

HYDROTHERMAL ACTIVITY ON MARS: CAN MAGMATIC WATERS PLAY A VIABLE ROLE?

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Introduction: Magmatic fluids contributed to the crust by shallow intrusions during second boiling may provide local groundwater and hydrothermal surface expressions [1-3] in the absence of wide-spread meteoric water. Such fluids may have been of particular importance during the periods of time when atmospheric conditions no longer supported liquid water on the martian surface, yet ongoing magmatism provided a continuing source of magmatic waters. Magmatic water-dominated systems may even have been present locally on Mars during the period of efficient atmospheric water cycling, as seen on Earth in epithermal Au deposits. But did martian magmas generate fluids capable of producing some of the alteration minerals, such as the phyllosilicates found in the Noachian terrain [4], or the sulfate and silica-rich horizons found in the vicinity of Home Plate [5, 6]? To answer such questions requires compositional information on martian magmatic fluids.

We have obtained compositional constraints on two types of Martian magmatic fluids through the study of melt inclusions in the Chassigny and MIL 03346 meteorites. The results suggest that *magmatic fluids* on Mars can give rise to (i) magmatic waters that on Earth are associated with the production of phyllosilicates upon interaction with wallrocks and (ii) acidic aqueous solutions that give rise to jarosite-hematite assemblages and highly acidic condensed vapor that produces extensive silica deposits in fumerolic environments.

Magmatic fluids from water-“rich” magmas: Inferences from the Chassigny meteorite. The volatile history of the silicate melt trapped in melt inclusions within cumulus olivine of the Chassigny meteorite was recently studied by [7]. The presence of F, Cl, and OH (recently determined by [8]) is evidenced in the minerals apatite, Ti-biotite, and kaersutite. As these volatiles build up in the melt, the presence of a significant amount of HCl in the melt likely caused early second boiling [9] at elevated pressure to produce a supercritical fluid (relative to the critical point of water). Retention of this fluid into the high-temperature hydrothermal regime is evidenced by subsolidus feldspar equilibration temperatures, almost binary alkali feldspar, and the high Cl and H₂O content (up to 1.2, and 0.3 wt% respectively) of maskelynite which appears to represent late-stage feldspar that contained fluid inclusions [7].

Upon second boiling, HCl would have partitioned strongly into the exsolving fluid and the accompanying

hydrolysis reactions with the feldspar components of the melt would remove some alkalis and leave behind an aluminosilicate-enriched silicate melt e.g., [10]. Above 500°C, these high-temperature fluids would contain primarily silica and un-ionized chlorides of Na, K, Fe and H (e.g., [11-14]). Continued crystallization would produce more fluid that would become progressively more dilute (water-rich). In fact, the absence of high Cl-bearing phases within the melt inclusion (such as Cl-amphibole) suggests the melt inclusions appear to have remained unbreached into the stability temperature field of this mineral. This suggests that the fluids were of relatively low salinity at least during the late magmatic stage.

The sodic nature of the mineral assemblage within the olivine-hosted melt inclusions suggests a high Na/K ratio of the trapped residual melt. With a partition coefficient for KCl and NaCl between melt and fluid of ~1 [11], the early-formed fluid would also have been predominantly sodic. Since Cl is strongly complexed with Fe in high temperature fluids [11], the exsolved fluids likely had elevated Fe contents.

H₂S also partitions strongly into the fluid e.g., [10]. At and below the oxygen buffer QFM, and at magmatic temperatures and elevated pressure, sulfur remains primarily as H₂S in the fluid, SO₂ not becoming of importance until late stages where diffusive loss of H₂ from the more water-rich late-stage fluids may oxidize the melts [15].

Such fluids produced outside of the melt inclusion are free to leave the magma and evolve compositionally during ascent, cooling, and reacting with wallrock. Dilute fluids may not undergo phase separation (into L+V) until low temperatures and pressures [16] and retain their bulk chemical signature of neutral to mildly alkaline pH with Cl as the dominant anion over much of their cooling history. Such fluids will not give rise to either alunite (or other sulfates) or silica minerals. They will produce instead typical phyllic alteration zones, with muscovite (sericite) and kaolinite dominant in wallrocks with abundant feldspar. That such alteration can be accomplished effectively with magmatic fluids was pointed out by [10]. If the magma ascended to shallower levels and such fluids were released there, low-temperature pyrophyllitization of the wallrocks could result. If the amount of K in the system were low enough, it is possible that paragonite would form, or at

lower temperatures, montmorillonite and chlorite (from more ferromagnesian phases) [10].

Magmatic fluids from water-“poor” magmas: Inferences from MIL 03346. Evidence for fluid compositionally quite distinct from that associated with melt inclusions in the Chassigny dunite is present in select mineral assemblages of pyroxene-hosted melt inclusions in the nakhlite MIL 03346. In one melt inclusion [17] observed K-jarosite finely intergrown primarily with hematite \pm Ti-magnetite (and in some areas with both hematite and goethite) surrounding magmatic pyrrhotite. The melt inclusion also contains Cl-rich amphibole and two intergrown potassic iron-silicon-rich phases. Both jarosite and Cl-amphibole require the presence of an aqueous phase, and suggest higher fluid concentrations of S and Cl relative to that inferred from the Chassigny meteorite. Retaining high concentrations of S and Cl through the final magmatic stage suggests that the melt itself was lower in water and higher in S and Cl than the melt residual to crystallization of the Chassigny dunite. A fluid exsolving from a relatively dry, Cl, S, and Fe-enriched potassic melt within a melt inclusion would share the chemical characteristics of the melt.

