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

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N91-25222

Abstract

Carbonaceous chondrites are usually believed to be the primary constituents of near-Earth asteroids and Phobos and Deimos, 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 H₂, H₂O, CH₄, CO₂ and CO. The relative abundances of these volatile species change as functions of temperature, and on a molar basis, H₂ 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% H₂O and 40 wt% CO₂. 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 (C1) and C2 (or CM) classes. However, the grain size of the volatile bearing phases are often too small (100 to 1000 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 co-existing 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) ₂ SiO ₄	(8)
Orthopyroxene	(Mg,Fe)SiO ₃	(8)
Periclase	(Mg,Fe)O	(23)
Quartz	SiO ₂	(17)
Cristobalite	SiO ₂	(17)
Hematite	Fe ₂ O ₃	(23)
Magnetite	Fe ₃ O ₄	(23)

Hydrous and Carbonate Phases

Anthophyllite	(Mg,Fe) ₇ Si ₈ O ₂₂ (OH) ₂	(8,27)
Talc	(Mg,Fe) ₃ Si ₄ O ₁₀ (OH)	(8)
Antigorite	(Mg,Fe) ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂	(8)
Chrysotile	(Mg,Fe) ₃ Si ₂ O 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)

<u>Vapor Phase</u>	C-O-H-S	(15,16,17)
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Species: H₂O, CO₂, CH₄, CO, O₂, H₂S, S₂, SO₂, 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 confined 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°) 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 Robie²⁺ and Hemingway (10) for the Mg- and Fe²⁺-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°) for Fe-talc and Fe-antigorite at 1 bar, 298 K are -4477.18 and -4784.0 KJ/mol of Fe²⁺, 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 $\text{Fe}_{27}\text{Si}_{36}\text{O}_{86}(\text{OH})_{26}$ as compared to that of $\text{Fe}_{27}\text{Si}_{36}\text{O}_{90}(\text{OH})_{18}$ for Fe-talc, and greenalite with a stoichiometry of $\text{Fe}_{48}\text{Si}_{32}\text{O}_{80}(\text{OH})_{64}$ compared to $\text{Fe}_{48}\text{Si}_{34}\text{O}_{85}(\text{OH})_{62}$ for Fe-antigorite. Anovitz et al. (12) have recently determined ΔG_f° of minnesotite and greenalite from phase equilibrium data. Their results, ΔG_f° (minnesotite) = -4577.78 KJ and ΔG_f° (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 (TU) 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 Fe²⁺- 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 $T > 600^\circ\text{C}$, 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 H₂S behave as H₂O, S₂ as

