



Coupled organic synthesis and mineral alteration on meteorite parent bodies

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Abstract—The hypothesis that the soluble fraction of the organic compounds present in carbonaceous chondrite meteorites was formed during aqueous alteration of the parent body was tested with mass-transfer, reaction-path calculations. In these calculations, we start with likely compositions of the original parent body and asteroidal fluids that are far from thermodynamic equilibrium, and metastable and stable equilibrium constraints are imposed as the total Gibbs free energy of the parent body environment is minimized. The results of these calculations suggest that the classes of soluble organic compounds present in carbonaceous chondrite meteorites could have formed during relatively low temperature aqueous alteration of the meteorite parent body or bodies. The main controls on the potential for synthesis and transformation of organic compounds were the oxidation state of the rock/fluid system, the bulk composition of that system, and the temperatures that were achieved during the alteration event or events. It also appears that the alteration mineral assemblages were influenced by the presence of soluble organic compounds and reaction among them.

INTRODUCTION

The CM and CI carbonaceous chondrites display evidence, in the form of hydrated phyllosilicate, carbonate and sulfate minerals, and replacement and vein textures, of having experienced relatively low temperature aqueous alteration on their parent body or bodies. Despite the alteration, the relative elemental composition (with the exception of volatile elements such as H, C, N, and O) of most carbonaceous chondrites is very close to the solar abundances (Anders and Ebihara 1982; Anders and Grevasse 1989), implying that these meteorites have not experienced significant element loss during the approximately 4.5 Gyr since their formation. Therefore, it is generally acknowledged that carbonaceous chondrites are samples of the early solar system. As such, they present an opportunity to study processes that occurred early in the solar system's history, a record that has long since been erased on Earth.

Although the carbonaceous chondrites are depleted in volatiles relative to the Sun, they do have a relatively high volatile-element content, including carbon, which is present at concentrations of 0.3 to >3.0 wt% (Cronin et al. 1988; Cronin and Chang 1993), and water, which comprises between 3 and 11 wt% (Sears and Dodd 1988). The carbon is present mostly

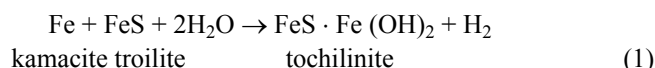
in the form of an extensive suite of organic compounds. The bulk of the organic carbon present in meteorites is in a complex, insoluble, macromolecular form, likened by many to kerogen found in terrestrial samples. Soluble forms of organic material are present in the Murchison meteorite at a concentration level of around 600 ppm (Cronin et al. 1988; Cronin 1989), and there is a great variety of organic compound classes represented. It has been suggested that the soluble fraction of the organic material formed during the same aqueous alteration events that produced the mineral assemblages (Bunch and Chang 1980; Chang and Bunch 1986; Shock and Schulte 1990; Schulte and Shock 1994). The processes that led to the formation of the complex organic assemblages in carbonaceous chondrite meteorites may be analogous to organic synthesis processes on the early Earth. If aqueous alteration is involved, any body in the solar system that has ever hosted liquid water may have experienced organic synthesis.

To date, efforts to model parent body processes have focused on the alteration of the mineral phases (Zolensky et al. 1987, 1989; Bourcier and Zolensky 1991, 1992; Rosenberg et al. 2001). Here, we consider the relationship between the appearance of alteration minerals and the soluble organic components observed in carbonaceous chondrite meteorites.

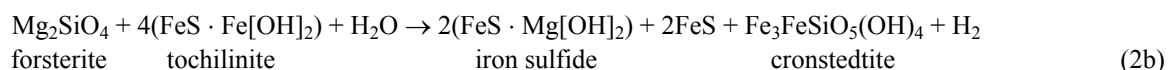
THE EVIDENCE FROM CARBONACEOUS CHONDRITES

Petrologic Observations

The petrography of the carbonaceous chondrite meteorites demonstrating evidence of aqueous alteration processes occurring on the parent body is well-documented (see reviews by Nagy [1975], Zolensky and McSween [1988], and Brearly and Jones [1998]), although some of these features can be attributed to nebular processes (Bischoff 1998; Ciesla et al. 2003). In an attempt to unravel the history of the processes responsible for the current state of this class of meteorites, Tomeoka and Buseck (1985) described the aqueous alteration scenario on the parent body of the Murchison meteorite in four stages, and more recently, Lauretta et al. (2000) presented a series of reactions based on the Tomeoka and Buseck (1985) model. Our interpretation of the reactions involved are summarized below, along with a more detailed description of what we believe occurred. First, kamacite (an iron-nickel alloy mineral) reacted with a sulfur-rich fluid inside chondrules and within the matrix (Hanowski and Brearly 2001) to produce a phase Tomeoka and Buseck (1985) called FESON, an acronym for the iron, sulfur, oxygen, and nickel it contains. FESON has been shown by Mackinnon and Zolensky (1984), Zolensky and Mackinnon (1986), and Zolensky (1984, 1987) to be a mineral named tochilinite, an interstratified Fe-Ni sulfide and Fe-Mg hydroxide. Therefore, we propose that this first stage of alteration can be represented by:



The naturally occurring minerals are represented in this reaction by ideal end member compositions to clarify the processes involved. Reaction 1 is likely to closely represent



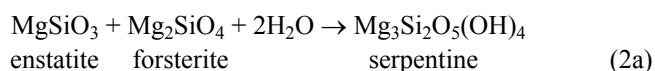
The combined result of Reactions 2a and 2b is that brucite and iron sulfide layers in tochilinite combine to form more Mg-rich tochilinite as the serpentine minerals appear in the alteration assemblage. It is possible that a portion of the serpentines and tochilinite become interlayered to form what Tomeoka and Buseck (1985) refer to as "Phase A," shown by Mackinnon and Zolensky (1984) to be an as-yet unnamed mineral that is composed of alternating layers of serpentine and tochilinite.

Notice that Reaction 2a does not involve the formation of $\text{H}_2(\text{g})$ and, therefore, cannot constrain the redox state of this stage. Reaction 2b, however, does involve the evolution of $\text{H}_2(\text{g})$ and could be used to track the redox state. Since Reaction 2b also involves the formation of Fe-rich serpentine containing trivalent iron (Fe^{+3}), we suggest that

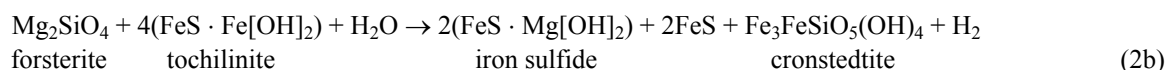
the natural process because kamacite is composed primarily of iron (with only up to 7 wt% or 6.66 mol% nickel; Van Schmus and Wood 1967; Sears and Dodd 1988), and although tochilinite contains a variety of cations within its structure, the iron (Fe^{+2})-bearing variety is the most common one found in carbonaceous chondrites. In Reaction 1, we have assumed that the source of sulfur for the sulfur-rich fluid is the dissolution of troilite, a common iron sulfide mineral in chondritic meteorites, including carbonaceous chondrites (Sears and Dodd 1988).

