MOBILITY OF PHOSPHORUS ON THE MARTIAN SURFACE AND IN A MARTIAN METEORITE.

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Introduction: On Mars the P abundance is about 10 times higher compared to Earth [1]. Assuming that most of the P is hosted in Ca-phosphates, their mobilization in an acidic environment, as found for the Martian surface, was studied for the Martian meteorite Zagami by leaching experiments and in soils and rocks on the Martian surface with the Alpha Particle X-Ray Spectrometer (APXS) onboard the NASA Mars Exploration Rovers (MER), Spirit and Opportunity.

The basaltic Martian meteorite Zagami: The fine-grained lithology of Zagami contains 0.48 wt.% of P_2O_5 in form of whitlockite, which accounts for 0.35 wt.% of Ca out of the 7.2 to 7.6 wt-% present [2, 3]. Whitlockite also hosts the majority of the lanthanides as trace elements in the form of phosphate minerals.

We studied the dissolution of phosphate by leaching crushed (46 - 75 µm) samples of Zagami at increasing acidity (pH 5 to pH 1) using 0.1 N buffer solutions. We measured residual Ca and lanthanides in the leached samples by neutron activation analysis, which is not suitable for a P determination. Residual Ca decreased from 7.4 to 7.1 wt.% on average, as the pH value of the leaching solution was lowered from 5 to 2. The observed constant Ca concentration in solution of pH 1 indicated that complete mobilization of phosphate via dissolution of whitlockite had already occurred at pH 2. The residual Ca is bonded in unreactive feldspar and pyroxene. As the relative uncertainty of Ca is 5 %, which is in the range of the Ca amount in whitlockite, a precise study of the phosphate dissolution was not possible via Ca determinations.

Therefore, the pH-dependence of lanthanides mobilization was determined by their residual concentrations (Fig. 1); see also [4]. The overall mobilization of Ca and lanthanides in whitlockite is similar. These leaching experiments indicate that mobilization of P occurred on the Martian surface when acidic brines reacted with the surface material.

Martian surface: The MER APXS measurements reveal similar P concentrations in soils of 0.36 wt.% [5, 6] at the two different landing sites, Gusev Crater and Meridiani Planum.

Gusev Crater: The P contents of the rocks in the Gusev plains (Fig. 2 see at the end) have a somewhat lower or similar P concentration as the soils, except for rock Mazatzal. However, in the Columbia Hills the P

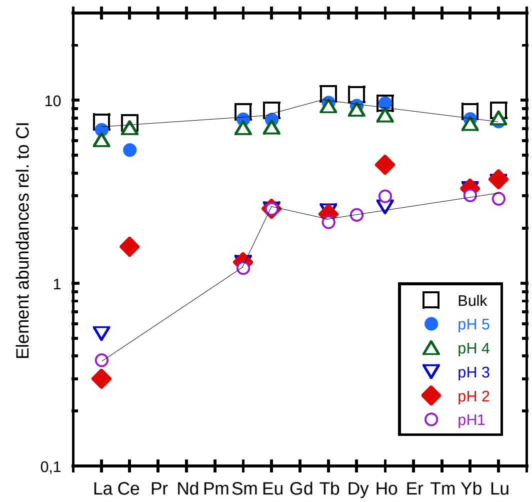

Fig. 1. REEs in residue of meteorite Zagami after leaching by buffered solutions at pH 5 to 1.

contents raise up to 2.0 wt.% [5] (Fig. 2). For the Gusev plains rocks, P show different concentrations for undisturbed (RU) surfaces, brushed (RB), and with the Rock Abrasion Tool (RAT) abraded rocks (RR). For Adirondack rock, P contents decrease from RU over RB to RR. Rock Humphrey shows similar P contents in RU and RB and a decrease in RR, whereas for rock Mazatzal the highest P concentration is measured in its weathering rind of RB [5]. This observation is an indication for a P-phase on the surface mobilized by aqueous processes.

The rocks in the Columbia Hills have a higher Fe^{3+}/Fe_T ratio [7] and all except the Peace-class are

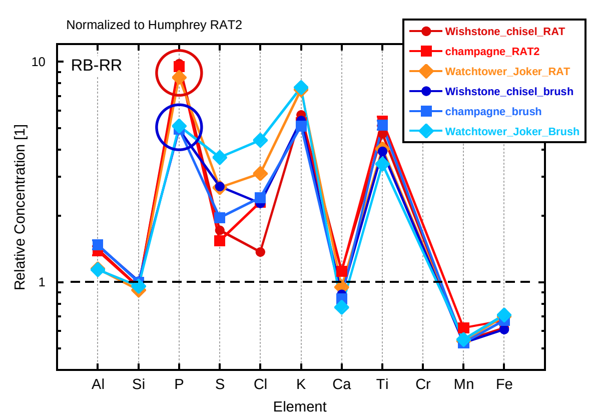

Fig. 3 Wishstone-class rocks: Only brushed samples lost phosphates (weathering rind) compared to abraded rocks.

enriched in P compared to the plains basalts (Fig. 2). For Wishstone-class rocks, the chemical compositions of brushed and abraded surfaces reveal the alteration of P-rich rocks in an acidic environment (Fig. 3). The P contents in the brushed samples are a factor of 2 lower than in the abraded surfaces [5]. A loss of Ca-phosphate, but, no loss of feldspar was found for the brushed surfaces. Phosphates dissolve readily in dilute acids, whereas plagioclase is stable as shown in our leaching experiments with Zagami [4].

