COPPER, GALLIUM, ZINC, AND GERMANIUM IN GALE CRATER SOILS: NEW CONSTRAINTS ON THE GLOBAL ENRICHMENT OF VOLATILE ELEMENTS ON THE MARTIAN SURFACE

J. A. Berger1*, S. J. VanBommel2, E. B. Rampe3, A. L. Knight2, G. K. Ustunisik4, K. Righter3. 1Jacobs JETSII at NASA JSC; 2Washington University in St. Louis; 3NASA Johnson Space Center; 4South Dakota School of Mines and Technology. *jeff.berger@nasa.gov.

Introduction: Curiosity’s Alpha Particle X-ray Spectrometer (APXS) has acquired 60+ soil measurements over the rover’s 30+ km traverse in Gale crater. The volatile-free composition is basaltic, with nearly the same composition as basaltic soils at the Spirit and Opportunity sites [1-2]. This apparent uniformity has led to the interpretation that basaltic soils represent the average global basaltic crust [2-4]. The volatile content of the soil, however, can be significant (up to ~8 wt%).

Multiple lines of evidence link the volatile fraction of soils to a global dust unit. Measurements of airfall dust show the same S/Cl (~3.4 molar) as soils measured by MER and MSL, but notably higher S+Cl (Fig. 1c, d) [2, 5]. Soils with higher volatile content have a much finer average grain size and concomitant cohesive properties (Fig. 1a, b). These characteristics define a continuum of soils that is sufficiently distinct to classify the coarser, lower-volatile, and more recently active aeolian materials as ‘sand’ (Fig. 1).

High concentrations of Zn correlate positively with the S and Cl in soils, indicating an enrichment in the global dust (Fig. 1d). Enrichment of volatile elements S, Cl, and Zn in surface materials provides evidence of volcanic activity and magmatic degassing, but limited constraints on the processes can be inferred. This is partly due to the abundant evidence of the mobility of the three elements in low temperature fluids. Here, we conduct an analysis of Curiosity’s APXS measurements of soils and sand to derive concentrations of Cu, Ga, and Ge for the first time, with the objective of providing constraints on volatile enrichment processes on the martian surface.

Methods: The sensitivity of APXS to trace elements is affected by multiple considerations (e.g., temperature, standoff distance) [6]. The duration of a measurement over one target affects overall statistics, including signal/noise, which increases with longer integration times. Rover measurements with integration times >8 hours are rare; the 16 major, minor, and trace elements reported by the APXS are routinely quantified in less time. To quantify trace elements that are usually below detection limits, we combined spectra from multiple measurements of soils with consistent compositions (Fig. 2). Additional processing using the methods of [6] were used to determine trace element abundances.

Results: Trace element results from composite APXS spectra of soil and sand are presented in Fig. 3 as ratios to the martian mantle concentrations calculated by [7]. Relative statistical (i.e., precision) error is ~5-10%.

Measurements of three compositional groups of unsieved soils were composited and analyzed: (i) high-volatile soil n = 12; (ii) low-volatile sand n = 23; and (iii) low-volatile, high Mg+Ni sand n = 15.
Relative to the martian mantle, Ga, Zn, Cu, and Ge are enriched in soil (~3×, ~5×, ~6×, ~8×, respectively), and concentrations correlate positively with increasing volatility in a silicate melt [8]. Sand has the same concentrations of Ga and Cu, but lesser enrichments of Zn and Ge (~4×, ~5×, respectively). Evidence of aeolian sorting in the Mg+Ni-rich sand introduces complexity, and it will not be discussed further here.

**Figure 3:** Trace element results for composite soil (brown circles) and sand (black diamonds) ratioed to the martian mantle [7] and ordered by increasing volatility in a silicate melt [8]. Shergottite data (thin lines, triangles) and mean concentrations (bold magenta line) from [7] are shown.

**Discussion:** Gallium in soil and sand is not highly enriched compared to the martian meteorites, and Ga/Al agrees with the ratio in meteorites (Figs. 3, 4) and in situ MER rocks [9]. Thus, Ga in martian soils is likely controlled primarily by fractionation of plagioclase by substitution with Al³⁺, as is common in terrestrial basalts (Fig. 4). This counterindicates enrichment via volcanic sulfides and/or meteoritic material.

Enrichments (10-1000×) in the moderately volatile elements Ge and Zn have been found in localized occurrences by *Spirit* and *Opportunity* [10, 11] and in >500 meters of sedimentary strata by *Curiosity* [12]. These enrichments are difficult to explain in terms of terrestrial analogues, and they have not been reconciled with data from other rover science instruments; the Ge- and Zn-hosting phase(s) is(are) not currently known. No definitive mineralogical assemblage has been detected in Gale crater by CheMin XRD that can account for the scale of the Ge and Zn enrichments (e.g., volcanic sulfide, gossan) [13].

Our new quantification of Ge enrichment in the martian soil is evidence that it is a global feature. Elevated Ge in Gale crater sedimentary rock has been linked to Ge depletion in martian meteorites [7, 14] (Fig. 3). There is uncertainty in this hypothesis because the enrichment in Gale sediment could be unique to the crater, rather than a global feature. However, our determination of Ge enrichment in martian soils supports the hypothesis of a long-term degassing input of volatile and moderately volatile elements to the martian surface [14, 15]. Soils likely retain a record of this degassing in Ge and Zn (and S, Cl) concentrations.

The quantification of both Ge and Ga in the soil is particularly useful because both elements are more likely to have relatively low mobility in low temperature fluids. This contrasts with S, Cl, and Zn, which have abundant evidence of mobility on the martian surface. As such, Ge and Ga may have preserved a record of martian magmatic processes for eons.

**Figure 4:** Ga vs. Al in Gale crater soil and sand, martian meteorites [e.g., 7], and Mauna Kea basalt [16].

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**References:**