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HIGH PRECISION, HIGH SPATIAL RESOLUTION ANALYSIS OF SULFUR ISOTOPES BY LASER COMBUSTION OF NATURAL SULFIDE MINERALS

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Abstract

Laser induced combustion provides a powerful new technique for sulfur isotope measurements in natural sulfides. A high power continuous laser, focused through a modified microscope system onto a sulfide mineral target, produces highly localized heating. The laser beam is focused to a spot 25 μm in diameter at the sample surface. In the presence of low pressure oxygen, temperatures at the centre of the spot are sufficiently high to produce localized oxidation. Resultant SO_2 is transferred to a gas source isotope ratio mass spectrometer, where the $\delta^{34}\text{S}$ can be measured to a precision better than 0.25 ‰. Sulfur isotopes are fractionated during the combustion by an amount which is reproducible, mineral specific and favours the lighter isotopes. The system is calibrated for given sulphide minerals and specified operating conditions. Laser combustion analysis of sulfur isotopes in pyrite "chimneys" from the Silvermines ore deposit in Ireland, illustrates the benefits of 100 μm spatial resolution possible with this technique.

Key words: Laser, combustion, sulfur, sulfide, geochemistry, geology, Nd-YAG, Argon Ion, ore genesis, isotopes.

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Introduction

Laser extraction techniques are a rapidly expanding area of stable isotope geochemistry. Early experiments using pulsed lasers extracted noble gases by small scale melting, as early as the late 1960's (Megreue, 1967). A similar technique was described by Franchi *et al.* (1986) for nitrogen isotope extraction from meteorites, later exploited by Franchi *et al.* (1988). Oxygen and carbon isotope measurements by the same technique proved less reliable. More recently extraction techniques have been developed using continuous wave (CW) or CW Q-switched lasers. Those which have been described thus far are; controlled combustion in oxygen for sulfur isotopes in sulfide minerals (Kelley and Fallick, 1990; Crowe *et al.*, 1990); thermal decomposition for oxygen and carbon isotopes in carbonates (Dickson *et al.*, 1990; Smalley *et al.*, 1989); controlled reaction with fluorinating agent such as BrF_5 or ClF_3 for oxygen isotopes in silicates (Sharp, 1990) and thermal dehydroxylation in vacuo for hydrous mineral hydrogen isotopes (Jenkin and Fallick, unpublished data). Preliminary experiments are also underway in use of fluorine to extract SF_6 for measurement of sulfur isotopes in sulfides (Rumble *et al.*, 1991).

The reasons for such a rapid blossoming of techniques are clear: firstly they offer high precision isotope ratio measurement combined with good spatial resolution *in situ* analysis. Secondly, they are relatively inexpensive to establish (measurements are made using conventional gas source Isotope Ratio Mass Spectrometers available in most isotope geochemistry labs). Laser techniques fill a niche between conventional "bulk" techniques and ultra small sample sizes analyzed by ion microprobe techniques (Deloule *et al.*, 1986; Chaussidon *et al.*, 1987; Eldridge *et al.*, 1987; Eldridge *et al.*, 1988; Chaussidon *et al.*, 1989).

The notation used throughout this text for reporting fractionation of natural sulfur isotopes is as the difference of the ratio $^{34}\text{S}/^{32}\text{S}$ from a standard sample, Cañon Diablo troilite. The units used are parts per thousand (‰); this is the standard notation used in isotope

geochemistry: for further details see Faure (1986).

Method

Combustion of sulfide minerals to produce SO₂ was one of the first laser extraction techniques fully described (Kelley and Fallick, 1990) and continues to advance, with better understanding of important parameters and processes involved. The laser combustion technique is essentially very simple. In this section we will describe the technique briefly: detailed discussion of the two main parameters effecting analysis, laser (power, wavelength, mode) and sample (reflectivity, thermal conductivity, form) appear below.

A sample of natural sulfide (either separated mineral grains or as part of a larger rock sample) is placed in a vacuum chamber mounted upon a microscope system (Figure 1). No chemical preparation is required, except that the sample be free from hydrocarbon contamination (i.e., samples may not be affixed using glue). Rock samples are generally sliced around 1-2 cm in diameter and a few mm thick, polished on at least one face. In order to complete the requirements for combustion, oxygen is admitted into the chamber at low pressure. Oxygen pressures used are between 8 and 26 torr, since at higher pressures separation of resultant SO₂ from the unreacted oxygen prove difficult. The chamber is isolated and the appropriate grain or area selected, by moving the remotely controlled microscope XY stage. The laser is directed by oxide coated, high reflector mirrors through a microscope. The beam is focused at the sample surface by the microscope objective, to a spot about 25 μm in diameter, producing localized, controlled combustion (Figure 1). Most natural sulfides combust in the range 400-600 °C (Burgess *et al.*, 1989).

During laser combustion SO₂ is the most abundant gas produced, with minor H₂O and CO₂. No SO₃ has been detected as a product. The SO₂ is purified using standard techniques (Kelley and Fallick, 1990) and passed to the mass spectrometer directly (Crowe *et al.*, 1990) or via a sealed sample vessel (Kelley and Fallick, 1990). It is particularly important to physically remove impurities from small SO₂ samples, ion-molecule collisions between SO₂ and other species in the mass spectrometer, lead to inconsistent and inaccurate results.

