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Carbonyl Extraction of Lunar and Asteroidal Metals

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Abstract

The century-old Mond process for carbonyl extraction of metals from ore shows great promise as an efficient, low energy scheme for producing high-purity Fe, Ni, Cr, Mn, and Co from lunar or asteroidal feedstocks. Scenarios for winning oxygen from the lunar regolith can be enhanced by carbonyl processing of the metallic alloy by-products of such operations. The native metal content of asteroidal regoliths is even more suitable to carbonyl processing. High-purity, corrosion resistant Fe and Ni can be extracted from asteroidal feedstocks along with a Co-rich residue containing 0.5% platinum-group metals. The resulting gaseous metal carbonyls can produce a variety of end products using efficient vaporforming techniques.

Introduction

The exploitation of extraterrestrial natural resources will be essential to the successful economic development of the space frontier. In particular, the surfaces of the Moon and near-Earth asteroids offer materials -- structural materials, propellants, and life support fluids -- that we cannot afford to ignore if we are to sustain a growing human presence beyond low-Earth orbit. Confronted with the remote, low-g vacuum environment of the lunar or asteroid surface, we should emphasize the use, whenever possible, of simple, proven terrestrial refinement schemes in our initial exploitation of space resources. In the case of lunar and asteroidal mining, the Mond process for carbonyl extraction of iron and nickel (as well as other valuable siderophiles) shows great promise as a practical refining technique, capable of producing high purity metals from the local regolith or other feedstocks. In this paper we discuss the general traits of the carbonyl process, examine its advantages and drawbacks, show its application to lunar and asteroidal scenarios, and mention some potential uses for the metals produced.

The Carbonyl Process

The groundwork for the gaseous carbonyl process was

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Fig. 1. Equilibrium pressure (p) and temperature (T) relations for iron carbonyl.

Fig. 2. Equilibrium pressure (p) and temperature (T) relations for nickel carbonyl.

Fig. 3. Equilibrium vapor pressures of iron and nickel carbonyl.

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laid near the turn of the century by the discovery of Fe and Ni carbonyls, culminating in the posthumous publication of a body of data on the synthesis, stability and reactions of a number of metal carbonyls by Mond et al. (1910). International Nickel adapted the process early in the century for use in its Sudbury, Ontario facility that alone produces nearly 60% of the global supply of nickel (Boldt, 1967).

The fundamental principle of the gaseous carbonyl process is simple. Metallic alloys of Fe, Ni, Co, etc. are exposed to carbon monoxide gas at modest pressures (about 10 bars) and temperatures on the order of 100 °C. Volatile carbonyls form spontaneously by reactions such as:

$$Fe + 5 CO = Fe(CO)_5 \quad (g) \qquad (1)$$

$$Ni + 4 CO = Ni(CO)_4 \quad (g) \qquad (2)$$
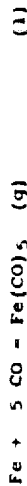
The conditions required for volatilization of iron and nickel are displayed in Figs. 1 and 2, respectively. These plots of the partial pressure of carbonyl gas at various values of $\log_{10}(P_{CO})$ and $1/T$ are derived from the equation for the gas equilibrium constant K_p. For example, using Eq. 1,

$$K_p = \frac{P_{Fe(CO)_5}}{a_{Fe} (P_{CO})^5} \qquad (3)$$

where P is the partial pressure of the particular gas and a is the activity of Fe, here assumed to be 1. Solving for P_{CO} and taking the log of both sides, we can write:

$$\log(P_{CO}) = 1/5 [\log(P_{Fe(CO)_5}) - \log K_p]. \qquad (4)$$

Since

$$Log K_p = -\Delta G^o/(2.303RT) \qquad (5)$$

substitution into (4) finally produces:

$$\log(P_{CO}) = \Delta G^o/(11.51)RT + (1/5)\log(P_{Fe(CO)_5}) \qquad (8)$$

This is the equation of a straight line, with variables $\log(P_{CO})$ and $1/T$, and a slope of $\Delta G^o/(11.51R)$. Choosing different values of $P_{Fe(CO)_5}$ generates a family of parallel straight lines (Figs. 1,2).

A close examination of these figures reveals the most favorable T,P environment for carbonyl formation. In Fig. 2, note that at 400 K (127°C), CO at a pressure of 1 bar (10^{-1} MPa) would be in equilibrium with nickel carbonyl gas with a partial pressure of 1 bar. As little as 0.02 bars of CO at room temperature would equilibrate to make 1 bar pressure of nickel carbonyl. High pressures are clearly unneeded; the equilibrium thermochemistry of the system
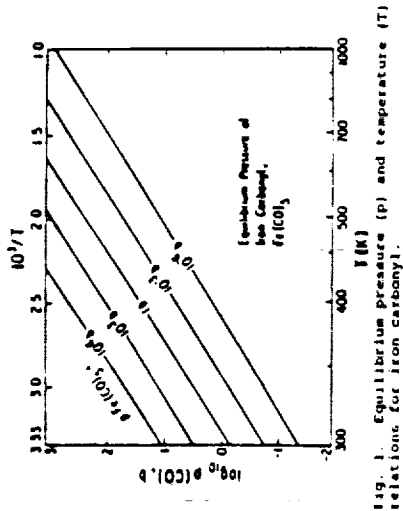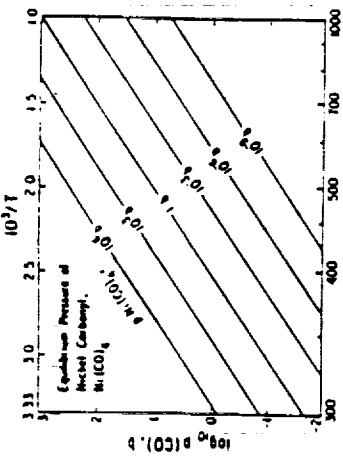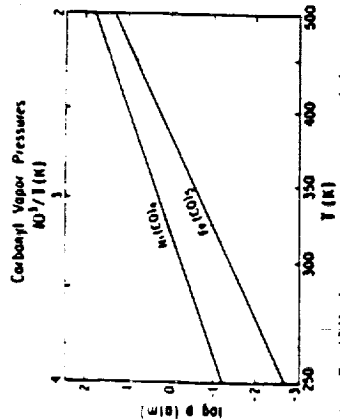
favors the best yield of carbonyls at the lowest temperatures. If, for other reasons (kinetic factors, or limited reactor volume), it is found desirable to operate at much higher gas densities and pressures, higher temperatures can be tolerated: a pressure of 10 bars of CO is sufficient to keep nickel carbonyl stable and abundant (a partial pressure of 1 bar) at up to about 500 K. Note that the pressure of carbonyl gas in Eqn. 4 varies as the fifth power of the CO pressure, and that the iron and nickel carbonyls have different equilibrium stabilities. Therefore, passing the reaction product gas through a collecting bed with the same temperature but 10 times lower CO pressure than in the reactor could precipitate out up to 99.99% of the iron carbonyl as metallic Fe particles. The CO released can be recycled through the reaction chamber indefinitely.

The same principles apply to the formation of the gaseous carbonyls of many other elements (e.g. Os, Co, Ir, Ru, Rh, Pt, and Pd). Stability data for a number are available (See the JANAF Thermochemical Tables; Roble et al., 1978; Sykes and Townshend, 1955; Tripathi et al., 1976a,b.)

