

GEOCHEMICAL ANOMALIES AND ROCK COATINGS ON MARS: SIGNIFICANCE TO MSR

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Introduction: As exploration of Mars has progressed, ever-more-complex scenarios for multiple episodes of aqueous alteration have been discovered. Previous study groups have set goals for sampling Mars that have emphasized mineralogical and rock types based on the experience of terrestrial geological investigations [1]. The extensive Mars rover missions --- Spirit (MER-A), Opportunity (MER-B), and Curiosity (MSL) --- have discovered unexpected geochemical extremes, dramatically demonstrating that the limited sampling range of the Viking and Pathfinder missions could not reveal the geochemical diversity of Mars. Beyond major/minor elements patterns of igneous rocks, certain trace elements show large enrichments beyond explanation by magmatic differentiation alone.

Geochemical Patterns of Alteration: Examples of desirable samples, identified by the MEPAG study group, include carbonate, chert, and gypsum [1]. Discoveries by the three rover missions include carbonate (Comanche, MER-A) and numerous Ca sulfate veins (MER-B, MSL). Strong silica enrichments also occur, e.g., the Kenosha soils, >90 wt% silica (MER-A), while Independence outcrop (MER-A) and Esperance boxwork fracture fill (MER-B) have high Al and Si, and low cation concentrations consistent with montmorillonite clays. The Buckskin sample (MSL) has ~75 wt% SiO₂, some of which is tridymite, with low Al but above-average TiO₂, similar to FuzzySmith (MER-A). In contrast, there are low-Si occurrences, including sulfate-rich sediments of the Burns Formation (MER-B), the Island rocks with high S, Mg and Mn (MER-B), and ferric sulfate-rich soil horizons (Samra, Ulysses by MER-A). Peace rock (MER-A) is a Mg-sulfate cemented sandstone.

Coatings: Thin coatings have been discovered on many samples, both sediments and igneous rock surfaces, at all three rover sites. These are typically Cl-enriched, implicating aqueous activity. Although coatings are thin, they could support an embedded microbial biofilm or provide UV shielding to a shallow endolithic biota.

Trace Element Anomalies: Other samples exhibit a geochemical profile that does not deviate so dramatically in the major and minor elements from either the global martian soil (average Mars) or the Shergottite samples from Mars. Yet, several exhibit major deviations in trace element composition that are difficult to explain without invoking aqueous alteration scenarios. The Stephen sample (exposed fracture fill) discovered by MSL is highly Mn- and Cl-enriched, whereas the Mn- and S-rich samples at MER-B (Island rocks) are low in Cl.

Strong deviations in several other trace elements have been discovered on Mars:

Nickel. Concentrations of 4000 ppm (Morrison, MSL) and 2000 ppm (Tisdale, MER-B) far exceed the 300 to 600 ppm in martian soils and the much lower levels in shergottites. Ni can be mobilized, but its mineralogical forms may also allow scaling of the total contribution of accreted exogenous carbonaceous material to global soil.

Chromium. Modest factors of enrichment occur, but perhaps most significant are the very low values (<0.1 wt%), along with low Ni, in two classes of rocks on Husband Hill (Wishstone and Watchtower classes, MER-A).

Manganese. Wide variations in Mn/Fe ratio's occur, implying changes in pH and redox conditions.

Phosphorus. Although maximum enrichments are modest (~10x over Shergotty), the element often, but not always, accompanies other evidence for aqueous activity. P is the most important trace element to astrobiology.

Zinc: Martian meteorites contain < 100 ppm, but some samples at MSL and MER-B approach 1 wt%.

Chlorine. Maximum concentration of 2.6 to 3.4 wt% occur across the three missions. These are 3x to 8x higher than soil concentrations. Cl occurs as chlorides, perchlorates, chlorates, and perhaps other species, each having important implications for sub-zero aqueous processes and astrobiological conditions.

Bromine. The typical soil content of Br, 40 ppm, is 40x times higher than in Shergotty. Occurrences are extremely variable, often not correlating with Cl, and reach 2000 ppm (MSL) or ~1500 ppm (MER-A and -B). Much of the history of wetting of martian materials is surely recorded in the variability of salts of S, Cl, and Br.

Germanium. Perhaps the most surprising trace element enrichment has been Ge, occurring at up to 850 ppm (MER-B) [2] and almost as high at Gale crater (MSL). This level is an enrichment factor of at least 400 above that in SNC meteorites and minerals [3]. Suggested explanations include volcanic outgassing, hydrothermal activity, and precipitation sequences of Si-rich fluids. Like Br, Ge enrichments are highly variable, but not for the same reasons.

Ba, Li, F, Y, Rb, Sr, and Zr. These elements are sometimes detected by ChemCam (LIBS) and/or APXS (XRF), but quantitations are still in progress. Their extremes may also help identify samples of special interest.

Conclusion: In addition to the classically-derived mineralogic components, the martian sediments, rocks and soils themselves provide geochemical clues where the secrets of past conditions, timing, and sequences are hidden.

References: [1] E2E-iSAG Report to MEPAG. 2011. JPL CL#11-5351. [2] Mittlefehldt D. W. et al. 2016. Abstract #2086. 47th Lunar & Planetary Science Conference. [3] Humayun M. et al. 2016. Abstract #2459. 47th LPSC.