The major constraint upon the amount of sample combusted, is the volume of SO₂ required for precise and accurate isotope ratio measurement on the mass spectrometer. Early experiments required 1-5 μmole SO₂ (measured on a VG602 dynamic mass spectrometer, Kelley and Fallick, 1990). Recent measurements on an improved mass spectrometer (VG SIRA II) and micro-inlet system are made in the 0.05-0.1 μmole range. Even with such small samples, no problems with memo-

ry effects have been encountered. The progress of the laser combustion reaction is also an important constraint. If the laser beam strikes the same spot for even a few seconds, the combustion process penetrates deep into the sample, often producing holes 100 μm wide and several mm deep. The technique aims to achieve high spatial resolution with an understanding of the precise composition and textural relationships of the material extracted. This is lost if material at depth is analyzed without knowledge of its relationship to the surface features. To gain an indication of the problems involved, consider a sample size of 0.05 mg sulfide, small, even for the laser technique. If the laser pit were 50 μm in diameter, the pit would have to be 1270 μm deep; for a 100 μm pit, 320 μm deep; and for a 200 μm pit, 80 μm deep. Since it is possible to follow visible zones or textures in the minerals, using the laser, we move the laser spot during combustion to produce trenches 50 μm wide, 50 μm deep and around 1 mm long. Resolution achieved in this manner is useful in practice, since the isotope variations being studied are often mirrored by the mineral zones or textures and the laser tracks can follow the zones (see the pyrite chimney example below).

Note that we do not get 100% conversion of sulfur in the sulfide to SO₂ with the laser technique, but in many cases the yields are high. For example, a 5 mm long trench, 100 μm wide and with a profile such as that shown in Figure 2c, yields approximately 1 μmole SO₂. The calculated yield, based upon the excavated volume (the length, width and depth of trenches were measured on secondary electron images), would be a maximum of 1.2 μmoles , indicating that 80% of the sulfur is extracted for analysis.

Parameters

Laser

Choice of laser power, wavelength and mode of operation can have a marked effect upon the manner in which the samples react under the laser beam. The laser is used essentially as a method of delivering intense heat to a precise area, while maintaining the rest of the sample at as low a temperature as possible to prevent secondary reactions. In the case of sulfide combustion, the oxygen atmosphere reacts so slowly with the sample surface at room temperature as to be negligible.

A pulsed Nd-YAG laser (Table 1) (yielding a power density of around 10¹¹ Wm⁻² at the sample surface), proved ineffective in extraction of SO₂, the sample was rapidly vaporized, producing little reaction with the oxygen and extremely low yields of SO₂. An Argon Ion laser (Table 1), delivering 6-7 W (multimode) in a continuous beam (Kelley and Fallick, 1990), however, produces very high yields of SO₂. When focused through

Table 1. Comparison of Laser Power Densities, Resolutions, and Wavelengths (see text for details).

Laser	λ (μm)	pulsed/ continuous	spot size (μm)	Power density (Wm^{-2})	Comments
Nd-YAG	1.064	pulsed, 200 ms	100	6×10^{11}	Very little SO_2 produced, rapid vaporization
Argon ion	0.488, 0.514	continuous	100	8×10^8	High yields of SO_2
Nd-YAG	1.064	continuous	25	2×10^9	Good yields and high spatial resolution
Nd-YAG	1.064	continuous	70	2.5×10^9	Good yields, lower spatial resolution
CO_2	10-10.6	continuous	100	5×10^8	Silicate and sulfide fluorination

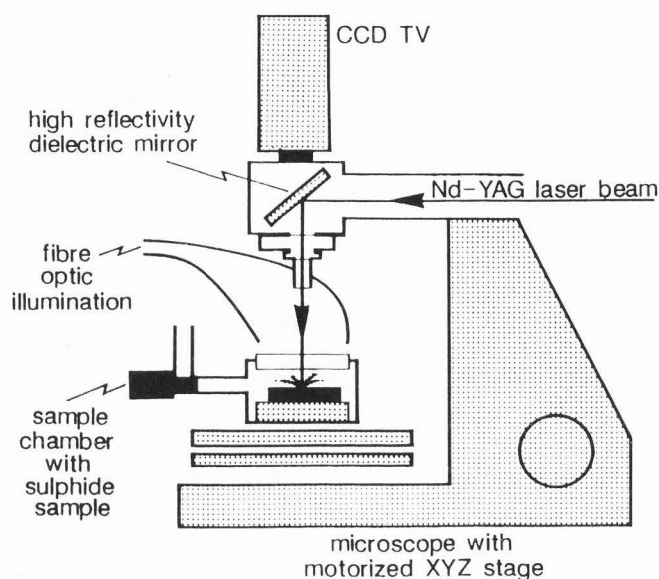


Figure 1. Schematic diagram of the laser beam path through the microscope and position of the sample chamber during laser combustion.

a microscope system to a $100 \mu\text{m}$ diameter spot, the power density at the sample surface was $8 \times 10^8 \text{ Wm}^{-2}$ (not $2 \times 10^8 \text{ Wm}^{-2}$ as originally reported, an error caused by taking the spot diameter as the spot radius). Lower power densities do not produce temperatures at the sample surface sufficient to cause combustion (sulfide combustion temperatures have been discussed by Burgess *et al.*, 1989). The probable temperatures produced are discussed below.

