GERMANIUM ENRICHMENTS IN SEDIMENTARY ROCKS IN GALE CRATER, MARS: CONSTRAINING THE TIMING OF ALTERATION AND CHARACTER OF THE PROTOLITH

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Introduction: Rocks enriched in Ge have been discovered in Gale Crater, Mars, by the Alpha-particle X-ray spectrometer (APXS) on the Mars Science Lab (MSL) rover, *Curiosity*. The Ge concentrations in Gale Crater (commonly >50 ppm) are remarkably high in comparison to Earth, where Ge ranges from 0.5-4.0 ppm in igneous rocks and 0.2-3.3 ppm in siliciclastic sediment [1]. Primary meteoritic input is not likely the source of high Ge because Ge/Ni in chondrites (~0.003) [2] and irons (<0.04) [1] is lower than in Gale rocks (0.08-0.2). Earth studies show Ge is a useful geochemical tracer because it is coherent with Si during magmatic processes and Ge/Si varies less than 20% in basalts [3]. Ge and Si fractionate during soil/regolith weathering, with Ge preferentially sequestered in clays [4]. Ge is also concentrated in Cu- and Zn-rich hydrothermal sulfide deposits and Fe- and Mn-rich oxide deposits [1]. Other fluid-mobile elements (K, Zn, Cl, Br, S) are also enriched at Gale [5] and further constrain aqueous alteration processes. Here, we interpret the sediment alteration history and present a possible model for Ge enrichments at Gale involving fluid alteration of the protolith.

Methods: Under typical deployment conditions, MSL-APXS, a combination of PIXE and XRF techniques, is capable of quantifying Ge at ≥20 ppm with ≥0.3 h integrations at low temperatures (< -20° C). Error is ~5% for long integrations (>1 h); uncertainty increases (~20%) for shorter integrations and lower concentrations. Ge concentrations for every MSL-APXS target (sols 0-831) were calculated from APXS spectra [6]. Ge results for most short integrations (<1 h) and from low-resolution spectra (FWHM Fe >200 eV) were near or below LOD; these targets were removed from the dataset and 60 remained.

Results: Ge concentrations (Fig. 1) have two broad ranges: soil, regolith, and mugearitic to trachyandesitic rocks (JakeM) have low Ge (<50 ppm), and all other rocks have high Ge (>50 ppm). Exceptions include 1) the Cratered Surface Unit (Caprock), which has low Ge but widely varying compositions, and 2) the sedimentary rocks of Bell Island, Darwin, and The Kimberley, which have variable Ge. Ge/Si does not have strong correlations with other elements analyzed by APXS ($-0.5 < r < 0.5$) including K_2O ($r = 0.05$) and Zn ($r = 0.39$), nor does it vary with the chemical index of alteration (CIA) [7] (Fig. 2).

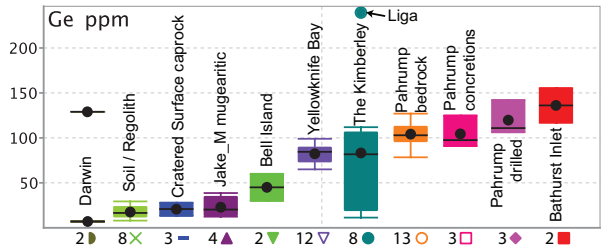

Fig. 1: *Ge levels in Gale Crater (sols 0-831) grouped by rock class [8]. Liga (The Kimberley; sol 601) and Halls (Bathurst Inlet; sol 537) have notably high Ge (239 & 155 ppm, respectively). Box includes 50%; whiskers show min and max that are not outliers; Liga is an outlier. The number of targets n is shown on the x-axis with the symbols used in Fig. 2.*

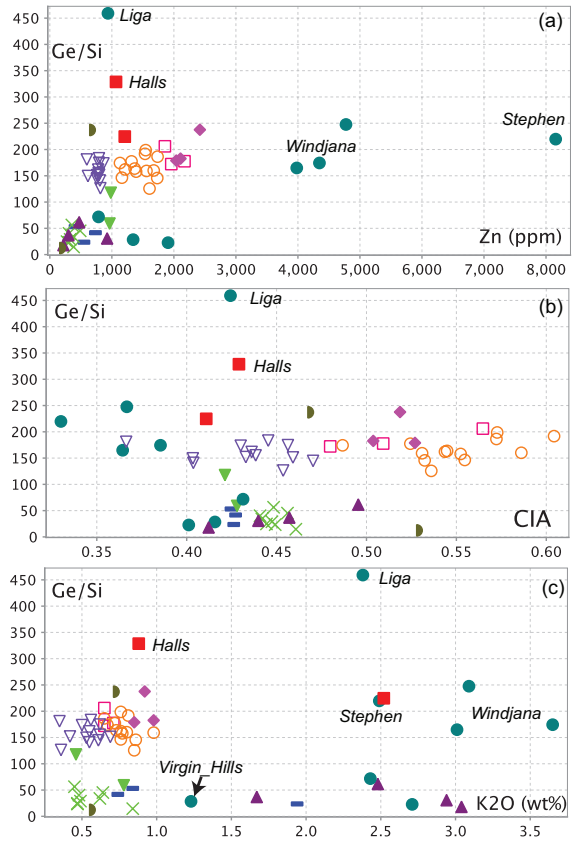

Fig. 2: *Variation of Ge/Si (μmol/mol) with (a) Zn, (b) CIA [$(Al_2O_3)/(Al_2O_3+Na_2O+K_2O+CaO)$], & (c) K_2O. Symbols denote the rock classes as shown in Fig. 1.*

