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Introduction: The S contents of rocks and soils are indicative of various alteration processes on Mars, e.g.[1]. It has been quantified along traverses at 4 landing sites – Pathfinder, both MERs and MSL – by the APXS [2,3]. At the MSL and MER sites, sulfur abundances, correlations with likely bound cations and other elements, and complementary mineralogical and textural data have provided important insights into alteration processes and periods of more habitable environments in the distant past.

Method: The APXS quantifies 16 major and trace elements between Na and Br with high precision, good accuracy and low detection limits, sulfur among them[4]. The elements are quantified by their characteristic x-ray peaks as their usual oxides and are normalized to 100 wt%, assuming a homogeneous and water- and carbonate-free sample. The assumption that sulfur is fully oxidized as SO₃ in the overwhelming number of cases is confirmed by quantification of low-Z elements – essentially oxygen – using the APXS scatter peak method [5].

Soils: Unconsolidated materials (soils) at all landing sites show similarity in overall composition and an abundance of sulfur equivalent to approximately 5% SO₃ [6]. Sulfur correlates well with chlorine and zinc in soils (fig 1), and with the Fe³⁺/Fe_T content from Mössbauer on MER. These phases likely represent the fine Martian dust and were linked to the amorphous component in Chemin XRD [7].

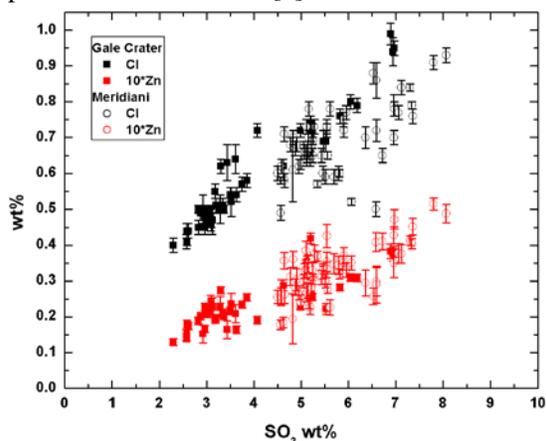


Figure 1: Cl and Z vs S in soils

Meridiani Planum: Bedrock on the plains at Meridiani is the Burns formation, a sulfate-rich sandstone

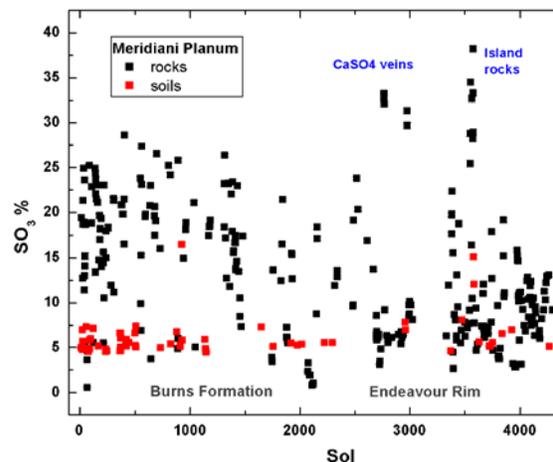


Figure 2: S vs sol number (traverse)

with up to 25% SO₃, and hematite and jarosite were identified by Mössbauer [8]. The traverse of ~45 km can be visualized through the sulfate content in rocks and soils in Fig. 2 against sol number. Abraded interiors of the Burns fm. have the highest sulfate content while brushed and as is surfaces have lower values through soil/dust cover or preferential abrasion of sulfate minerals from the rocks surface. The overall composition of the Burns fm. is remarkably constant over 30 km. However, sections in two impact craters have parallel ~30% reduction of magnesium and sulfur in 1:1 molar ratios with depth [3]. Fig. 3 shows that Mg and Fe are not diluted by the addition of sulfur, indicating that the Burns fm. likely contains Mg- and

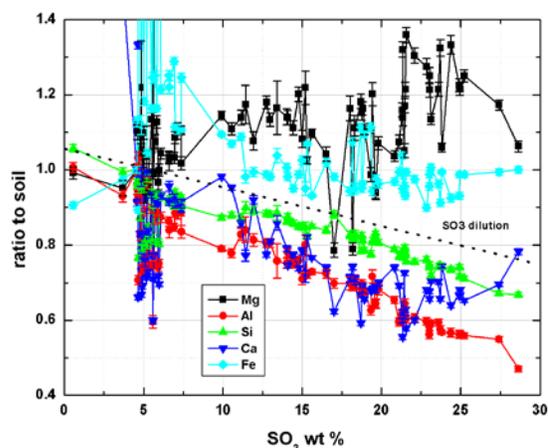


Figure 3: Major element content vs S

Fe-sulfates. Calcium tracks Al and Si, indicating that Ca-sulfates are not a major component.

On sol 2700 the rover reached the rim of Endeavour Crater, predating the Burns fm. Rocks on the rim are essentially of average-Mars-crust composition and have lower S contents (Fig. 2). Localized alteration zones occur, and for the first time, CaSO_4 veins (of unknown hydration state) were encountered [9].