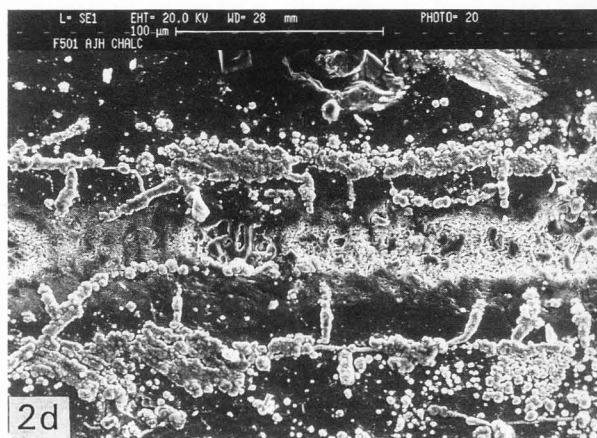
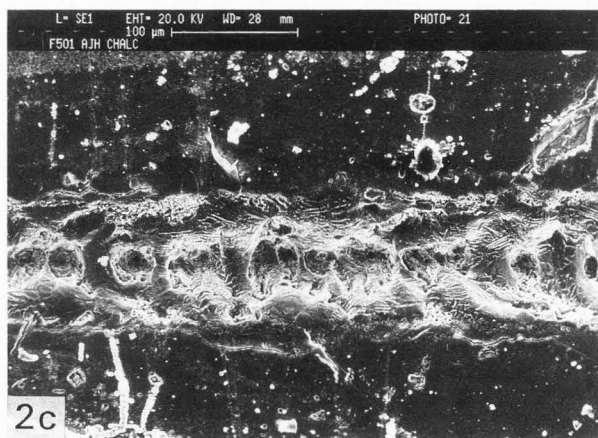
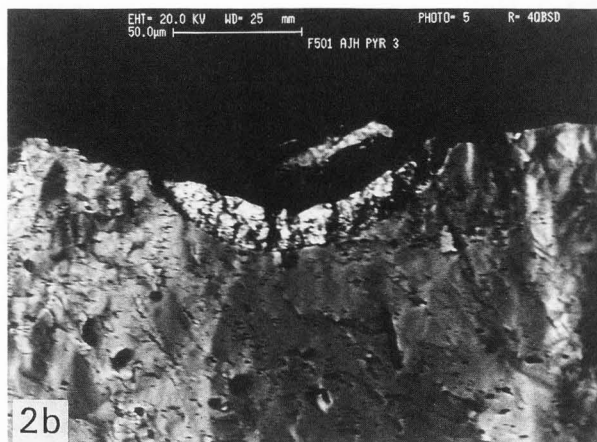
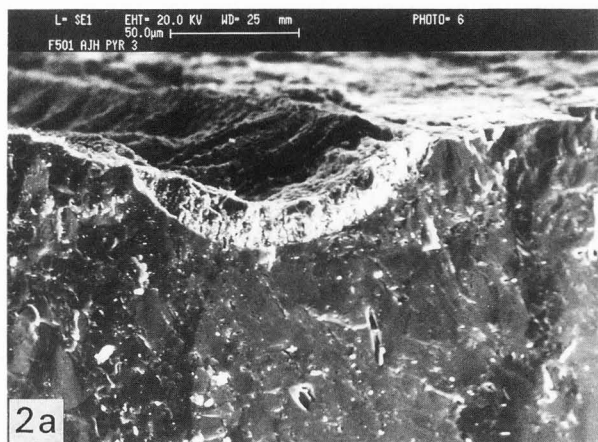
Continuous Nd-YAG lasers have also been used for SO_2 extraction, by Crowe *et al.* (1990) (Table 1) and Fallick *et al.* (1990) (Table 1). The Nd-YAG systems have the advantage of being solid state (the lasing medium is a rod of yttrium aluminium garnet), and are thus more efficient than argon ion lasers. Nd-YAG lases at $1.064 \mu\text{m}$, in the infra-red, and the Spectron

Laser Systems SL902TQ, used in our experiments yielded a continuous power of up to 20 W (TEM_{00}). Focused through a modified Leitz Metallux 3 microscope system using high reflector mirrors and a standard objective lens, the laser produced a spot size of $25 \mu\text{m}$ (Figure 1). This yields a power density of up to $4 \times 10^{10} \text{ Wm}^{-2}$. Such high power levels are, however, undesirable. High power levels produce increased vaporization, less reaction (combustion) and thus lower yields of SO_2 . Suitable levels were found to be around 1 W, yielding a power density of $2 \times 10^9 \text{ Wm}^{-2}$, a power density similar to that used by Crowe *et al.* (1990), with a 10 W Nd-YAG beam focused to a $70 \mu\text{m}$ spot. The efficacy of CO_2 laser systems is as yet unproven for SO_2 extraction from sulfides, though it has been used to great effect in the extraction of oxygen from silicates by the fluorination technique (Sharp, 1990) and a recent preliminary report described the use of a CO_2 laser to produce SF_6 for sulfur isotope measurements (Table 1) (Rumble *et al.*, 1991). Many silicates have low absorption coefficients at the $1.064 \mu\text{m}$ wavelength but absorb strongly at $10.6 \mu\text{m}$ (the CO_2 wavelength) making the CO_2 laser advantageous; sulfides, however, do not exhibit such a strong dichotomy of absorption characteristics.

Sample

The precise mechanism by which combustion occurs is still not entirely clear, and is currently the subject of further study, but several sample attributes influence the laser/solid interaction. Most important of these are, reflectivity at the given laser wavelength, form (powder/solid) and thermal conductivity. None of these parameters is easily quantified, since they are all temperature dependent and as such will vary during the analysis.

