ORTHOPYROXENITE HYDROTHERMAL ALTERATION PATHWAYS: LOW VS. HIGH TEMPERATURE

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Much of the debate about the possibility that there is evidence in ALH84001 for life on Mars will hinge on determining the origin of the carbonate in that meteorite. There are presently at least two schools of thought concerning the origin of the ALH84001 carbonate. One idea is that the carbonate formed at very high temperature (>650°C) [1,2]. Evidence used for this temperature determination is the solid-solution chemistry of the carbonates. It was observed that many of the ALH84001 carbonate analyses coincided with determinations of terrestrial carbonate solid-solutions if the temperature of deposition was >650°C [2]. This temperature is consistent with formation from a fluid with a mole fraction of CO_2 (X_{CO2}) in excess of 85%. These conditions render impact-driven metasomatism as a likely candidate for the carbonate formation process. In this case evidence for life in ALH84001 is highly unlikely.

The other proposal for the origin of the ALH84001 carbonate suggests a much lower temperature of deposition [3]. The evidence supporting this hypothesis comes from carbon and oxygen isotopic analyses. Specifically the $\delta^{18}O$ analysis shows a fractionation between the carbonate and host-rock resulting in an estimate of hydrothermal deposition in a thermally decaying system with a maximum temperature ~80°C. Recent research has proposed a maximum temperature of 250°C [4]. The $\delta^{13}C$ values of the carbonate suggest the system was in contact with the atmosphere [3,4]. This evidence is one of the pillars supporting the plausibility of evidence in ALH84001 for life on Mars.

These lines of evidence are contradictory. To test whether either explanation is plausible, we have conducted theoretical models of hydrothermal alteration of an orthopyroxenitic rock using established methods of geochemistry [5-7]. During aqueous alteration of an orthopyroxenite, there are many possible outcomes, dependent on temperature, pressure, fluid composition and extent of equilibration. There are, however, two endmember possibilities that should be easily distinguished. One path leads to an anhydrous assemblage, the other to a hydrous assemblage. These two possibilities can be generalized by the carbonation reaction

$$MgSiO_3 (Enstatite) + CO_2 \Rightarrow MgCO_3 (Magnesite) + SiO_2 \quad (1)$$

or a hydration reaction such as

$$MgSiO_3 + SiO_2 + H_2O \Rightarrow Mg_3Si_4O_{10}(OH)_2 (Talc). \quad (2)$$

Talc represents one of several hydrous products, including serpentine, that may form depending on temperature. The alteration of ALH84001 appears to be anhydrous [1-3], so pathway (1) is of interest. This implies that either talc (or other hydrous minerals) did not form or was replaced during alteration by the reverse of reaction 2 or via

$$Mg_3Si_4O_{10}(OH)_2 + 3CO_2 \Rightarrow 3MgCO_3 + 4SiO_2 + H_2O. \quad (3)$$

As in the case of reaction (1) the extent to which this reaction proceeds depends on the X_{CO2} in the fluid.

Figure 1 shows a Temperature vs. X_{CO2} diagram for the system of interest, assuming SiO_2 to be quartz. At equilibrium,

magnesite and enstatite can coexist without talc only in the field labeled Q-E-M. At 7 kbars and 650°C, this requires a $X_{CO2} > 0.75$. The invariant point, labeled 1 in the figure, moves to lower temperature and higher mol fraction of CO_2 at lower pressure, reducing the size of the field where enstatite is in equilibrium with magnesite and quartz. However, if the carbonate in ALH84001 did not form in equilibrium with the pyroxene, then equilibrium T-X diagrams may only provide maximum temperatures.

At first glance, the lack of hydrous phases in the alteration assemblage might be thought to rule out a low temperature origin for the carbonate. However, there are combinations of temperature and CO_2 partial pressure (P_{CO2}) that are consistent with anhydrous alteration. Figure 2 shows the relevant system at 75°C. This figure shows the activity of silica in the fluid vs. the ratio of the activity of Mg^{+2} to H^+. The solid lines represent saturation curves for minerals of interest. At equilibrium without CO_2, the fluid composition is constrained to plot within the field denoted by the heavy solid lines. The dotted horizontal lines (A & B) indicate the saturation state of magnesite for two different P_{CO2}'s. In both cases, the range of fluid compositions is further constrained. It can be seen that for a specific value of P_{CO2} (167 mbars for this case) the magnesite saturation line crosses the point of intersection of the talc and quartz saturation lines; this value can be called the critical value of CO_2 for anhydrous alteration. Any solution in equilibrium with $P_{CO2} > 167$ mbars can not reach talc saturation, and the resulting alteration should be anhydrous.

Exploring the sequence of alteration at low temperature, various P_{CO2} values, and water to rock ratios (W/R), can be accomplished with mass transfer calculations for 75°C as seen in Figure 3A-F. Figure 3A vs. 3C shows a comparison of alteration calculations with values of P_{CO2} below and above the critical value. In 3A P_{CO2}=150 mbars and the assemblage is dominated by talc. In 3C (P_{CO2}=200 mbars) the system is prevented from reaching talc saturation with the resultant assemblage dominated by quartz and magnesite. Figures 3B-D show that W/R (from 0.1 to 10) at 75°C has little effect on the final alteration products; the assemblages are nearly identical. This means that an anhydrous alteration assemblage could have been produced in a hydrothermal system with a high W/R. Figures 3E (P_{CO2}=500 mbars) vs. 3C demonstrate that above the critical value of P_{CO2}, there is very little difference in alteration products. From these calculations it can be seen that at low temperatures the X_{CO2} (see Table) can be substantially lower than that needed for the equivalent anhydrous alteration at high temperatures.

