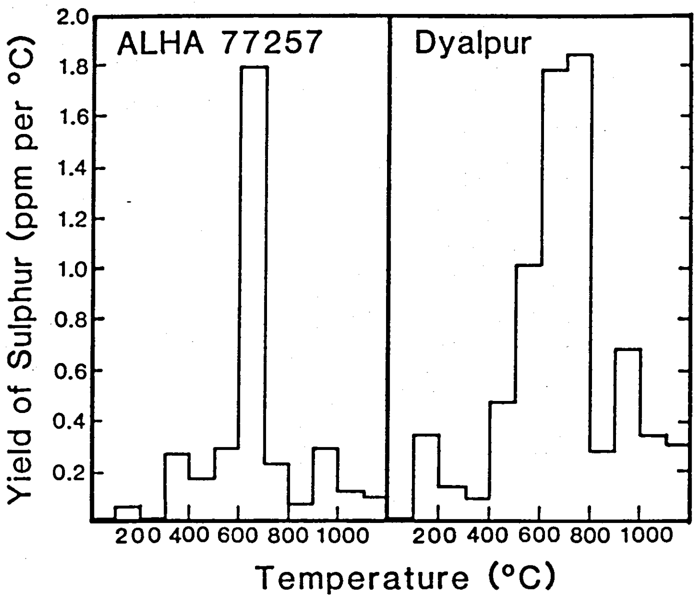


Figure 6.1 Sulphur released (—) upon stepped combustion of two ureilites.

sulphur-rich aluminosilicates in shergottite Elephant Moraine A79001. Stepped combustion analysis enables the sulphur from most sulphides and sulphates to be distinguished on the basis of combustion temperature and may be a useful technique for quantifying and obtaining isotopic measurements of such sulphur minerals of SNC meteorites.

Figure 6.1 shows the sulphur release profiles obtained for two ureilites Allan Hills A77257 and Dyalpur. Both profiles give evidence for three sulphur components, a low temperature release occurring between 100 and 300°C, a main release between 400 and 800°C and a high temperature one between 900 and 1200°C. Tentatively, these three releases may be attributed, in order of increasing temperature, to:

- Elemental sulphur.
- A sulphide (probably troilite).
- A sulphate or possibly oldhamite.

Ramdohr (1973) found oldhamite in veins in Havero as well as indications of daubréelite in solid-solution with troilite. Wacker

> (1986) has related the noble gas-bearing carbon of ureilites to enstatite chondrites and considered that this material may have formed in a similar region of the nebula as the enstatite chondrites which was separate from that of the rest of the meteorite. Significantly, the profiles shown in Figure 6.1 are similar to many of those obtained from enstatite chondrites. This preliminary investigation of sulphur in ureilites shows that stepped combustion has the potential to provide valuable information about the formation and evolution of meteorites, even in groups that contain only trace quantities of sulphur.

This thesis has detailed efforts made to measure the abundance and isotopic constitution of sulphur in meteorites using a stepped combustion technique. Since sulphur data for materials not previously investigated, can be obtained by this method, it has many potential applications in disciplines outside the sphere of meteoritics.

Appendix A

The application of sulphur hexafluoride for sulphur isotope analysis

A.1 Background

Sulphur isotopic fractionation by ordinary chemical reactions and physical transport processes (e.g. diffusion) are controlled by the relationships (Hulston and Thode, 1965a):

$$\delta^{33}S = \delta^{34}S/1.94$$
$$\delta^{36}S = 1.89\times\delta^{34}S$$

These two equations hold for $\delta^{34}S$ values of <150‰ (Hulston and Thode, 1965a), which encompasses the range for terrestrial samples (Nielsen 1979). Therefore, measurement of variations in the abundances of the minor isotopes of sulphur (^{33}S and ^{36}S) in geological samples is of limited value to geochemists. However, there is unequivocal evidence that some extraterrestrial samples contain small quantities of certain elements with anomalous isotopic compositions, these elements include: oxygen (Clayton et al, 1973; Clayton et al, 1977; Clayton and Mayeda, 1977a,b), magnesium (Lee and Papanastassiou 1974; Lee et al., 1976), calcium (Lee et al., 1978; Lee et al., 1979) and titanium (Heydegger et al., 1979; Niederer et al., 1980) among others. Isotopic anomalies of this type are currently thought to be due to inhomogeneities present in the solar nebula prior to condensation. An objective approach to the study of sulphur in meteorites must therefore include the notion that the effects of nuclear processes (e.g. nucleosynthesis in stars, photochemistry, plasma reactions, spallation etc.) are possible and relative enrichments in one or more of the sulphur isotopes may be expected (Clayton and Ramadurai, 1977). It was shown by Hulston and Thode (1965a) that data for separated sulphur-bearing minerals from a number of meteorites, fall on the mass-dependent fractionation line for plots of $\delta^{33}S$ vs. $\delta^{34}S$

and $\delta^{36}S$ vs. $\delta^{34}S$, suggesting that the early solar nebula may have had a uniform sulphur isotopic composition.

The relative abundances of the three isotopes of oxygen has proved to be particularly useful for unravelling genetic relationships between different meteorite groups. Meteorites derived from an initial oxygen isotopic reservoir will fall on a straight line on a graph of $\delta^{17}O$ vs. $\delta^{18}O$. The position of this line is dependant on the original abundance of ^{16}O and different meteorite groups have been shown to have a variable initial amount of ^{16}O. Clayton and Mayeda (1978) have shown that there is an association between IAB irons and enstatite chondrites using results from oxygen isotope analyses of silicate inclusions. Re-examination of the sulphur isotopic compositions of all the meteorite classes using three isotope plots is desirable so that a comparable framework of meteorite classification can be constructed. Sulphur isotope data provide an especially promising approach to tackling the problem of relationships between iron and stony meteorites. Silicates are rare or absent from most iron meteorites (particularly members of the groups II, III and IV), in contrast, troilite is usually common (Buchwald, 1975).

Some experiments are described herein which were performed as preliminary to the investigation of sulphur isotopes in meteorites using sulphur hexafluoride gas, a species which allows measurement of ^{32}S, ^{33}S, ^{34}S and ^{36}S. Although sulphur dioxide is used conventionally for sulphur isotope measurements, sulphur hexafluoride has certain advantages. The most important of these is that fluorine is monoisotopic and there are no isobaric interferences, as there are from oxygen in sulphur dioxide. Consequently it is possible to determine all three isotope ratios of sulphur ($^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}S/^{32}S$). The disadvantage is that the preparation of sulphur hexafluoride is invariably more difficult and potentially hazardous, involving the use of highly toxic and very reactive fluorine-containing agents. During the course of this study, experiments were undertaken in an attempt to synthesise sulphur hexafluoride gas from certain sulphur-bearing samples using:

1. Chlorine trifluoride gas.
2. Fluorine gas generated by dissociation of two solid metal fluorides (gold trifluoride and cobalt trifluoride).

Most importantly, experiments were carried out to try and fluorinate sulphur dioxide gas directly, in an attempt to produce sulphur hexafluoride from sulphur dioxide samples formed during stepped combustion of geological samples to provide compatibility with the studies discussed in the main body of this thesis.

To facilitate simultaneous measurement of the three isotope ratios, $^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}S/^{32}S$, substantial modification of a V.G. Micromass 602E mass spectrometer was necessary (Section 2.1.1). The most important of the changes was the inclusion of an electromagnet for high mass resolution and use of four Faraday buckets for collection of ion beams at m/z 127, 128, 129 and 131 (Section A.3).

A.2 Previous experimental work

The first sulphur isotope analysis using sulphur hexafluoride was apparently undertaken by Hoering (1962), quoted in Hulston and Thode (1965a). The gas was synthesised by reaction of sulphides with bromine trifluoride and purified by gas chromatography. Hulston and Thode (1965a) formed sulphur hexafluoride by reaction of silver sulphide and fluorine gas. Yields of up to 75% were achieved by this method, but negligible isotopic fractionation was incurred. Puchelt et al. (1971) reacted bromine trifluoride with separated sulphides (PbS, CdS, HgS etc.) in a sealed metal vessel at 200°C overnight to form sulphur hexafluoride. The reaction products were passed through metal scrubbing traps filled with sodium hydroxide pellets to remove any acid constituents (HF, HBr) and bromine. Final purification was carried out by gas chromatography. Some sulphide minerals gave low yields using this method, especially pyrrhotite and troilite, and it was thus considered necessary to convert these two minerals to cadmium sulphide prior to fluorination. Thode and Rees (1971) report the use of bromine pentafluoride to fluorinate silver sulphide samples prepared from separated sulphur-bearing minerals. During these experiments a twenty molar excess of bromine trifluoride was used for 16 hours at 300°C. A cryogenic purification was followed by separation of the products by gas chromatography.

In a series of publications, Yugoslavian scientists (Leskovšek et al., 1969a,b; Leskovšek et al., 1974; Pezdič and Slivnik, 1970) investigated the reactions of fluorine gas with a number of different sulphides under various experimental conditions. Using 18 to 22 atm of fluorine gas at −196°C, sulphides could be quantitatively converted to sulphur hexafluoride in twenty minutes. The reaction between metal sulphides and fluorine is exothermic so the actual reaction temperature was estimated to be about 20°C. Using these conditions yields of 95% (± 2%) were obtained from most of the sulphides studied. After excess fluorine was removed, the gaseous products were cleaned of any acidic constituents using sodium hydroxide. Yields of less than 95% were found to be accompanied by appreciable isotopic fractionation (Leskovšek et al., 1974) which is in contrast to the results of Hulston and Thode (1965a).

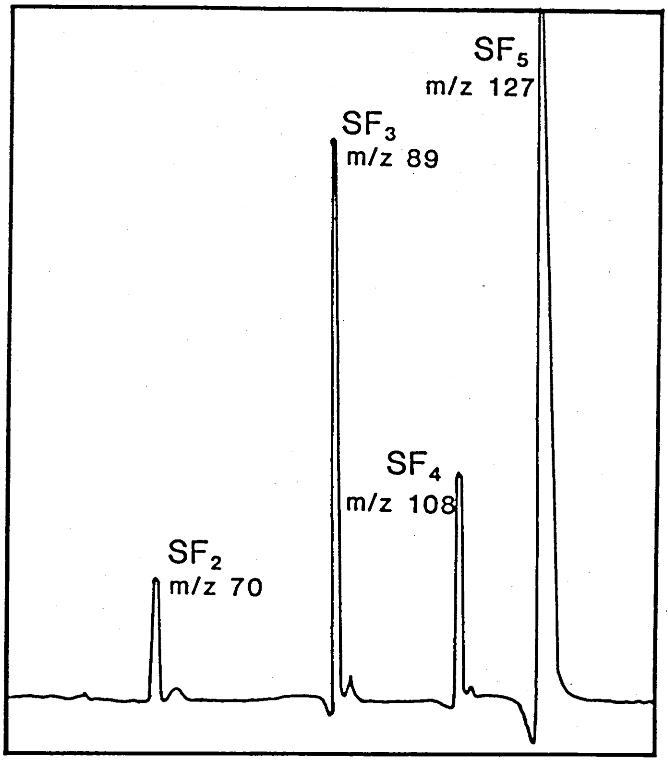


Figure A.1 The mass spectrum of sulphur hexafluoride.