A further implication of the data given in Fig. 1 and 2 is that deposition conditions can easily be chosen so as to separate very pure Fe while retaining all the Ni in the gas phase. The commercial Mond process can produce Fe and Ni with purities of about 99.95% in a single step by taking advantage of this trait. Such ultra-high purity Fe and Ni, ideal for making tough, corrosion-resistant single crystals of very high tensile strength, cannot be made by either fractional distillation or zone refining, despite literature claims to the contrary, because of the very high mutual solubility of solid and liquid Fe and Ni. (The eutectic composition in the Fe-Ni is near 60% Ni, not near the pure end-member composition, and Ni and Fe have very similar vapor pressures.)

An entirely separate approach to carbonyl separation is available: the vapor pressures of the liquid carbonyls are large enough at and near room temperature to permit their fractional distillation. The vapor pressure data in Fig. 1 illustrate this alternative. By holding an Fe-Ni carbonyl liquid mixture at, say, 300 K, Ni carbonyl will have about 10 times the vapor pressure of Fe carbonyl, allowing preferential separation of the former. This process is even more effective at lower temperatures.

For process design, the kinetics of carbonyl formation and decomposition are just as important as thermodynamic stability. Literature data for Fe and Ni are available (Garratt and Thompson, 1934a,b; Carlton and Oxley, 1965, 1967; Kim et al., 1973; Oxley, 1966). The speed of volatilization of metallic feedstocks is striking, as is the temperature dependence of the formation rate of the

gaseous carbonyls. Rhee et al. (1973) have shown that the optimum temperature for Fe carbonyl formation is about 394 K (121°C). At lower temperatures the reaction rate is more sluggish, while at higher T the rate of decomposition of the carbonyls accelerates markedly. Above 400 K the rate of the net forward reaction varies as about $1/T^2$. As an example, an iron powder consisting of 100 μm grains, subjected to 21 bars of CO at 394 K for four hours, will be 50% converted into Fe carbonyl. Nickel, because of the greater stability of its carbonyl, reacts faster (Sykes and Townshend, 1955).

The advantages of the carbonyl process for space application are numerous. The only reactant required is CO, recoverable at the time of metal deposition and recyclable indefinitely. The basic process uses very little electric power, requires few moving parts, and can achieve the entire range of process temperatures by passive thermal control. The process is ideally suited for automatic operation. As the thermodynamics and kinetics of formation and decomposition are well-understood for the major carbonyls, process design can begin at once. For space applications, perhaps the most attractive of these is the low energy requirement. Passive solar heating and radiative cooling can provide the entire range of process temperatures.

The carbonyl process exhibits several obvious disadvantages. Nickel and iron carbonyls are extremely toxic, so contamination of any workers and their living facilities must be prevented. Another drawback for lunar applications is that CO will initially have to be delivered from Earth, but the gas is recyclable, and can be supplemented by combustion of organic wastes. In the asteroidal case, as we shall see, CO is easily derived from nearly every asteroid type suitable for metals extraction.

Lunar-specific Applications

Any scheme for producing oxygen from the lunar regolith could be enhanced by applying the Mond process to the solid by-products of such an operation. Among the suite of minerals in the lunar regolith, the one which seems most amenable to oxygen extraction would be ilmenite ($FeTiO_3$).

Ground and orbital studies from the Apollo missions indicate that ilmenite concentrations are highest in the lunar maria, particularly in Mare Tranquillitatis and southern Mare Serenitatis, where Apollo 11 and 17, respectively, found ilmenite making up to 10% of the mode of some soils. Studies of electrostatic techniques for beneficiation of lunar ilmenite from such soils indicate that grades and recoveries in the 90%+ level could be achieved (Agosto, 1984).
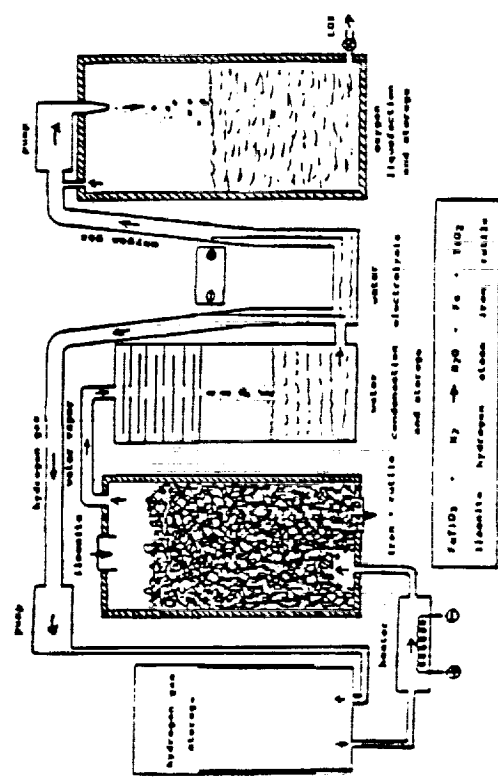
A promising method for extracting oxygen from ilmenite is through the hydrogen-reduction process (Fig.4). The relevant reaction is:

$$FeTiO_3 + H_2 \rightarrow Fe + TiO_2 + H_2O .$$

The H_2O can then be broken down to H_2 and $1/2$ O_2 via electrolysis with the hydrogen being recycled and the desired oxygen drawn off and liquified for storage and later shipment. Some hydrogen will be lost in this process, but some solar wind implanted hydrogen will also be released from the ilmenite feedstock.

The above reaction is endothermic, but not terribly so, with a ΔH of 9.7 Kcal/gm-mol at 900°C. At moderate temperatures of 700-1000°C, the per pass production of H_2O is 5% or less (Williams, 1984). The energy cost of the process is 5000 calories per gram of oxygen produced. Running the process at higher temperatures will produce higher yields, but that raises the associated problems of increased hydrogen loss rates through diffusion, sintering of solid reactants and products and, of course, higher energy usage.

Further tests of the hydrogen-reduction process are needed. Specifically, it must be determined how efficient the process is when the ilmenite feedstock contains no Fe^{3+}. Extraterrestrial ilmenites used in such tests could come from the lunar sample collection or from meteorites.

The solid residue of the hydrogen reduction process is a mass of native Fe and rutile (TiO_2). The Mond process could be effectively used to separate this residue into its components. Exposure to CO volatilizes Fe carbonyl which can then be thermally decomposed to yield high-purity iron for use in structural members. The left-over rutile can be used in products that require a refractory constituent or used as a feedstock for the production of pure Ti.