Notice that $\text{H}_2(\text{g})$ is a product of Reaction 1. Therefore, the hydrogen fugacity (f_{H_2}) could be calculated from the equilibrium constant for this reaction. If that was possible, it would serve to track the redox state of the processes involved in the early stage of aqueous alteration of the Murchison meteorite. The hydrogen fugacity can be used to couple the processes involved in the mineral alteration with the alteration thought to have affected the organic composition of the Murchison meteorite. Since this first stage involves reactions with native metals and sulfides, it probably took place at conditions more reducing than any of the stages that follow.

The second stage of Tomeoka and Buseck's scenario involves the formation of much of the present matrix, which is predominantly Fe- and Mg-serpentines together with tochilinite that is slightly more Mg-rich than that formed in the first stage. Tomeoka and Buseck (1985) propose that these phases form through aqueous alteration of olivines, pyroxenes, and the previously formed iron-rich tochilinite. We represent this second stage in two parts, one involving the hydration of Mg-olivine and Mg-pyroxene and the other involving Mg-olivine and the iron-rich tochilinite. Therefore, there are two reactions:



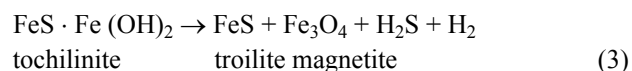
and:



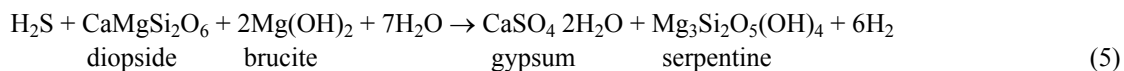
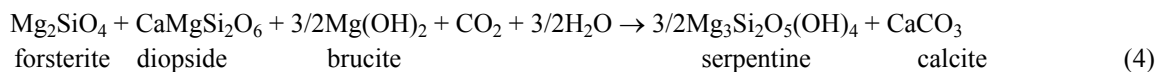
this second stage of alteration is somewhat more oxidizing than stage 1.

The third stage described by Tomeoka and Buseck (1985) is a mechanical mixing stage ("regolith gardening") whereby the tochilinite and serpentines become poorly crystalline. Based on the discussion in the literature, it appears that no chemical reactions occur in this stage.

The final stage of Tomeoka and Buseck's scenario is one in which the tochilinite reacts to produce serpentines, magnetite, troilite, and pentlandite and in which serpentines mix and exchange cations. The reaction of tochilinite to produce sulfides and oxides can be represented by:



Again, this reaction has been written for ideal end member compositions of some of the phases. For example, tochilinite is assumed to be strictly an Fe-bearing variety, and pentlandite, an iron-nickel sulfide, is simplified to an iron-only sulfide. Reaction 3, which we have written to represent what Tomeoka and Buseck describe for this stage, involves the formation of $H_2(g)$. Until data for tochilinite are available, it is unclear how the fH_2 corresponding to Reaction 3 relates to that for Reaction 2b.



Such reactions are consistent with the observation of intergrown serpentines and calcite; thin, short, discontinuous veins of carbonates and sulfates throughout Murchison and other carbonaceous chondrite meteorites; the greater Mg content of the matrix with increased extent of alteration; and the increased degradation of tochilinite and intermixing of tochilinite with Mg-rich phyllosilicates in the final alteration products (McSween 1979a, b; Tomeoka and Buseck 1985; McSween 1987; Zolensky and McSween 1988; Browning et al. 1996).

This final stage of alteration that produces carbonate and sulfate minerals is likely to have been produced by the most oxidized of the fluids responsible for mineral alteration. Comparison of the reactants and products involved in Reactions 1, 2b, 3, and 5 suggests a relative trend of decreasing fH_2 over the full course of mineral alteration. It should be noted that Lauretta et al. (2000) have presented a series of reactions based on the Tomeoka and Buseck (1985) work that, while similar, differs in a number of details; their interpretation is based on their petrographic observations of the ALH 81002 CM chondrite. The most significant difference between their scenario and ours is that they do not include the generation of gaseous hydrogen during the mineral alteration.

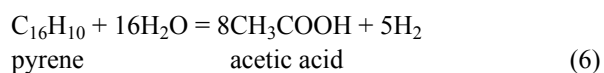
The Organic Connection

In light of the petrologic evidence of such pervasive alteration in carbonaceous chondrite meteorites, it is difficult to imagine that any organic material originally present did not also undergo extensive secondary processing. Indeed, recent work indicates a strong association between alteration minerals and organic matter in several carbonaceous chondrite meteorites (Pearson et al. 2002). Alternatively, if organic compounds were not initially present, they may have formed during the aqueous alteration event(s). Formation of the organic material in carbonaceous chondrites has been suggested to have occurred during aqueous phase alteration events on the parent body (Bunch and Chang 1980; Peltzer et

al. 1984; Chang and Bunch 1986; Shock and Schulte 1990). Although not accounted for by Tomeoka and Buseck, the very last stage of alteration may have involved the formation of carbonates and sulfates present in the Murchison meteorite and many other carbonaceous chondrites. Reactions leading to the formation of calcite and gypsum could have proceeded simultaneously with the reactions above (Barber 1981). The following reactions represent the formation of calcite and gypsum, respectively:

al. 1984; Chang and Bunch 1986; Shock and Schulte 1990). With redox conditions constrained by mineral assemblages and reactions, it would be possible to test whether these conditions are consistent with reactions that could have produced the organic compounds now present in carbonaceous chondrites. As a guide, we refer mostly to the Murchison meteorite, which contains numerous organic compounds, including amino acids, carboxylic acids, hydroxy acids, hydrocarbons (aliphatic and aromatic), nitrogen-bearing compounds, including urea and heterocycles (e.g., quinoline), alcohols, amines, amides, ketones, aldehydes, and insoluble organic carbon (Cronin et al. 1988).