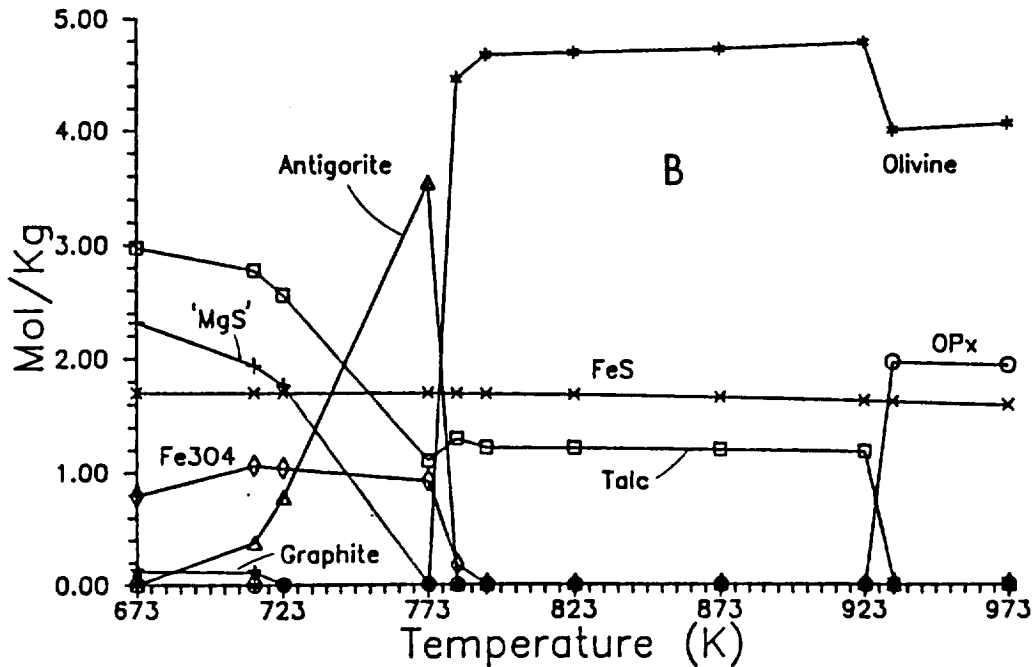
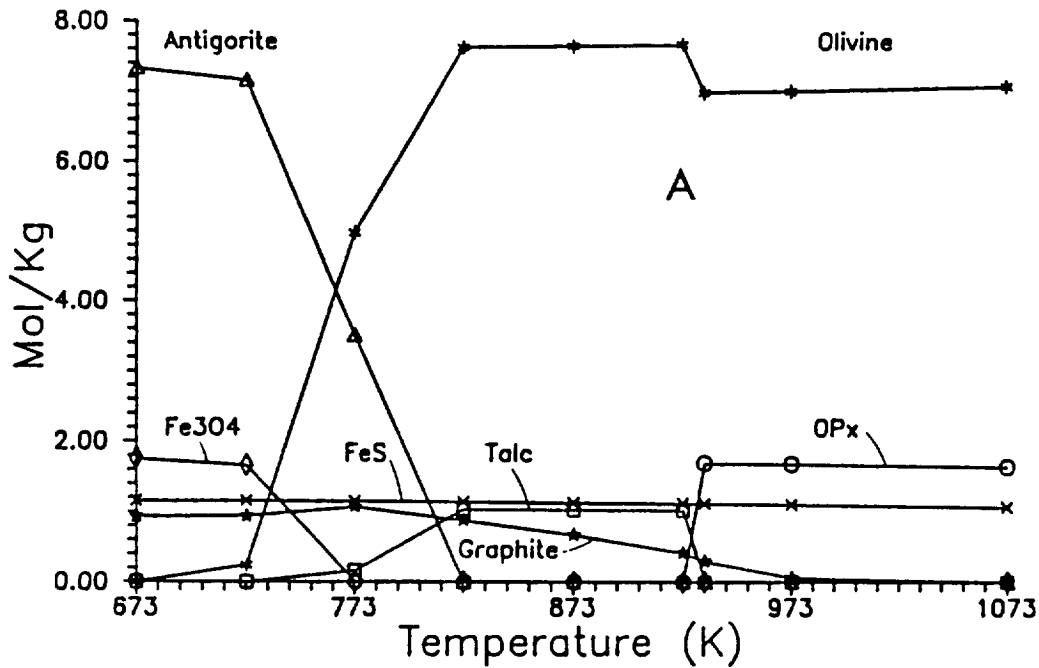


Fig. 1 Calculated modal abundances of minerals per kilogram of rock in (a) C1 and (b) C2 carbonaceous chondritic bulk compositions as functions of temperature at 2 Kb. The steps in the calculations are shown by symbols.

O_2 , and SO_2 and COS as CO_2 , 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 $T > 400^\circ C$. 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-

