

EARLY ALTERATION OF MATRICES IN PARENT BODIES OF CI/CM CARBONACEOUS CHONDRITES: KINETIC-THERMODYNAMIC MODELING. M. Yu. Zolotov¹ and M. V. Mironenko²,

¹School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404; e-mail: zolotov@asu.edu. ²Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia; e-mail: mironenko@geokhi.ru.

Introduction: Fine-grained matrices of CI and CM carbonaceous chondrites are mainly presented by hydrated and oxidized minerals [1-4] that could have formed through alteration of anhydrous and reduced precursors. Matrices are dominated by Mg-rich phyllosilicates and contain cronstedtite (in CM chondrites), tochilinite (in CM), magnetite (mostly in CI), secondary sulfides, carbonates, sulfates, organic matter and presolar grains. Primordial phases could have been presented by ~1 μm size grains of forsterite, low-Ca pyroxene, kamacite, troilite and amorphous silicates that formed in the solar nebula [e.g., 5]. Although some hydration and oxidation could have been possible in local nebular environments [6], the majority of aqueous alteration occurred on parent asteroids that accreted water ice together with mineral particles [e.g., 7,8].

Release of radioactive heat from short-lived radionuclides caused melting of ice shortly after accretion [9,10]. Initial alteration occurred at ~0°C or below [11] in the presence of water ice. Very early fluids could have been acidic [12], possibly because of dissolution of HCl hydrates that accreted with ice [11]. The composition of aqueous fluids was mainly controlled by dissolution and precipitation of solids. Aqueous oxidation of kamacite and schreibersite led to production of H₂ that preferably separated into the gas phase [e.g., 13,14]. Diffusion of H₂-rich gas toward the surface could have prevented explosive disruption of typical asteroids until pressure (P) reached ~10² bar [15]. Here, we evaluated the timing of water-solid reactions that drove an early evolution of matrices and corresponding aqueous solutions.

Approach: Aqueous alteration of individual primary solids in matrices was investigated through numerical modeling. The model includes pH-dependant dissolution kinetics of primary and secondary solids [16], the oxidation rate of Fe-rich metal by liquid H₂O, as well as chemical equilibration among solutes, precipitates and dissolved gases. At each time step, dissolution rates are computed at the current solution pH and surface area of specific mineral grains. In the model, secondary phases form through dissolution of primary minerals, all species in aqueous solution are in chemical equilibrium and secondary precipitation is controlled by solubilities of solids. A thermodynamic block of the model is based on the GEOCHEQ code [17], which uses the Gibbs free energy minimization

method to calculate equilibria. We used this approach to model acid weathering of basalts [18].

Alteration was modeled for $T = 0^\circ\text{C}$ and total $P \leq 10^2$ bar in the system H-O-Fe-Mg-Ca-Al-Si-Na-K-S-Cl-C. The system was open with respect to H₂ to model H₂ removal. Fugacity (f) of H₂ was equal to total P . The bulk composition of matrices was assumed to be solar and the original mineralogy was represented by forsterite, enstatite (low-Ca pyroxene), diopside, feldspars, Fe-rich metal and troilite. Initial carbon matter was presented by insoluble polyaromatic polymer. We explored effects of mineral grain size, a degree of grain's exposure to aqueous solution, water/rock (W/R) mass ratio and $f\text{H}_2$. Nominal calculations were performed for 1 μm grains and W/R ratio ≥ 0.1 -1 that corresponds to O isotope data [e.g., 19]. Freshly melted water was represented by 0.044 molal HCl solution [cf. 11]. Initial solution also contained CO (10⁻⁵ molal) added to represent water-soluble carbon compounds (CO₂, methanol etc.) accreted with ice. Formation of CH₄ and other light hydrocarbons was suppressed because of the inhibition of their formation at low T .