The physical properties of the sulfide have a strong influence upon the progress of the reaction, and may affect both the production rate of SO_2 and the degree of isotopic fractionation accompanying oxidation. Temperatures in the laser spot can be calculated for a steady



state, assuming no phase changes, using the formula of (Ready, 1971) which simplifies to:

$$T = (F_0 r \sqrt{\pi}) / 2K \quad (1)$$

where T = temperature rise at the centre of the laser spot ($^{\circ}$ C); F_0 = Flux density at the centre of the laser

spot; r = gaussian radius of the laser spot; and K = thermal conductivity of the sample.

Equation (1) is valid for a semi-infinite solid, where $D^2/4\kappa t \gg 1$ (where D = sample dimension, κ = diffusivity and t = time scale of interest). For $\kappa = 10^{-6} \text{ m}^2/\text{s}$ (typical value for rocks) and time of 1 second, D must be $\gg 2 \text{ mm}$.

Laser combustion of natural sulfide minerals

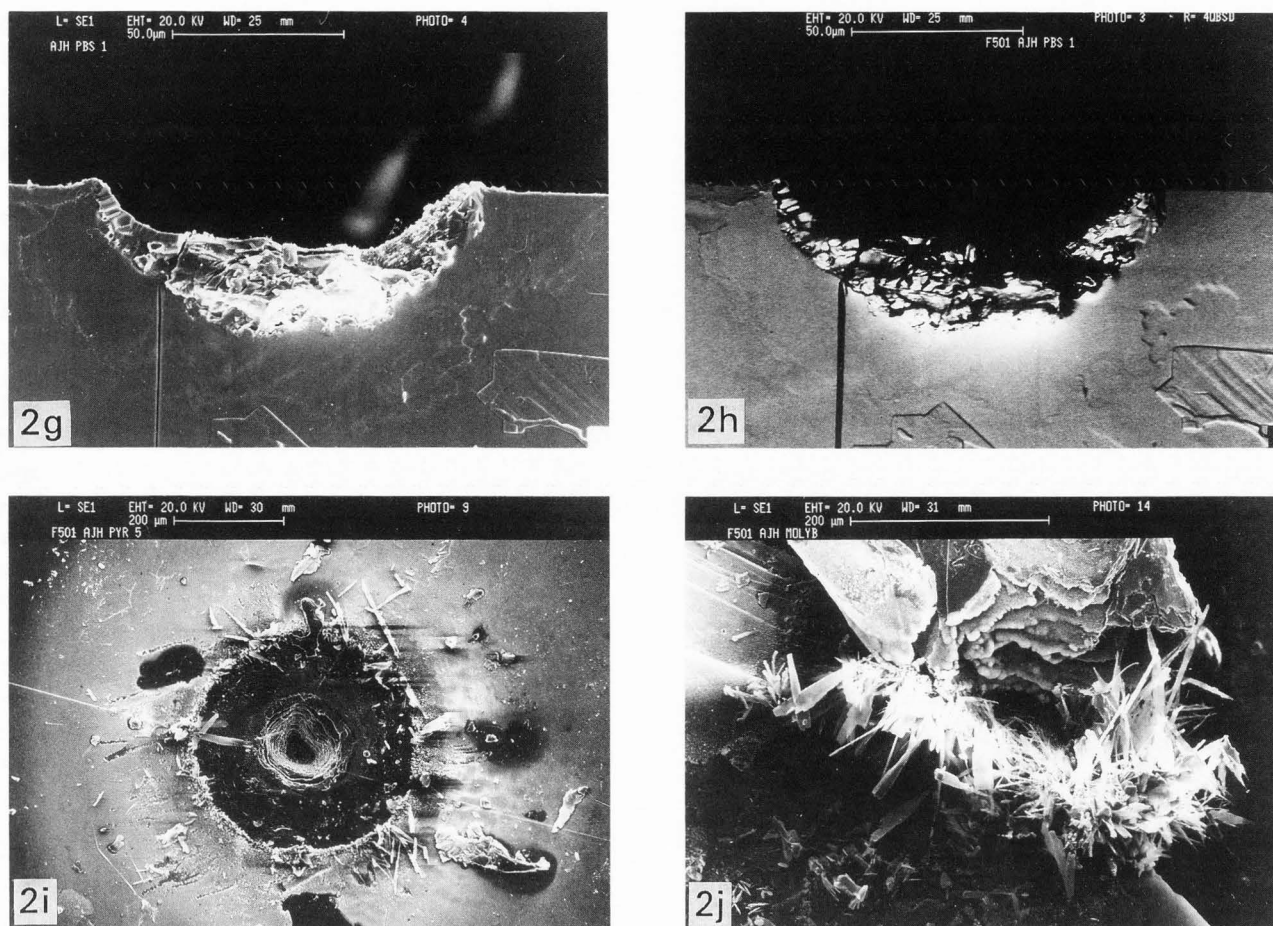


Figure 2. a. Secondary electron image of a cross section through a laser trench in pyrite (FeS_2). The reaction halo is clearly visible. The Iron oxide coating (darker in color) has been broken slightly further back, revealing the surface of the altered pit base. Laser power 0.5 W. b. Backscattered electron image of the same laser trench in pyrite, illustrating the contrast between composition of the pyrite and that of the halo. c. Secondary electron image of a laser trench in chalcopyrite (CuFeS_2), in vacuum (laser power 1 W). Sample exhibits melting textures within the laser trench. d. Secondary electron image of a laser trench in chalcopyrite, with oxygen present. Note the different texture within the trench. A higher proportion of iron was found in the trench, with Copper being ejected along with the sulfur. Surface deposits measured semi-quantitatively using energy dispersive x-ray analysis, are rich in copper, sulfur and probably oxygen. e. Secondary electron image of laser combustion tracks in galena (PbS). The morphology of the high power (4W) track in the lower half of the image, contrasts with the smoother low power tracks (1W) in the upper half. f. Backscattered electron image of the same tracks as in Figure 2e. Note the ejecta showing up as dark shadows surrounding the laser tracks. g. Secondary electron image of a track in galena. Laser power 0.5 W. Note that the partially reacted halo geometry is similar to that of pyrite, but all material is ejected so that no oxide coating remains. h. Backscattered electron image of the same area as in Figure 2g. i. Secondary electron image of a laser combustion pit in molybdenite (MoS_2). The pit was excavated using a 5W beam for 2 seconds. The morphology of the pit is strongly effected by the sheet-like structure of the mineral. On the surface, the pit is surrounded by a clear area of around $100 \mu\text{m}$ with a composition indistinguishable from MoS_2 , where no oxides were deposited. Outside that, at least two oxides were deposited on an unaltered surface of molybdenite, one as large prismatic crystals and one in powder form. Large pieces of partially reacted molybdenite excavated from the pit are also seen on the surface. j. Close up of the molybdenum oxide crystals.