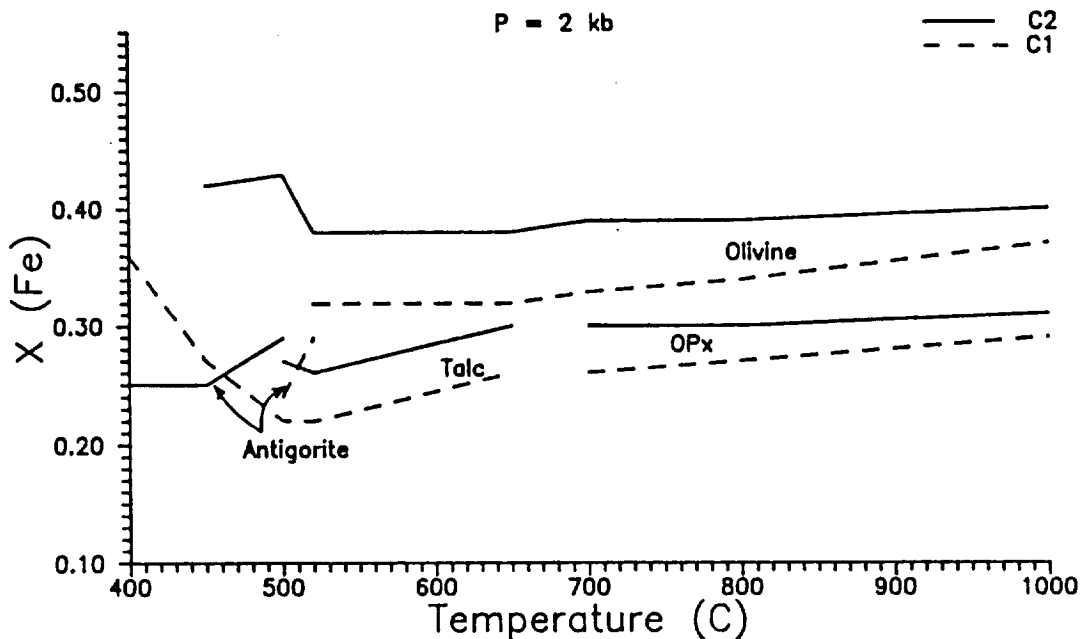


Fig. 2 Calculated compositions of the silicate phases in C1 and C2 carbonaceous chondrites as functions of temperature at 2 Kb.

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 $Tc + Ol = 5 OPx + H_2O$. Antigorite and magnesite crystallize at $T < 550^\circ C$, but magnesite is absent in C2 bulk composition at $T \geq 400^\circ C$. 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 $T \leq 500^\circ C$. 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 devolatilize 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 $T > 550^\circ C$.

In contrast to the C2 chondrites, the volatiles given off by C1 material above 400°C consist essentially of H_2O and CO_2 at 1 bar pressure. Per kilogram of material, the total yield of volatile is about 306 grams of which nearly 60 wt% is H_2O .