A.3 Mass spectrometry

Isotopic measurements of sulphur hexafluoride gas were made by conventional dynamic mass spectrometry using the modified V. G. Micromass 602E instrument described in Section 2.1. This mass spectrometer has four fixed collectors positioned such that all four isotopic species from the SF_5^+ ion can be collected at m/z 127, 128, 129 and 131. Apart from SF_5^+, other fragment ions of sulphur hexafluoride are produced in the ionization source of the mass spectrometer. These ions (SF_4^+, SF_3^+, SF_2^+ and SF^+) were not used for isotopic measurements because:

1. They are not produced as efficiently as SF_5^+.
2. They occur at masses similar to those of likely contaminants (e.g. silicon tetrafluoride).

The mass spectrum of sulphur hexafluoride is shown in Figure A.1 from which it can be seen that SF_5^+ is the dominant species produced in the ion source of the mass spectrometer. The ion source operating parameters for

Half-plate voltage	+7 V
Ion repellor voltage	-7 V
Electron energy	65 eV
Trap current	200μA
Magnet current	3.5 A
Accelerating voltage (m/z 127)	1.9 KV

Table A.1 Ion source operating parameters for sulphur hexafluoride.

Parameter	SF_6	SO_2
Mass spec. temp. (°C)	21	110
Ionic species analysed	SF_5^+	SO_2^+, SO^+
Masses (m/z)	127, 128, 129, 131	66, 64, 50, 48
No. collectors	4	2
δ-measurements	$\delta^{33}S$, $\delta^{34}S$, $\delta^{36}S$	$\delta^{34}S$
Analysis time	≈10 mins	≈20 mins
Minimum sample size (μg sulphur)	0.5	1

Table A.2 A comparison of sulphur dioxide and sulphur hexafluoride mass spectrometric analyses.

sulphur hexafluoride analysis are given in Table A.1 and the mass spectrometer operating conditions for sulphur dioxide and sulphur hexafluoride measurement are compared in Table A.2.

For a number of reasons the isotopic analysis of sulphur hexafluoride is considerably more straightforward and less time-consuming than that of sulphur dioxide. As already stated, fluorine is monoisotopic, therefore no isobaric corrections need be applied to the raw mass spectrometric data obtained from sulphur hexafluoride, this in turn leads to increased precision of the isotopic measurements compared to those determined using sulphur dioxide. It is not necessary to heat the mass spectrometer as the behaviour of sulphur hexafluoride in the instrument is similar to that of carbon dioxide and argon (Section 2.1.2). Furthermore during sulphur hexafluoride analysis only the SF_5^+ species is considered, thus there is a significant reduction in analysis time over sulphur dioxide for which the SO^+ fragment is also analysed.

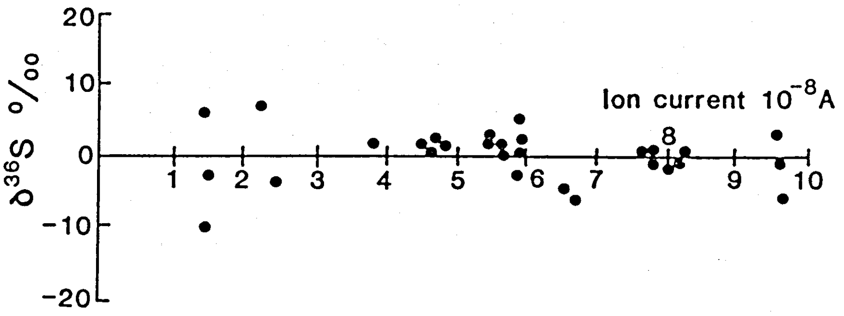


Figure A.2 Zero enrichment tests for δ^{36}S using different sample sizes.

The measurement procedure adopted for sulphur hexafluoride is similar to that described for sulphur dioxide in Section 2.1.4. Six reference/sample comparisons are made, during each a total of 400 ratio measurements are obtained for the three ratios; 128/127, 129/127 and 131/127. These are plotted in real-time on a computer VDU screen as δ128, δ129 and δ131 values. Mean values of the 400 ratio measurements are calculated for each reference/sample comparison and the δ-values are derived directly from these. The standard errors for the δ-values so obtained are ± 0.7‰, ± 0.1‰ and ±3‰ for δ^{33}S, δ^{34}S and δ^{36}S respectively. These errors are a reflection of the relative abundances of the stable isotopes and are greatest for the least abundant isotope. The relative abundances are as follows (Ault and Jensen, 1962):

$$^{32}S = 94.941\%$$
$$^{33}S = 0.769\%$$
$$^{34}S = 4.273\%$$
$$^{36}S = 0.017\%$$

The results of δ^{36}S measurements for successive zero enrichments of sulphur hexafluoride reference gas are shown graphically in Figure A.2. The error in the measurement of the δ^{36}S values is too large to be useful at major ion beam intensities below 2×10^{-8} amps, but precision improves substantially with larger samples.

The minimum sample size of sulphur hexafluoride measurable in the mass spectrometer is equivalent to 0.5μg of sulphur which is an improvement on that using sulphur dioxide (where a factor of two more was required). The normal working pressure of sulphur hexafluoride in the ion source is 2×10^{-8} mb which gives a major ion beam intensity (m/z 127) of 4×10^{-7} amp.

A cylinder of sulphur hexafluoride gas (BDH Chemicals Ltd, Poole, England) was obtained for use as a laboratory isotopic reference gas. The isotopic composition of this gas was calibrated relative to CDT by using the results described in A.4.1 and has a δ^{34}S value of +4.2‰.

A.4 Preparation of sulphur hexafluoride

A.4.1 Chlorine trifluoride

In order to assess the possibility of producing sulphur hexafluoride from sulphides using chlorine trifluoride, experiments were performed using a semi-automatic system developed originally for the purpose of extracting oxygen from silicates for isotopic analysis (built by Dr D.P. Mattey and Mr S.J. Prosser). The metal part of the extraction line is shown in Figure A.3 and required only minor modification for sulphur hexafluoride production. The reaction vessel is made of a solid bar of nickel which was drilled out to give an internal volume of about 33cm^3. Prior to use several aliquots of chlorine trifluoride were reacted with the interior walls of the reactor at 550°C for 8 hours. This operation was repeated several times to remove contaminants introduced during drilling and to form a protective layer of nickel difluoride on the interior surfaces of the vessel (Dr D.P. Mattey, personal communication). The nickel difluoride coating prevents further reaction between nickel and chlorine trifluoride and avoids the unwanted depletion of chlorine trifluoride during reaction with samples. If the Ni-reactor is not properly conditioned in this way it was found to give a low yield of gas when extracting oxygen from silicates.

Prior to loading a sample for fluorination, the metal line was flushed with argon (at 1 atm pressure). If the conditioned Ni-vessel was opened directly to atmosphere during sample loading, the metal walls adsorb water and oxygen causing blank problems. Samples of separated sulphide minerals (2 to 5mg) were transferred into small teflon buckets, which are threaded at the sealed ends so that they could be screwed onto metal rods. The samples, contained in the teflon buckets, were loaded in a musket-like fashion into the detached Ni-reactor and emptied by inverting the vessel. During loading, care was taken not to scrape the walls of the Ni-reactor as this could damage the protective fluoride coating. It was also important to ensure that all the sample was emptied at the bottom of the tube and not onto the walls of the vessel, thus ensuring that the sample was heated to a uniform temperature during reaction with chlorine trifluoride. The reactor was reconnected to the manifold using a high vacuum screw-coupling and pumped to high vacuum. During evacuation, the reactor was heated to 200°C using a wire-wound resistance furnace to remove all traces of air and water. When the vacuum was better than 10^{-6} torr some chlorine trifluoride was distilled from the main reservoir and by a continuous sequence of sublimation and freezing cycles impurities (e.g. oxygen and nitrogen) were removed. Allowing the chlorine trifluoride to warm to room temperature generated enough vapour for about a 10 molar excess of this compound for reaction with the sample