Another promising technique for winning oxygen from ilmenite is the carbothermal reduction process (Cutler and Krag, 1984). In this process, ilmenite feedstock is mixed with a carbon reductant and an anorthite fluxing agent and melted, causing the following endothermic reaction:

$$FeTiO_3 + C \rightarrow Fe + CO + TiO_2$$
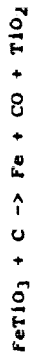
The resulting iron is contaminated with carbon and can be subjected to the Mond process to purify the iron. When reacted with H_2, the CO (some of which could be removed for use as the Mond process reactant) can be converted to hydrocarbons and water through the Fischer-Tropsch process:

$$yCO + (2y+1)H_2 \rightarrow yH_2O + C_yH_{2y+2}$$

Fig. 4. The hydrogen-reduction of ilmenite produces oxygen with an Fe-TiO2 residue.
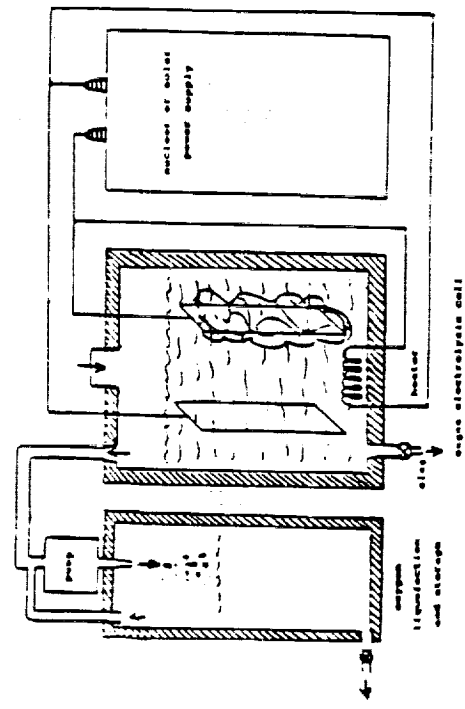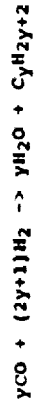
Fig. 5. Electrolysis of molten silicates produces oxygen at the anode while various metals plate out on the cathode.

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Oxygen can then be recovered via electrolysis and the original carbon reactant can be recovered via hydrocarbon cracking. The cost of carbothermal reduction is approximately 17,000 calories per gram of oxygen produced.

Although carbothermal reduction is an involved process, it does have some significant advantages over hydrogen reduction of ilmenite. Most notably, carbon removes more than 1.25 times its mass of oxygen per pass while hydrogen only removes 0.4 to 0.9 times its mass per pass. Also, carbon can be recovered from garbage and CO_2 waste gases and should be an easier reducing agent to handle than hydrogen. Disadvantages of the process are that it is more energy intensive than hydrogen-reduction and requires more processing steps.

While ilmenite makes up, at best, 10% of lunar soils, silicate minerals are as abundant as they are on Earth. While liberating oxygen from silicates is an energy intensive process, one proposed extraction scheme stands out because of its conceptual, if not practical, simplicity. Lindstrom and Haskin (1979) have experimented with a system of magma electrolysis (Fig. 5). A feedstock of silicates is melted and two electrodes are inserted into the melt; when an electric current is applied, oxygen is liberated at the anode while the cathode is plated with a mixture of Fe, Cr, Mn, Ti and possibly Si. The process requires 3000 calories of thermal and electrical energy per gram of feedstock. For reasonable oxygen yields (10% of the mass of solids) the cost per gram of oxygen is 30,000 calories. Note that instead of melting bulk lunar silicates, the feedstock could just as easily be ilmenite. In this case, the cathode deposit would consist dominantly of Fe and Ti. By exposing the cathode deposit to CO, the constituent metals can be volatilized and extracted.

Of the hydrogen reduction, carbothermal and magma electrolysis methods, the first appears more viable. It operates at lower temperatures, does not require massive sources of electrical power (all the process energy could be provided by a solar furnace), and is more energy-efficient than either the carbothermal process or electrolysis. Should future experimentation with magma electrolysis show that a free metal and a silica residue product are produced, then the additional expense of the latter process may be justified.

Application to Asteroidal Metals

The carbonyl process is especially suited to the extraction, separation, and refinement of the native metal alloys plentiful in the regoliths of certain types of asteroids, those corresponding to the unequilibrated ordinary chondrite meteorites. Metal content for the H and L (high and low iron) chondrites ranges up to 20%. (See

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Table I.) The parent bodies of these meteorites have not undergone the melting and geochemical differentiation experienced on Earth and the Moon, and hence have not concentrated most of their metals in inaccessible cores. Because of the very low oxygen fugacity in metal-bearing meteorites, all the siderophile elements are readily available for direct extraction from the metal phase, not locked up in very dilute oxide solid solutions or microscopic inclusions in silicates. For example, after Fe/Ni carbonyl extraction, the remaining metallic residue contains mostly Co and small but significant amounts (0.5%) of the platinum-group siderophiles (Pd, Pt, Os, Ir, Au, Rh, Ru, Cu, etc.) which are worth roughly $10,000 per kg. Their recovery may be an attractive by-product of the process.

TABLE I: Fe and Ni Concentrations in Ordinary Chondrites

	CLASS		
	LL	L	H
meteorite total metal (%)	4±1	9±2	16±3
Ni concentration in metal	25±5	15±3	10±2
Co concentration in metal	1.2±0.2	0.7±0.1	0.5±0.1

The ordinary chondrites make up some 75% of the current terrestrial meteorite flux, implying that their parent bodies are well-represented in the near-Earth asteroid (NEA) population. Spectral analogs of ordinary chondrites are rare in the few dozen near-Earth asteroids classified so far; this situation is offset somewhat by the sheer numbers of NEA available. Shoemaker (1983) projects that there are some 1300 NEA > 1 km in diameter, and about 100,000 > 0.1 km across. Even more encouraging, about 1/5 of these objects should require less ΔV to reach from low Earth orbit (LEO) than does the lunar surface (for 1982 DB, 0.1 km s⁻¹ vs. 6 km s⁻¹). Radar studies of NEA indicate that most objects are covered with a dusty regolith; metal grains may be easily beneficiated using a magnetic rake or separator. Where regolith is scarce or absent, the relatively low crushing strengths of the ordinary chondrites may permit grinding the surface rocks to an easily stored powder. The return vehicle would need bulk storage for the ore and a heat shield for an aerobraking return to LEO. We think the carbonyl processing facility is best located in LEO --asteroid operations should be limited to automated functions like bulk ore handling and perhaps magnetic separation.

The major advantage of asteroidal feedstocks for the carbonyl process is the low energy required to deliver mining equipment to the NEA and return useful ore to LEO.

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Not only are many NEA more accessible (from LEO than the lunar surface) in terms of ΔV, but the return energy requirements are even lower (for a well-chosen asteroid like 1982 DB, the ΔV required is less than 100 m s⁻¹.) These asteroidal ores can be subjected immediately to the Mond process without any of the reduction or melting steps required for lunar feedstocks. Further, simple heating of any class of chondritic meteorite can supply all the necessary CO.

The major drawback to the exploitation of asteroid targets is the long flight-time associated with the low launch and return energies, typically on the order of 1 to 3 years. Moreover, the most energetically attractive asteroids have the longest synodic periods; launch windows occur for a given asteroid occur at typical intervals of about 5 years. As a result, dozens of energetically favorable asteroids would have to be discovered and characterized in order to support large scale mining.

Uses of Carbonyl-Derived Metals

Yet another attractive feature of carbonyl processing is that the separated metals are available as very pure powders, or in the gas phase as carbonyls. In the latter case the metal can be deposited directly onto a heated mold or mandrel. Nickel "vaporforming," as the process is called, is a successful commercial process that is today invading markets for precision nickel components previously supplied by machining, electroplating, casting, and other vapor deposition techniques (Melnel, 1985). Vaporformed nickel produced by a division of Formative Products Co. has a tensile strength of over 200,000 psi (> 1400 Mpa); surfaces of optical quality can be produced directly from the mold.