Little data on the thermal conductivity of natural sulfides exists, though Horai (1971), lists data for pyrite (FeS_2), chalcopyrite (CuFeS_2) and galena (PbS), (19.2,

8.2, and 2.3, $\text{W m}^{-1} \text{K}^{-1}$, respectively). From this the maximum theoretical laser spot temperatures can be calculated, using the known spot radius, which is 12.5

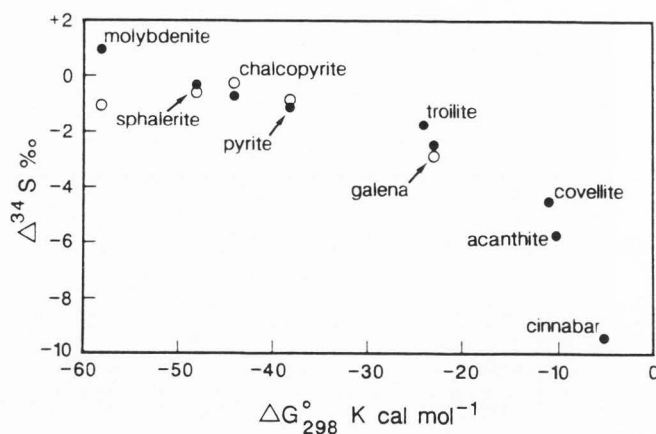


Figure 3. Plot of sulfur isotope fractionation against bond energy monitored by D. Closed circles are fractionations determined using the argon ion system (Kelley and Fallick, 1990), open circles are fractionations determined using the Nd-YAG system at similar power densities (see text).

μm for the present CW Nd-YAG system at SURRC. For pyrite, the maximum temperature rise in a steady state, without reaction, is 1153 °C. Assuming the sample was initially at room temperature, this corresponds to a temperature of around 1180 °C.

Pure metals generally have high reflectivities to infra-red light (some are used as mirrors for high intensity far infra-red applications) and sulfides also exhibit high reflectivities in the infra-red. Standard reflectivity measurements of polished specimens using visible light yield reflectivities in the range 46-56 % (Uytenbogaart and Burke, 1971). Simple measurement of laser beam reflection (1.064 μm wavelength) from polished pyrite indicated 50 % reflection, suggesting that the actual laser spot temperature is around 600 °C. This was corroborated by our observation that without the presence of oxygen, pyrite does not glow or decompose in the 1 W laser beam (Kajiwara *et al.*, 1981, achieved only slow pyrite decomposition to pyrrhotite in vacuo at 600 °C). However, in the presence of oxygen, pyrite combustion initiates at around 400 °C. This has the dual effect of reducing reflectivity by destroying the surface and increasing the temperature due to the exothermic combustion reaction with the result that material in the laser spot glows (i.e., temperatures above 800 °C). Sulfur isotopes are fractionated less during laser combustion of pyrite (1 ‰, using the argon ion laser) than most other sulfide minerals. Semi-quantitative measurements using energy dispersive x-ray analysis, indicate that Laser combustion of pyrite leads to the formation of an iron oxide rich crust, over a zone having a composition close to FeS (pyrite is FeS₂) and a sharp boundary to pyrite (Figures 2a, b), following a similar oxidation route to

that noted by Remond *et al.* (1981) in a layered structure caused by polishing of sulfides. Little material is ejected from the pit, though the margins tend to be raised (Figures 2a, b). The halo of partially reacted material is only around 15 μm wide, an order of magnitude less than the halo reported by Crowe *et al.* (1990).