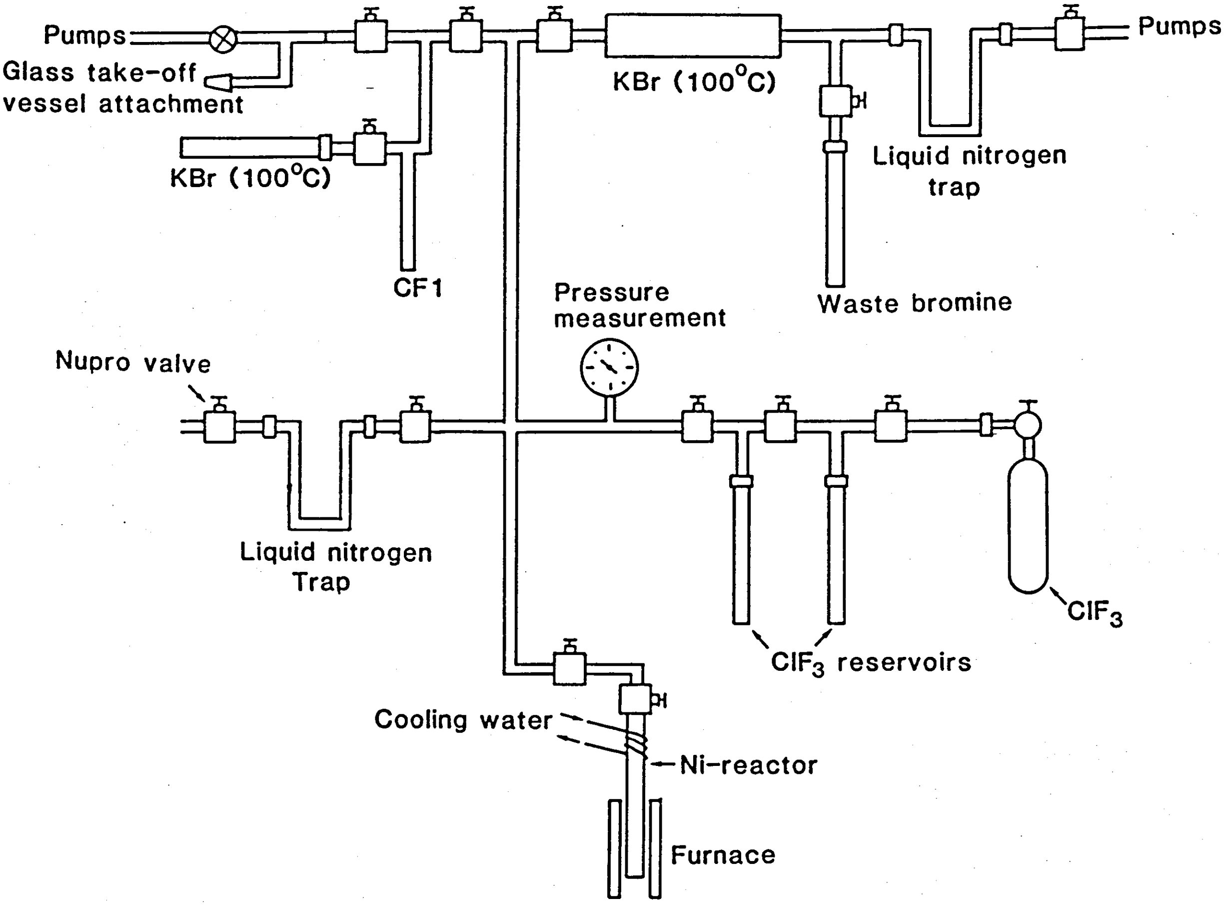


Figure A.3 Schematic diagram of the metal extraction system used for synthesising sulphur hexafluoride by the reaction of chlorine trifluoride with sulphides. (Built by Dr D.P. Mattey and Mr S.J. Prosser).

(up to 40mg chlorine trifluoride). The reagent was expanded into the reactor which was then isolated from the rest of the extraction line. Water was cycled through copper pipes attached to the top of the Ni-reactor to cool the teflon washer of the high vacuum screw-coupling whilst the vessel was heated to 600°C for 12 hours. The reaction of chlorine trifluoride with a sulphide (e.g. sphalerite) is:

$$8ClF_3 + 3ZnS \rightarrow 3ZnF_2 + 3SF_6 + 4Cl_2$$

After the reaction period the gases were frozen onto a metal 'cold finger' using liquid nitrogen (CF1 in Figure A.1). This trap was then warmed to room temperature and the gases allowed to remain in contact with potassium bromide at 150°C for 1 hour. The potassium bromide removes many of the unwanted constituents (such as chlorine and fluorine) by displacement of bromine. Sulphur hexafluoride freezes at approximately −125°C in a vacuum and can be readily separated from bromine (boiling point 58°C freezing point −7°C) with a methanol slush bath (−100°C). Following this cryogenic separation, pure sulphur hexafluoride is transferred (using liquid nitrogen) into a detachable glass vessel and delivered to the mass spectrometer for isotopic analysis. Any impurities inadvertently frozen along with the sulphur hexafluoride are apparent as yellow (chlorine trifluoride), or red (bromine), discolourations in the frozen mixture. Otherwise, the main impurities are silicon tetrafluoride (SiF_4), thionyl fluoride (SOF_2) or sulphuryl fluoride (SO_2F_2). The silicon and oxygen in these compounds is derived either from the walls of the Ni-reactor or possibly from silicate contaminants in the sulphide.

Sulphides like chalcopyrite, sphalerite and pyrite usually gave between 60% and 70% of the theoretical yield of sulphur as sulphur hexafluoride. However troilite (from the Bella Roca iron meteorite) did not readily react with chlorine trifluoride under the conditions specified above and yields of greater than 10% were unobtainable from this material.

The results for the isotopic analysis of sulphur hexafluoride prepared by fluorination of sulphide minerals using chlorine trifluoride are shown graphically in Figure A.4. The $\delta^{33}S$ and $\delta^{34}S$ values define a straight line:

$$\delta^{33}S = \delta^{34}S/2.28$$

The $\delta^{34}S$ values obtained for the compounds other than troilite are close to the quoted values, despite the relatively low yields. The data from Bella Roca troilite, which gave the lowest yields, shows a spread of δ-values along the mass fractionation line (Figure A.4) which are higher than the true value ($\delta^{34}S = -0.45$‰, $\delta^{36}S = -0.23$‰). It is considered that the partial reaction between this mineral and chlorine trifluoride has resulted in production of isotopically fractionated sulphur hexafluoride (depleted in ^{32}S). The $\delta^{36}S$

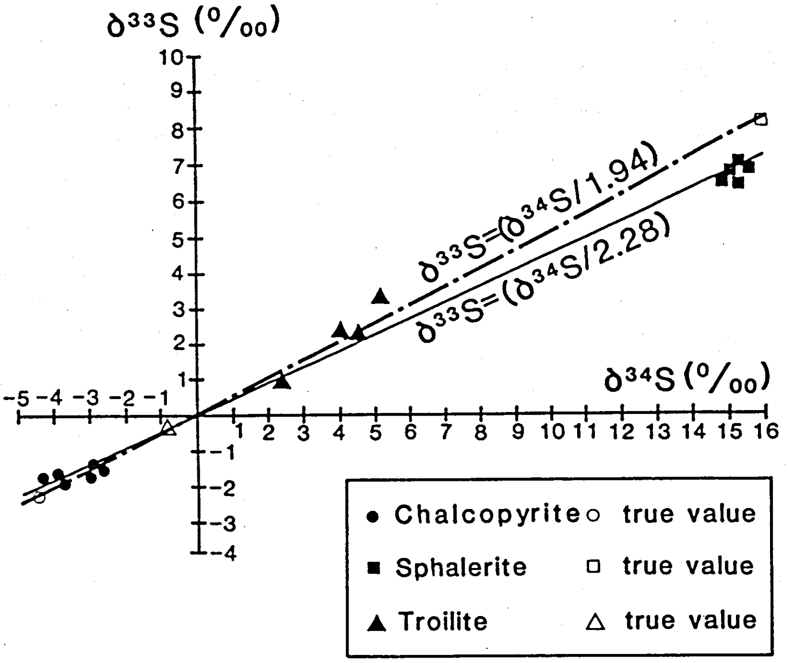


Figure A.4 A graph of $\delta^{33}S$ versus $\delta^{34}S$ for three different sulphide minerals. Filled symbols – values obtained by fluorination (SF_6), open symbols – values obtained by bulk combustion (SO_2).

values obtained were rendered meaningless by an interference at m/z 131 ($^{36}SF_5^+$) from an unidentified contaminant in the sample gas (Figure A.5). Careful purification of the sample gas aids in reducing the effect, but it is not possible to completely remove the contaminant using cryogenic separation. This impurity is probably the same as that found by Thode and Rees (1971) which they removed using gas chromatography.

The reaction of sulphur dioxide with chlorine trifluoride was also investigated as a means of producing sulphur hexafluoride from sulphur dioxide generated by stepped combustion. The reaction of interest being:

$$SO_2 + 3F_2 \rightarrow SF_6 + O_2$$

Two 1mg samples of sulphur as sulphur dioxide were reacted with 10mg aliquots of chlorine trifluoride overnight:

1. At room temperature.
2. At 100°C.

Both experiments were unsuccessful in forming sulphur hexafluoride, the final product being sulphuryl fluoride. The failure of this experiment may be explained by the relatively low temperatures involved. Kwasnik (1963) states that sulphur hexafluoride can be prepared by burning sulphur dioxide with excess fluorine at 650°C, the main impurity being thionyl fluoride.

A.4.2 Metal fluorides

The hazardous nature of chlorine trifluoride necessitates extensive safety procedures and specialized handling techniques. The experiments described above were carried-out in a separate laboratory from that containing the mass spectrometer. An effort to find a simpler, safer and more convenient method of preparing sulphur hexafluoride was attempted using two solid metal fluorides, cobalt trifluoride (CoF_3) and gold trifluoride (AuF_3).

1. Cobalt trifluoride (CoF_3): Cobalt trifluoride is a buff-coloured powder which begins to decompose at 100°C to form pink cobalt difluoride.

$$2CoF_3 \rightarrow 2CoF_2 + F_2$$

2. Gold trifluoride (AuF_3). Bright yellow needles of gold trifluoride can be prepared by the reaction of fluorine and gold powder or precipitate using a high pressure of fluorine at 350°C for 12hrs (Einstein et al., 1967). In the present study gold trifluoride was prepared using the oxygen extraction system described previously (Figure A.3), by the reaction of gold strips (with dimensions 1mm×2mm×0.5mm) in a Ni-reactor vessel with 60mg chlorine trifluoride at 300°C for 12 hours.

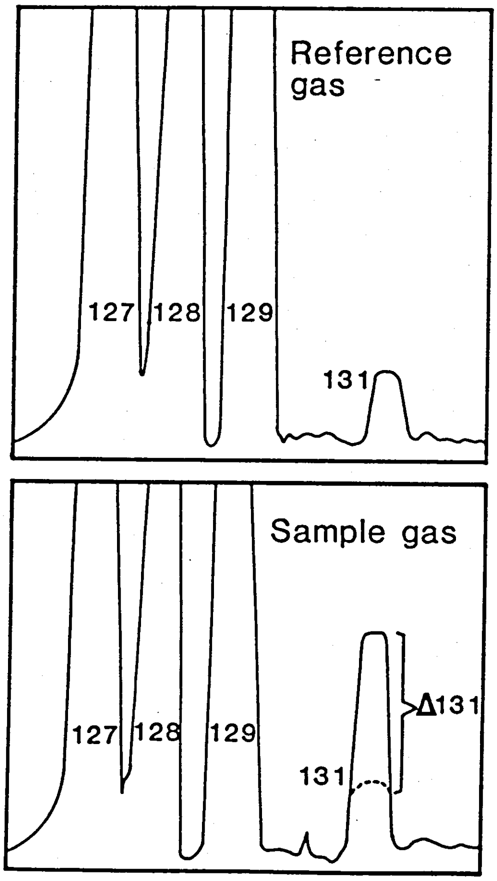


Figure A.5 Segments of the mass spectra of sample and reference gases showing the presence of a contaminant species at m/z 131 in the sample gas.

