

ACIDIC FLUIDS ACROSS MARS: DETECTIONS OF MAGNESIUM-NICKEL SULFATES. A. S. Yen¹, D. W. Ming², R. Gellert³, D. W. Mittlefehldt², E. B. Rampe⁴, D. T. Vaniman⁵, L. M. Thompson⁶, R. V. Morris², B. C. Clark⁷, S. J. VanBommel³, R. E. Arvidson⁸, ¹JPL- Caltech (Albert.Yen@jpl.nasa.gov), ²NASA-JSC, ³University of Guelph, ⁴Aerodyne Industries, ⁵Planetary Science Institute, ⁶University of New Brunswick, ⁷Space Science Institute, ⁸Washington University in St. Louis.

Introduction: Calcium, magnesium and ferric iron sulfates have been detected by the instrument suites on the Mars rovers. A subset of the magnesium sulfates show clear associations with nickel. These associations indicate Ni^{2+} co-precipitation with or substitution for Mg^{2+} from sulfate-saturated solutions. Nickel is extracted from primary rocks almost exclusively at pH values less than 6, constraining the formation of these Mg-Ni sulfates to mildly to strongly acidic conditions. There is clear evidence for aqueous alteration at the rim of Endeavour Crater (Meridiani Planum), in the Murray formation mudstone (Gale Crater), and near Home Plate (Gusev Crater). The discovery of Mg-Ni sulfates at these locations indicates a history of fluid-rock interactions at low pH.

Mars Rovers: The Mars Exploration Rovers (MER), Spirit and Opportunity, landed in January 2004 at Gusev Crater and Meridiani Planum, respectively. Spirit traversed over 7.7 km through 2210 sols of surface operations, and Opportunity is currently on the degraded rim of Endeavour Crater after 4600 sols and 44 km of traverse. The MER instrument payload includes an Alpha Particle X-ray Spectrometer (APXS) measuring elemental chemistry and a Mössbauer spectrometer for iron redox and mineralogy on each rover. The Curiosity rover landed in Gale Crater in August 2012 to explore past and present martian habitability and has since traversed over 15 km through ~1600 sols of surface operations. Curiosity's instrument suite includes an arm-mounted APXS for elemental chemistry and the CheMin X-ray diffraction analytical lab instrument for quantitative mineralogy.

Abundant Sulfates: Sulfur is ubiquitous on the surface of Mars (Fig. 1). Of the ~1100 distinct APXS measurements made by the three rovers, only ~20 samples have less than 1% sulfur. Elemental correlations with sulfur indicate the presence of calcium (Fig. 2) and magnesium (Fig. 3) sulfates at all three landing sites. The MER Mössbauer spectrometers have detected ferric iron sulfates and hydroxysulfates (jarosite). Gypsum, bassanite, anhydrite and jarosite have been identified at Gale Crater by the CheMin instrument. Sulfates occur in a variety of settings: As distinct light-toned veins, as a distributed component within sedimentary rocks, as fine-grained deposits in soils, and in the X-ray amorphous fraction of many martian samples.

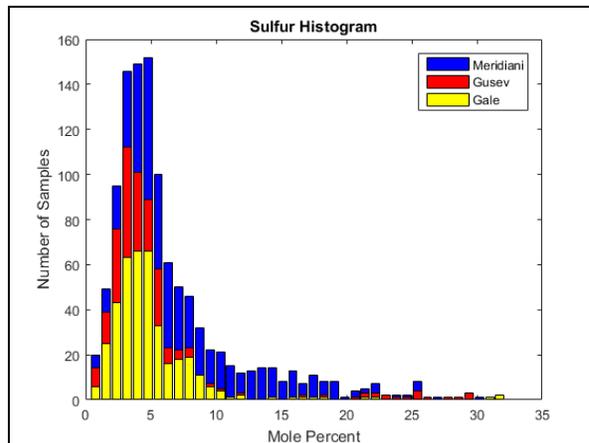


Fig 1: Histogram showing significant concentrations of sulfur in APXS analyses by the three Mars rovers (mean value: 6.6%).