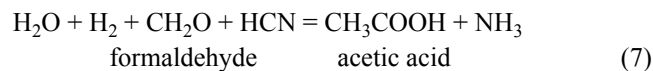
The nature of the original carbon present in the parent body is controversial. Shock and Schulte (1990) chose polycyclic aromatic hydrocarbons (PAHs) as starting compounds for model calculations. PAHs are thought to form in the molecular envelopes of red giant stars (Frenklach et al. 1989) and may be present in comets (Cronin et al. 1988). Therefore, they could have been incorporated into a meteorite parent body. PAHs are also found in hot-water extracts of the Murchison meteorite. An example of reactions to form other organic compounds from PAHs is:



The product of this reaction, acetic acid, has been detected in the Murchison meteorite (Yuen et al. 1984). As shown by Shock and Schulte (1990), there may have been a thermodynamic drive to form acetic acid, and other aqueous organic compounds, during aqueous alteration. Notice that Reaction 6 involves H_2 . Therefore, this reaction will be affected by, and affect reactions involved in, the mineral alteration that also includes hydrogen gas. Linking reactions of this type with mineral alteration reactions through fH_2 illustrates the interdependence of organic and inorganic reactions during aqueous alterations processes.

Another reasonable starting point is a volatile composition consistent with the volatile content of the outer asteroid belt, presumably in the form of a melting mixture of

ices; as such, it would consist of an aqueous solution of CO, CO₂, simple organic compounds, N₂, and NH₃ (Cronin et al. 1988; Fegley 1993). Cometary volatile compositions have also been proposed (e.g., Bunch and Chang 1980), and these ices would likely contain volatiles as simple organic compounds, HCN, CO, CO₂, and NH₃ (Fegley 1993). An example of a reaction to form the constituents of carbonaceous chondrite organic material from these "simpler" starting materials is:



Notice that hydrogen gas is a reactant here instead of being a product, as in the cases of all of the mineral alteration reactions considered above. This suggests that mineral alteration by fluids derived from cometary ice may drive the generation of acetic acid and other organic compounds from molten ice. As in the case of Reaction 6, constraints placed on the hydrogen fugacity by the mineral reactions will affect Reaction 7 as well. Also, notice also that ammonia is produced in Reaction 7. The presence of ammonia in Murchison is manifest by nitrogen-bearing organic compounds like amino acids and the possible presence of ammoniated minerals of undetermined composition (Kung and Clayton 1978).

Alteration Conditions

The great abundance of hydrated silicate and carbonate minerals in the Murchison and other meteorites provides compelling evidence (corroborated by oxygen isotope data) that aqueous geochemical processes occurred on the CM parent body. The conditions attending the mineral and organic alteration of carbonaceous chondrites has been the subject of a lot of attention. DuFresne and Anders (1962) were the first to attempt to place constraints on the source of the fluid, oxidation state, pH, and temperatures of the alteration of carbonaceous chondrites. They concluded that the temperature was near 25 °C, the pH was between 6 and 10, the Eh was less than −0.2 V, the fluid contained various amounts of NH₃, CO₂, SO₂, and minor H₂S, and the processes occurred near equilibrium. Bunch and Chang (1980) explicitly addressed the concept of aqueous organic chemistry on parent bodies and concluded only that formation of water-soluble organic compounds is consistent within the context of the mineral alteration at temperatures less than 125 °C. They further suggested that the parent body contained some cometary material that was responsible for the source of the fluid and dissolved volatiles. Based on mineral phase relations, Zolensky (1984) concluded that the presence of tochilinite constrains the alteration to low temperature (less than 170 °C), Eh to much less than 0 V, pH to 10–12, and a high partial pressure of S₂. Computer models by Zolensky et al. (1989) led them to suggest that the conditions of alteration

were temperatures of 1–150 °C, Eh of −0.3 to −0.8 V, total solution carbon of at least 10^{−2} m, pH of 7–10, and wide ranges of water/rock ratios.

Oxygen isotope data (Clayton and Mayeda 1984) suggest that the temperatures of alteration were 20 °C or less for Murchison (and other CM chondrites) with water/rock ratios of approximately 1:2 by volume, while the CI group experienced higher temperatures (as much as 140 °C) and larger volumes of water (approximately 1:1 by volume). It is possible that these results reflect the final steps of alteration and do not preclude earlier alteration events at higher temperatures that may have been subsequently overprinted (Grimm and McSween 1989). Other attempts to determine the temperatures of alteration have resulted in estimates of 85 °C for the CI group and 105–125 °C for the CM group (Hayatsu and Anders 1981).

Grimm and McSween (1989) investigated the thermal evolution of carbonaceous chondrite parent bodies and discuss the possible heating sources that could have increased in temperature on the parent body, melted the ice, and raised the temperature of alteration. They concluded that two heating mechanisms are the most feasible: solar electromagnetic induction and the decay of ²⁶Al, a short-lived radionuclide (half-life = 0.75 Myr). Although they were concerned with constraining the alteration temperatures to those determined by the oxygen isotope data of Clayton and Mayeda (1984), their results do not preclude much higher temperatures being reached during the heating events responsible for the aqueous alteration.

CONCEPTUAL MODEL

To determine the feasibility that the soluble fraction of the organic matter present in carbonaceous chondrites formed during aqueous alteration of the parent body or bodies (Bunch and Chang 1980; Chang and Bunch 1986; Shock and Schulte 1990; Schulte 1997; Sephton et al. 1998), we have conducted mass-transfer, reaction-path calculations that explicitly account for geochemical changes during the aqueous alteration events. Simultaneous solution of mass-action and mass-balance equations allows calculation of the distribution of aqueous inorganic and organic compounds and assemblages of stable mineral phases. Although the approach used for this study is general, much of the discussion will be influenced strongly by studies of the Murchison (CM2) meteorite.

In this paper, we describe results of geochemical models designed to test the likelihood that organic compounds found in the meteorite were formed by the same aqueous fluids responsible for the alteration of the primary, anhydrous minerals that originally coalesced to form the parent body. This work builds on our earlier efforts in this area (Shock and Schulte 1990) but represents a major improvement now that we can take explicit account of simultaneous mineral alteration and organic compound synthesis. In addition, we

have included many more groups of organic compounds in the calculations and have considered a wider variety of starting compositions for fluids and minerals.

Studies of a variety of environments suggest that formation of graphite, CH₄, and other stable equilibrium products from CO₂ is kinetically inhibited in natural systems (see Shock 1988, 1992). Furthermore, some of the alkane fraction extracted from the Murchison meteorite shows evidence of terrestrial contamination (Cronin and Pizzarello 1990), although the indigenous presence of many of these compounds in the meteorite has been firmly established. However, light hydrocarbons are often lost during extraction procedures, leading to suggestions of a period of heating and volatile loss on the parent body (Cronin and Chang 1993). Based on these considerations, the formation of graphite and light aliphatic hydrocarbons was suppressed during the model calculations to simulate metastable equilibrium states that are typically attained in geochemical systems (Shock 1988; Helgeson et al. 1993; Seewald 1994).

