Inferred Impact-Generated Hydrothermal Mineral Assemblages in Basaltic Regions of Mars.

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Introduction: Impact cratering can produce hydrothermal systems within crater fill and throughout an aureole in the surrounding country rock, even where water may otherwise be completely locked up in a frozen state. Impact-generated hydrothermal systems and the alteration minerals they produce have been found at several terrestrial analogue sites [e.g., 1–4]. Thermal models of those systems on Earth [e.g., 5, 6] and Mars [7, 8] indicate that they can be long-lived and have the potential to chemically and mineralogically alter vast volumes of Mars’ crust. Indeed, those models suggested heavily cratered Noachian terrains were altered substantially more than younger terrains, a prediction that has been confirmed by ESA’s Mars Express mission [9 and references therein]. In this contribution, we expand those earlier thermal models [8] to explicitly calculate alteration mineral assemblages that would be produced at various depths in impact-generated hydrothermal systems, so that the interpretation of spacecraft data can be enhanced.

Modeling – code and conditions: We use the computer code CHILLER [10, 11] to evaluate mineral phases that are produced when hydrothermal water interacts with Martian subsurface rocks. Impact-generated hydrothermal systems can extend to depths of several kilometers, so a plutonic shergottite (LEW88516) rather than an eruptive lava is taken as the protolith. The chemical composition is the weighted mean of [12–14]. Ten mole-% of the iron is distributed as Fe₂O₃ and 90% as FeO per mineralogical analyses by [14]. Sulfur abundance as SO₂ is taken from [12]. Initially, we model an aqueous (rather than carbonic) fluid who’s chemistry is derived from the host rock. The system at depth is closed so that the fluid does not interact with the atmosphere, consistent with observations at a terrestrial crater [15]. Concentrations in our initial fluid are (in moles) [Fe³⁺] = 9.19×10⁻³, [Mg²⁺] = 20.53×10⁻³, [Ca²⁺] = 2.5×10⁻³, [HCO₃⁻] = 1.68×10⁻³, [SO₄²⁻] = 2.85×10⁻³, and [Cl⁻] = 0.68, which is also consistent with fluids venting from Deccan basalt units [16].

Results: At a depth of 5 km (P=550 bar), a 300 °C hydrothermal fluid at water/rock (W/R) values of 1 to 30 will produce phyllosilicates (serpentine; 52–56%), mica (chlorite), amphibole, garnet, and minor magnetite, quartz, hydroxylapatite, pyroxene, and pyrite. Garnet quickly becomes a trace phase as W/R approaches 30. At W/R ~ 30 the major anions in the fluid are Ca, Na and Mn and pH is ~5. Chlorite is present at low W/R only and is replaced by talc gradually as W/R increases from ~80 to 150. At W/R ~1000 the dominant phase is hematite accompanied by serpentine and diaspore. Interestingly, the abundance of water sequestered by the alteration assemblage is higher (16 wt% in serpentine) at lower W/R values than at higher W/R values (5 wt% in hematite–diaspore assemblage).

At intermediate temperatures (300 °C>T>150 °C), the assemblage at W/R~1 is composed mostly of serpentine, chlorite, amphibole, actinolite, and iron oxides (hematite, magnetite) with garnet (andradite). Fluid pH is ~6 and ions are dominated by Na, K, and Ca. Amphibole disappears quickly as W/R approaches 30. Chlorite disappears at higher W/R, although it is not replaced by talc at any W/R in this T interval. At 250 to 200 °C and W/R>1000, kaolinite is stable in addition to the minerals present at higher T. At lower temperatures (~150 to 90 °C) and W/R<30, the assemblage is serpentine, amphibole, and chlorite. At W/R ~30 to 1000 the assemblages is serpentine, hematite, and chlorite (with 15 wt% bound water) and at W/R>1000 the assemblage is nontronite–hematite with (with 2½ wt% bound water). The ratio of kaolinite and nontronite also changes as a function of T in this interval, with kaolinite being progressively replaced by nontronite at the lowest T.