In perhaps the most demanding application tried to date, rhenium thrust chambers for advanced solar-powered rockets have been vaporformed in an analagous process from rhenium carbonyl. Carbonyl deposition is also widely used to apply thin films of Pt and Cr to mass-produced items like razor blades. Another technique for production of thin films is laser chemical vapor deposition, where metal is deposited on a surface heated by a focused laser. The beam dwell time and focus determine the film thickness. In space, this technique could produce lightweight films for solar collectors, solar power satellite structures, and electrical components.

With Fe the most plentiful metal in lunar and asteroidal ores, vaporforming of pure Fe as well as Fe-Ni alloys from a carbonyl gas mixture should be investigated as a high priority. Even if such processes prove unworkable, powder metallurgy may provide another means to

use the high-purity iron produced by carbonyl extraction. Indeed, because of its corrosion resistance and strength, iron castings may be worth producing despite the high energy costs.

Conclusions

The gaseous carbonyl process offers significant advantages in lunar and asteroidal resource exploitation. To bring the method to a practical level of development for space application, we recommend: (1) Theoretical process design based on thermodynamic and kinetic data; (2) Construction of a boilerplate laboratory extraction system to test the process on synthetic metal alloys and on chondritic and iron meteorite samples; (3) Zero-g testing of the process on the shuttle or space station using actual meteorite samples; (4) evaluation of lunar and asteroidal ores through space-based geochemical observation and ground-based spectroscopy; and (5) deployment of an automated processor in the selected venue. Spacecraft observations could begin with lunar survey missions designed by Japan's NASDA for the mid-1990's. The Soviets have also announced an ambitious series of probes aimed at asteroid resource targets, beginning with the twin-spacecraft Phobos mission to the Martian moons in July 1988. If funded adequately under a revived U.S. space sciences program, the proposed Lunar Geosciences Observer and Near-Earth Asteroid Rendezvous missions can provide the specific compositional data needed to implement a space-based carbonyl extraction program.

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APPENDIX D

THEORETICAL PREDICTION OF VOLATILE-BEARING PHASES AND VOLATILE RESOURCES IN SOME CARBONACEOUS CHONDRITES
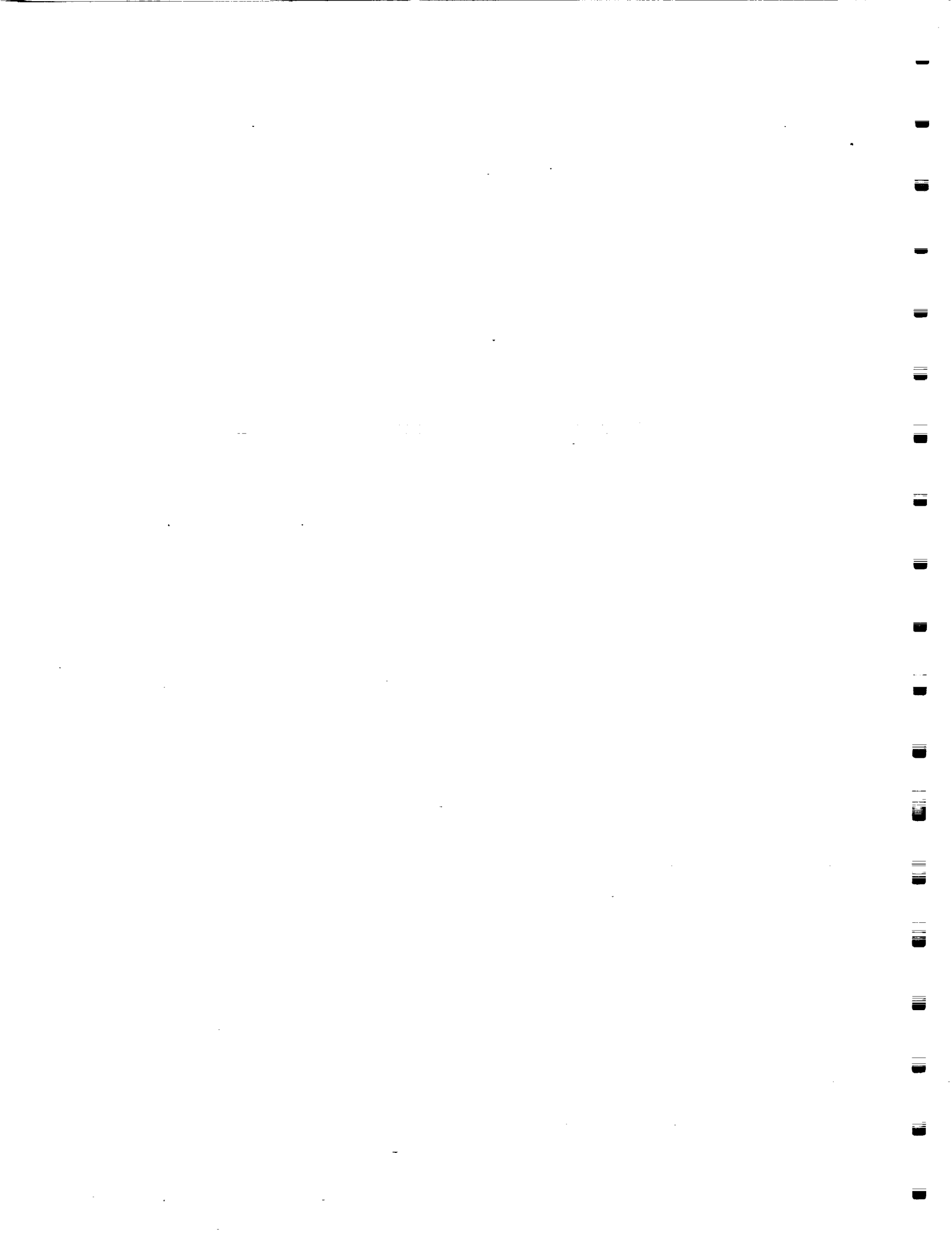
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THEORETICAL PREDICTIONS OF VOLATILE BEARING PHASES AND VOLATILE RESOURCES IN SOME CARBONACEOUS CHONDRITES

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Abstract

Carbonaceous chondrites are usually believed to be the primary constituents of near-Earth asteroids and Phobos and Diemos, and are potential resources of fuels which may be exploited for future planetary missions. In this work we have calculated the nature and abundances of the major volatile bearing and other phases, including the vapor phase, that should form in C1 and C2 type carbonaceous chondrites as functions of pressure and temperature. The results suggest that talc, antigorite ± magnesite are the major volatile bearing phases and are stable below 400°C at 1 bar in these chondritic compositions. Simulated heating of a kilogram of C2 chondrite at fixed bulk composition between 400 and 800°C at 1 bar yields about 135 gm of volatile, which is made primarily of H_2O, H_2O, CH_4, CO_2 and CO. The relative abundances of these volatile species change as functions of temperature, and on a molar basis, H_2 becomes the most dominant species above 550°C. In contrast, C1 chondrites yield about 306 gm of volatile under the same condition, which consist almost completely of 60 wt% H_2O and 40 wt% CO_2. Preliminary kinetic considerations suggest that equilibrium dehydration of hydrous phyllosilicates should be attainable within a few hours at 600°C. These results provide the framework for further analyses of the volatile and economic resource potentials of carbonaceous chondrites.