Sulfides other than pyrite, notably chalcopyrite (CuFeS₂) and galena (PbS), melt and decompose under the 1 W laser beam without the presence of oxygen. This is the result of both lower thermal conductivity and lower reflectivity. The theoretical 1 W steady state temperature for chalcopyrite, from equation (1), is 2750 °C. Typical reflectivities of 44-51 % (Uytenbogaart and Burke, 1971) indicate a maximum spot temperature of 1530 °C, sufficient to cause melting (Figure 2c) and ejection of some material. Laser pits drilled in chalcopyrite in the presence of oxygen, remain similar in size though the material ejected changes, again following a similar oxidation route to that noted by Remond *et al.* (1981) (Figure 2d). Sulfur isotope fractionations measured by Kelley and Fallick (1990), were similar to those of pyrite. The much lower thermal conductivity of galena causes even more energetic reaction (Figures 2e, f). Material is vigorously ejected from the pit in galena even without the presence of oxygen. With oxygen present, a black deposit coated the sample surface in proximity to the laser pits (Figures 2e, f). In addition, higher laser powers seemed to cause uneven combustion, resulting in more variable pit morphologies (Figures 2e, f). The theoretical maximum temperature for steady state heating of galena, from equation (1), is 9750 °C. Taking into account measured reflectivities of around 44 % (Uytenbogaart and Burke, 1971), actual temperatures of around 5460 °C might be predicted. These temperatures are, however, never reached, since the beam is rapidly obscured by material being continuously ejected from the pit during irradiation. Galena exhibits a greater sulfur isotope fractionation (2.6 ‰, using the argon ion laser) than either pyrite or chalcopyrite.

The contrast in theoretical spot temperatures for pyrite, chalcopyrite and galena, serves to illustrate the tremendous difference between the response of pyrite and galena to the same laser beam. Despite this difference, however, the underlying pit morphology of laser combusted galena is similar to pyrite (Figures 2g, h). There is a shallow zone of partially altered material and a sharp boundary to unaltered material. This similarity of morphology may go some way to explaining the relatively small differences in sulfur isotope fractionation. Which even in the more extreme cases such as molybdenite, (which forms a range of molybdenum oxides, including coarsely crystalline laths, Figures 2i, j), lead to sulphur isotope fractionations of less than 7 ‰.

Sulfur isotope fractionation is related to variation in

laser/sample interaction and is only indirectly sensitive to the laser spot temperature, since temperature fluctuations are likely to be large even during a single analysis, yet reproducibility between analyses and even different samples is very good (better than 0.25 ‰).

Another important factor in understanding the laser combustion process is sample form (grain size). The porosity and roughness of the sample surface can have marked effects upon the laser/solid interaction. If the sample is presented as a powder (less than about 10 μm grain size), the form of the reaction changes. In this case, the ready supply of oxygen to all hot areas of the sample is facilitated by the spaces between the grains. The exothermic nature of SO_2 formation means that the reaction can become virtually self sustaining and combustion continues for several seconds after lasing has ceased. Probably as a result of this "cigarette effect", the isotope fractionations produced by analyses of powder were more erratic than solid samples. The laser extraction technique was always intended for analysis *in situ*, so the erratic nature of powder extraction did not present a problem except that most of the laboratory and international standards for sulfur analysis were in powder form!

Calibration

Sulfur isotopes in the SO_2 produced by laser combustion are fractionated by an amount which appears to be reproducible and linear (insensitive to variations in the sulfur isotope ratio of the mineral) (Kelley and Fallick, 1990, Crowe *et al.*, 1990). In order to calibrate laser combustion, a range of sulfide minerals (acanthite, cinnabar, chalcopyrite, covellite galena, molybdenite, pyrite, sphalerite, troilite), were analyzed by the conventional "bulk" combustion technique to determine their $\delta^{34}\text{S}$ value. Laser analysis of the same samples yielded $\delta^{34}\text{S}$ values which were generally less than the conventional value (richer in the light isotope, ^{32}S), but no relationship was observed between the $\delta^{34}\text{S}$ value and the amount of laser induced fractionation.

Kelley and Fallick (1990) found a strong correlation between sulfur isotope fractionation and sulfide bond strength, monitored by the value of ΔG_{298}^0 - the Gibbs free energy at 25°C. Minerals with high bond energies yielded SO_2 with only slightly fractionated sulfur isotopes, whereas those with lower bond energies yielded larger isotope fractionations. The fractionation factors of Kelley and Fallick (1990) are reproduced in Figure 3, along with more recent results using a Nd-YAG laser at high power (around 5 W). The earlier fractionation factors determined using the argon ion laser were reproduced by the Nd-YAG, using similar power densities, though molybdenite fractionation did not follow the

trend. The newer data points are the result of fewer analyses; more are needed to verify the precise correction factors. However, they illustrate the fact that changing the laser wavelength while maintaining similar power densities does not strongly alter the sulfur isotope fractionation. Crowe *et al.* (1990) using lower power densities (see above), also observed sulfur isotope fractionation enriching the SO_2 in ^{32}S , though the correlation with bond strength was not as apparent.

It seems likely that, in a similar manner to fractionations produced during ion microprobe measurements of sulfur isotopes (Deloule *et al.*, 1986; Chaussidon *et al.*, 1987; Eldridge *et al.*, 1987; Eldridge *et al.*, 1988; Chaussidon *et al.*, 1989), the precise fractionation varies with conditions of the analysis. Sulfur isotope fractionations produced by the laser combustion technique (0 ‰ to 7 ‰) are however, an order of magnitude less than those produced by ion microprobe techniques (up to 60 ‰). Precision in the measurement of sulfur isotopes by the laser combustion and conventional mass spectrometry (± 0.25 ‰) is also around an order of magnitude less than ion microprobe measurements (± 1 to 2%).