CONSTRAINTS ON PARENT BODY MINERAL AND FLUID COMPOSITIONS

Because of the extensive alteration of the mineral phases in carbonaceous chondrites, the original mineralogic and petrologic record has been largely eradicated, making it difficult to assess the initial conditions on the parent body before alteration occurred. However, a number of clues allow us to place constraints on the geochemical models. We have chosen to adopt an average bulk composition of the CM chondrite meteorites from Dodd (1981), Jarosewich (1971), and Fuchs et al. (1973) rather than rely on attempts to reconstruct the primary mineralogy (Browning and Bourcier 1998). Because the carbonaceous meteorites have retained approximately solar abundances of the major rock-forming elements, we assume that the bulk composition measured for these elements is representative of the original parent body composition. As a consequence, the models presented here are isochemical with respect to the major rock-forming elements.

A significant amount of water that may have been initially present is retained in hydrous silicate phases of carbonaceous chondrites, which contain up to 10 wt% H₂O (DuFresne and Anders 1962; Sears and Dodd 1988). Despite this fact, there is no direct record of the composition of the fluid involved in the alteration event or events, and searches for fluid inclusions in the mineral record of carbonaceous chondrites have not been successful (Rudnick et al. 1985; Zolensky and McSween 1988). We considered a range of water:rock ratios and have found that the results that most closely match the gross characteristics of the meteorites are for water:rock ratios on the order of 10:1 to 1:1 by weight.

It has been suggested that carbonaceous chondrites are the remains of devolatilized comets (see Anders [1975],

Cronin et al. [1988], and Zolensky and McSween [1988] for discussion and references). As such, their original fluid compositions would have been those of cometary ice, which has been studied by mass spectrometry and spectral instruments. The volatile composition of some comets has been measured (see review and summary by Fegley [1993]), and models similar to the ones described here for hydrothermal systems on Triton have been discussed using these ranges of volatile contents (Shock and McKinnon 1993). The idea that carbonaceous chondrites are fragments of comets has been convincingly challenged, however, and currently seems unlikely to be the case (Anders 1975; Zolensky and McSween 1988; Wetherill and Chapman 1988).

However, if it can be assumed that the carbonaceous chondrite parent body originated in the asteroid belt, thermodynamic considerations of condensation temperatures of volatile species (Prinn and Fegley 1989) can be used to further constrain approximate ice compositions, from which the parent body fluids would have been derived. The assumption that most meteorites, including the carbonaceous chondrites, originated in the asteroid belt is widely accepted (Barber 1985; Wetherill and Chapman 1988). The evidence indicating an asteroidal source outweighs problems associated with the idea. The lines of evidence include reflectance spectra taken for many asteroids that qualitatively resemble those of meteorites; orbital determinations based on photographic records of meteorite falls placing them in the asteroid belt; petrologic and geochemical constraints limiting the size of the body from which meteorites could be derived (with the exception of the SNC meteorites of putative martian origin and those demonstrably of lunar origin); and implanted solar gases, solar flare tracks, and microcraters indicating that the meteorites originated in the inner solar system (i.e., ruling out cometary derivation). Most reservations with total acceptance of the hypothesis are due to lack of quantitative matches between reflectance spectra of the most common meteorites (the ordinary chondrites) and those of the asteroids that are most likely their source (the S-type asteroids). This so called "spectrophotometric paradox" (Wetherill and Chapman 1988) appears to be satisfactorily explained, based on recent results from both the Galileo fly-by of Gaspra and Ida and the NEAR mission to Eros, as being due to the effects of space weathering (Chapman 1996; Clark et al. 2001; Nittler et al. 2001). On the other hand, the composition of the major rock-forming elements of Comet Halley measured by spacecraft agrees with that of carbonaceous chondrites to within a factor of two (Fomenkova et al. 1992), and secondary minerals indicative of aqueous alteration were determined to be present. Therefore, a cometary origin cannot be ruled out completely on these grounds.

The carbonaceous chondrites, because of their high volatile content and spectrophotometric similarities with C type asteroids (Wetherill and Chapman 1988), most likely originated in the outer asteroid belt. Water, in the form of ice,

would have condensed and been incorporated with dust into the parent asteroid of the carbonaceous chondrites (Prinn and Fegley 1989; Fegley 1993). The volatile elements C, H, N, and O also would have been incorporated into the parent asteroid (Prinn and Fegley 1989; Fegley 1993) in a variety of forms, including CO, N₂ (the most common forms of carbon and nitrogen, respectively, in the inner solar nebula), NH₃ (from grain-catalyzed reactions of N₂), and CH₄ (representing hydrocarbons and other organic compounds that may have formed in the solar nebula). Zolensky et al. (1989) calculated that the CO₂ content required to stabilize carbonates during aqueous alteration was at least 10⁻² molal. We have used a variety of starting fluid compositions to determine the effects of changing the relative amounts of C, H, N, and O in the asteroidal fluid. This, along with the observed depletion in volatile elements in the carbonaceous chondrites, implies that the volatile content was higher than presently measured in the meteorites; the volatiles may have resided in the ice/fluid and were subsequently lost during or after the alteration event(s). In addition, fluid compositions at the distance of the asteroid belt may have been much higher in volatile content than those assumed in these calculations, depending on the amount of cometary flux to the inner solar system (W. McKinnon, personal communication), the potential for incorporation of hydrogen and carbon as hydrocarbons or other organic compounds, and the mixing rates of volatiles throughout the solar nebula (Prinn and Fegley 1989; Fegley 1993).

On the other hand, since comets are unlikely to be the parent bodies of carbonaceous chondrites, C, H, N, and O contents of the fluids must be less than those of comets. The carbonaceous chondrites probably originated near the outer edge of the asteroid belt (Wetherill and Chapman 1988), and we have selected compositions of volatiles with the minimum range of cometary compositions as an upper bound, assuming that the more oxidized forms of volatiles (as listed above) are consistent with origin in the inner solar nebula. Within these constraints, the results of model calculations provide tests of fluid composition when compared with observations of the mineral and organic assemblages in the meteorites. We find that the form of the starting materials is less influential than the absolute abundance of the volatile elements. The potential for forming organic material is strongly controlled by the redox state of the system.

GEOCHEMICAL MODELS OF PARENT BODY AQUEOUS ALTERATION

Using the major element composition in Table 1 and various fluid compositions, we have minimized the Gibbs free energy for closed chemical systems using stable and metastable equilibrium constraints and simulated heating of the CM parent body to temperatures that may have been reached during the alteration process. Due to the nature of the

Table 1. Average bulk composition of the major elements of CM carbonaceous chondrite meteorites used in this study (from Jarosewich [1971] and Fuchs et al. [1973] as reported by Dodd [1981]).