Introduction

The near-Earth asteroids are potential resources of volatiles which can be used as propellants and life supporting purposes for planetary missions. As emphasized by Lewis and Lewis (1), these asteroids are at times the nearest bodies to Earth, and many of them can pass between Earth and Moon. These authors have also shown that within any arbitrary three-year period, there are roughly 300 and 90,000 launch opportunities to respectively kilometer and 100-meter sized asteroidal bodies as compared to 39 lunar launch windows. These facts and the potential volatile resources make the asteroids important candidates for detailed analyses for supporting future planetary missions.

Cost-effective or energy-efficient extraction of volatiles from the asteroids require knowledge of the nature and modal abundances of the constituent minerals in which the volatile components are structurally bound. There has been several studies on reflectance spectroscopy of near-Earth asteroids to characterize the nature of the volatile bearing minerals (2,3). While these studies report absorption band near 3 μm suggesting presence of hydrous phyllosilicates, more precise characterizations were equivocal. An obvious alternative approach to the resolution of the problem is to examine directly the asteroidal materials.

The spectral and density characteristics strongly suggest that a significant fraction of the near-Earth asteroids are made of carbonaceous chondrites (1,4). The most volatile rich of these meteorites are what are commonly known as C1 (or CI) and C2 (or CM) classes. However, the grain size of the volatile bearing phases are often too small (100 to 1500 Å) (5) to permit identification under optical microscope, and are best observed under high resolution transmission electron microscopy (HRTEM). Zolensky and McSween (5) have recently presented a summary of volatile bearing phases identified in the carbonaceous chondrites.

The primary objective of this work is to carry out theoretical calculations to predict modal abundances and compositions of the major mineral phases, along with the abundance and composition of the coexisting vapor phase, that could develop in the bulk compositions of C1 and C2 chondrites as functions of pressure and temperature. The results would provide the framework for engineering designs for the extraction of volatile components from asteroids as well as Phobos and Deimos, the two small natural satellites of Mars, which are also likely to be made of carbonaceous chondrites (1).

Theoretical Method

Principles

According to Duhem's theorem in classical thermodynamics (6,7), the equilibrium state of a closed system (i.e., a system of fixed composition and mass) is completely determined if any two variables are fixed regardless of whether these are intensive, extensive, or a combination of both. Ganguly and Saxena (7) have recently reviewed the various methods by which one may carry out the actual computation of the equilibrium assemblages. The

Table 1 Bulk chemical compositions of C1 and C2 carbonaceous chondrites

	C1	C2
Si	10.40	12.96
Ti	0.04	0.06
Al	0.84	1.17
Cr	0.23	0.29
Fe	18.67	21.56
Mn	0.17	0.16
Mg	9.60	11.72
Ca	1.01	1.32
Na	0.55	0.42
K	0.05	0.06
P	0.14	0.13
Ni	1.03	1.25
Co	0.05	0.06
S	5.92	3.38
H	2.08	1.42
C	3.61	2.30
O	45.61	41.74

method used in this study obtains the compositions and abundances of the equilibrium phase assemblages by minimizing the Gibbs Free Energy (G) of the system at fixed P-T conditions. The minimization is constrained to conserve the various elemental masses of the system through the method of Lagrangian multipliers (7). Because of the extremely small grain size of the phyllosilicates observed in carbonaceous chondrites, one should consider the effects of surface free energy on the formation of these phases. As a first approximation, we have, however, ignored this effect. Therefore, the actual equilibrium temperatures of volatile bearing phases could be lower than those predicted by our calculations.

System, Phases and Data Base

Table 1 shows the bulk compositions of C1 and C2 carbonaceous chondrites. These compositions are based on analyses of a number of fragments of Orgueil and

Table 2 Phases in the system Mg-Fe-Si-C-H-O-S considered in this work

The sources of thermochemical data are shown by reference numbers within parentheses. The Heat of Formation of the Fe-end members of the hydrous phyllosilicates are derived in this work.

Anhydrous Silicates and Oxides

Olivine	$(Mg,Fe)_2SiO_4$	(8)
Orthopyroxene	$(Mg,Fe)SiO_3$	(8)
Periclase	$(Mg,Fe)O$	(23)
Quartz	SiO_2	(17)
Cristobalite	SiO_2	(17)
Hematite	Fe_2O_3	(23)
Magnetite	Fe_3O_4	(23)

Hydrous and Carbonate Phases

Anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$	(8,27)
Talc	$(Mg,Fe)_3Si_4O_{10}(OH)$	(8)
Antigorite	$(Mg,Fe)_{48}Si_{34}O_{85}(OH)_{62}$	(8)
Chrysotile	$(Mg,Fe)_3Si_2O_5(OH)_4$	(8)
Brucite	$(Mg,Fe)(OH)_2$	(17,24)
Magnesite	$(Mg,Fe)CO_3$	(17,25)

Sulfides and Elements

Troilite	FeS	(17)
Pyrite	FeS_2	(17)
Iron	Fe	(26)
Sulfur	S	(17)
Graphite	C	(17)

Vapor Phase	C-O-H-S	(15,16,17)

Species: H_2O, CO_2, CH_4, CO, O_2, H_2S, S_2, SO_2, COS

Murchison meteorites, respectively, and are summarized in Dodd (22). It can be easily seen from this table that the subsystem Mg-Fe-Si-C-H-O-S (MFCHOS) constitutes almost 96% by weight of the bulk compositions of C1 and C2 chondrites. In order to somewhat simplify the computational problem, we have contined the G minimization calculation to this subsystem, but evidently the phases whose compositions form outside of this subsystem cannot be major constituents of these chondrites.

Table 2 shows the list of phases that we have considered as possible crystallizing phases within the above subsystem along with the sources of the thermochemical data. The choice of these phases have been guided by the published reports of the mineralogy of carbonaceous chondrites whose compositions lie within the system MFCHOS (e.g., Zolensky and McSween (5)). The selection of thermochemical data in the system Mg-Si-O-H is based on the critical analysis of Chatterjee (8,11) for consistency with both calorimetric and experimentally determined phase equilibrium measurements. These data are similar to those of Berman (9). However, unlike those in Berman, the data are also consistent with high P-T experimental data involving distribution of Fe and Mg among coexisting silicates.

The heat capacities (C_p) and entropies (S^0) of the phases, if not available in any of the recent systematizations of self-consistent data set, are estimated by stoichiometric summation of the properties of oxides and structurally analogous compounds, as discussed in a number of publications (13,14).

There are no thermochemical data for the Fe-end members of the phyllosilicates listed in Table 2. The enthalpies of these phases are estimated according to the known relative properties of Fe- and Mg-end members of biotite, which is also a phyllosilicate. The data derived by Chatterjee (8) and Robie and Hemingway (10) for the Mg- and Fe^{2+}-end members (phlogopite and annite, respectively) yield an enthalpy difference of -359.566 KJ per mole of divalent cation at 1 bar, 298 K. We have used these values to estimate the enthalpies of formation from elements of Fe-end members of phyllosilicates at 1 bar, 298 K from the available data for the Mg-end members. The results are as follows (KJ/mol of Fe). Fe-talc: -1606.80; Fe-antigorite: -1127.53 and Fe-chrysotile: -1094.87. The corresponding values of the free energy of formation from elements (ΔG_f^0) for Fe-talc and Fe-antigorite at 1 bar, 298 K are -4477.18 and -4784.0 KJ/mol of Fe^{2+}, respectively.