Application

The increased spatial resolution of the laser combustion technique allows for variations in the $\delta^{34}\text{S}$ of sulfides to be determined at the sub-100 μm scale. Microisotopic variations were measured on a sample from a massive zinc-lead-barite ore deposit, formed in the Lower Carboniferous period, around 360 Myrs ago at Silvermines, in Central Ireland (Boyce *et al.*, 1983, Samson and Russell, 1987). Within the deposit which formed close to the seabed, two types of sulfide (pyrite) chimneys were generated at small vents in the sea floor. The chimneys, typically 1 cm in diameter, formed as hydrothermal metal rich fluids, poured out of the ground at temperatures of 150 °C. They entered a dense brine pool in a depression in the sea floor, where sulfide reducing bacteria formed mounds and chimneys of sulfide minerals. Their development presents a problem which might be illuminated by high resolution laser combustion analysis.

Measurement of the sulfur isotope variations within two types of chimney was undertaken by Boyce *et al.* (1983). They were able to separate the chimneys into three zones, by drilling out samples for analysis by the conventional "bulk" technique. Texturally simple type II chimneys displayed no detectable isotope zonation, exhibiting $\delta^{34}\text{S}$ values of around -20 ‰. The texturally complex type I chimneys yielded tantalizing zonations from $\delta^{34}\text{S}$ values as low as -42.5 ‰ at the margins to around -30 ‰ in the central zone. Boyce *et al.* (1983) offered several hypotheses. The favoured hypothesis ex-

plained the sulfur isotope signature of the texturally simple type II chimneys as the interaction of hydrothermal Fe(II) with bacteriogenically-reduced sulfur from sea water ($\delta^{34}\text{S} = +20\text{‰}$) to yield pyrite with a $\delta^{34}\text{S}$ value of -20‰ . The sulfur isotope zonation of type I chimneys was ascribed to a complex mechanism initiated by reoxidation of reduced sulfur ($\delta^{34}\text{S} = -20\text{‰}$). This sulfur mixed with normal sea water sulphate at the halocline (the boundary between the high density brine and normal sea water), to yield $\delta^{34}\text{S}$ values close to 0‰ . Bacteriogenic reduction of this mixture then resulted in sulfur isotope values in the pyrite of -40‰ , the value observed at the margins of type I chimneys.

A corollary to this hypothesis is that the sulfur isotope ratios in type I chimneys would vary erratically as conditions in the sea water changed. If this were the case, the sulfur isotope zonation within the type I chimneys might range from -20‰ to -40‰ , greater than that shown by the drilling experiments. A series of chimneys were analyzed, one of which we use here as illustration (Figure 4a). The chimney was 3.6 mm in diameter, and 17 analyses were undertaken between centre and margin, yielding a resolution of close to $100\text{ }\mu\text{m}$ (contrast with $600\text{ }\mu\text{m}$ from the drilling experiment). The chimneys also presented a challenge to the laser technique since their textural zones ranged from coarsely crystalline pyrite, to crumbling pyrite rubble. The results of the laser combustion analysis were surprising (Figure 4b), they showed variation within the zones was as great as that seen by Boyce *et al.* (1983) between zones. In addition, the only overall variation was between the innermost textural zone and all the others. Some within zone variation was expected, since sulfur products of ancient bacteriogenic processes characteristically show this pattern but it was not expected to dominate the pattern.

The laser combustion analysis forced a reappraisal of the earlier hypothesis. In all samples analyzed, the central textural zone had $\delta^{34}\text{S}$ noticeably lower than outer zones. This is now interpreted as debris filling the empty chimney after hydrothermal activity ceased, and as such is unconnected with other zones. The textural zones do not mark sudden changes in isotope signature, rather the sulfur supply has a constant signature throughout chimney formation. Only one point lies significantly distant from the mean, that analyzed at $350\text{ }\mu\text{m}$ from the chimney centre (Figure 4b), which is most likely the result of a mixture between a sub-surface extension of the central "fill" and crystalline pyrite.

Full discussion of the geochemical interpretation of the data is beyond the scope of the present paper and will be published elsewhere. However, the presence of a stable sulfur isotope signature implies that sulfur in the type I chimneys came from a stable source, not in the

water column but rather from within the sediment on the sea floor, a conclusion with important ramifications for the interpretation of other ore deposits.

Conclusion

In an earlier experiment, using the laser combustion technique, large and sudden variations were detected in the $\delta^{34}\text{S}$ of a galena sample (Kelley and Fallick, 1990), thought to contain only limited, smooth zonation. In the pyrite chimneys illustrated above, where we might have expected variation, our results indicate $\delta^{34}\text{S}$ variations within textural zones, as great as that between the zones. The detailed sulfur isotope patterns being detected as a result of this new technique, challenge the concepts developed using lower resolution "bulk" techniques. Laser combustion is rapidly becoming an essential part of detailed sulfur isotope studies.