Element	Composition (wt%)
Si	12.96
Ti	0.06
Al	1.17
Fe	21.56
Mg	11.72
Ca	1.32
Na	0.42
K	0.06
Ni	1.25
S	3.38
H	1.42
C	2.30
O	41.74
Total	99.36

calculations, the exact nature of the starting minerals and volatiles is not significant. The more important considerations are the bulk composition of the system and the redox and compositional disequilibrium between the "solid" material (i.e., the rock component) and the fluid with which it reacts. It is worth noting that reduced nitrogen, as well as additional carbon, has been added to the fluid composition. We explored a range of concentrations of each of these volatile components; the results described in this paper correspond to a total carbon and nitrogen abundance of 2 molal. We have modelled heating events on the parent body that raised the temperature of the system to temperatures as high as 200 °C; the pressure is sufficient in these calculations that boiling does not occur.

In these calculations, we have assumed a single episode of aqueous alteration, although textural evidence from the meteorites suggests that there was probably more than one (Richardson 1978; Tomeoka and Buseck 1985; Zolensky et al. 1987, 1993; Zolensky and McSween 1988) or that there may have been cycles or pulses of fluids (Benedix et al. 2003). Departures from equilibrium, caused by changes in the flow of fluid through pore spaces and/or dissipation of water from the parent body, also could result in the preservation of any or all of the minerals calculated to precipitate over the course of the reaction progress in preference to the final equilibrium assemblage.

The thermodynamic database used for this study is the most comprehensive available, especially in the number and variety of aqueous organic compounds included. Methods are available to estimate the thermodynamic properties of aqueous organic compounds (Shock and Helgeson 1990; Schulte and Shock 1993, Forthcoming; Shock 1995). This database was used with the EQ3NR and EQ6 software packages (Wolery 1992; Wolery and Daveler 1992) to conduct the reaction-path calculations described in the next section.

RESULTS AND DISCUSSION

Reaction-path calculations that simulate heating from the ice melting point to a number of temperatures yield calculated mineral and organic assemblages remarkably similar to those observed in the matrices of the carbonaceous chondrite meteorites. Below, we describe the results of these calculations.

Mineral Paragenesis

The calculations described here are equilibrium calculations. As such, they define where water/rock reactions are headed and reveal what can happen along the way. To compare these calculations with petrographic observations of meteorites, the scale of local equilibrium must be established. For the most part, overall equilibrium is rarely recorded in the meteorites at the thin section scale. In fact, it is more likely that the scale of local equilibrium may be at the scale of mineral grain boundaries. It is also possible that the parent body hydrothermal systems approached but did not reach equilibrium at any given temperature and that minerals that formed at higher temperatures during the alteration were protected against further destruction during the period when the parent body cooled. Model calculations that simulate alteration of the parent body as heating occurs to temperatures as high as 200 °C result in the equilibrium mineral assemblages shown in Fig. 1. Examination of this figure reveals that the equilibrium assemblages include serpentines, magnetite, chlorites, carbonates, talc, and sulfides.

At 2 °C, the calculated mineral assemblage consists predominantly of chrysotile (45.9%), followed in abundance by chlorite, greenalite, cronstedtite, troilite, carbonates, nickel, and biotite. Chrysotile is a magnesium-bearing serpentine, and greenalite and cronstedtite are iron-bearing phyllosilicates. The bulk of the carbonate calculated to form is calcite with minor amounts of magnesite and siderite, which is in agreement with the distribution of carbonate minerals in CM chondrites (Fuchs et al. 1973; Bunch and Chang 1980; Barber 1981; Zolensky and McSween 1988; Hanowski and Brearly 2001; Benedix et al. 2003). Clinocllore and daphnite are the chlorite minerals calculated to occur. Chlorites have long been suspected of being the “spinach phase” prevalent in CM chondrites (Zolensky and McSween 1988) and, indeed, have been positively identified in CM chondrites by Lauretta et al. (2000).

At 25 °C, the mineral assemblage is similar to the one at 2 °C, except that antigorite replaces chrysotile as the most abundant phase (47.6%) and the most abundant serpentine. In addition, cronstedtite is calculated to become more abundant than greenalite. The other minerals are approximately in the same proportions. The results at 50 °C are largely identical to those at 25 °C.

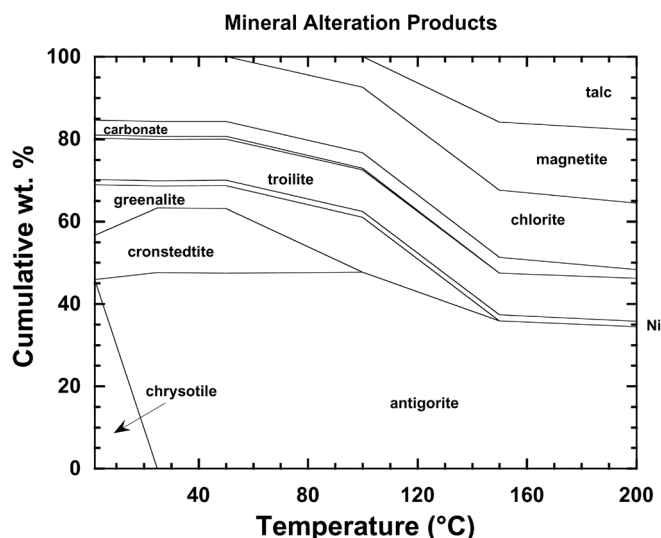


Fig. 1. Alteration mineral assemblages, in cumulative weight percent as a function of temperature for the reaction-path calculation of a carbonaceous chondrite parent body alteration.

Magnetite first appears in the calculation between 50° and 100 °C. At the same temperatures, cronstedtite no longer appears in the alteration mineral assemblage. There is a greater abundance of greenalite than previously calculated, but the remainder of the minerals are in roughly the same proportions as before. However, by 150 °C, greenalite and biotite are no longer in the alteration assemblage, and instead, talc appears. Magnetite becomes more abundant, while antigorite decreases in abundance (from roughly 50 wt% of the alteration assemblage to about 36 wt%), and the other minerals remain about the same. The results for 200 °C are nearly identical to those at 150 °C; however, at 200 °C, fayalitic olivine is calculated to begin forming. This result appears to be anomalous; however, recent work indicates that olivine does appear to form during aqueous alteration of the carbonaceous chondrites (Krot et al. 2000; Chizmadia et al. 2002).