The above results are subject to considerable uncertainties owing to the

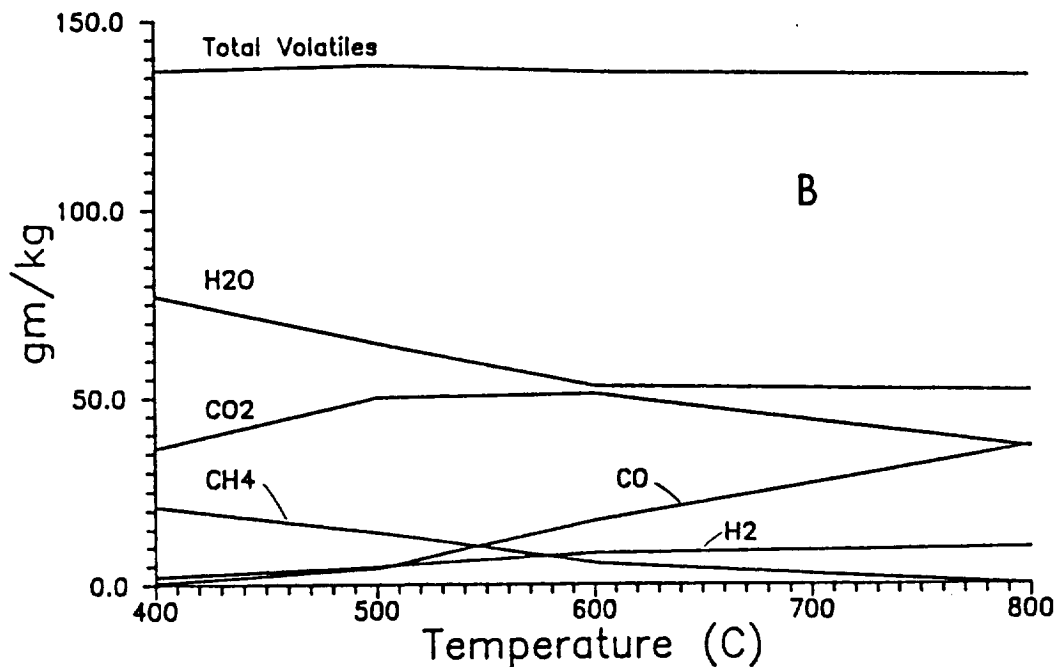
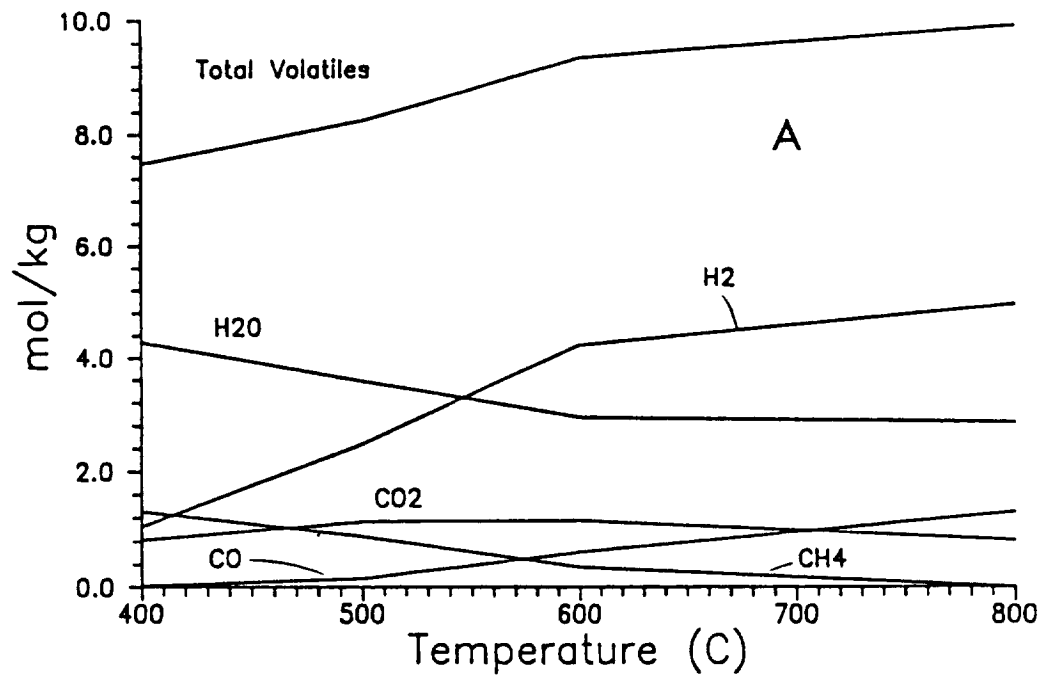


Fig. 3 Calculated equilibrium (a) molar and (b) mass abundances of the volatile species per kilogram of C₂ chondritic material.