Fluids high in Cl and S and low in water can undergo phase separation even at elevated pressure [16]. The vapor will be enriched in HCl, SO₂ (+H₂S, HF, Si, B, and Cu); the aqueous liquid would become enriched in alkali, alkaline earth, and Fe chlorides and sulfates [18-22]. Within a melt inclusion, both aqueous liquid and vapor would coexist, changing their composition upon cooling. The overpressure induced by phase separation, however, may drive H₂ from the melt inclusion resulting in gradual oxidation of the fluid. Alternatively, phase separation of the fluid phase in the magma external to the melt inclusion and loss of the vapor would increase the oxidation state of the magma as a whole (because SO₂ partitions less strongly into the vapor than H₂S [15]) and drive H loss from the melt inclusion. In either case, both the aqueous liquid and vapor would become oxidized over time. This would produce more SO₂ and H₂ in both aqueous liquid and vapor, destabilizing previously precipitated magmatic pyrrhotite and further enriching the liquid in S. Upon further cooling, SO₂ in the aqueous liquid would hydrolyze to produce H₂S and H₂SO₄ and metal sulfides could precipitate through homogeneous reactions between H₂S and metal chlorides, thereby increasing the fH₂SO₄ of the aqueous liquid and eventually decreasing the pH at even lower temperatures.

Upon cooling and dissociation of the Cl- and S-bearing complexes in the liquid, a variety of hydrolysis reactions could take place. The Al-poor nature of the jarosite in the melt inclusion studied suggests that at low temperatures the pH was so low in the aqueous

liquid that Al hydrolysis and subsequent Al incorporation into the jarosite structure did not occur. The potassic nature of the jarosite suggests a continued high K⁺/Na⁺ ratio (>3.8) of the aqueous liquid [23-25]. The presence of the assemblage jarosite, hematite and goethite imply that: (i) the pH reached values between 1.9 and 1.2, (ii) the log fO₂ was at least -34, and (iii) the aqueous liquid was retained to at least 100°C.

In the main magma body, the aqueous liquid and vapor would likely separate. At low temperatures, the vapor phase would become highly acidic upon dissociation of the high-temperature sulfate species, and produce the vuggy quartz and kaolinite-alunite (jarosite on Mars) alteration observed in fumeroles on Earth [14]. This vapor is low in chlorinity and can condense to produce highly acidic groundwater of primarily magmatic origin with a surface expression of hot-springs [26].

Summary: Our work has identified two types of magmatic aqueous liquids may have been contributed to the near-surface and surface environments of Mars. One is typically associated with phyllic alteration on Earth. The other produces highly acidic vapor which, upon condensation leads to silica precipitation, and oxidized aqueous liquids which can precipitate sulfates such as jarosite. Without re-hydration of the mantle by subduction, it is likely that younger martian magmas were progressively lower in water and early phyllic alteration would give way to jarosite/hematite assemblages and fumerolic silica as the groundwater became more acidic.

References: [1] Vennemann T. W. et al. (1993) *Econ. Geol.*, 88, 55-71. [2] Wallier S. et al. (2006) *Econ. Geol.*, 101, 923-954. [3] Einaudi M.T. et al. (2003) *Econ. Geol. Spec. Pub.* 10, 285-313. [4] Michalski J. et al. (2007) AGU Abstract #P11E-06. [5] Ruff S. et al. (2007) AGU Abstract #P23A-1097 [6] Morris R. et al. (2007) AGU Abstract #P21C-02: [7] McCubbin F. and Nekvasil H. (2008) *Am. Min.* 93. [8] McCubbin F.M. et al. (In prep) [9] Webster J. D. and Rebbert R. (1998) *Contrib. Mineral. Petrol.* 132, 198-207. [10] Burnham C. W. (1979) In *Geochemistry of Hydrothermal Ore Deposits* 2nd Ed., 71-133. [11] Kilinc I. A. (1969) Ph.D. Dissertation, The Pennsylvania State University. [12] Kilinc I. A. and Burnham C. W. (1972) *Econ. Geol.* 67, 231-235. [13] Holland, H.D. (1972) *Econ. Geol.* 67, 281-301. [14] Webster J. D. and Mandeville C. W. (2007) *Rev. Mineral. Geochem.* 65, 313-362. [15] Ohmoto H. and Rye R. O. (1979) In *Geochemistry of Hydrothermal Ore Deposits* 2nd Ed., 509-561. [16] Liebscher A. (2007) *Rev. Mineral. Geochem.* 65, 15-47. [17] McCubbin F. M. et al. (2008) LPSC XXXIV. [18] Schmulovich K. I. et al. (1995) In *Fluids in the Crust: Equilibrium and transport properties*. 193-214. [19] Bischoff J. L. et al. (1996) *GCA* 60, 7-16 [20] Schmulovich K. I. et al. (2002) *Contrib. Mineral. Petrol.* 144, 257-273 [21] Hedenquist J. W. and Lowenstern J. B. (1994) *Nature* 370, 519-527. [22] Baker T. et al. (2004) *Geol* 32, 117-120. [23] Alpers C. N. et al. (1989) *Sci. Geol. Bull.* 42, 281-298. [24] Stoffregen R. (1993) *GCA* 57, 2417. [25] Brophy G. P. and Sheridan, M. F. (1965) *Am. Min.* 50, 1595. [26] Dreisner T. and Geiger S. (2007) *Rev. Mineral. Geochem.* 65 187-212.