As temperatures approach the pre-impact geothermal gradient value (65 °C at 5 km depth; [8, 17]), talc is stable with chlorite, serpentine, and amphibole when W/R~1 to 30. In general there are two assemblages at intermediate W/R: talc–serpentine–chlorite at W/R about ~70 and nontronite–hematite at W/R about 900. If the W/R is even higher, hematite makes up more than 60 % of the assemblage and is accompanied by chlorite. The water content of the alteration assemblage is about 9 and 2.5 wt% for the talc–serpentine–chlorite and the nontronite–hematite assemblage, respectively.

Many of the same minerals are found near the top of the hydrothermal system, within 10 m of the surface. At 90 °C and 50 °C the mineral assemblage at W/R of 1 is comparable to the assemblage at 65 °C and 5 km depth. At lower temperatures talc precipitates at low W/R, which is not seen at 90 °C. At all temperatures nontronite is the most abundant phase in a W/R range between ~850 and 10000. At all model temperatures (90, 50, and 1 °C) and very high W/R (>10000) a dominating Fe-oxide/hydroxide phase is formed, which is hematite for the higher temperatures
and goethite at 1 °C. The water content of the resulting mineral assemblages is comparable to that observed at higher temperatures.

At nearly all W/R and T values (and, thus, nearly everywhere in the system), S and P precipitate as pyrite and apatite, respectively.

One of the uncertainties in our model calculations is the distribution of iron between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) states. Several of the above calculations were repeated for a range of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) values, from pure \( \text{Fe}_2\text{O}_3 \) to pure \( \text{FeO} \). This variation does not affect the general attributes of the assemblages above, but does modify the W/R values at which minerals replace each other. In addition, when iron is dominated by \( \text{Fe}_2\text{O}_3 \), a gas phase (mainly \( \text{H}_2 \) and \( \text{H}_2\text{O} \)) is produced at the top of the hydrothermal system. Similar gas phases have been observed in modeling low temperature alteration of Martian rocks [18, 19]. The mineral assemblages described above are fairly robust over a wide variety of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) values, except in the extreme condition when all Fe is partitioned into \( \text{Fe}^{3+} \) and W/R<30.

**Implications:** This initial set of calculations suggests that impact-generated hydrothermal systems within basalt protoliths will create phyllosilicate-dominated assemblages at moderately-high T (300 °C). As W/R values rise, the phyllosilicate serpentine is replaced by talc. The same is true at lower T, although kaolinitic clay also becomes important. At the lowest T, alteration assemblages again contain talc and serpentine at low W/R, but increasingly contain nontronite as W/R rise. Iron oxides are present in all cases and become major components of the assemblage at W/R values >700 at high T. As temperature decreases, the W/R value at which iron oxides become the dominating phases increases, reaching 10000 at 1°C. When W/R values are limited to ~1 at moderate to high T, then the assemblage is essentially a thermal metamorphic product with chlorite and garnet.

Similar results were found for volcanically-driven hydrothermal systems on Mars in similar protoliths by Griffith and Shock [20, 21]. Although volcanic hydrothermal systems certainly occurred on Mars, we have previously argued that Noachian terrains may be dominated by impact-generated hydrothermal systems. Thus, it is interesting to compare our results with observations made by OMEGA on Mars Express, which reveal several alteration products in Noachian terrains. In an early report [22] nontronite was described at the northern margin of Syrtis Major in the Nili Fossae region. Subsequent observations of the Nili Fossae region revealed smectite, an undetermined mineral that may be a second smectite, chlorite, vermiculite, or talc, and a third undetermined hydrous mineral [9]. If these minerals were produced by impact-generated hydrothermal activity, then they point to potentially diverse hydrothermal conditions. Based on the above model calculations, nontronite implies moderately high W/R (≥900) and intermediate to low T (below 200 °C). On the other hand, if the unidentified phyllosilicate is serpentine, as proposed by [9], this implies W/R<1000 and intermediate to relatively high T (>200 °C) or, alternatively, W/R<100 at T<200 °C. Although ~300 °C hydrothermal temperatures can be produced in craters as small as 30 km diameter [8], those conditions are short-lived. Significant quantities of a high-temperature mineral assemblage are more likely to be produced in the vicinity of larger (e.g., >100 km diameter) craters on Mars where relatively high T conditions can persist for 10^4 to ≥10^5 yrs.

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