

Trace Elements in Martian Fines: Contributions by Magmatic Gases, N. Zimmermann¹, M. Safari¹, H. Nekvasil¹, ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, natalie.zimmermann@stonybrook.edu

Introduction: Both rover and orbital analyses have confirmed that Martian fines are compositionally distinct from terrestrial fines, showing major enrichments in S, Cl, and Fe [1-5]. They are also compositionally distinct from Martian rock substrate and soil, suggesting that a widespread process, such as volcanic gas condensation perhaps on ash, could have played a role in its formation [1,2,7]. [6] showed that a S- and Cl-bearing magma of Backstay composition with low water content can deliver a significant load of vapor-deposited chlorides, sulfides, and oxides to the surface. These workers noted an important lack of Ca and Mg in these deposits, but it is unknown whether this result simply reflected the low concentration of these in the Backstay composition magma. Those experiments also could not elucidate halogen- and S-mediated trace element volatility from Martian magmas, nor the nature of the vapor-deposited phases through which they could be added to the fines. Yet it is vital to understand the nature of the phases produced during condensation because they constrain reactivity that leads to their transformation and degradation over time.

In order to elucidate the effect of magma composition, specifically Ca, P, and trace element content on the nature of vapor-deposited phases, we degassed a P-Ca-Ti rich basaltic source of Wishstone composition [11] doped with S, Cl, Br and the trace elements Rb, Sr, Mn, Ge, Pb, Ga, Zn, Cs, Se, Sr, Cu, La, and Lu.

Methods: Mixtures of oxides, sulfides, chlorides, and silicates were made to simulate Wishstone composition doped with varying amounts of S, Cl, Br (0-2.5 mol% each) and 0-0.25 mol% of the trace elements listed above. The ferrous/ferric Fe ratio used was dictated by that computed for the magma if the fO_2 were that of the NNO buffer at 1300 °C. Glasses were made of these mixtures (after drying in a 120 °C vacuum oven overnight) by melting at 1300 °C and 1 GPa in Fe-soaked Pt capsules in a piston cylinder apparatus. Water content of the glasses was analyzed via micro-FTIR and found to range from 0.83 - 2.26 wt% H₂O (± 0.054 - 0.200 wt%).

One hundred fifty mg of each volatile-doped synthetic glass was placed in Au₈₀Pd₂₀ capsules at the bottom of a 30 cm long silica glass tube. The tube was then evacuated and sealed, and loaded into a vertical furnace with the source glass at 1200°C. Tubes were allowed to degas for 12-96 hours under a strong thermal gradient. (Note: upon removal from the furnace, subsequent and overlapping phases form upon cooling and the assemblage will oxidize even while sealed.)

Resulting deposits were analyzed via SEM/EDS, TES, synchrotron XANES, and EPMA.

Results: Condensed phases coating the interiors of degassed tubes form distinct bands of precipitates in discrete temperature zones. The figure below shows a cooled tube for an experiment with high water content; the source capsule is on the far left.



Mineral phases were identified by element associations in SEM spectra and crystal systems seen in EDS.

Table 1. Phases identified in experiments and their associated temperature range within the primary pre-cooling thermal gradient.

Group	Phases	Temp. Range
Chlorides	NaCl, KCl, RbCl ₂ , CsCl, ZnCl ₂ , PbCl ₂ , SiCl ₄ , FeCl _x	25-725 °C 1125-1175 °C
Bromides	NaBr, KBr, PbBr ₂ , ZnBr ₂	175-1125 °C
Sulfides	Pyrrhotite (monoclinic Fe _{(1-x)S}), Pyrite (cubic FeS ₂), Sphalerite (cubic (Zn,Fe)S), Wurtzite (hexagonal (Zn,Fe)S)	175-375 °C
Sulfates	CaSO ₄ , K ₂ SO ₄ , Na ₂ SO ₄	175-1125 °C
Phosphates	Chlorapatite (Ca ₅ (PO ₄) ₃ Cl)	375-1125 °C
Oxides	Hematite (hexagonal Fe ₂ O ₃), Magnetite (Fe ₃ O ₄), Maghemite (cubic Fe ₂ O ₃), GeO ₂ (α-quartz type crystal structure), GeO ₂ -Ge microcubes	375-725 °C
Silicates	Aegirine CPX with Ge (NaFe(Si,Ge) ₂ O ₆), Fe-Ge CPX (Fe(Ge,Si)O ₃), Opal-C, SiO ₂ 'nano-fiber' morphology, SiO ₂ spherical morphology	CPX:375-725 °C SiO ₂ polymorphs: 375-1125 °C

SEM images of selected phases are included below.

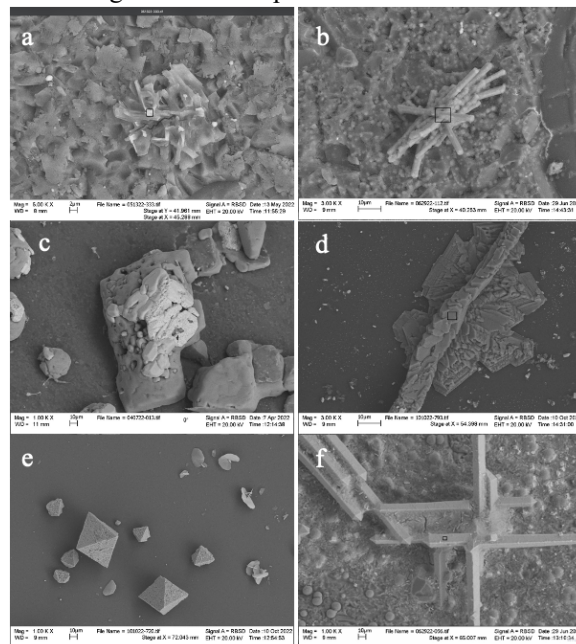


Figure 1. (a) Chlorapatite (b) K_2SO_4 (c) layered chlorides ($NaCl$, $RbCl_2$, $CsCl$ on top) (d) Pyrrhotite and Pyrite (e) maghemite (octahedra) and hematite (flakes; on right) (f) Fe-Ge clinopyroxene