The validity of the estimated thermochemical properties of the Fe-end members of the phyllosilicates may be tested as follows. The Fe-end members of talc and

antigorite are unstable. Instead, the stable phases are closely analogous compounds, namely, minnesotite, which has a stoichiometry of $Fe_{27}Si_{36}O_{86}(OH)_{26}$ as compared to that of $Fe_{27}Si_{36}O_{90}(OH)_{18}$ for Fe-talc, and greenalite with a stoichiometry of $Fe_{48}Si_{32}O_{80}(OH)_{64}$ compared to $Fe_{48}Si_{34}O_{85}(OH)_{62}$ for Fe-antigorite. Anovitz et al. (12) have recently determined ΔG_f^0 of minnesotite and greenalite from phase equilibrium data. Their results, ΔG_f^0 (minnesotite) = -4577.78 KJ and ΔG_f^0 (greenalite) = -4799.50 KJ, differ in the right direction from the corresponding values of Fe-talc and Fe-antigorite, considering the relative stabilities of the phases.

The stereochemical environments of divalent cations in biotite are quite similar to those in talc, both being 2:1 (TOT) layer silicates, and partly similar to those in antigorite, which is an 1:1 (TO) layer silicate (28). Thus, these phyllosilicates should have similar differences between the enthalpies of formation of the Fe- and Mg-end members. Further, since on the basis of observational data, the predicted compositions of the mineral phases in carbonaceous chondrites are expected to be Mg-rich, the effects of errors in the Fe-end member thermochemical properties and solid solution model will be relatively small. This can be easily understood by considering the form of G-X curve of a stable solution and evaluating the effects of errors in above properties near Mg-terminal segment.

The thermodynamic mixing properties of the Fe^{2+}- and Mg-end member components of the anhydrous silicates are taken from the self-consistent summary of Chatterjee (8), while those of the phyllosilicates are assumed to be ideal for the lack of any data. The latter assumption is likely to be approximately valid at $T \geq 600^0 C$, since at these conditions biotite solid solution is found to behave approximately ideally (7). At lower temperature, the phyllosilicates may deviate from ideal solution behavior, but perhaps not too dissimilarly to significantly affect their relative stabilities. Magnesite is also assumed to be an ideal solution of Fe-Mg components. As emphasized by Ganguly and Saxena (7), the computed dehydration conditions are not very sensitive to errors in activity-composition relations since the devolatilization equilibria are characterized by large enthalpy changes. The iron oxides and sulfides are considered to be stoichiometric phases since the solid solutions of Mg are around a few percent at the temperatures of interest.

The fluid properties are taken from Saxena and Fei (15,16) and Robie et al. (17). The "corresponding state method" of estimating P-V-T relation, as discussed by these authors, is extended to include the sulfur species. For mixing data, we have assumed that H_2S behave as H_2O, S_2 as
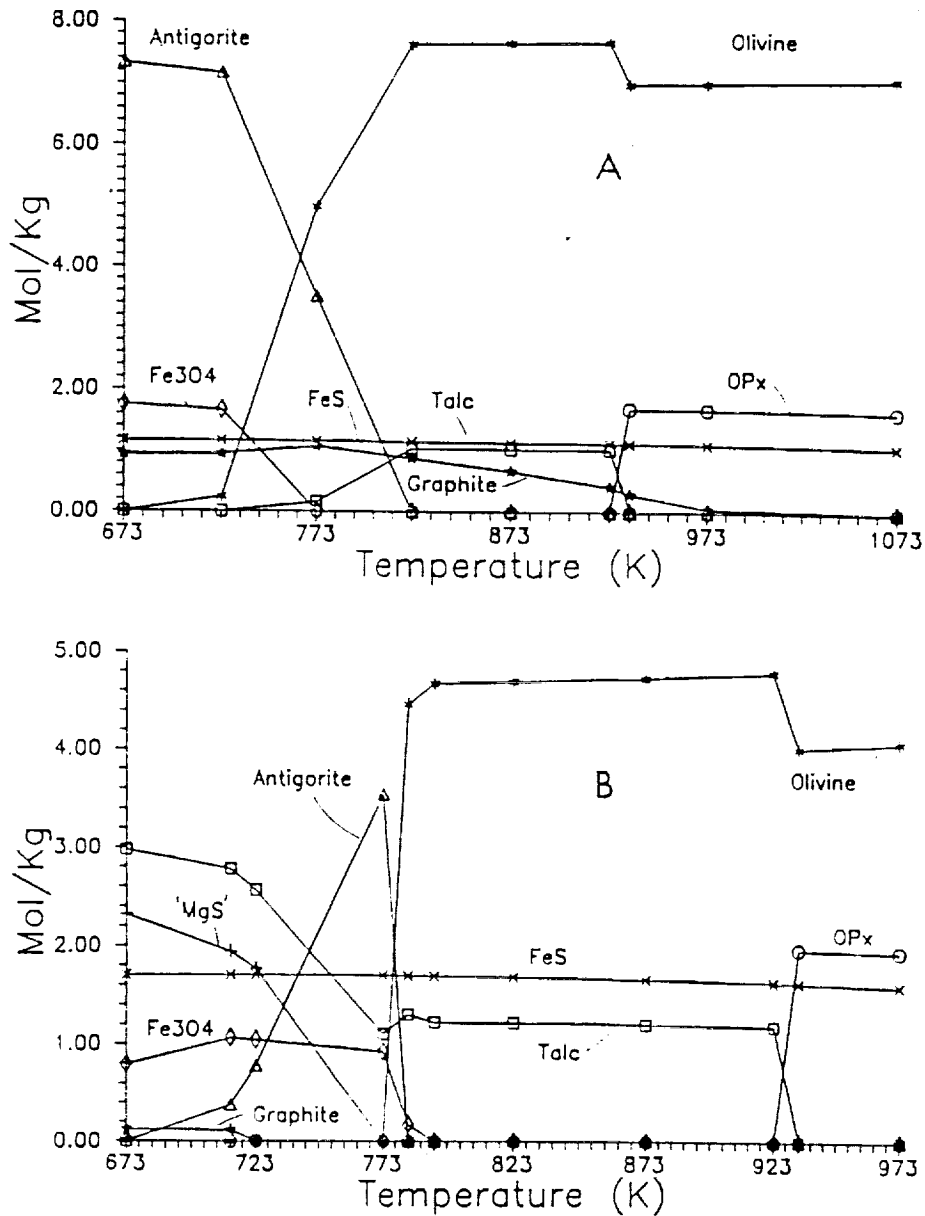
Fig. 1 Calculated modal abundances of minerals per kilogram of rock in (a) C1 and (b) C2 carbonaceous chondritic bulk compositions as functions of temperature at 2 Kb. The steps in the calculations are shown by symbols.

O₂, and SO₂ and COS as CO₂, and used the equivalent binary interaction parameters from Saxena and Fei (15).