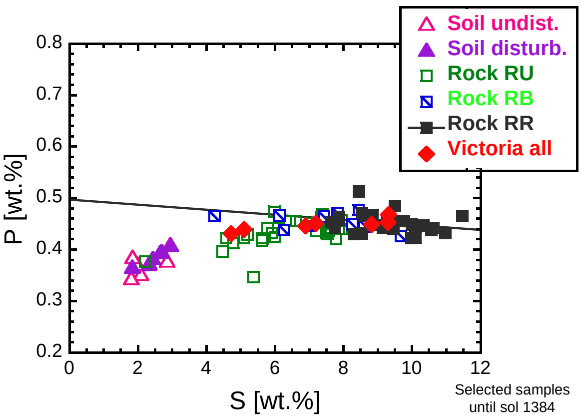

Fig. 4 Phosphorus versus S for Meridiani soils and rocks, undisturbed (RU), brushed (RB), and abraded (RR). All rocks from Victoria crater are shown separately. For the abraded rocks (RR), there is no correlation of P with S.

Meridiani Planum: Most of the rocks are of sedimentary origin, a similar P content of about 0.45 wt.% was measured in all outcrops with the APXS [6]. Figure 4 demonstrates the relatively constant P abundances in rocks that are independent of their S content. Since S concentrations are markedly high in all measured outcrops, the concentration of major elements can provide constraints on the composition and the relative proportion of the S compounds in the outcrops.

In a simple two-component mixing model it could be assumed that one component, which may be of basaltic or siliciclastic nature, contains all Si-bearing minerals, while the other component consisting of minerals that likely precipitated from brines, contains most of the S. Mass balance consideration and Fe-bearing mineralogical results from the Mössbauer spectrometer point to sulfate being the predominant oxide of S [8]. As P in the outcrops is not diluted by the sulfate phase, as observed for Si or Al for example [9], it must be a part of this component. The sorption of phosphate from dissolved $Ca_3(PO_4)_2$ in weakly acidic solution by igneous rocks has been demonstrated experimentally [10]. The reactivity increases with increasing concentration of Al and Fe in the rocks and with decreasing pH in moderately acidic solutions [10]. Compared to Earth the Martian rocks have a two to three times higher Fe content. The easy dissolution of Ca-phosphates from rocks in weakly acidic water, but, also the sorption of dissolved Ca-phosphates by rocks could be the reason for the uniform distribution of P in the S-rich outcrops.

Ares Vallis: Phosphorus concentrations of 0.4 wt.% in rocks and soils were measured with the APXS of the Pathfinder Mission (MPF). As the MPF APXS was less sensitive as the MER APXS, the relative error of P was 30 % [11]. Nevertheless, this is consistent with the MER results. In Ares Vallis, fluvial activities may have mobilized P and caused its uniform distribution.

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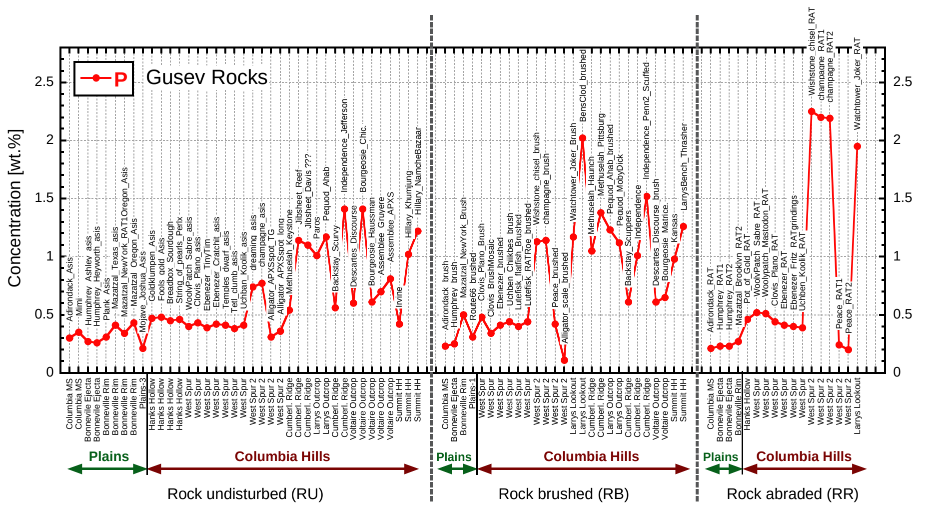

Fig. 2 Concentration of P in rocks along the traverse from the plains to the Columbia Hills at Gusev Crater. The rocks are first sorted by surface treatment and then by increasing sol.