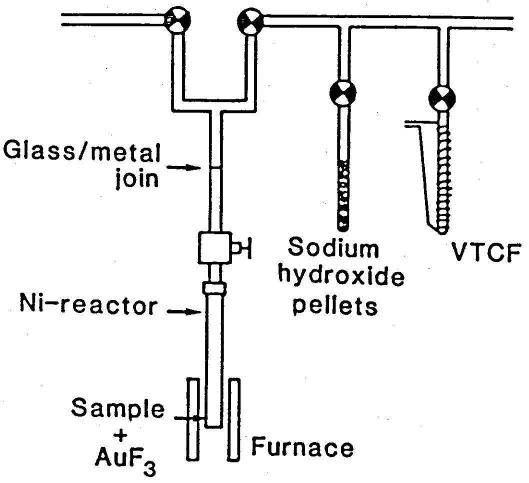


Figure A.6 Section of the extraction line modified for reacting samples with metal fluorides (part metal).

After reaction, the surfaces of the gold strips appeared tarnished and etched due to the formation of gold trifluoride which probably occurs as a surface coating. Fluorine is liberated from gold trifluoride at temperatures in excess of 400°C.

$$2AuF_3 \rightarrow 2AuF_2 + F_2$$

The gold strips coated with gold trifluoride resumed their 'normal' gold colour after heating and could be re-fluorinated for further use.

Similar experiments were performed using gold trifluoride and cobalt trifluoride and both compounds gave similar results. Samples of sulphide, or elemental sulphur (each about 1mg) and cobalt trifluoride (5mg) or gold trifluoride (5mg, but gold trifluoride maybe a surface coating) were weighed into a teflon bucket and loaded into a Ni-reactor using the method described previously. The reactor and a Nupro-valve were connected to a glass vacuum line in the arrangement shown in Figure A.6. A variety of experimental conditions were tested in order to discover a method of preparing sulphur hexafluoride. Unfortunately the only product compounds identified in the mass spectrum, were silicon tetrafluoride, sulphur dioxide and thionyl and sulphuryl fluorides. An example spectrum is shown in Figure A.7. Curiously even simple heating of gold trifluoride and cobalt trifluoride, with no sulphur bearing material present, gave these products.

Silicon tetrafluoride probably formed by the reaction of fluorine and glass when the reaction gases were let out of the reactor into the rest of the system. An attempt to alleviate this problem was made by freezing all the

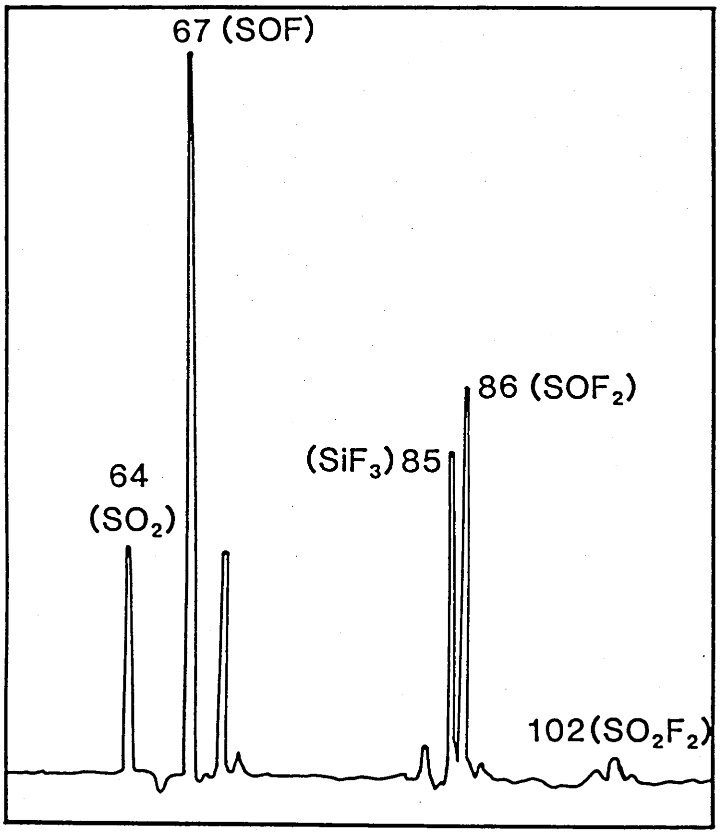


Figure A.7 Mass spectrum of the products formed by the reaction of elemental sulphur with CoF_3 at 100°C.

products in the reactor using liquid nitrogen whilst unreacted fluorine was removed by pumping. However, silicon tetrafluoride was still identified in the mass spectrum of gases obtained from these experiments. The oxygen required to form thionyl and sulphuryl fluorides could originate either from glass or from an inadequately conditioned reactor. Repeated fluorinations of the reactor with chlorine trifluoride at 500°C using the oxygen preparation line did not reduce the amount of the sulphuryl or thionyl fluorides formed.

Gold trifluoride and cobalt trifluoride were step-heated in an attempt to identify a temperature at which formation of silicon tetrafluoride and SOF-bearing compounds were at a minimum. Changes in the relative quantities of some of the products occurred e.g. heating cobalt trifluoride with elemental sulphur from room temperature to 100°C gives mainly silicon tetrafluoride and sulphur dioxide, whilst at 450°C sulphuryl fluoride is the main product. However, there was no temperature at which sulphur hexafluoride was formed, or where minimal amounts of impurities were encountered. Kwasnik (1963) reports that the reaction of cobalt trifluoride with elemental sulphur proceeds readily at 130°C in quartz glass to give mainly SF_4 but with a small quantity of sulphur hexafluoride. So the absence of sulphur tetrafluoride from the analogous experiment in a nickel vessel in the present study is surprising.

During the latter part of this study it was found that there was an unexpectedly high background level (blank) of both sulphur dioxide and silicon tetrafluoride in the system which derived, in part from the glass section, but mainly from the reactor. The blank is considered to be a memory effect since it could be significantly reduced by pre-heating the vessel at 600°C for half-an-hour before sample loading.

The configuration of the preparation line was altered to that shown in Figure A.8 and was constructed of quartz glass. The alterations were undertaken partly to remove the Ni-reactor from the line (as this was suspected as being a major contributor of oxygen during fluorinations) and also to enable greater control over the reactions of interest by loading the sulphur-bearing material and the fluorinating agent into separate arms of the reactor (Figure A.8). The arm containing the sample was pre-heated to 800°C before the sample was dropped to the base of the tube and the cobalt trifluoride was also pre-heated, at 100°C, to remove any traces of adsorbed air and water. The entire reactor assembly was wrapped in heater tape and maintained at 100°C to remove traces of water adsorbed onto the walls of the glass.

During the experiments, the cobalt trifluoride was heated to 500°C and the sample could be heated to temperatures of up to 1200°C (using the Ni-reactor the maximum temperature possible was 600°C). Usually elemental sulphur was heated to 100°C to avoid sublimation and sulphides were heated to between 400 and 500°C. At the begining of the experiment a methanol

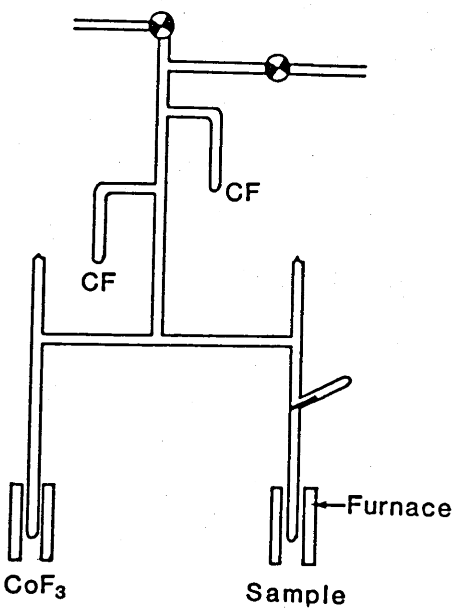


Figure A.8 Section of the extraction line modified for reacting samples with metal fluorides (quartz glass).

slush (−100°C) was placed on one of the cold fingers to freeze-out any water as it formed. At the end of half-an-hour a liquid nitrogen trap was placed on the second cold finger to trap the reaction products and unreacted fluorine was pumped away. The product gases were then transferred to the mass spectrometer for analysis. Even with such close control over the reaction conditions neither sulphur hexafluoride or sulphur tetrafluoride could be generated by this method, the reaction products being identical to those observed from previous experiments (i.e. thionyl and sulphuryl fluorides and silicon tetrafluoride).

Despite being unsuccessful for preparing sulphur hexafluoride, the use of metal fluorides could be an effective method for obtaining silicon tetrafluoride gas from silicates. Silicon tetrafluoride is used for isotopic analysis of silicon and is usually formed by direct fluorination of meteorite samples (Epstein and Taylor, 1970). The use of metal fluorides may provide both a simpler and safer technique for producing silicon tetrafluoride gas.

A.5 Conclusions and future developments

Chlorine trifluoride like other halogen halides is a powerful fluorinating agent which reacts with elementary sulphur and many sulphide minerals (but not troilite) to liberate sulphur hexafluoride. The stringent safety requirements

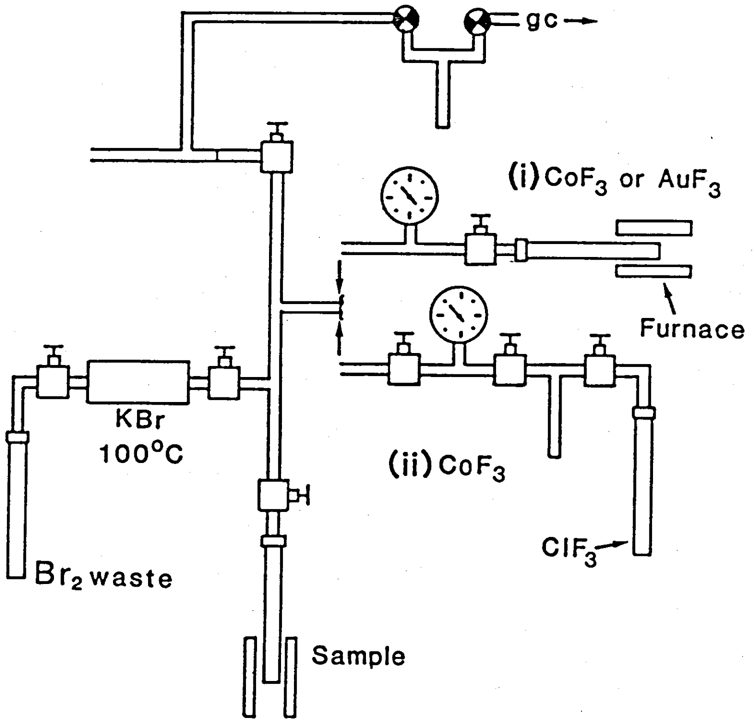


Figure A.9 Possible design for a metal system to fluorinate sulphides using, (a) CoF_3, AuF_3 or, (b) ClF_3.

and its ineffectiveness with troilite, is likely to limit its use with meteorites where troilite is the major sulphur-bearing mineral. Less reactive metal fluorides which liberate fluorine gas when heated, favoured the formation of silicon tetrafluoride, thionyl fluoride and sulphuryl fluoride when heated with sulphur-containing species.