Figure 3 also shows effects of temperature on orthopyroxenite alteration. Calculations for higher temperature alteration are shown in Figures 3F-H. Figure 3F (150°C) is remarkably similar to 3A; in both cases the P_{CO2}
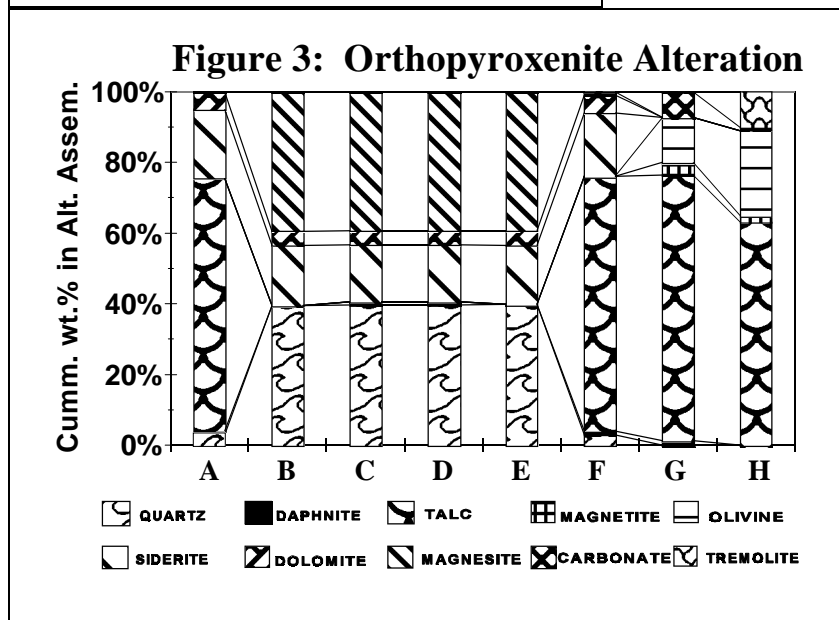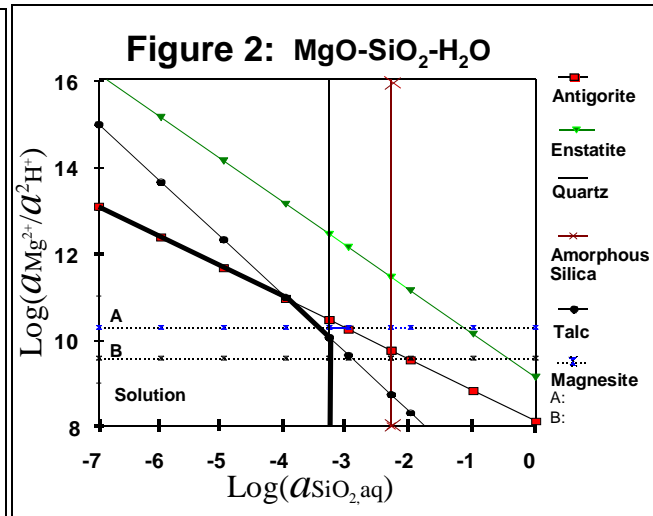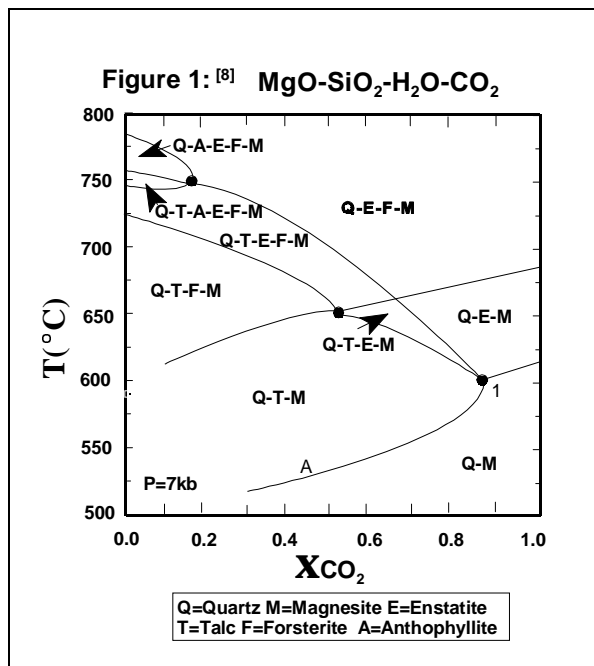
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is slightly less than the critical P_{CO_2} value at that temperature. At the higher temperatures of 350 and 450°C (Fig. 3G&H) even large amounts of CO_2 do not push the system onto the anhydrous pathway.

In conclusion additional data from sources such as isotopes and trace elements are needed to help constrain the temperature and pressure of origin of the carbonates in ALH84001. Once conditions are better constrained, the types of models described here will help identify the fluid composition responsible for the alteration and provide new avenues for exploring the possible connection between hydrothermal processes and life, including

providing a framework from which to search for evidence of hydrothermal systems on Mars.

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Figure 1: [8] MgO-SiO$_2$-H$_2$O-CO$_2$

Q=Quartz M=Magnesite E=Enstatite
T=Talc F=Forsterite A=Anthophyllite

Figure 2: MgO-SiO$_2$-H$_2$O

Figure 3: Orthopyroxenite Alteration

	T(°C)	W/R	X$_{CO_2}$
A	75	1	0.15
B	75	0.1	0.20
C	75	1	0.20
D	75	10	0.20
E	75	1	0.50
F	150	1	0.21
G	350	1	0.61
H	450	1	0.90