

EVALUATING THE INFLUENCE OF MAGMATIC SULPHIDES ON CHALCOPHILE ELEMENT ENRICHMENTS IN THE BRADBURY ASSEMBLAGE, GALE CRATER, MARS, USING APXS MEASUREMENTS. M. R. M. Izawa^{1,2*}, M. E. Schmidt¹, J. A. Berger³, R. Gellert³, ¹Dept. Earth Sciences, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, Ontario, Canada L2T 3V8, ²Planetary Science Institute 1700 East Fort Lowell, Suite 106 Tucson, AZ 85719-2395, ³Guelph-Waterloo Physics Institute, University of Guelph, Guelph, ON N1G 2W1, Canada, *matthew.izawa@gmail.com

Introduction: Among the rocks encountered by the Mars rover, Curiosity, are igneous rocks and (nearly) isochemically-derived sediments that appear to reflect two magmatic reservoirs: Jake-M class rocks characterized by elevated Na₂O, K₂O, Al₂O₃ and SiO₂, and the Bathurst Inlet class characterized by high MgO, FeO_{total}, MnO, and Zn and low SiO₂ [1]. Sedimentary processes, chemical weathering reactions, and hydrothermal alteration of source rocks appear to have affected little mineralogical change in many Bradbury group rocks analyzed by the Curiosity rover [2]. This may point to a role of magmatic sulphide mineralization in the formation of the enrichments in Zn and other chalcophile elements in the Bradbury Group [3]. Primary magmatic sulphides would have been subjected to post-emplacement hydrothermal redistribution of mobile elements. Weathering and transport of magmatic and hydrothermal sulphides could then lead to the dispersal of chalcophile element rich material into the Bradbury assemblage sediments.

Methods: To assess the potential role of magmatic sulphide mineralization in the Bradbury assemblage, we have used whole-rock chemistry measurements from the Alpha Particle X-ray Spectrometer (APXS) instrument [4]. Estimated Sulphide Concentrations at Sulphide Saturation (SCSS) values were calculated according to the formulations of Ding et al. [5] and Righter et al. [6] from the APXS-measured compositions. Because the empirical equations of Ding et al. are calibrated for FeO-rich compositions, we have used this formulation in this work. Because there are no measurements of iron valence for the analyzed rocks, we take assume that all Fe occurs as FeO. Further, the APXS analyses are initially normalized to 100% and then recalculated without SO₃ and Cl following common practice [e.g., 7]. Therefore, the SCSS values calculated here represent upper bounds.

Viscosities were calculated for anhydrous melts of the APXS-measured compositions (normalized to 100%, then renormalized with SO₃ and Cl set to 0 with all Fe as Fe²⁺), and therefore represent upper bounds. The addition of water and other volatiles would be expected to decrease melt viscosity. The

assumed temperature was 1270°C, changing the temperature will affect the quantitative but not the qualitative character of the relationships.

Discussion: Estimated sulphide concentration at sulphide saturation for Gale crater igneous rocks and isochemically-deposited sediments, including Jake_M and Bathurst, are up to ~13500 ppm (Fig. 1), depending on the choice of parameters used. As stated above, these calculated SCSS values are upper bounds. Qualitatively, these SCSS calculations show that the Jake_M and Bathurst Inlet melts would have been efficient carriers of sulphur and chalcophile elements. Upon sulphide super-saturation (potentially triggered by decreasing pressure or temperature, or changing composition), viscosity will influence the segregation of immiscible sulphide melts. Calculated viscosity for measured igneous rock compositions (soils and John Klein mudstone sediment excluded) shows an inverse relationship between melt viscosity and concentrations of Ni, Cr₂O₃, and Zn (Fig. 2). The relationship with Cr may indicate a segregation of dense oxide (Cr-spinel) or be coincidental due to the mafic to ultramafic character of the Bathurst-type melts.

Assimilation of crustal sulphur may have played a key role in causing the primary magmas to reach sulphide saturation [8]. Impact melts, are initially superheated and therefore able to erode and assimilate 'country rock', and are emplaced in surface rocks, may be ideally suited to form 'magmatic' sulphide deposits. Impact melts are also likely to be highly inviscid, which can enhance the segregation of immiscible sulphides. Martian surface rocks contain abundant sulphur, predominantly as sulphate. Interaction of crustal sulphate with reducing magmas may therefore allow the incorporation of additional S [8]. Pyrrhotite is the only sulphide mineral definitively detected thus far by XRD in Gale crater rocks, in addition to a single possible detection of pyrite in a John Klein sedimentary sample [2], and is the most common sulphide mineral observed in Martian meteorites including the regolith breccia samples of the NWA 7034 group [9]. Evidence for sulphide minerals on the Martian surface also comes from pyrolysis

results from the Sample Analysis at Mars (SAM) instrument [10].

Treating the compositions of Bradbury assemblage sediments as melt compositions is subject to many uncertainties. Samples analyzed by CheMin are dominated by igneous minerals in plausible original modal proportions [11], indicating little chemical alteration or physical fractionation. Modeling of the crystallization of Jake M class rocks [12] shows that they represent plausible melting products of the Martian mantle. The Bradbury assemblage rocks fall on an apparent mixing trend between Jake_M and Bathurst class rocks in Mg/Si vs. Al/Si space, suggesting mixing between two igneous sources [13].