Gusev Crater: The Gusev Plains' rock population is dominated by primitive, olivine-bearing basalts [10]. Rock surfaces were measured as is, brushed or abraded, with lowest SO_3 values for abraded rocks, down to $\sim 1\%$. Some rocks showed alteration rinds with S, Cl, and Zn contents higher than the values in basaltic soils [10]. At Gusev, a variety of localized sulfates were encountered: Peace is cemented with $\sim 20\%$ MgSO_4 ; Halley_Brunt contains $\sim 10\%$ CaSO_4 ; and the soil trench Boroughs exposed $\sim 10\%$ excess MgSO_4 [11]. However, the highest SO_3 contents occur in whitish subsurface soils exposed by the rover wheels. PasoRobles on the Columbia Hills contains $>30\%$ SO_3 . Most other elements are diluted with the notable exception of Fe. Several other deposits of sulfate-rich soil were found within the Columbia Hills over a traverse of several km. Mass balance shows that these Paso-Robles-class soils consist of basaltic sand mixed with Fe^{3+} , Mg- and Ca-sulfates, and excess SiO_2 (Fig. 4). These soils were interpreted as remnants of acidic leaching resulting from fumerolic activity. The scatter peaks indicate an excess of oxygen of ~ 15 wt% in these soils, pointing towards hydrated ferric sulfates [5].

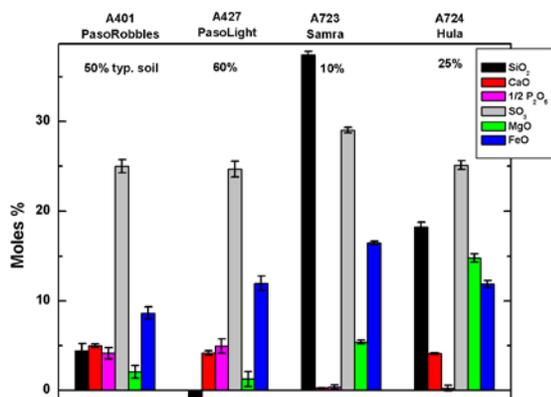


Figure 4: Excess sulfates and silica in PasoRobles soils

Gale Crater was selected on the basis of evidence from orbit for a sequence of sulfates, clays, and hematite. The rover has yet to reach the sulfate unit, but it has found ample occurrences of sulfates and clays. The bedrock at Yellowknife Bay, contains $\sim 20\%$ clays and is notably low in sulfate with $\sim 1\%$ SO_3 . Sulfates at Gale are predominant late-stage CaSO_4 veins. A SO_3 vs. CaO plot (Fig. 5) shows a clear trend of

CaSO_4 addition. The largest veins were found at Garden City where a Ca-rich, but S-free phase was identified in association with enrichments in germanium and manganese [12]. Local MgSO_4 pebbles and concretions were identified in the Murray and Stimson formations. Minor Fe-sulfates like jarosite, detected by Chemin, demonstrate excess sulfate over CaO as expected [13].

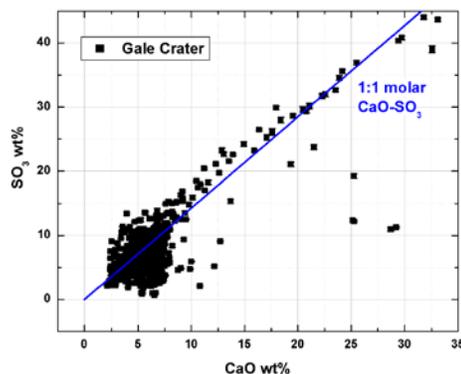


Figure 5: CaSO_4 addition at Gale Crater

Summary and Discussion: The ability to detect and quantify sulfur is crucial for understanding and comparing alteration processes at all landing sites. The extensive Burns formation at Meridiani Planum with $\sim 25\%$ SO_3 content is in sharp contrast with the low contents of sulfate at the older Endeavour and Gale Craters, where circumneutral water formed clays, documenting the transition from neutral water activity to a much more acidic period in Martian history.

The capability to detect and quantify sulfur and associated elements will be crucial for the upcoming exploration of the sulfate unit at Gale Crater to map the extent of this formation, to localize the most promising drill samples, to compare ground observations with orbital mapping, and to extend the understanding of alteration processes in early Mars history [14].

References: [1] King, McLennan, (2010), Elements, 6, [2] Rieder et al. (2003), JGR, Vol 108, E12, [3] Gellert, Clark, (2015) Elements, 11, [4] Gellert et al, (2006), JGR, Vol 111, E12, [5] Campbell et al, (2008), JGR, Vol 113, E6, [6] Yen et al. (2005) Nature, 436, 7047, [7] Blake et al., (2013), Science, Vol 341, 6153, [8] Clark et al., (2005), EPSL, 240, 1, [9] Squyres et al. (2012), Science, Vol 336, 6081, [10] Gellert et al., (2004), Science, Vol 305, 5685, [11] Ming et al. (2007), JGR, Vol 113, E12, [12] Berger et al., (2017) JGR, Vol 122, E8, [13] Rampe et al. (2017), EPSL, 471 [14] Grotzinger et al., (2012) SSR, 170

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