A design for a system which may be suitable for synthesising sulphur hexafluoride using cobalt trifluoride or gold trifluoride is shown in Figure A.9. A reservoir of cobalt trifluoride (about 50g) is placed in a Ni-reactor which has previously been extensively treated with chlorine trifluoride (to form a protective nickel difluoride coating). Heating cobalt trifluoride to 400°C would produce fluorine gas, the pressure of which can be monitored. The sample (elemental sulphur or a sulphide) is loaded, or if gaseous (sulphur dioxide) frozen, into a pre-baked Ni-reactor (which again has been previously conditioned with chlorine trifluoride) and an aliquot of fluorine gas expanded into the vessel for the reaction to form sulphur hexafluoride. The temperature of the reaction can be controlled (and varied) using a wire-wound resistance furnace connected to a variable transformer. At the end

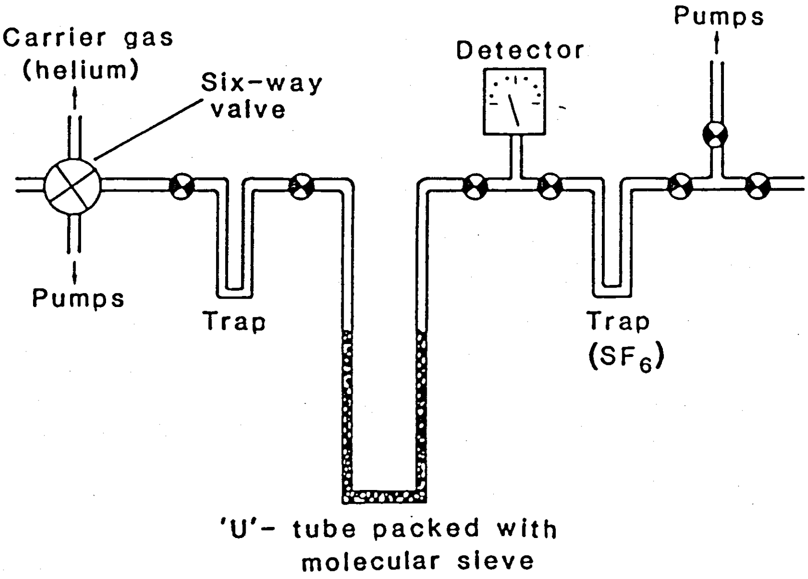


Figure A.10 A design for a simple gas chromatography system for use of separating impurities from SF_6.

of the reaction excess fluorine can be re-adsorbed onto the cobalt trifluoride at 200 to 300°C by conversion of difluoride to trifluoride. The products (including fluorine) can be allowed to contact with either sodium hydroxide or potassium bromide at 100°C. This will remove any residual fluorine before the product gases are transferred to the glass line. A methanol slush placed on the waste trap will freeze-out bromine. Sulphur hexafluoride and any remaining impurities are passed into the glass section for a carefully controlled final cryogenic separation using a variable temperature cryogenic finger. The yield of sulphur can be measured using a capacitance manometer before the sulphur hexafluoride is passed on for mass spectrometric analysis. The inability of cryogenic separations to remove the contaminant species at m/z 131, thus preventing $\delta^{36}S$ determinations, means that it will be necessary to subject the sulphur hexafluoride to a final purification stage using gas chromatography. A proposed design for a simple gas chromatography system is shown in Figure A.10. The carrier gas is helium and the presence of sulphur hexafluoride can be identified by a detector, possibly of the thermal conductivity type. Immediately the gas is detected it can be frozen into a cold finger using liquid nitrogen and the helium diverted to a waste pump. The pure sulphur hexafluoride can then be delivered to the mass spectrometer.

A modified version of the fluorination system for use of chlorine trifluoride is shown in Figure A.9. A reservoir of chlorine trifluoride is attached to the extraction line, in a teflon vessel. The chlorine trifluoride having initially been distilled from a cylinder of the liquid kept in isolation elsewhere (e.g. a fume cupboard). A small amount of chlorine trifluoride from the reservoir is expanded into a metal finger so that the gas can be purified by successive freezing-sublimation cycles before it is expanded into the reaction vessel. Once again, the pressure of chlorine trifluoride gas can be measured. After reaction the procedure is identical to that just described for cobalt trifluoride with successive purification of the sulphur hexafluoride using potassium bromide (or sodium hydroxide), followed by cryogenic separation and gas chromatography.

Appendix B

Details of meteorite samples analysed

Meteorite	Class	Source & Sample No.
Abee	EH4	UCSD (1,1,02,0)
Allan Hills A77257	Ureilite	AMWG
Allende	CV3	Dr B. Simoneit
Al Rais	CR2	BM 1971,289
Atlanta	EL6	BM 1959,1001
Bella Roca	IIIB	BM 64206
Bustee	Aubrite	BM 32100
Coolidge	CV4	Wiik
Daniel's Kuil	EL5	BM 42507
Dyalpur	Ureilite	BM 63625
Felix	CO3	BM 1919,89
Indarch	EH4	BM 86948
Ivuna	CI1	USNM
Karoonda	C4	Wiik
Khairpur	EL6	BM 51366
Kivesvaara	CM2	Wiik
Kota-Kota	EH3	BM 1905,355
Mighei	CM2	BM 86947
Mulga West	CV5/6	WAM 13205
Murchison	CM2	BM 1970,6
Murray	CM2	BM 1966,48
Nogoya	CM2	NHM, Vienna
North West Forrest	EL6	WAM 13194
Norton County	Aubrite	BM 1959,758
Orgueil	CI1	BM 1920,328
Ornans	CO3	BM 42474
Renazzo	CR2	Wiik
Saint Mark's	EH5	BM 1970,339
Semarkona	LL3.0	USNM 1805
Shallowater	Aubrite	BM 1937,377
South Oman	EH4	SOA 1028
Vigarano	CV3	Wiik
Yilmia	EH5	BM 1972,132
Yamato 6903	CV4	NIPR
Yamato 82042	CM1	NIPR

AMWG–Antarctic Meteorite Working Group; BM–British Museum (Natural History), London; NHM, Vienna– National History Museum, Vienna, Austria; NIPR–National Institute of Polar Research, Tokyo; SOA–Dr S.O. Agrell, Cambridge; UCSD–Dr K. Marti, Univ. California at San Diego (consortium study, clast 1,1,02,0); USNM–United States National Museum, Washington; WAM–Western Australia Museum, Perth; Wiik– Dr H.B. Wiik.

Appendix C

Meteorite stepped combustion data

Sample Wt (mg)	Al Rais 5.162			Ivuna 3.579			Kivesvaara 6.162		
Temp. (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	–	–	–	0.13	36	ND	0.09	146	ND
150	0.17	33	ND	0.27	75	ND	–	–	–
200	0.53	103	ND	11.62	3247	+0.1	7.35	11928	+1.0
250	0.20	39	ND	12.35	3451	+3.48	–	–	–
300	0.68	132	ND	1.59	444	ND	9.28	15060	ND
350	1.66	322	ND	0.53	148	ND	–	–	–
400	24.17	4683	−1.6	0.86	240	ND	12.76	20707	+1.0
450	16.80	3255	−1.4	3.59	1059	−2.0	–	–	–
500	7.11	1377	−3.0	0.73	204	ND	4.64	7530	+2.0
550	3.25	630	−4.1	0.93	260	ND	–	–	–
600	1.05	203	ND	0.80	224	ND	3.95	6410	+0.8
650	1.79	347	−3.7	0.53	148	−4.5	–	–	–
700	3.85	746	+1.9	2.79	780	−4.3	5.96	9672	−4.0
750	4.25	823	+2.6	10.23	2858	−3.4	–	–	–
800	5.58	1081	+1.8	25.90	7237	+0.6	28.55	46322	+0.6
850	2.99	579	−1.9	6.77	1892	+1.9	–	–	–
900	5.31	1029	0.0	5.78	1615	+0.3	15.24	24732	+3.0
950	4.83	936	−1.4	–	–	–	–	–	–
1000	4.65	901	−1.0	10.76	3006	+0.7	10.29	16699	+1.4
1050	2.17	420	−0.8	–	–	–	–	–	–
1100	1.43	277	ND	8.10	2263	−0.4	6.19	10045	+1.8
1200	1.72	333	ND	0.93	260	ND	2.86	4641	+3.6
Total	94.19	18046	−1.1	105.39	29447	+0.25	107.16	158902	+1.1

Sample Wt (mg)	Mighei 4.775			Murchison 10.430			Murray 7.242		
Temp.	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$
(°C)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)
100	ND	ND	ND	0.77	738	ND	0.12	166	ND
150	0.07	15	ND	–	–	–	–	–	–
200	0.53	111	ND	10.83	10384	ND	1.16	1602	ND
250	0.73	153	ND	–	–	–	–	–	–
300	0.66	138	ND	7.74	7421	ND	5.42	7484	ND
350	1.26	264	ND	–	–	–	–	–	–
400	19.19	4019	−1.7	26.30	25216	ND	58.79	81179	ND
450	20.72	4340	−2.8	–	–	–	–	–	–
500	8.63	1807	−2.0	61.89	59338	−1.2	19.34	26705	ND
550	4.71	986	−4.2	–	–	–	–	–	–
600	1.39	291	ND	33.26	31889	+0.6	20.89	28846	−1.7
650	1.20	251	ND	–	–	–	–	–	–
700	5.78	1211	−3.9	13.92	1335	−0.8	6.89	9514	−1.6
750	19.52	4088	−0.1	–	–	–	–	–	–
800	9.56	2002	+4.1	100.57	96424	−0.6	44.09	60881	−1.0
850	6.44	1349	+4.0	–	–	–	–	–	–
900	4.25	890	+4.2	30.94	29664	+4.4	33.26	45927	+4.0
1000	8.90	1864	−0.2	35.59	34123	+2.2	18.27	25642	+3.9
1100	10.29	2155	−1.9	20.11	19281	+2.4	8.51	11751	+3.8
1200	2.66	557	ND	10.81	10364	ND	5.42	7484	+5.1
Total	126.49	26491	−0.76	352.73	307181	+1.3	222.46	265713	+1.2