Discussion: Many of the same gas-deposited phases were formed from Wishstone magma and Backstay composition magma, suggesting a set of vapor-deposited minerals ($NaCl$, $FeCl_x$, maghemite, hematite, pyrrhotite and pyrite) that are ubiquitously contributed to the globally dispersed Martian fines. However, P-rich magmas further allow for the vapor transport of P and Ca and the formation of vapor-deposited apatite and $CaSO_4$. For the F-absent compositions studied here, the apatite is chlorapatite but other apatite may form if F and H_2O are dissolved in the magma.

In these experiments, the magmatic major elements Si, Fe, Na and K were common in vapor-deposited phases; Na and K formed primarily chlorides, while Fe formed chlorides, sulfides and oxides. Pb, Zn, Rb, and Cs were also frequently observed in vapor deposits, usually forming halide salts. In contrast, Sr, Cr, Se, La, and Lu, along with the major elements Ti and Al were rarely to never observed in the vapor-deposited phases. The igneous trace elements Mn, Ge, and Ga, along with Mg, were observed well distributed in temperature space but in minor amounts, often substituting for other cations in mineral structures. Ca and P were predominantly seen in chlorapatite/apatite deposits.

Secondary minerals. Magmatic gas delivers magmatic major and trace elements to the surface and upon cooling, the dissolved solute condenses to form micron-sized minerals. It is likely that on the Martian surface the vapor-deposits would be modified as they react with the oxidizing atmosphere and/or dissolve into hydrothermal, surficial, or groundwater. These processes could free ions to be redistributed via sedimentary processes.

Large scale chloride deposits have been identified on the Martian surface [12,13], occurring in small but globally wide-spread deposits [12], and comprising an estimated 10-25% of Martian soil/dust [14]. Bromine has also been detected, in what has been interpreted to be hydrous bromide salts [5]. The current dry climate of Mars favors the stability of halide salts, but these compounds are highly soluble and would likely have formed brines in the presence of high humidity or liquid water. Upon dissolution, freed chlorine or bromine ions may oxidize to form chlorates or bromates [15].

Iron(II) sulfides, including those found in these experiments, may oxidize to Iron(III) sulfates ($\pm S$) on Mars [1]. In the presence of liquid water, Fe(II) sulfides are likely to oxidize to Fe_2O_3 ($+S$) rather than

$FeSO_4$, as soluble sulfide/sulfate ions would be freed by solution to form compounds with other available cations [1].

Iron(II) oxides would similarly oxidize in the Martian atmosphere to Iron(III) oxides. Magnetite likely oxidizes to hematite, with maghemite as an intermediate phase[1]. Hematite is insoluble in water and abundant on the Martian surface [7]. Additionally, iron oxides could form secondary phases with vapor-deposited sulfides to produce jarosite, akaganéite, or iron oxychloride [6]. GeO_2 , on the other hand, is soluble in water, which could free Ge cations to be redistributed through sedimentary processes [8,9].

Conclusion: Degassing a volatile and trace element doped Wishstone basalt produces a variety of unique phases that could be contributed to Martian surface fines. These minerals include chloride salts, bromide salts, sulfides, sulfates, chlorapatite, iron-oxides, germanium-oxides, clinopyroxenes, and SiO_2 polymorphs. These phases formed directly from gas condensation, and they are likely to react, oxidize, or degrade on the Martian surface. In the presence of liquid water or high humidity, several phases produced could dissolve to form brines or acidic solutions, which would further accelerate the weathering process.

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References: [1] Gooding, J.L. (1978) *Icarus*, 33(3), 483-513. [2] Berger, J.A., et al. (2016) *Geophys. Res. Lett.*, 43, 67-75. [3] Gellert, R., et al. (2006) *JGR*, 111. [4] Ojha, L., et al. (2018) *Nat Comm.*, 9, 2867. [5] Yen, A., et al. (2005) *Nature*, 436, 49-54. [6] Nekvasil, H., DiFrancesco, N.J., et al. (2019) *JGR: Planets*, 124, 1592-1617. [7] Weast, R.C. (1979) *Handbook of Chem.&Phys.* 60th ed. [8] Gan, N. et al. (2015) *ECS Trans.*, 69, 277. [9] Butterman & Jorgenson (2002) *Germanium: USGS Mineral Commodity Summ.*, 70-71. [10] Hausrath, E.M. & Tschauner, O. (2013) *Astrobio.*, 13(11), 1049-1064. [11] McSween, H.Y., et al. (2006) *JGR*, 111. [12] Osterloo et al. (2008) *Science*, 319(5870), 1651-1654. [13] E.B. Rampe, et al. (2020) *Geochem.*, 80 (20). [14] Glotch, T.D., et al. (2016) *JGR: Planets*, 121, 454-471. [15] Clark, B. (1981) *Icarus*, 45(2), 370-378. [16] Williams, Parks & Crerar (1985) *J Sed. Res.*, 55 (3), 301-311. [17] Rapin, W., et al. (2018) *JGR: Planets*, 123, 1955- 1972.