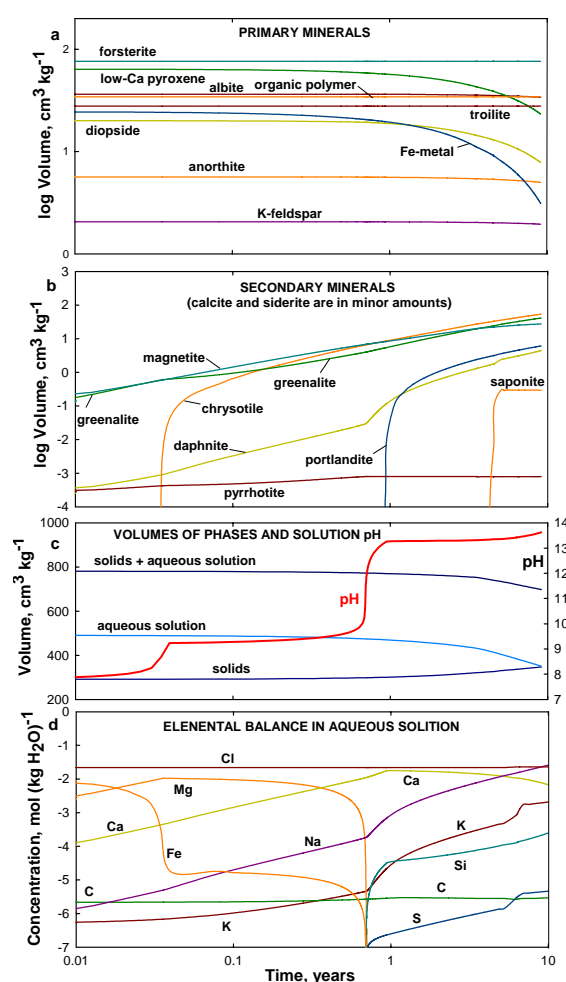
Results and discussion: Modeling demonstrates rapid oxidation of Fe⁰-metal via reaction $3\text{Fe}^0 + 4\text{H}_2\text{O}(\text{liq.}) = \text{Fe}_3\text{O}_4 + 4\text{H}_2(\text{aqueous/gas})$. Fe-rich metal, low-Ca pyroxene, diopside and feldspars alter faster than forsterite. The abundance of troilite does not change much, as exemplified in Fig. 1a. At early stages of alteration, magnetite and Fe-rich serpentine minerals (e.g., greenalite) are major secondary phases (Fig. 1b). Formation of these Fe-minerals is accounted for by oxidation of metal and high Fe(II) concentrations in the aqueous phase (Fig. 1d). At later stages, significantly altered matrices mostly consist of Mg-Fe-serpentine, magnetite, Ca-Na-K-Fe bearing saponite, a Fe(II)-chlorite, some pyrrhotite and mostly unaltered troilite and polyaromatic polymer. Formation of tochilinite could have needed longer time while significant organic transformations required higher temperatures. (Tochilinite and cronstedtite yet to be considered). Some of the following minor phases were also observed in calculated assemblages: amesite, andradite, portlandite, brucite, talc, calcite, siderite and cohenite (at high $f\text{H}_2$). At later stages, magnetite partially dissolves and reduces, and Fe goes to phyllosilicates and fayalite, which can form before consumption of solution [cf. 14].

Table 1. Modeled concentration (mole/kg H₂O) of major species in typical aqueous solution in contact with partially altered matrix minerals of CM/CI chondrites*

Na ⁺	0.15	NaHSiO ₃	2.4E-3
Cl ⁻	8.7E-2	H ₂	2.3E-3
OH ⁻	8.6E-2	NaCl	1.1E-3
K ⁺	7.7E-3	HSiO ₃ ⁻	1.7E-4
Ca ⁺²	4.9E-3	KOH	1.0E-4
NaOH	4.7E-3	pH=13.7	

*0°C, 10 bar total pressure, $f_{H_2} = 10$ bar.

Fig. 1. Changes in mineralogy and solution composition during very early aqueous alteration of matrix minerals in CI/CM chondrites (0°C, 10 bar total P , $f_{H_2} = 10$ bar, $W/R=0.5$, 10% of grain surface area is exposed to solution).



Total volume of solids increases in time, while the amount of solution decreases because of hydration and H₂ formation (Fig. 1c).

Rapid neutralization of the original acidic fluid leads to an alkaline solution with pH > 12. Variations in pH and solution composition are affected by precipitation of secondary phases. At very early low-pH

stages, Cl⁻, Fe²⁺, Mg²⁺, and Ca²⁺ were the dominant solutes. At advanced alkaline stages, Na⁺, Cl⁻ and OH⁻ dominate (Table 1). Carbon is mostly presented by carbonate aqueous species. Sulfur is in sulfide form (HS⁻ + S²⁻).

Although timing of alteration depends on several factors, major alteration of micron-sized grains at 0°C could occur within ~10²-10³ yr. Alteration is slower at larger grain sizes, higher W/R ratio and lower exposure of grains to solution [cf. 18]. At $W/R \sim 0.1$ and micron-sized grains, solution could be completely consumed in ~10 years. The timescales shown in Fig. 1 represent a fast alteration scenario. However, changes in rock volume (Fig. 1c) could have decreased effective surface area and make alteration slower.

Summary: The models demonstrate that matrix mineralogy and fluid composition evolved dramatically during the first ~10³ yr after beginning of ice melting. Early phyllosilicates were Fe-rich and more oxidized. Pervasive alteration of micron-sized mineral particles led to alkaline NaCl-rich aqueous solutions that slowly approached equilibrium with secondary phases. At low W/R ratios, alteration was terminated by consumption of solution.

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