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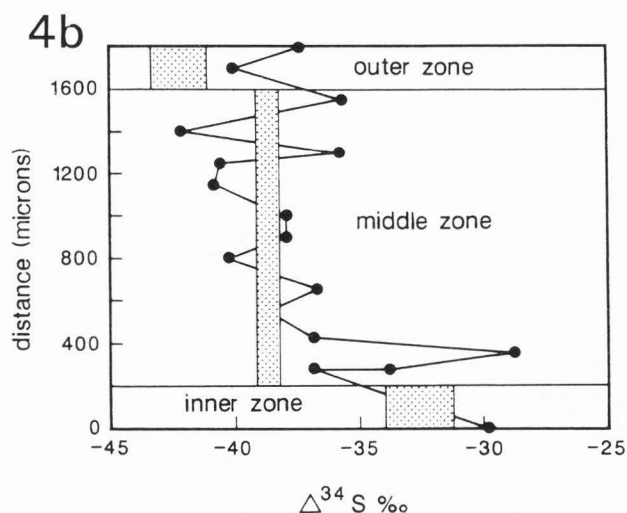
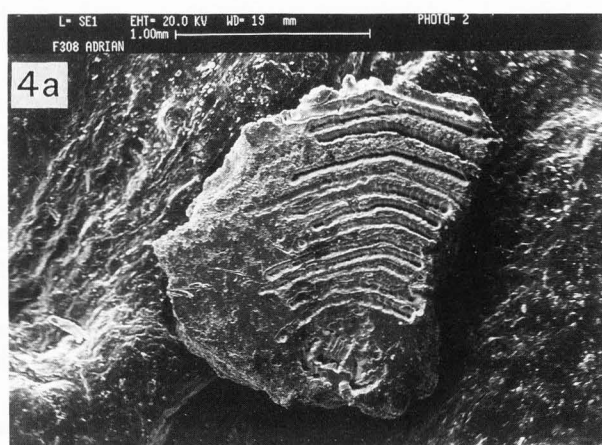


Figure 4. a (at left). Secondary electron image of a fragment of a pyrite chimney from Silvermines, after analysis for sulfur isotopes. The laser tracks follow original textural zones which were concentric about the centre of the chimney. **b (at right).** Plot of the laser combustion analyses of the Silvermines pyrite chimney (Closed squares) and mean values for samples drilled from the three textural zones and analyzed by conventional techniques (Shaded rectangles), illustrating the increase in resolution. The natural sulfur isotope ratio is plotted against distance.

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Discussion with Reviewers

G. Remond: How were the ablated volume of material and composition of the halo material measured and have the authors any analytical data to support their conclusions on the nature of the compounds in the laser trace?

R. Gijbels: Was the chemical composition of the partially reacted material around the crater measured by electron microprobe X-ray analysis?

Authors: The ablated volumes were estimated by measuring the depths of the laser pits at various points by breaking the sample perpendicular to the pit after analysis, see Figure 2. We attempted to measure the composition of ablated material from several sulfide minerals using energy dispersive X-ray analysis and gained some semi-quantitative data, however, the nature of the ejecta prevented precise analysis using that technique. More precise data were obtained by removing ejecta (this is a simple procedure since the ejecta has a powder form and does not adhere to the mineral surface) and using X-ray fluorescence analysis. The results of this analysis are presented in Kelley and Fallick, 1990. The nature of the material in the laser trace, was measured by grinding the sample subsequent to the experiment to reveal the material at the base of the laser pit.

G. Remond: Although the mechanical effect induced by the laser beam may lead to the removal of some particulate materials, heating is probably the most important factor as mentioned by the authors. The vapour created above the specimen surface may condense to form sub-microscopic particles reacting with the oxygen in the specimen chamber. Could such a possible mechanism affect the accuracy of the isotopic analyses?

Authors: It is extremely difficult to be clear about precisely what mechanisms are operating above the laser pit during combustion, and sub-microscopic particles certainly do form since we see them as ejecta around the laser pit. The mechanism by which they might affect the isotopic analysis is if they were ejected forcefully from the laser path as partially reacted material. This would produce a variable isotope fractionation and therefore unreproducible results. This does not seem to be a problem with the low power beam used on solid material, but is probably a contributory factor in the more erratic results obtained from powders.

G. Remond: What is the composition of the dark ring defined by the authors as the clear area around the crater as compared to that of the brighter area (oxidised sur-

face?) on the secondary electron image of MoS₂, Figures 2i, 2j. Could this dark ring result from either an exfoliation mechanism or a temperature gradient as suggested by the possible presence of droplets of fused materials at the boundary between the dark ring and the bright area in Figure 2i?

Authors: The dark ring around the pit in Figures 2i, 2j, is the polished surface of the mineral free of any coating, the composition was measured using energy dispersive X-ray analysis. Beyond that zone, the surface has a coating of Molybdenum oxides, the gap may be a product of the condensation temperature of the oxides.

R. Gijbels: Which laser parameters and sample characteristics appear to be mainly determining the usefulness of the laser for micro combustion of sulphides in oxygen atmosphere?

Authors: The usefulness of the laser combustion technique is its ability to achieve both high accuracy and precision at high spatial resolution. The parameters which contribute most to this phenomenon are the low combustion temperatures of the sulfides and ability of the focused laser beam to heat very small areas rapidly.

R. Gijbels: Please indicate reference(s) for "sulfide bond strength". How were these data obtained? Are ΔG_{298}^0 values the molar standard free enthalpies of formation at 298K?

Authors: We used data compiled by Barchinski (Economic Geology, 64, 56-65, 1969), for many of the important sulfide minerals which had been determined by a variety of techniques. More data is now available though the bond strengths (molar free energy of formation at 298K) vary by only around 1 % from those quoted by Barchinski.

C.S. Eldridge: Is there any documentation available concerning the linearity of fractionation in the laser combustion process? I have seen several talks and papers concerning this process and multiple matrices have been investigated, but usually only on one isotopic composition per matrix. So, how confident are we that this process is linear in its behaviour and to what degree do memory effects come in to play in handling the small samples for mass spectrometry?

Authors: Kelley and Fallick (1990), analyzed sulfides with a wide range of $d^{34}\text{S}$ values and found the same fractionation factor throughout, indicating a linear response. In most of the analyses we present here, the samples are sufficiently large that memory effects are unimportant (samples greater than 1 micromole). We are currently pursuing the problem of smaller samples with a new mass spectrometer and micro inlet system.