These results are summarized in Fig. 1 and Table 2, where the calculated mineral assemblages at each final temperature are shown schematically. The formation of two of the phyllosilicate minerals (cronstedtite and chrysotile) is restricted to temperatures of 50 °C or below, suggesting that the presence of these minerals in CM meteorites limits the alteration temperatures. This agrees with previous temperature estimates for alteration of the CM meteorites, which have been interpreted as peak temperatures (Clayton and Mayeda 1984). However, the serpentines could form during cooling from higher temperatures. Alternately, these minerals could have formed at low temperatures and been preserved during further heating. It is reasonable to assume that a range of temperatures was reached during the alteration event, and this may be reflected in ranges of mineral stabilities, especially for the serpentine minerals.

Table 2. Mineral paragenesis results for the equilibrium geochemical model calculations described in the text, indicating the appearance of alteration phases.

Minerals	200 °C	150 °C	100 °C	50 °C	25 °C	2 °C
Magnetite	✓	✓	✓			
Nickel	✓	✓	✓	✓	✓	✓
Chlorite	✓	✓	✓	✓	✓	✓
Cronstedtite				✓	✓	✓
Chrysotile						✓
Troilite	✓	✓	✓	✓	✓	✓
Greenalite			✓	✓	✓	✓
Carbonate	✓	✓	✓	✓	✓	✓
Biotite			✓	✓	✓	✓
Antigorite	✓	✓	✓	✓	✓	
Talc	✓	✓				

These results generally agree with the alteration scenario described above. The presence of troilite at all of the temperatures considered is consistent with Reaction 1, in which primary troilite becomes incorporated into tochilinite (a layered sulfide-hydroxide mineral). The calculated dominance of chrysotile and antigorite among the alteration phases agrees with the mechanism proposed in Reaction 2a, while the calculated occurrence of cronstedtite, greenalite, and troilite agree with the mechanism proposed in Reaction 2b, which is presumed to be simultaneous with Reaction 2a. The final stage described by Tomeoka and Buseck (1985), which involves the formation of magnetite (as represented by Reaction 3) is restricted in the model to temperatures at or above 100 °C. This is in accordance with the higher temperatures suggested for the CI chondrites, which contain abundant magnetite, but contrary to peak temperature estimates for the CM chondrites. The presence of magnetite in CM chondrites (Fuchs et al. 1973; Bunch and Chang 1980; Barber 1981) may indicate that 100 °C temperatures were, in fact, reached during alteration of the CM group. The appearance of carbonate in the models along with serpentines is consistent with Reaction 4 and observations of CM chondrite matrices.

Organic Compound Synthesis

The organic compounds calculated to occur in the alteration sequence are also consistent with those observed in CM meteorites (summarized by Cronin et al. [1988] and Cronin and Chang [1993]). Alcohols, amino acids, carboxylic acids, ketones, hydroxy acids, amides, and amines all appear in the models during the alteration sequences, as summarized in Table 3. The carboxylic acids, amides, and metal-organic compounds dominate the speciation at all model temperatures. All other compound classes that were considered decrease in abundance with decreasing temperature, excluding the dicarboxylic acids, which are most abundant between 25 and 100 °C. Carboxylic acids, which are the most abundant soluble organic compounds present in the Murchison meteorite, are also the

most abundant soluble organic compounds calculated to form during the reaction-path calculations. Similarly, the calculated relative proportions of other organic compounds at all temperatures are generally in agreement with the relative abundances observed in the Murchison meteorite.

An example of the speciation of carbon in the fluid (as a percentage of the total amount of carbon in the system) as a function of temperature is shown in Fig. 2. The final temperature of this calculation is 200 °C, and it is representative of the approach toward equilibrium for each of the final temperatures considered. The dominant group of organic species at all temperatures are the carboxylic acids, and amides are the second most abundant compounds at temperatures to 150 °C. However, as can be seen from Fig. 2, the metal-organic complexes are calculated to increase in abundance at temperatures >150 °C. We note that shorter-chain compounds are calculated to be the most abundant for each class of compound (Fig. 3), especially at temperatures at or below ~125 °C. This is consistent with observations of decreasing concentration with increasing chain length for the soluble organic compounds extracted from the Murchison meteorite. The abundances of longer-chain organic compounds increase at temperatures above 125 °C. Furthermore, anionic forms of the organic acids tend to be more abundant than neutral analogues owing to the basic pH calculated in these models (see Fig. 4). This result is in agreement with previous estimates of pH during alteration (DuFresne and Anders 1962; Zolensky et al. 1989).

The reasons for the increased potential for organic synthesis during the alteration as temperature increases can be inferred from the plot in Fig. 5, which shows the logarithm of the hydrogen fugacity as a function of temperature. Also shown in this plot are the curves corresponding to values of $\log f_{H_2}$ set by mineral buffer assemblages; HM refers to the hematite-magnetite assemblage, the presence of which controls the hydrogen fugacity through the reaction:

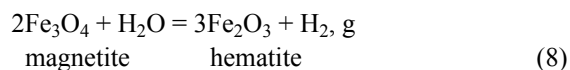


Table 3. Aqueous organic compound speciation results for the equilibrium geochemical model calculations described in the text. The number of plus signs indicate the total concentrations of each group of compounds according to the scale: +++++ = 10^{-2} molal, ++++ = 10^{-4} molal, +++ = 10^{-6} molal, ++ = 10^{-8} molal, and + = 10^{-10} molal.

Organic compounds	200 °C	150 °C	100 °C	50 °C	25 °C	2 °C
Carboxylic acids	+++++	+++++	+++++	+++++	+++++	+++++
Amides	+++++	+++++	+++++	+++++	+++++	+++++
Metal-organic	+++++	+++++	+++++	+++++	+++++	++++
Ketones	++++	++++	+++	++	++	+
Aldehydes	++	++	+			
Hydrocarbons	+++	+++	++	+	+	
Alcohols	++++	+++	+++	+++	++	++
Amines	++++	+++	+++	+++	+++	++
Hydroxy acids	+					
Amino acids	+	+	+			
Dicarboxylic acids	+	++	++	++	++	+
Esters	+	+				