Discussion: The enrichment of Ge is accompanied by high concentrations of other fluid-mobile elements (K, Zn, Cu, Cl, Br, S) [5]. Volcanic hydrothermal or metasomatic alteration of igneous materials similar to JakeM (mugearitic to trachyandesitic) and soil (average Mars basalt) are possible enrichment processes [9, 10]. In detail, however, these elements do not have strong correlations with Ge, and their concentrations vary widely across similar rocks, particularly in Kimberley rocks. This leads us to ask: are high Ge, Zn, and K a signature of a metasomatized sediment source, *or* have diagenetic processes further affected Ge, Zn, and K such that the characteristics of the source region are obscured?

Differences in concentration between the moderately volatile siderophile elements Ge and Zn may give insight to the relative timing and nature of alteration events (Fig. 2a). The Kimberley rocks demonstrate a decoupling of Ge and Zn under the conditions that deposited the Zn- and Mn-rich (8150±245 ppm) fracture fill (Stephen; sol 627) only a few cm from the Windjana target (Zn ~4300 ppm; sols 612-622). Ge/Si does not vary between these two targets, indicating that Ge was not mobilized by the highly oxidizing fluids proposed for Stephen's formation [11]. Other evidence includes: 1) high Ge/Si Bathurst_Inlet (Halls) and Kimberley (Liga) targets, which lack a corresponding increase in Zn and 2) low Ge/Si in Kimberley targets does not vary despite Zn ranging from 785-1900 ppm.

The relationship between Ge/Si and the CIA (Fig. 2b) further constrains the enrichment of fluid-mobile elements. Higher CIA values indicate that Pahrump is more altered than Yellowknife Bay (YKB) [12], possibly caused by a slightly more open system alteration that allowed limited leaching of highly soluble cations (assuming circumneutral pH). There is not, however, a corresponding increase in Ge/Si, which suggests open system weathering was not pervasive enough to affect the Ge/Si. This scenario for limited weathering is unlikely to be related to the high Ge in Gale sediments. For example, extensive weathering at a site in Hawai'i increased Ge from 1.6 ppm of parent basalts to 5 ppm in soils, with a respective increase of Ge/Si from 3 to 35 µmol/mol, but only with extensive leaching of SiO_2 to 7 wt% [4]. We suggest that the Ge-rich sediments at YKB and Pahrump, ~6 km apart and representing Aeolis Palus and Aeolis Mons rocks, respectively, were elevated in Ge prior to deposition, and the Ge/Si ratio was unaffected by subsequent in situ weathering and diagenesis.

Similar to Zn, Ge/Si does not correlate with K. This is largely because low Ge JakeM rocks have high K_2O up to 3.6 wt% (Fig. 2c). Nevertheless, separately evaluating low Ge rocks (Ge/Si < 100; $r = 0.14$) and high Ge rocks (Ge/Si > 100; $r = 0.23$), correlation with K is still low. K is enriched in rocks with low Ge as well as high Ge, which leads to two possible interpretations: 1) Ge is concentrated in zones during fluid alteration and/or 2) K may be enriched in K-feldspar, clays, or amorphous phases by one or more processes that do not fractionate Ge/Si (igneous, metamorphic, hydrothermal, authigenic). The first interpretation is consistent with the wide variation of Ge in similar rocks (Bathurst, Bell Island, and The Kimberley [8, 13]), which is plausibly due to the erosion of a source region with Ge-rich zones. The second interpretation is currently a topic of discussion [14].

Conclusion: The Ge discoveries in Gale so far are consistent with a sediment source that was heterogeneously enriched in Ge. The Peace Valles source region possibly includes pockets of Ge-rich materials. The source region of Pahrump was possibly also enriched, although this is the only outcrop of Aeolis Mons rocks studied as of sol 831 and further investigation is needed to support this hypothesis. Ge/Si was not subsequently fractionated during limited weathering and diagenetic processes, or by highly oxidized fluids that mobilized Zn, Mn, and other metals. Our interpretation is ambiguous because the process for K enrichment is unknown and may be associated with K-feldspars, clays, or amorphous phases formed by several different processes. Nevertheless, Ge has potential to be an important tracer for constraining Gale Crater's fluid alteration histoy. We encourage longer APXS integrations on future targets so that Ge can be analyzed with higher certainty.

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