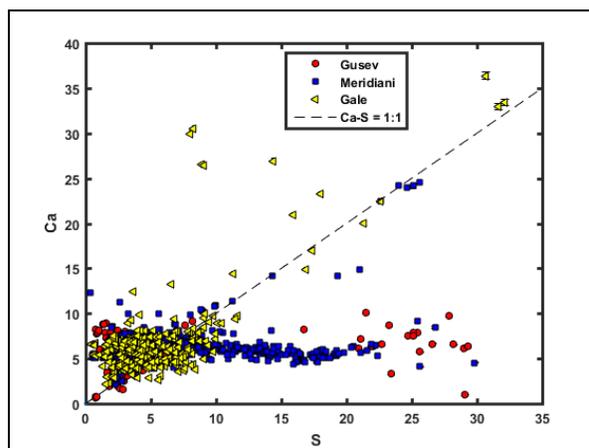


Fig. 2: Molar Ca versus S for all APXS measurements from the three landing sites showing clear evidence for calcium sulfates.

Magnesium-Nickel Sulfates: Calcium sulfates feature prominently in the in-situ dataset, but there are also instances of magnesium sulfates. Several of these latter occurrences have clear associations with nickel.

Pahrump Hills, Gale Crater. The Murray formation mudstone, finely laminated sediments deposited in a lacustrine setting [1], includes localized occurrences of erosion-resistant diagenetic features. Measurements of these raised clusters/nodules typically have >10 wt% SO_3 , an Mg-S molar ratio of ~1.4, and 2000 to 4000 ppm Ni. These are the samples with the highest Ni

concentrations measured thus far at Gale Crater. Deconvolution models also indicate the likelihood of Mg-Ni sulfates, with Ni concentrations of ~4500 ppm after subtraction of the background bedrock, in the diagenetic features in the Murray mudstone [2].

Endeavour Crater rim, Meridiani Planum. Fluid percolation through fractures within the rim of Endeavour Crater produced localized Mn enrichments and associated sulfates [3] as well as curvilinear zones of reddish altered rocks [4]. The Mn-rich samples (“Island Rocks”) show elevated MgO (11-16 wt%), SO₃ (25-38 wt%), and Ni (up to 1000 ppm), indicative of Mg-Ni sulfates (Figs. 3, 4). Approximately 3 km south of the Island Rocks and less than 10 cm from an exposure of the reddish altered rocks, a small (~2 cm), sub-surface pebble (“ECann”) was uncovered by the Opportunity wheels. Multiple APXS measurements of this pebble show clear Mg-Ni-S correlations with Ni concentrations approaching 2000 ppm (Figs. 3, 4).

Home Plate vicinity, Gusev Crater. Fumarolic deposits consisting of Mg, Ca and ferric-iron sulfates were discovered at various locales within Gusev Crater [5]. An APXS analysis of the “Hula” sample (Figs. 3, 4) shows elevated MgO (11 wt%), SO₃ (33 wt%), and Ni (900 ppm), suggestive of Mg-Ni sulfate.

Implications: Minor occurrences of Mg-Ni sulfates may seem insignificant, but quite the opposite is true. The solubility of Ni²⁺ is limited to mildly to strongly acidic fluids and thus the association of Ni²⁺ with Mg²⁺ constrains the fluid chemistry at the time these sulfates formed. For samples where other constraints, such as the presence of ferric iron sulfates, clearly establish an acidic formation environment, the discovery of Mg-Ni sulfates provides supporting information. In other cases where an acidic alteration history is not so obvious, the presence of Mg-Ni sulfates constrains at least one of the alteration episodes to low pH.