Sample Wt (mg)	Nogoya 7.921			Orgueil–a 6.008			Orgueil–b 5.332		
Temp. (°C)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)
50	–	–	–	0.05	8	ND	0.31	58	ND
100	0.12	165	ND	0.13	22	ND	1.42	267	ND
150	–	–	–	0.35	58	ND	8.63	1621	+2.4
200	3.37	4622	+3.0	0.60	100	ND	12.09	2272	+2.0
250	–	–	–	8.77	1460	+5.0	9.70	1822	+3.8
300	5.42	7434	ND	0.99	165	ND	1.59	299	ND
350	–	–	–	1.82	303	ND	1.06	199	ND
400	17.02	23344	+0.5	1.93	321	+2.7	2.86	537	−1.3
450	–	–	–	9.89	1647	−1.0	13.02	2446	−0.9
500	24.76	33960	+0.5	12.29	2046	−0.3	9.23	1734	−1.8
550	–	–	–	6.77	1127	−3.7	2.31	434	−5.0
600	14.70	2016	−0.9	1.93	321	−1.1	1.06	199	ND
650	–	–	–	1.86	310	−4.1	–	–	–
700	32.49	44562	−1.8	4.18	696	−4.8	–	–	–
750	–	–	–	11.55	1923	−3.6	–	–	–
800	52.60	72144	+2.5	40.77	6786	−1.4	–	–	–
850	–	–	–	24.04	4002	+4.5	–	–	–
900	27.08	37142	+4.2	6.51	1084	+3.5	–	–	–
950	–	–	–	8.57	1427	+1.6	–	–	–
1000	21.66	29708	+0.7	8.04	1338	+1.0	–	–	–
1050	–	–	–	12.15	2022	+1.6	–	–	–
1100	6.50	8915	+5.7	5.91	984	+1.4	–	–	–
1150	–	–	–	0.73	122	ND	–	–	–
1200	1.24	1701	ND	0.73	122	ND	–	–	–
Total	209.96	265713	+1.2	170.56	28391	+0.38	63.28	11889	+0.66

Sample	Renazzo			Yamato 82042		
Wt (mg)	6.630			2.547		
Temp.	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$
(°C)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)
100	0.12	18	ND	1.42	558	ND
200	0.03	5	ND	6.87	2697	+0.7
300	0.11	17	ND	3.03	1190	+6.7
400	0.17	26	ND	3.45	1355	+1.2
450	1.27	192	ND	–	–	–
500	3.85	581	−2.6	4.63	1818	+0.3
550	3.65	551	−2.3	–	–	–
600	3.82	576	−2.9	1.79	703	ND
650	3.39	511	−1.9	–	–	–
700	3.59	542	−1.1	2.60	1021	−2.3
750	4.83	729	−1.4	–	–	–
800	11.82	1783	−1.8	20.55	8068	−0.1
850	11.95	1802	+0.3	–	–	–
900	7.84	1183	+2.4	8.35	3278	+3.1
950	4.53	683	+2.2	–	–	–
1000	4.36	658	−1.2	9.13	3585	−0.1
1050	2.57	388	−1.0	–	–	–
1100	0.92	139	ND	8.47	3325	−3.1
1200	0.50	75	ND	3.02	1186	+1.2
Total	69.32	10459	−0.65	73.31	28784	+0.4

Orgueil and Murchison residues

Sample Wt (mg)	ME 11.743			MEW1 12.240			MEW2 7.111		
Temp. (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	0.23	19	ND	1.31	107	ND	0.36	50	ND
200	0.77	66	ND	2.82	230	ND	0.38	53	ND
300	7.74	659	ND	30.88	2523	ND	1.10	155	ND
400	42.54	3623	−3.4	76.60	6258	+1.2	11.06	1555	−1.7
500	44.87	3821	−3.3	55.00	4493	ND	54.15	7615	−0.5
600	16.25	1384	−5.6	26.30	2149	−5.7	20.11	2828	−1.3
700	7.73	66	−1.8	30.17	2465	−3.2	19.34	2720	−2.0
800	89.97	7662	+0.7	29.40	2402	+3.1	13.15	1849	+2.8
900	15.47	1317	+8.4	47.96	3918	+3.9	9.28	1305	+5.8
1000	17.02	1449	+6.1	21.76	1778	+5.6	11.29	1588	+4.2
1100	7.74	659	+5.2	13.92	1137	+5.6	8.95	1259	+1.9
1200	3.87	330	+5.2	6.96	569	ND	4.27	600	+1.9
Total	254.19	21647	−0.2	343.08	28030	+1.3	153.44	21578	+0.4

Sample Wt (mg)	MEW2R –			MEH 10.195			MEN 8.230		
Temp. (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	0.20	ND	ND	0.38	37	ND	5.57	678	+4.0
200	0.19	ND	ND	124.55	12217	+2.7	158.60	19271	+0.1
300	0.84	ND	ND	8.66	849	+3.8	10.68	1298	+5.5
400	0.46	ND	ND	41.16	4037	+0.9	5.58	678	+4.8
500	0.35	ND	ND	14.39	1411	+1.1	8.97	1090	+5.2
600	0.47	ND	ND	4.24	416	+4.3	2.58	313	ND
700	1.30	ND	ND	1.25	123	ND	0.28	34	ND
800	0.70	ND	ND	1.34	122	+2.0	0.30	36	ND
900	1.70	ND	−3.7	2.35	230	+2.8	0.02	2	ND
1000	4.5	ND	−1.0	0.82	80	ND	0.54	66	ND
1100	4.60	ND	+0.4	0.49	48	ND	0.06	7	ND
1200	1.70	ND	+1.0	0.40	39	ND	0.53	66	ND
Total	17.0	ND	−0.5	200.03	19647	+2.27	193.71	23537	+0.88

Sample Wt (mg)	MHF 1.267			OHF 0.770		
Temp. (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	0.64	505	ND	0.16	208	ND
200	6.11	4822	−0.5	0.80	1040	ND
250	14.01	11058	+3.0	7.04	9148	+3.7
300	31.28	24688	+1.1	7.90	10265	+5.8
350	11.16	8808	−6.2	0.80	1036	ND
400	11.95	9432	−3.4	6.00	7796	+1.4
450	22.38	17664	−0.9	3.00	3898	+5.0
500	14.54	11476	+1.2	1.06	1377	ND
550	5.05	3986	+5.0	–	–	–
600	0.53	418	ND	0.20	260	ND
700	0.40	316	ND	0.60	780	ND
800	0.07	55	ND	ND	ND	ND
900	–	–	–	ND	ND	ND
1000	7.84	6188	+1.9	0.06	78	ND
1200	0.13	103	ND	ND	ND	ND
Total	126.09	99518	+0.0	27.62	35885	+3.97

C3 to C6 carbonaceous chondrites

Sample Wt (mg)	Allende 4.143			Allende–1 20.101			Coolidge 9.042		
Temp. (°C)	Yield (μg S)	 (ppm S)	δ^{34}S (‰)	Yield (μg S)	 (ppm S)	δ^{34}S (‰)	Yield (μg S)	 (ppm S)	δ^{34}S (‰)
100	–	–	ND	4.56	227	ND	0.05	6	ND
200	0.08	19	ND	1.82	91	ND	0.03	3	ND
300	0.03	7	ND	19.14	227	–	0.04	4	ND
400	1.05	253	ND	19.14	952	–	0.04	4	ND
450	21.05	5081	−2.2	–	–	–	0.19	21	ND
500	23.97	5786	−2.1	196.89	9795	−0.6	0.66	73	ND
550	14.14	3413	−1.0	–	–	–	2.06	228	−5.3
600	6.65	1605	−4.3	79.39	3950	−1.1	3.85	426	−7.1
625	3.15	760	−4.8	–	–	–	–	–	–
650	3.54	855	−3.2	–	–	–	4.98	551	−4.0
675	3.02	729	−0.4	–	–	–	–	–	–
700	2.71	654	+3.2	86.60	4308	+0.6	8.04	889	−1.5
750	1.50	362	ND	–	–	–	2.79	309	−4.1
800	0.51	123	ND	32.82	1633	+2.6	1.59	176	+2.7
900	–	–	–	20.47	1043	ND	1.59	176	+2.1
1000	–	–	–	8.20	408	ND	1.46	161	ND
1100	–	–	–	4.56	227	ND	–	–	–
1200	2.69	649	+1.8	10.03	499	ND	2.12	234	+0.3
Total	84.09	20296	−1.9	469.54	23360	−0.2	29.49	3261	−2.7

Sample Wt (mg)	Felix 4.736			Karoonda 14.190			Mulga West 13.625		
Temp (°C)	Yield (μg S)	(ppm S)	δ^{34}S (‰)	Yield (μg S)	(ppm S)	δ^{34}S (‰)	Yield (μg S)	(ppm S)	δ^{34}S (‰)
100	–	–	–	ND	ND	ND	0.07	5	ND
200	–	–	–	0.11	8	ND	0.07	5	ND
300	0.07	15	ND	0.11	8	ND	0.13	10	ND
400	0.10	21	ND	0.48	34	ND	0.28	21	ND
450	7.70	1626	−2.6	42.83	3018	−3.7	0.25	18	ND
500	27.77	5863	−2.6	34.27	3018	−3.7	0.07	5	ND
550	13.28	2804	−2.8	10.76	758	−3.9	0.13	10	ND
600	9.63	2033	−4.8	8.63	608	−9.1	0.07	5	ND
650	8.17	1725	−5.0	10.03	707	−8.6	0.03	2	ND
700	6.18	1305	−3.7	11.82	833	−6.0	0.03	2	ND
750	4.25	897	+3.6	29.29	2064	−1.6	–	–	–
800	1.36	393	+2.9	21.18	1493	+2.7	0.16	12	ND
850	–	–	–	5.64	397	+4.4	–	–	–
900	2.72	574	+4.0	1.99	140	+4.3	–	–	–
1000	1.33	281	ND	1.59	112	+1.8	5.51	404	+7.7
1100	–	–	–	–	–	–	0.73	54	+4.3
1200	1.26	266	ND	2.79	197	+1.3	0.86	63	ND
Total	84.32	17803	−2.5	181.52	1292	−2.7	8.39	616	+7.3