Results

At 1 bar, the free energy minimization calculations do not yield any volatile bearing phase at T ≥ 400°C. At the present state of the thermochemical data, we do not believe that our calculations

are reliable at lower temperatures. Indeed, we find results at lower temperatures which do not seem to follow the systematics of the results obtained at higher temperatures. Thus, we have calculated the equilibrium phase assemblages at a pressure of 2 Kb so that the volatile bearing phases appear at higher temperatures. This procedure at least permits recognition of the major volatile bearing phases. Some of these phases may be re-
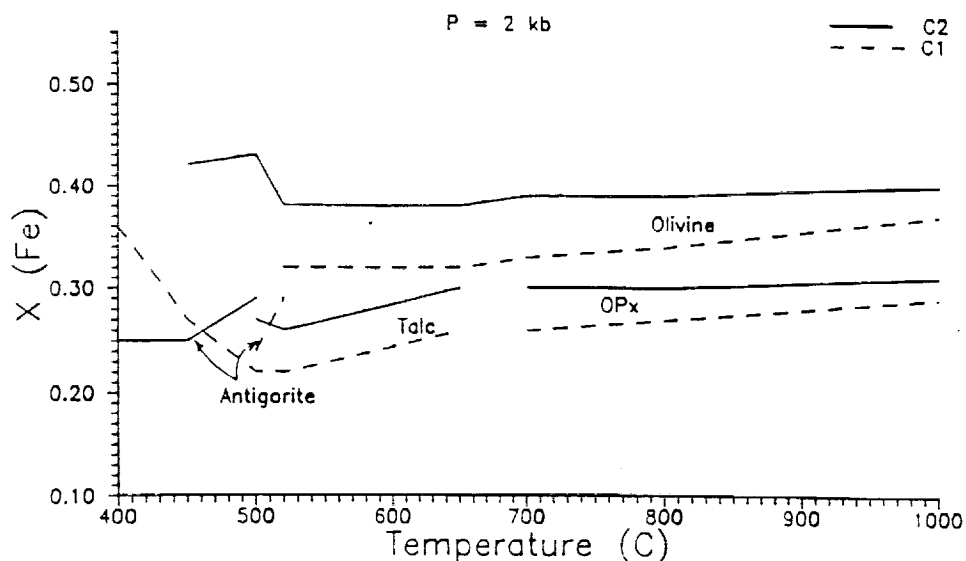
Fig. 2 Calculated compositions of the silicate phases in C1 and
C2 carbonaceous chondrites as functions of temperature at 2 Kb.

placed by more stable assemblages at lower temperature, but should reappear during heating experiment. The results, which are illustrated in Figure 1, show that the primary volatile bearing phases in the C1 and C2 bulk compositions are talc, antigorite ± magnesite. Talc is stable to around 650°C at 2 Kb, and dehydrates to orthopyroxene (OPx) at higher temperature according to Tc + Ol = 5 OPx + H₂O. Antigorite and magnesite crystallize at T < 550°C, but magnesite is absent in C2 bulk composition at T ≥ 400°C. FeS is a stable phase at all temperatures investigated in this work. We, however, did not consider the formation of sulfate or pyrrhotite. Magnetite becomes a stable phase at T ≤ 500°C. Elemental sulfur found in C1 chondrite is invariably associated with pyrrhotite ($Fe_{1-x}S$) (5). This suggests decomposition of troilite (FeS) to pyrrhotite and sulfur.

Figure 2 shows the compositions of the ferromagnesian phases as function of temperature at 2 Kb for the C1 and C2 bulk compositions. Calculations at 1 bar also yield similar compositions. The observed compositions of these phases in the carbonaceous chondrites vary widely in Fe/Mg ratio. One way to achieve this diverse Fe/Mg ratio is by aqueous alteration which seems to be a characteristic of the carbonaceous chondrites. Fe^{2+} fractionates very strongly into an aqueous phase relative to the silicates (18). Thus, varying degrees of equilibration with an aqueous phase could lead to a spectrum of Fe/Mg compositions of the ferromagnesian sili-

cates. Aqueous alteration may not be the sole reason, but is likely to be an important contributing factor in the development of variable Fe/Mg ratio of the ferromagnesian silicates in carbonaceous chondrites.

The abundances of volatile species in equilibrium with the solids per kilogram of total mass of C2 chondrites are illustrated in Figure 3. Figures 3a and 3b illustrate the molar and mass abundances, respectively, as functions of temperature at 1 bar. It should be noted that the total mass of the volatiles do not change above 400°C, which means that under equilibrium condition C2 chondritic material will completely devolatize if heated above 400°C. The total yield of the volatile is about 14% of the initial mass of C2 chondrites. The change in the abundance of various species above 400°C is due to homogeneous reactions within the fluid phase. Above 550°C, hydrogen has the highest molar concentration in the vapor phase. Hydrogen is a very good propellant and reducing agent which may thus be preferentially extracted by heating the C2 chondritic material to T > 550°C.

In contrast to the C2 chondrites, the volatiles given off by C1 material above 400°C consist essentially of H₂O and CO₂ at 1 bar pressure. Per kilogram of material, the total yield of volatile is about 306 grams of which nearly 60 wt% is H₂O.

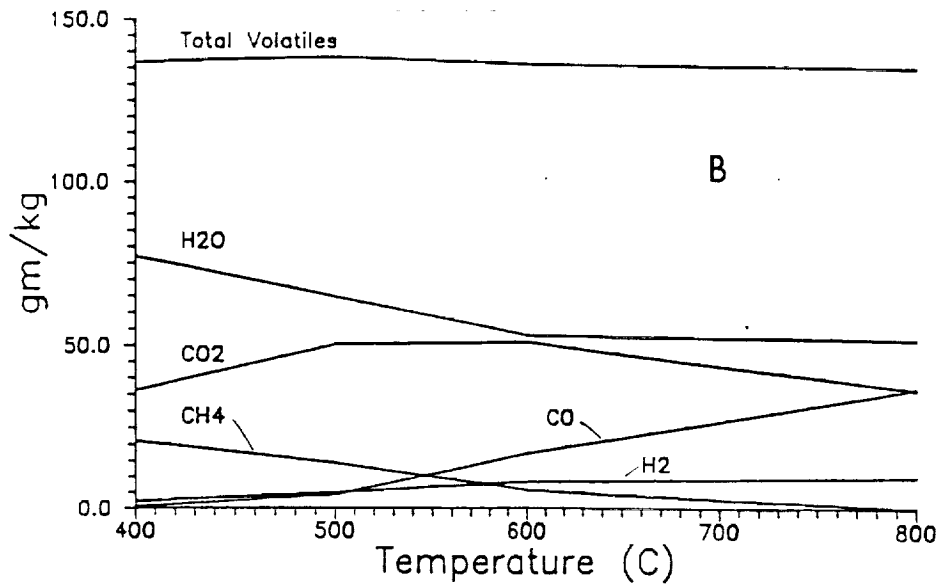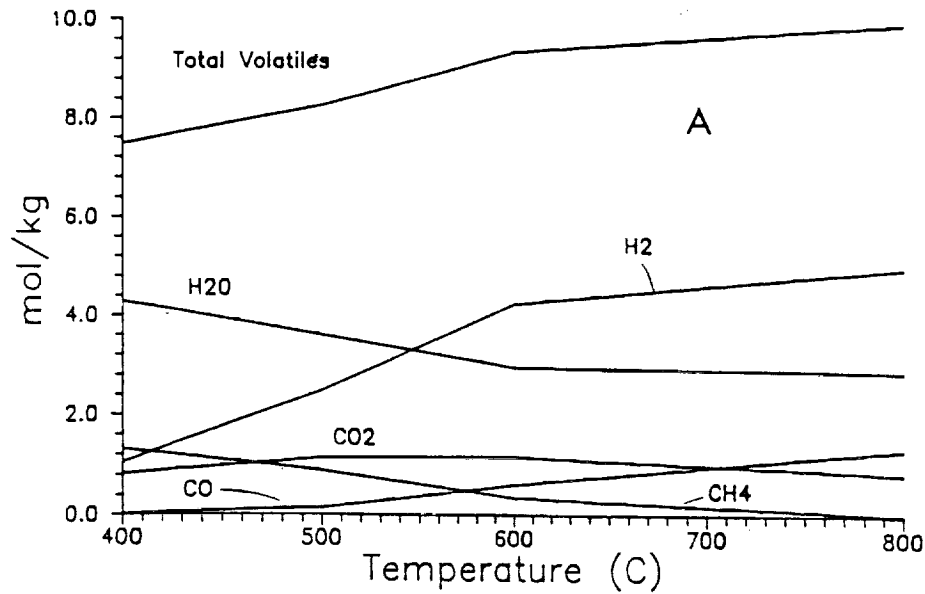The above results are subject to considerable uncertainties owing to the