Mg-Ni associations are observed in martian meteorites [6], as Ni²⁺ readily substitutes for Mg²⁺ in magmatic processes, though these rocks are low in S (<0.3 wt% S). The alternative possibility that the Mg-Ni-S associations are due to the addition of sulfur to concentrated accumulations of Mg-Ni-rich igneous material was considered given the existence of mafic sand grains with >10 wt% MgO and nearly 1000 ppm Ni (El Dorado sands at Gusev Crater). With the possible exception of the ECann pebble at Meridiani, each of the samples identified as Mg-Ni sulfate is clearly secondary in nature, with clear context for aqueous alteration and likely precipitation from solution.

Another possible scenario involves the initial liberation of Ni from primary rocks at low pH, precipitation of readily soluble Ni complexes, and subsequent remobilization of Ni with Mg and S by fluids not necessarily

at an acidic pH. While this scenario cannot be ruled out with the available observations, there is no evidence to suggest that secondary compounds are available to provide the source of Ni for these Mg-Ni sulfates.

Summary: Chemical associations established by the APXS on the Curiosity, Opportunity and Spirit Mars rovers indicate the presence of Mg-Ni sulfates in erosionally-resistant diagenetic features in the Murray mudstone at the base of Mount Sharp at Gale Crater, in the rim of Endeavour Crater at Meridiani Planum, and near Home Plate in Gusev Crater. These sulfates most likely precipitated from acidic fluids.

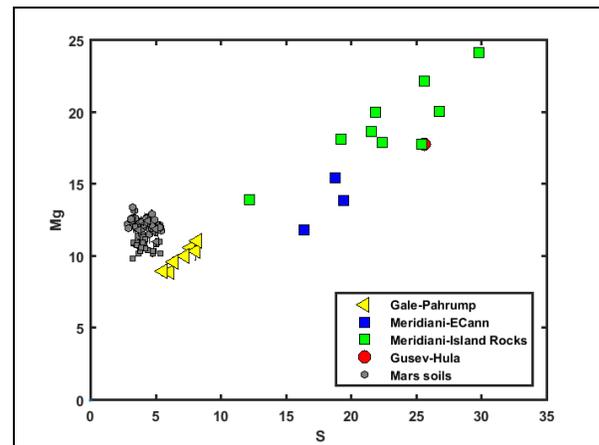


Fig. 3: Molar Mg versus S showing samples at the three rover landing sites containing Mg-sulfate.

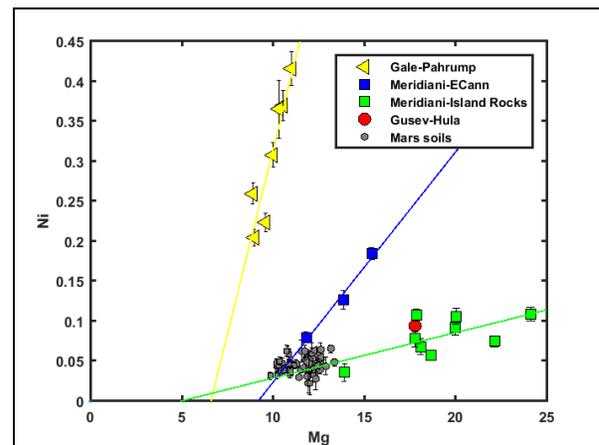


Fig. 4: Molar Ni versus Mg for the same points plotted in Fig. 3 showing Ni correlations with Mg.

References: [1] Grotzinger, J. P. et al. (2015) *Science* **350**, aac7575. [2] VanBommel, S. J. et al. (2016) *X-ray Spectrom.* doi:10.1002/xrs.2681. [3] Arvidson, R. E. et al. (2016) *Am. Min.* **101**, 389-405. [4] Mittlefehldt, D. W. et al. (2016) *47th LPSC* #2086. [5] Yen, A. S. et al. (2008) *J. Geophys. Res.* **113** E06S10. [6] Ming, D. W. et al. (2006) *J. Geophys. Res.* **111** E02S12.