Sample Wt (mg)	Ornans 7.561			Vigarano 4.482			Yamato 6903 10.441		
Temp (°C)	Yield (µg S)	(ppm S)	δ^{34}S (‰)	Yield (µg S)	(ppm S)	δ^{34}S (‰)	Yield (µg S)	(ppm S)	δ^{34}S (‰)
100	–	–	–	0.03	7	ND	–	–	–
200	0.16	21	ND	0.16	22	ND	0.33	32	ND
300	0.13	17	ND	0.30	67	ND	0.19	16	ND
400	0.05	7	ND	0.09	20	ND	0.19	16	ND
450	5.11	676	−3.4	3.74	846	+1.3	15.27	1463	−3.8
500	26.03	3443	−1.7	11.49	2563	−1.4	38.98	3733	−2.7
525	–	–	–	–	–	–	8.37	802	−3.9
550	28.82	3812	−2.5	15.74	3512	−2.6	5.31	509	−4.4
575	–	–	–	–	–	–	4.25	407	−5.5
600	33.67	4453	−2.1	6.91	1542	−4.0	3.72	356	−5.7
625	–	–	–	–	–	–	4.18	400	−6.8
650	19.47	2575	−2.5	4.65	1037	−5.1	5.18	496	−5.7
675	–	–	–	–	–	–	6.57	629	−5.7
700	20.12	2661	−1.7	3.92	875	−2.3	7.24	693	−4.0
750	8.90	1177	+0.6	4.18	933	+1.7	13.61	1304	−0.9
800	6.57	869	+1.5	1.26	281	+1.4	7.11	681	−2.3
850	4.25	562	+1.8	–	–	–	5.71	547	−2.2
900	2.26	299	+2.3	2.99	667	+0.6	4.52	433	+3.2
1000	3.05	403	+2.3	1.66	370	+2.0	3.10	297	+6.1
1200	2.30	304	+3.5	1.13	252	ND	2.19	210	ND
Total	166.89	21279	−1.5	58.24	12994	−1.7	136.00	13026	−3.0

Enstatite chondrites and aubrites

Sample	Abee			Atlanta			Bustee		
Wt (mg)	3.701			4.119			10.221		
Temp (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	1.95	527	ND	0.22	53	ND	0.05	5	ND
200	0.33	89	ND	0.03	7	ND	1.26	123	−2.9
300	1.26	340	ND	0.02	5	ND	0.33	32	ND
350	0.50	135	ND	–	–	–	–	–	–
400	6.91	1867	−2.0	0.19	46	ND	0.13	13	ND
450	13.98	3777	−3.48	8.85	2149	−6.7	–	–	–
500	40.94	11062	−3.6	37.45	9092	−3.3	12.35	1208	−2.2
550	46.02	12435	−3.6	37.85	9189	−3.1	–	–	–
600	11.49	3105	−3.5	17.93	4353	−3.4	42.96	4203	−2.4
650	12.82	3464	−4.3	9.50	2306	−2.4	–	–	–
700	9.63	2602	−4.3	5.98	1452	−1.2	54.45	5327	−3.7
750	13.75	3715	−4.0	2.06	500	+1.8	–	–	–
800	17.66	4772	−2.3	0.66	160	ND	10.29	1007	−4.6
850	15.61	4218	+1.6	0.46	112	ND	–	–	–
900	15.61	4218	+1.6	0.46	112	ND	15.41	1508	−3.5
950	17.27	4666	−0.9	–	–	–	–	–	–
1000	21.78	5885	−0.4	0.60	146	ND	27.49	2690	+0.7
1050	6.64	1794	+0.3	–	–	–	–	–	–
1100	4.85	1310	+0.9	–	–	–	10.36	1014	+1.7
1200	2.92	789	+0.7	1.06	257	ND	0.93	91	ND
Total	261.92	70770	−2.86	123.32	32639	−3.2	176.01	17221	−2.3

Sample Wt (mg)	Daniel's Kuil 4.217			Indarch 2.846			Khairpur 3.825		
Temp (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	ND	ND	ND	0.41	144	ND	0.27	71	ND
200	0.31	31	ND	1.33	467	+1.5	0.13	34	ND
300	0.22	52	ND	0.27	95	ND	0.13	34	ND
350	–	–	–	3.39	1191	−2.2	–	–	–
400	0.46	109	ND	27.43	9639	−3.6	0.20	52	ND
450	2.79	662	−2.8	27.43	19952	−2.9	3.92	1025	−2.4
500	13.28	3149	−2.7	13.28	4667	−2.5	6.84	1788	−3.2
550	34.46	8172	−3.9	8.04	2825	−3.9	20.79	5436	−3.2
600	43.10	10221	−3.9	7.70	2706	−4.4	28.09	7606	−3.7
650	22.31	5291	−4.5	8.50	2987	−4.0	15.14	3959	−2.9
700	5.71	1354	−3.7	9.43	3314	−1.6	4.85	1268	−0.5
750	0.27	64	ND	5.98	2101	+0.7	1.93	505	−0.8
800	0.99	235	+3.2	5.38	1891	+0.7	1.93	505	−0.8
850	–	–	–	4.32	1518	+1.6	2.66	695	0.0
900	2.59	614	−1.1	3.32	1167	+1.7	4.25	1111	−2.2
950	–	–	–	1.99	699	+2.4	5.84	1527	+0.3
1000	4.58	1086	−3.2	1.53	538	ND	4.12	1077	+2.6
1050	–	–	–	–	–	–	0.60	157	ND
1100	0.53	126	ND	0.45	158	ND	–	–	–
1200	0.40	95	ND	0.13	46	ND	0.10	26	ND
Total	131.82	31261	−3.7	159.66	55901	−2.5	102.25	26734	−2.5

Sample Wt (mg)	Khairpur* 4.583			Kota-Kota 2.517			N.W. Forrest 4.265		
Temp (°C)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (μg S)	Yield (ppm S)	δ^{34}S (‰)
100	0.22	48	ND	0.84	334	ND	ND	ND	ND
200	0.30	65	ND	1.99	791	+0.3	ND	ND	ND
300	0.10	22	ND	0.93	369	ND	0.86	202	ND
350	–	–	–	0.20	79	+0.3	ND	ND	ND
400	0.13	28	ND	1.93	767	−4.7	0.14	33	ND
450	1.47	321	ND	22.71	9023	−2.0	0.07	16	ND
500	5.83	1272	−4.1	29.95	11899	−2.6	0.28	66	ND
550	10.76	2348	−3.9	18.53	7362	−3.3	3.19	748	−3.2
600	12.15	2651	−2.6	7.57	3008	−6.3	4.81	1128	−6.7
650	7.11	1551	−3.4	8.67	3445	ND	6.24	1463	−3.2
700	2.31	504	−2.6	3.92	1557	−1.0	4.58	1074	+0.7
750	–	–	–	3.45	1371	−3.2	2.52	591	+3.0
800	0.52	113	ND	2.52	1001	−0.5	1.33	312	+0.70
850	0.21	46	ND	2.79	11.08	−0.7	–	–	–
900	0.09	20	ND	2.79	1347	−2.3	2.32	544	+0.7
950	–	–	–	3.65	1450	−0.9	–	–	–
1000	0.05	11	ND	2.19	870	−2.4	2.59	607	+1.0
1100	–	–	–	–	–	–	0.46	108	ND
1200	0.42	92	ND	1.70	675	+1.6	0.47	110	ND
Total	41.67	9092	−3.3	117.19	46559	−2.5	29.86	6936	−1.4

*Acetic acid residue.

Sample Wt (mg)	Norton County 14.571			St. Mark's 4.368			Shallowater 13.155		
Temp (°C)	Yield (μg S)	(ppm S)	δ^{34}S (‰)	Yield (μg S)	(ppm S)	δ^{34}S (‰)	Yield (μg S)	(ppm S)	δ^{34}S (‰)
100	–	–	–	0.24	55	ND	–	–	–
200	1.22	84	ND	0.14	32	ND	0.15	11	ND
300	0.28	19	ND	0.09	21	ND	0.29	22	ND
400	0.07	5	ND	1.73	396	ND	1.75	133	−1.2
450	0.96	66	ND	20.98	4804	−3.2	5.01	381	−2.4
500	4.33	297	−1.6	20.21	4627	−3.5	8.49	645	−5.0
550	8.35	573	−3.1	13.02	2981	−3.1	14.86	1130	−5.5
600	7.03	482	−3.6	10.09	2310	−4.0	15.60	1186	−5.7
650	4.34	298	−5.1	5.38	1232	−4.9	12.02	914	−2.16
700	3.64	250	−6.0	3.92	898	−1.9	12.24	930	+1.6
750	1.08	74	−3.7	4.98	1140	−3.0	7.51	571	+3.3
800	1.06	73	ND	4.85	1110	−3.8	5.54	421	+3.9
850	1.64	113	−3.0	5.51	1262	−5.3	2.62	199	+4.0
900	2.35	161	−2.9	10.03	2296	−2.8	1.88	143	+2.9
950	6.56	450	−1.3	17.80	4075	−0.5	1.22	93	+3.8
1000	4.95	340	−0.5	12.88	2949	+0.7	0.69	52	ND
1100	3.64	250	−2.1	9.63	2205	+0.3	–	–	–
1200	0.32	22	ND	8.04	1841	−1.2	0.75	57	ND
Total	51.82	3557	−2.9	149.52	34234	−2.4	90.62	6888	−1.9

Sample	South Oman			Yilmia		
Wt (mg)	2.768			5.452		
Temp	Yield		δ^{34}S	Yield		δ^{34}S
(°C)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)
100	0.09	33	ND	0.09	17	ND
200	0.15	54	ND	0.67	123	ND
300	0.27	98	ND	0.60	110	ND
350	0.27	98	ND	–	–	–
400	1.86	672	+1.3	0.46	84	ND
450	5.84	2110	−3.1	3.85	706	−0.5
500	5.05	1824	−2.6	19.32	3544	−2.3
550	5.38	1944	−3.8	22.58	4142	−3.7
600	9.56	3454	−3.9	24.37	4470	−2.8
650	7.70	2782	−5.6	13.24	2432	−2.5
700	8.43	3046	−5.1	5.78	1060	−2.6
750	9.03	3262	−4.5	2.46	451	−4.9
800	9.03	3262	−3.1	1.99	365	−1.1
850	6.71	2424	−3.7	1.93	354	−1.6
900	5.51	1991	−3.4	3.72	682	−3.4
950	8.23	2973	−0.1	6.24	1145	−0.3
1000	5.11	1846	+0.8	4.52	829	−1.6
1100	3.45	1246	+1.7	3.72	682	−0.8
1200	7.90	2854	−3.5	0.66	121	ND
Total	99.57	35973	−3.1	116.17	21317	−2.5