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Fig. 3 Calculated equilibrium (a) molar and (b) mass abundances of the volatile species per kilogram of C2 chondritic material.

approximate nature of the thermochemical properties of the phyllosilicate solid solutions, and also since we have ignored the effects of surface free energy on the formation of extremely fine grained crystals. Further, carbonaceous chondrites of any given type do not have homogeneous compositions, but instead probably represent agglomeration of materials formed at different conditions at different parts of the solar system. However, these calculations are still useful in providing an idea of the relative stabilities, as well as upper stabilities of the volatile bearing phases and their average abundance. It is interesting to note that recent reflectance spectroscopic studies of carbonaceous chondrites seem to corroborate the predictions made above as to the nature of the most abundant hydrous phases (Gaffey, pers. comm.).

Kinetics of Devolatilization

The equilibrium calculations presented above provide a framework for the

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$$7Talc \rightarrow 3Anth + 4Qz + 4H_2O$$
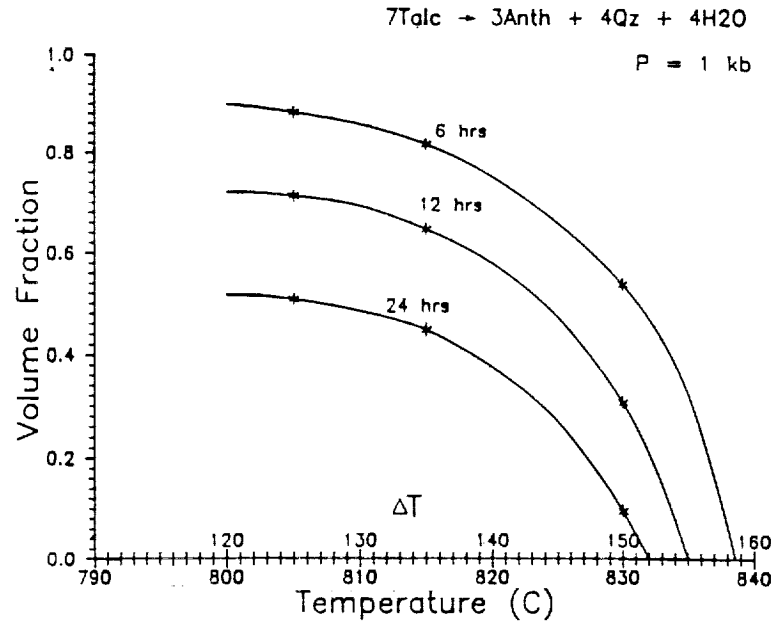
P = 1 kb

Fig. 4 Dehydration of talc as functions of time, temperature and extent of overstepping above the equilibrium dehydration boundary at 1 Kb. Volume fraction is that of talc remaining after reaction. Experimental data points, shown by asterisks, are from Greenwood (19).
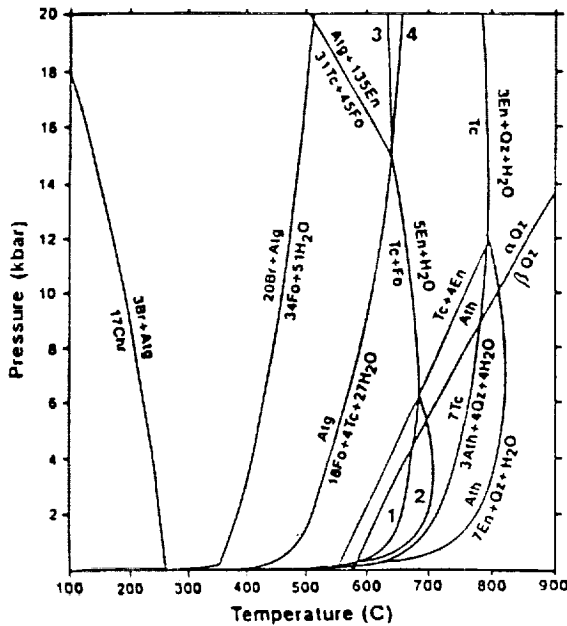

Fig. 5 Equilibrium relations of talc, antigorite and brucite along with other minerals in the system $MgO-SiO_2-H_2O$. Reproduced from Evans and Guggenheim (21).

evaluation of the volatile as well as some mineralogical resource potential of C1 and C2 carbonaceous chondrites. The actual extraction of volatiles as a function of temperature and heating rate, however, depends on the kinetics of the devolatilization process. For kinetic analysis, it is essential to identify the minerals in which the volatiles are most likely to be structurally bound. The above results suggest that talc, antigorite and magnesite are likely to be the major volatile bearing phases in carbonaceous chondrites.

Except for pure Mg-talc, there are no kinetic data for the other volatile bearing phases. The dehydration kinetics of talc was determined by Greenwood (19). At a given temperature, the rate of reaction depends on the rate constant, K', and the extent of departure from the equilibrium boundary. This is expressed in transition state theory (20) according to the relation Rate = K'(1-exp(nΔG/RT)), where n is a constant, commonly assumed to be unity, and ΔG is the Gibbs free energy of the reaction at the P,T condition of interest. Figure 4, which is constructed from Greenwood's experimental data, illustrates the dehydration kinetics of talc as functions of time, temperature and extent of overstepping (ΔT) above the equilibrium dehydration boundary at 1 Kb. It is evident from this figure that essentially complete dehydration of talc can be achieved within

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6 hours at about $160^{\circ}C$ above the equilibrium boundary.

The stability fields of the pure Mg-end members of various phyllosilicates of interest in this study are summarized for the condition of $P_{total} = P_{H2O}$ in Figure 5, which is reproduced from Evans and Guggenheim (21). According to our results, talc and other phyllosilicates completely dehydrate at $\geq 400^{\circ}C$ at 1 bar in C1 and C2 bulk compositions. This is compatible with the phase relations shown in Figure 5. Thus, based on the results shown in Figure 4, one would anticipate that essentially complete dehydration of all phyllosilicates in C1 and C2 chondritic material is likely to be achieved in a matter of a few hours at $T \geq 600^{\circ}C$. Detailed studies of the devolatilization kinetics of both phyllosilicates and carbonates as functions of temperature, fluid composition, and grain size are currently under way to evaluate the practical limitations of the extraction of volatiles from carbonaceous chondritic materials.

Acknowledgments

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