Conclusions: The initial formation of magmatic sulphides during the emplacement of Martian melts (of endogenic and impact origin) can provide initial enrichment in chalcophile elements, which can later be mobilized and redistributed by hydrothermal, weathering and sedimentary processes.

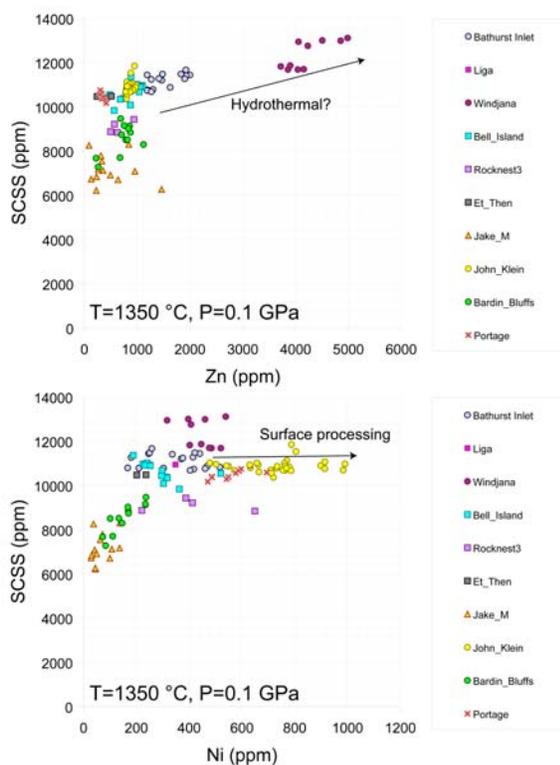


Figure 1: Upper bound case for Sulphide Concentration at Sulphide Saturation (SCSS), $T=1350\text{ }^{\circ}\text{C}$, $P=0.1\text{ GPa}$, all Fe as FeO, and measured composition first normalized to 100% then renormalized without SO_3 and Cl. Formulation of Ding et al. [5]: $\ln(S\text{ in ppm})_{\text{SCSS}} = 14.25 - 3948.51/T - 0.06P - 2.81[\text{SiO}_2]_{\text{melt}} - 7.33[\text{Al}_2\text{O}_3]_{\text{melt}} + 0.97\ln([\text{FeO}]_{\text{melt}})$. Calculated SCSS values correlate with

chalcophile elements Ni and Zn. Soils and sediments show decoupling of Ni from Zn, possibly due to different mobilities of these elements in hydrothermal or weathering processes, or the concentration of Ni in mudstones from meteoritic infall and Ni accumulation in Mg-sulphates (nickel-hexahydrate component).

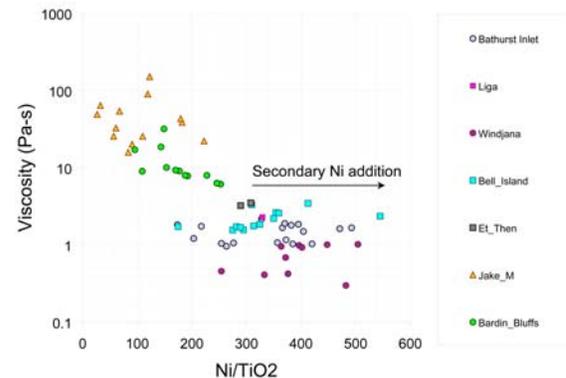


Figure 2: Calculated melt viscosity for APXS analyses thought to represent plausible melt compositions (soils and John Klein mudstones excluded) using the formulation of Shaw et al. [14]. The inverse relationship of viscosity with Ni/TiO_2 ratio is consistent with concentration of Ni in lower-viscosity melts. Viscosity is strongly dependent on SiO_2 and FeO concentrations and the anticorrelation of viscosity and [Ni] in part reflects this, but this is also consistent with enhanced sulphide segregation in the low viscosity (low SiO_2 , high FeO melts).

References: [1] Schmidt et al., 2014 *J. Geophys. Res. Planets*, 119(1). [2] Treiman et al., 2016 *J. Geophys. Res. Planets*, accepted. [3] Berger et al., 2015 *LPSC XLVI Abs.* #1564. [4] Gellert et al. 2015 *Elements*, 11 (1), 39-44. [5] Ding et al., 2014 *GCA* 131 (2014) 227–246. [6] Righer et al., 2009 *EPSL* 288 235–243. [7] Ming et al. 2008 *J. Geophys. Res. Planets*, 13, E12S39. [8] Baumgartner et al. 2015 *Ore Geol. Reviews* 65 400–412. [9] Agee et al. 2013 *Science* 339, 780–785. [10] MacAdam et al. 2014 *J. Geophys. Res., Planets* 119, 373-393. [11] [12] Stolper et al., 2013 *Science* 341(6153). [13] Schmidt et al. 2016 *this meeting* [14] Shaw 1972 *Am. J. Sci.* 272, 870-893.

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