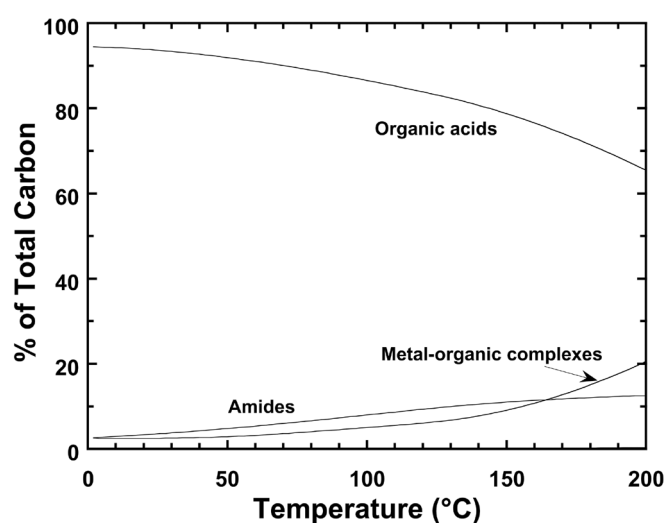
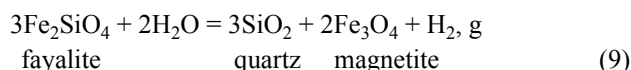
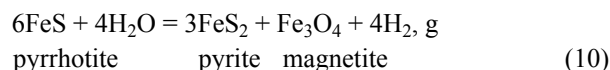


Fig. 2. Speciation of carbon (as a percentage of total carbon) during alteration of a carbonaceous chondrite parent body to 200 °C, as a function of temperature. Note that the bulk of the organic matter calculated at all temperatures is in the form of organic acids, consistent with observations from meteorites.

FMQ stands for the fayalite-magnetite-quartz assemblage, the reaction for which is:



and PPM represents the pyrite-pyrrhotite-magnetite assemblage, given by the reaction:



It can be seen that the alteration path becomes progressively more reduced relative to the mineral buffer values as temperature increases. The fluid is initially set to a $\log f_{\text{H}_2}$ value consistent with the hematite-magnetite mineral assemblage. As the fluid/rock system approaches equilibrium

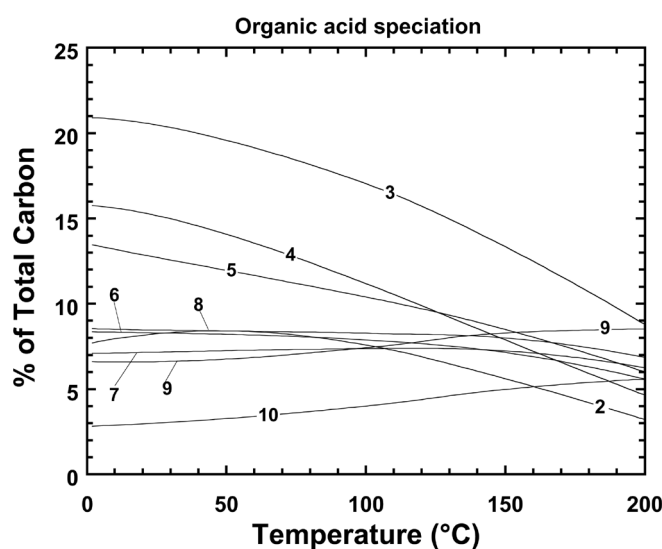


Fig. 3. Distribution of carbon among the carboxylic acids during alteration of a carbonaceous chondrite parent body to 200 °C, in terms of percentage of total carbon as a function of temperature. The numbers on the curves refer to all of the acids with the same number of carbons in the alkyl chain; for example, “3” refers to the sum of propanoic acid + propanoate.

at the final temperature, the hydrogen fugacity increases above the values set by the fayalite-magnetite-quartz mineral assemblage at about 75 °C. As discussed above, many of the mineral/fluid reactions likely to have occurred during the alteration could generate hydrogen, thus accounting for the increasing reducing power to create organic compounds from inorganic precursors.

Close examination of Table 3 reveals that the formation of detectable concentrations of amino and hydroxy acids is not favored during the alteration until the temperatures approach 100 °C and 200 °C, respectively. How can this result be reconciled with the oxygen isotope data indicating peak alteration temperatures of approximately 20 °C (Clayton and Mayeda 1984)? There are a number of possibilities. First, it is

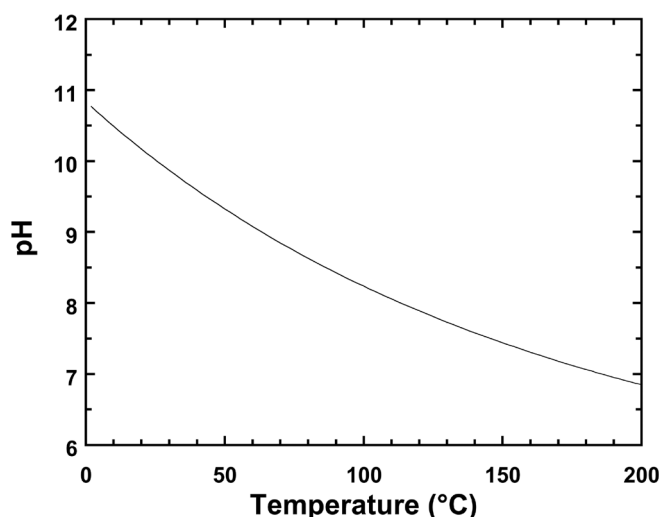


Fig. 4. pH as a function of temperature during the alteration of a carbonaceous chondrite parent body to 200 °C.

possible that the oxygen isotope data were interpreted with inappropriate assumptions. Because experimental data for water-phyllsilicate oxygen isotope fractionation are not available for the phases that occur in the CM meteorites, Clayton and Mayeda (1984) compared the calcite-water fractionation to either estimated values or data for allegedly similar phyllosilicate minerals to obtain the alteration temperature estimates. Taking these considerations into account, however, would likely result in lower temperature estimates (Clayton and Mayeda 1984). Second, and perhaps more likely, the temperature recorded by the oxygen isotopes may indicate only the last temperature at which the isotopes were able to equilibrate as the parent body cooled. If so, some organic products of the alteration, like amino acids, may have been preserved and not affected by subsequent cooling, heating, or aqueous alteration events. It is possible that this question could be resolved if more detailed information was gathered on the spatial relationships between the mineral and organic components of the meteorites. Work by Pearson et al. (2002) indicates that there is a strong relationship between phyllosilicate particles and organic matter in carbonaceous chondrites. Such information may resolve the relative timing and extent of alteration of the various components involved in the alteration. This may also be evidence that more extensive fluid flow (as described in the model of Young et al. [1999]) could transport organic compounds formed at one temperature and incorporate them in silicate alteration products at another location that did not experience the same temperature range.

