

Experimental leaching processes and the formation of sulfates with sulfuric acid on terrestrial rocks, martian-like rocks and the martian meteorite Tissint related to the formation of ILD's on Mars.

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Introduction: Spectral data from Mars, obtained from the CRISM and OMEGA instruments show sulfate-rich regions not only along the equatorial zone. These sulfate deposits with thicknesses up to several kilometers were identified and discussed by various authors [1], [2] and [3], and consist dominantly of Mg-, Fe- and Ca-rich sulfates. According to [1] it is reasonable to assume that their deposition is the result of chemical reactions between aqueous, sulfur-containing species and the martian regolith involving evaporation processes at the late Noachian/early Hesperian boundary.

Chemical reaction between sulfuric acid (H_2SO_4) and rocks at elevated temperatures is potentially an important geochemical process because advective and diffusive fluid flow is probably widespread and perhaps still active on and within the martian surface to near subsurface.

An experimental design is presented of H_2SO_4 -leaching of various terrestrial source rocks, minerals and the martian meteorite Tissint. The investigations aim to tackle the hypothesis that the sulfate occurrence on Mars is related to evaporation. This might suggest that the martian crust was altered by sulfur acidified water at temperatures between 0 and 25°C resulting in the exchange of ions. The experiments are performed with sulfuric acid of medium to low pH values and temperatures between 0 - 25°C to produce sulfate-forming solutions.

Sample description: The mineralogical composition of the massive Mg-, Ca- and Fe-rich sulfate depositions on Mars is controlled not only by the quantity of aqueous influx but also by the mineralogical composition of the source rocks which serve as ion donors.

The samples used contain Mg, Na, K, Ca, Mn, Fe and Al ions. Ten suitable terrestrial samples including two standards, the major rock forming minerals, ortho- and clinopyroxene, olivin and plagioclase and 4 mafic to ultra mafic rocks were examined in this study (Tab. 1), whereas the two standards (provided by the U.S. Geological Survey) also refer as martian analogues.

Our sample selection such as olivine, pyroxene, plagioclase -and the rocks: including volcanic glass, basalt and komatiite as analogues for martian lithologies are in accordance with in situ measurements

of soil, performed during the NASA's MER-mission and APXS-data (Alpha Particle X-ray Spectrometer) collected during the most recent MSL-mission.

The ages of the samples range between 3.5 Ga (komatiites, Onverwacht group, Barberton Greenstone Belt) up to recent ages (volcanic glass, Mt. Kilauea, Hawaii, USA). The alteration and weathering state also reflects the different history and environment.

Table 1: Terrestrial rocks and minerals used in our experiment as martian analogues and the martian meteorite Tissint.

<i>Name</i>	<i>Material</i>	<i>Location</i>
Tissint	martian Meteorite, Picritic Shergottite	Morocco
San Carlos	Olivine	San Carlos, AZ, USA
CPx	Clinopyroxen	Eifel, GER
Opx	Orthopyroxen	Lake Onatchiway, Québec, CAN
Bytownite	Plagioclase	Crystal Bay, MN, USA
House Park	Volcanic glass	Kilauea, HI, USA
11-102	Komatiite unweathered	Barberton greenstone belt, Komati River, SA
Spinnifex	Komatiite weathered	Barberton greenstone belt, Komati River, S. Africa
Vogelsberg	Xenolithe/Mantle peridotite	Hessen, GER
Standard 1/BIR-1a	Olivine tholeiite, Reykjavik dolerite	Iceland
Standard 2/DTS-2b	Twin Sister dunite	Twin Sister massif, WA, USA

In addition the most appropriate and for such destructive studies available martian rock sample was selected. Tissint, the youngest fall of a martian meteorite (observed on July 18th, 2011), is a direct sample from Mars that is almost unaffected by terrestrial weathering. It thus provides the unique opportunity to investigate the water/rock interaction in a scientifically comprehensible way with respect to leaching-, alteration- and weathering processes on Earth [4].

Experimental setup: The experimental setup is based primarily on standardized procedures which are common in aqueous geochemistry and hydrogeology. The total amount of the solid samples was dried at around 106°C for 24 h. Thereafter, the samples were ground with a disc mill to fine powder. Three grams of

each of the contemplated samples were sub sampled into three parts. For each test run 1 gram of rock powder together with 100 ml H_2SO_4 (medium and low pH values) was placed into a 100 ml PET-test tube (batch cup). The batch cups were placed in an overhead shaker, in an attempt to simulate time and fluid flow while leaching, and remained there for about 30 days (Fig.1).

Leachates were filtered through 11 μm standard Schleicher & Schuell cellulose filters.

The pH parameters of the resulting leachate were measured at each batch cup with a standard pH-electrode (pH-meter WTW pH 196).

A fifteen-ml aliquot of each of the untreated, filtered solution was analyzed by ICP OES Optima 2100 from PerkinElmer in order to measure the bulk-ion-concentration (Fe^{3+} , Mg^{2+} , Ca^{2+} , K^+ , Na^+ , Mn^{2+} , Al^{3+} , Cl^- and PO_4^{3-}).



Figure 1: Experimental acid-sulfate leaching process of various source rocks, minerals and the martian meteorite Tissint in an overhead shaker in the laboratories at the Freie Universität Berlin, Germany.

Major and trace element analyses of the solid samples were performed using a PANalytical Axios (XRF). The mineralogical composition of the samples was measured by powder X-ray diffractometry (PXRD) using a Bruker AXS Discover diffractometer at the German Research Centre for Geosciences (GFZ) in Potsdam, Germany.

Figure 2 presents the result of PXRD analysis showing the mineralogical composition of the representative sample “Vogelsberg” containing fosterite ($Mg_2[SiO_4]$) and enstatite ($Mg_2[Si_2O_6]$) as expected [5].

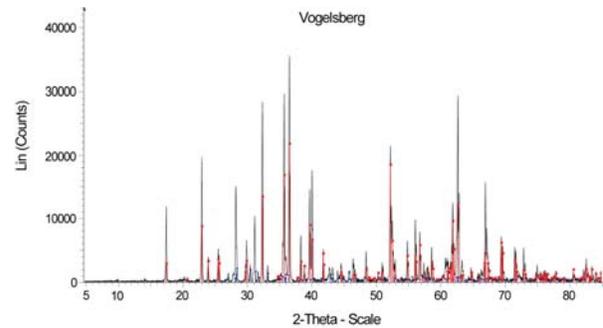


Figure 2: X-ray diffractogram showing the mineralogical composition of the sample “Vogelsberg” containing ■ fosterite and ◆ enstatite.

Approach: We assume that, besides of weathering and alteration, evaporation to be the main process responsible for the massive deposition of polyhydrated- and monohydrated sulphates, comparable with the formation of the Zechstein evaporite complexes in northern Europe [6]. The formation of almost monomineralic $MgSO_4 \cdot H_2O$ (kieserite) can only be reasoned by evaporation. The evaporation products thus had to be soluted in liquids or brine on Mars. Investigating the leaching behaviour of martian rocks and rock analogues will aid in improving our understanding of the ions available in martian liquids and the composition of the evaporation products. This study will be the basis of upcoming investigations in principle following the procedures which were already described by [7].

References:

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