Miscellaneous samples

Meteorites

Sample Wt (mg)	ALHA 77257 9.654			Dyalpur 9.708			Semarkona 4.299		
Temp. (°C)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)
100	0.01	1	ND	0.01	1	ND	0.10	23	ND
200	0.06	6	ND	0.33	34	ND	0.07	16	ND
300	0.01	1	ND	0.14	14	ND	0.13	30	ND
400	0.26	27	ND	0.09	9	ND	0.12	28	ND
450	–	–	–	–	–	–	8.23	1915	−3.9
500	0.16	17	ND	0.49	47	ND	29.62	6751	−2.8
550	–	–	–	–	–	–	14.94	3476	−2.6
600	0.28	29	ND	1.06	109	ND	4.85	1128	−3.0
650	–	–	–	–	–	–	2.79	649	−5.6
700	1.73	179	+3.8	1.73	178	+3.8	3.32	772	−3.7
750	–	–	–	–	–	–	2.99	696	−0.7
800	0.23	24	ND	1.79	184	−1.6	2.59	603	−0.1
900	0.07	7	ND	0.27	28	ND	2.32	540	−0.1
1000	0.29	30	ND	0.66	68	ND	1.06	247	ND
1100	0.12	12	ND	0.33	34	ND	–	–	–
1200	0.09	9	ND	0.29	30	ND	1.79	416	ND
Total	3.31	342	+3.8	7.16	736	+1.1	74.32	17290	−2.8

Reference materials

Sample Wt (mg)	Calcium sulphide 0.276			Chalcopyrite 4.000			Chalcopyrite (S080) 0.343		
Temp. (°C)	Yield (µg S)	Yield (ppmS)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)
100	0.08	290	ND	0.91	228	ND	–	–	–
200	ND	ND	ND	0.64	160	–	–	–	–
300	Nd	ND	ND	10.02	2505	ND	0.60	1751	ND
400	0.03	109	ND	507.70	126925	−3.8	23.90	69740	−7.2
450	–	–	–	–	–	–	38.85	113364	−6.4
500	0.04	145	ND	344.60	86150	−3.7	13.26	38693	−5.5
550	–	–	–	–	–	–	12.31	35924	−6.7
600	0.05	181	ND	104.80	26200	−3.6	4.88	14240	−4.6
700	0.27	978	ND	51.05	12763	ND	–	–	–
800	0.40	1448	ND	56.15	14038	+0.6	–	–	–
900	3.85	13939	+7.6	87.51	21878	−1.5	3.27	9542	+0.7
1000	19.67	71217	+7.6	1.73	433	ND	–	–	–
1100	31.21	112998	+10.3	0.82	205	ND	–	–	–
1200	10.09	36531	+9.3	0.46	115	ND	ND	ND	ND
Total	65.69	237836	+9.18	1166.39	291600	−3.34	97.07	283254	−6.19

Sample Wt (mg)	Epsomite 6.350			Ferrous sulphate 1.360			Gypsum 3.136		
Temp. (°C)	Yield (μg S)	 (ppm S)	$\delta^{34}S$ (‰)	Yield (μg S)	 (ppm S)	$\delta^{34}S$ (‰)	Yield (μg S)	 (ppm S)	$\delta^{34}S$ (‰)
100	–	–	–	–	–	–	0.15	48	ND
200	–	–	–	–	–	–	0.02	6	ND
300	–	–	–	1.70	1250	ND	0.54	172	ND
400	–	–	–	1.54	1132	ND	31.72	10115	+1.0
500	13.67	2153	ND	8.51	6257	+20.0	13.92	4439	+4.9
600	6.38	1005	ND	100.57	73949	−1.7	9.28	2959	ND
700	3.65	575	ND	12.38	9103	+37.7	309.44	98673	+4.1
800	10.03	1580	ND	7.74	5691	+26.2	119.13	37988	+1.6
900	100.27	15791	ND	4.64	3412	ND	6.96	2219	ND
1000	321.77	50672	+7.4	3.87	2846	ND	9.28	2959	ND
1100	11.02	1735	ND	5.41	3978	ND	0.77	246	ND
1200	30.99	4880	ND	6.19	4551	ND	0.16	51	ND
Total	497.78	78391	+7.4	152.55	112169	+5.20	501.36	159875	ND

Sample Wt (mg)	Reference mixture 1.320			Reference mixture 0.180		
Temp. (°C)	Yield (μg S)	 (ppm S)	$\delta^{34}S$ (‰)	Yield (μg S)	 (ppm S)	$\delta^{34}S$ (‰)
100	9.28	7030	+20.7	1.27	7056	ND
200	4.64	3515	+24.2	1.32	7333	ND
300	1.55	1174	ND	0.60	3333	ND
400	3.87	2932	ND	3.68	20444	+4.3
500	69.62	52742	−2.2	15.39	85500	−3.7
600	13.15	9962	−1.5	7.08	39333	+1.3
700	1.55	1174	ND	1.36	7556	ND
800	9.28	7030	+12.3	1.46	8111	ND
900	62.66	47469	+13.4	1.51	8389	ND
1000	10.05	7614	+11.1	0.61	3389	ND
1100	61.27	46417	+9.1	0.53	2944	ND
1200	15.47	11720	+12.1	0.35	1944	ND
Total	262.39	157004	+7.6	35.16	195333	−1.2

Sample Wt (mg)	Elemental sulphur 0.630			Tochilinite 1.108		
Temp. (°C)	Yield (μg S)	(ppm S)	δ^{34}S (‰)	Yield (μg S)	(ppm S)	δ^{34}S (‰)
100	241.56	383429	+15.1	0.05	45	ND
200	55.60	88254	+19.9	0.09	81	ND
300	36.46	57873	+15.0	0.15	135	ND
400	21.88	34730	ND	3.09	2789	−7.0
500	19.14	30381	ND	150.90	13691	−9.5
600	–	–	–	105.71	95406	−7.7
700	–	–	–	2.24	2022	−8.2
800	–	–	–	18.60	167687	−5.8
900	–	–	–	9.90	8935	+6.6
1000	–	–	–	3.79	3420	+2.0
1100	–	–	–	5.03	4540	+0.3
1200	–	–	–	2.17	1958	+1.0
Total	374.64	594667	+15.92	301.72	272309	−7.69

Bella Roca troilite samples

Sample Wt (mg)	S016 0.610			S079 0.390			S082 0.422		
Temp. (°C)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)
100	2.72	4459	ND	–	–	–	–	–	–
200	0.79	1295	ND	0.44	1129	ND	–	–	–
300	0.65	1066	ND	0.42	1078	ND	0.08	189	ND
350	–	–	–	0.77	1976	ND	–	–	–
400	13.95	22869	+0.5	8.93	22915	−3.3	0.08	189	ND
425	–	–	–	34.53	88607	−2.9	–	–	–
450	–	–	–	29.88	76674	−3.1	–	–	–
475	–	–	–	27.49	70541	−3.6	–	–	–
500	192.63	315787	−0.3	28.82	73594	−2.6	0.80	1895	ND
525	–	–	–	19.66	50449	−2.4	–	–	–
550	–	–	–	6.98	17911	−2.4	–	–	–
600	30.90	50656	+0.8	2.69	6903	−0.6	30.78	72904	−4.5
650	–	–	–	–	–	–	82.48	195358	−2.8
700	2.27	3721	ND	–	–	–	13.31	31525	−1.3
800	0.98	1607	ND	1.47	3772	+3.9	0.20	474	ND
900	0.90	1475	ND	–	–	–	–	–	–
1000	0.58	951	ND	0.48	1232	ND	–	–	–
1100	0.34	557	ND	–	–	–	–	–	–
1200	0.20	328	ND	0.09	231	ND	0.09	213	ND
Total	246.88	404771	−0.11	162.65	417372	−2.85	127.82	302747	−3.02

Sample Wt (mg)	S083 0.275			S084 0.365			S085 0.186		
Temp. (°C)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)	Yield (µg S)	Yield (ppm S)	δ^{34}S (‰)
300	0.34	1235	ND	0.18	494	ND	1.52	8172	ND
400	2.41	8751	−0.5	9.55	26186	−0.3	3.47	18656	+1.6
450	29.51	105846	−2.2	34.33	94132	−1.3	12.36	66452	−0.9
500	40.57	147313	−2.1	57.51	157691	−1.4	28.89	155323	−1.3
550	14.94	54248	−1.8	18.00	49356	−2.0	9.56	51398	−0.6
600	2.67	9695	−0.4	3.90	10694	−3.8	6.36	34194	−1.2
900	1.53	5556	ND	–	–	–	1.73	9301	+4.0
1200	0.56	2033	ND	2.06	5648	ND	0.35	1882	ND
Total	92.17	334677	−2.0	125.53	344201	−1.45	64.24	344201	−1.5

Sample Wt (mg)	S086 0.326			S087 0.224			S088 0.224		
Temp.	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$
(°C)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)
300	0.26	797	ND	0.27	1208	ND	–	–	–
400	2.80	8584	ND	5.06	22630	−1.3	2.30	9446	−2.6
450	24.04	73697	+1.6	12.64	56530	−2.3	18.39	75524	−2.3
500	59.30	181790	−2.0	23.57	105411	−2.8	45.55	187064	−2.6
550	7.30	22379	−1.0	17.60	78712	−1.6	7.47	30678	−3.1
600	3.10	9503	ND	3.70	16547	−1.3	1.16	4764	ND
1200	–	–	–	3.20	14311	−3.0	1.12	4600	ND
Total	96.80	478540	−1.0	66.04	295349	−2.2	75.99	312076	−2.6

Sample Wt (mg)	S089 0.371			S090 0.309			S091 0.273		
Temp.	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$	Yield		$\delta^{34}S$
(°C)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)	(μg S)	(ppm S)	(‰)
400	3.74	10078	−1.2	12.02	38900	+0.0	–	–	–
450	–	–	–	–	–	–	19.92	73047	−1.6
500	77.16	207922	−1.4	61.96	200518	−1.4	44.56	163403	−2.0
600	29.62	79817	−0.6	9.96	32233	−1.9	14.74	54052	−3.1
800	5.69	15333	−1.6	–	–	–	–	–	–
1200	0.94	2533	ND	1.06	3430	−2.0	1.69	6197	ND
Total	117.15	315683	−1.2	85.00	275081	−1.3	93.14	341547	−2.0

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