The results of these geochemical models indicate that the alteration of the CM parent body occurred at temperatures perhaps as high as ~150 °C at a water/rock ratio greater than 1 and involved a fluid with concentrations of carbon and nitrogen greater than 0.1 molal. The fluid was initially more oxidizing than the rock, the pH of the fluid was much greater

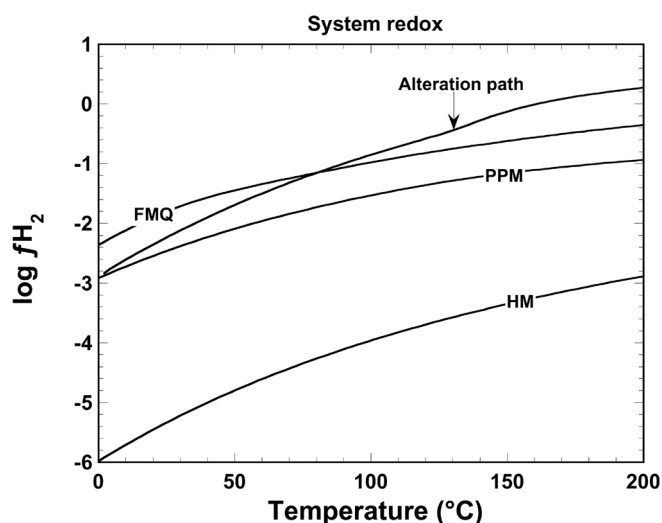


Fig. 5. Oxidation state, in terms of the logarithm of the hydrogen fugacity, as a function of temperature during the alteration of a carbonaceous chondrite parent body to 200 °C. HM indicates values of $\log f_{H_2}$ set by the hematite-magnetite mineral assemblage, PPM indicates values of $\log f_{H_2}$ set by the pyrite-pyrrhotite-magnetite mineral assemblage, and FMQ indicates values of $\log f_{H_2}$ set by the fayalite-magnetite-quartz mineral assemblage (see text).

than neutral, and the inherent disequilibrium between the rock and the fluid was the drive for the formation of alteration minerals and organic compounds. Our results also suggest that a great deal of volatiles were lost during or after the alteration of the CM parent body. Furthermore, organic compounds exert influence on the nature of the alteration by supplying or consuming reducing agents such as hydrogen or oxidizing agents such as oxygen, forming metal-organic complexes, and changing the pH of the fluid by acid-dissociation and association reactions. The high concentrations of carbon- and nitrogen-bearing constituents, suggested by these calculations to be in the fluids reacting with the rock to produce a diverse suite of soluble organic compounds, are inconsistent with the fact that carbonaceous chondrites are depleted in these volatile elements, implying that the depletions occurred during or after the aqueous alteration history of the parent bodies was complete.

These results are consistent with our earlier work (Shock and Schulte 1990) and do not preclude the possibility that the original source of the carbon for the soluble organic compounds was pre-existing macromolecular organic material (Sephton et al. 1998). In fact, Sephton et al. (1998) conclude that both the formation of higher molecular weight compounds from simpler molecules and the production of smaller molecules from larger precursors contributed to the observed “free organic inventory” of the Murchison meteorite. This scenario would also help explain the isotopic composition of various organic components of the Murchison meteorite. For example, the alteration of PAH (polycyclic aromatic compounds) to produce amino acids requires isotopically heavy carbon and nitrogen in the aqueous phase

(Shock and Schulte 1990). On the other hand, isotopic trends in other components (light hydrocarbons $\delta^{13}\text{C} = +2.4$ to $+9.2\%$, Yuen et al. 1984; carboxylic acids $\delta^{13}\text{C} = +4.5$ to 22.7% , Yuen et al. 1984; and amino acids $\delta^{13}\text{C} = +5$ to $+44\%$ and $\delta^{15}\text{N} = +90\%$, Cronin and Chang 1993) appear to indicate that they could not have originated from macromolecular precursors. However, these trends may reflect metastable equilibria among these compounds and redox reactions involving either macromolecular organic precursors and isotopically heavy carbon and nitrogen in the aqueous phase or only isotopically heavy, simple precursors. Either case would be consistent with the carbon isotopic composition of CO_2 ($\delta^{13}\text{C} = +29\%$, Yuen et al. 1984), carbonates ($\delta^{13}\text{C} = +20$ to $+80\%$, Sephton et al. 2003) and “extractable nitrogen” ($\delta^{15}\text{N} = +70$ to $+98\%$; Cronin and Chang 1993) from Murchison.

CONCLUDING REMARKS

Organic chemistry on carbonaceous chondrite parent bodies demonstrates the pervasive nature of organic compounds throughout the solar system. These samples of the early solar system record ancient processes that led to the formation of biologically significant compounds and show the influence of bulk composition, oxidation state, and temperature on the processes that may have also operated on the early Earth and contributed to the emergence of life. Furthermore, they represent clear snapshots captured during or after hydrothermal alteration on a primitive object and demonstrate the common nature of such processes in the solar system, much like hydrothermal systems on Earth.

The calculations described in this study also point out how reactions involving organic compounds are inextricably linked with the inorganic components with which they co-exist. The formation and transformation of organic compounds strongly influences the conditions of alteration during fluid/rock interactions (Schulte 1997). The calculated occurrence of a wide variety of aqueous organic compounds is consistent with the presence of the diverse suite of organic compounds observed in carbonaceous chondrite meteorites like Murchison. These results suggest that a great deal of volatile elements were lost during or after the aqueous alteration events that produced them.

Additional models of this type could test reaction pathways to see if relative concentrations of various groups of organic compounds are consistent with the mineral assemblages present in Murchison. The framework outlined here should make it possible to test whether a Strecker synthesis mechanism for amino and hydroxy acids (Peltzer et al. 1984; Cronin et al. 1993; Cronin and Pizzarello 1997) is consistent with the type and extent of mineral hydration recorded in the meteorite. Also, it would be possible to explore the entire range of fluid compositions that can be derived from known cometary compositions and hypothetical

asteroidal fluids. In this way, we can generalize, from the results described here, processes that could occur throughout the asteroid belt and on icy satellites.

Because of the easy potential for synthesis of organic compounds in hydrothermal systems (Shock and Schulte 1998), the introduction of intact organic compounds by comet or meteorite impacts may have been a major source of C, H, O, N, and S to the early Earth (Oró 1961; Anders 1989; Zhao and Bada 1989; Chyba et al. 1990; Zahnle and Grinspoon 1990; Chyba and Sagan 1992; Huebner and Boice 1992; Oberbeck and Aggarwal 1992; Steel 1992; Tingle et al. 1992). The normal geologic consequences of water-rock reactions are to transform these organic compounds under metastable or stable states depending on the temperature of alteration, the oxidation state, and the bulk composition of the system. Such a scenario could potentially provide a mechanism to reconstitute organic material that may have been destroyed during impact. This is especially true if life did, in fact, originate on the early Earth in an environment like present-day submarine hydrothermal systems, as appears probable or even likely (Corliss et al. 1981; Woese 1987; Schulte and Shock 1995).

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