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

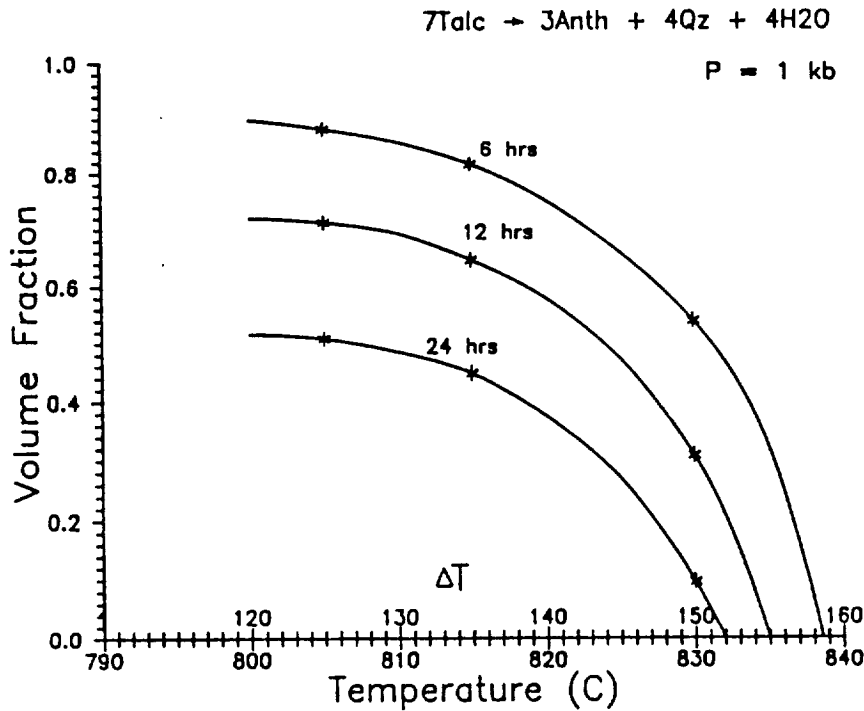


Fig. 4 Dehydration of talc as functions of time, temperature and extent of overstepping above the equilibrium dehydration boundary at 1 Kb. Volume fraction is that of talc remaining after reaction. Experimental data points, shown by asterisks, are from Greenwood (19).

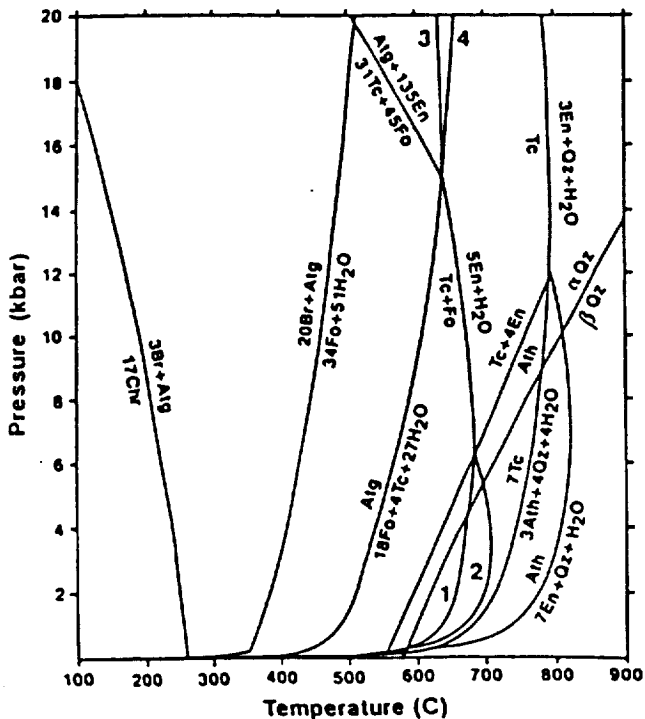


Fig. 5 Equilibrium relations of talc, antigorite and brucite along with other minerals in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$. Reproduced from Evans and Guggenheim (21).

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 $\text{Rate} = K(1 - \exp(-n\Delta G/RT))$, 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

6 hours at about 160°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 $P_{\text{total}} = P_{\text{H}_2\text{O}}$ in Figure 5, which is reproduced from Evans and Guggenheim (21). According to our results, talc and other phyllosilicates completely dehydrate at $\geq 400^\circ\text{C}$ 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 $T \geq 600^\circ\text{C}$. 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

This research was supported by a NASA grant NAGW-1332 administered through the Center for Utilization of Local Planetary Resources at the University of Arizona. Thanks are due to Professor John Lewis for his invitation to join the NASA project and helpful discussions, to Dr. Larry Anovitz for making available his thermochemical data for minnesotaite and greenalite before publication, and to Dr. Nilanjan Chatterjee and Kunal Bose for their help in the preparation of the manuscript. The skillful production of the manuscript in camera ready form by Jo Ann Overs is greatly appreciated.

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