BASALT WEATHERING EXPERIMENT IN SULFURIC ACID BRINE TO BETTER UNDERSTAND MARTIAN MINERAL ALTERATIONS.
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Introduction: Cold brines, especially acidic ones (from sulfuric volcanic outgasing) are among the few candidate liquids in the Amazonian period on Mars [1,2,3]. Because of the low freezing point and evaporation rate, they could be ephemerally present even today. To understand the low temperature acid brine produced mineral changes we started experiments with basalt samples from the Earth and H_2SO_4 to characterize the changes, composition and other specific characteristics of the liquid. The long term aim is to understand there are such solved chemicals produced by acid basalt weathering under Mars like conditions that could be used by hypothetical extreme organisms there. As a first step, the result of a simple experiment series is outlined here made at room temperature and at -20 °C to provide background to even lower temperatures.

Methods: The basalt sample came from Alsórákosi (no. RAC 15, collected by Sági T. [4], was composed of homogeneous, olivine basalt without much void spaces. It has weakly wavy oriented porphiric texture with 0.5-1 mm-(max. 2 mm) grain diameter, but smaller ones are also present with continuous size distribution. The main composition is olivine, augite with small Cr-spinell incusions. Elongated plagioclase grains and few opaque (magnetite) minerals are also present.

Two types of specimen were prepared: polished thin section plates and powder with grain size 1.0-0.05 mm for the following tests (Fig. 1.):

I. Room temperature + saturated H_2SO_4 (slice+powder)
II. Room templerature + H_2O (slice+powder)
III. -20 °C + saturated H_2SO_4 (slice+powder)
VI. -20 °C + saturated H_2O (powder)
V. -20 °C + saturated H_2O (slice)
-20 °C + saturated H_2SO_4 (powder)
VII. no effect, control sample (slice+powder)

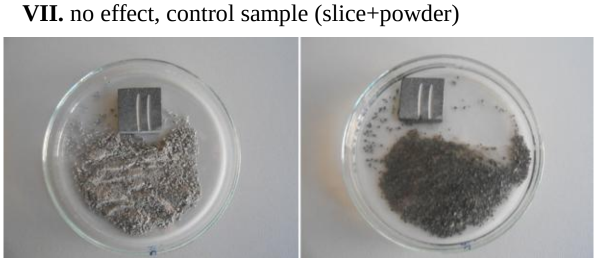

Figure 1. Example of the test III. before (left) and after (right) with powder (bottom) and slice (top). The dark colour on the right came from the hygroscopic acid

Results: Intact and weathered areas of the samples could be separated by microscopic appearance: in the weathered patches the mineral grains are smaller, have resorbed perimeter, highly fractured, together with many dark clay-like mineral with non-reflecting colour, submiscroscpic grain assemblage and occurred around te weathered grain edges.

Discussion: Comparing the H_2SO_4 driven weathering at + and – 20°C: the rate of the weathered area varies between 20 and 70% at +20°C (calculating at 3x3 mm diameter field of view), at -20°C between 50-70%. The weathering rate is characterized by tiny (300-500 μm) and large weathered patches (1-3 mm), in the case of +20°C these patches occur mainly around the sample's edge, but also almost everywhere, but starting from fractures (Fig.2).

At +20°C, the large weathered patches contain submicroscopic clay minerals occasionally with grayish-green thin cover (characteristic to smectites), whereas at -20°C instead of large weathered zones, almost continous vesicular weathered zones are present and filled by 50% clay and 50% eroded phenocrysts of earlier less weathered minerals. Phenocrysts in the highly fully weathered and clay containig zones have strongly eroded rim, whereas the minerals in vesicular weathered zones (where next to resorbed depressions feldspars are still present) at -20°C the erosion was concentrated along fractures, possibly formed by the temperature decrease, but relatively well-preserved rim. The olivine in low-weathered zones show etched surface with inclusions and FeO and clay-filled fractures, and the olivine is strongly iddingsited along fractures. The feldspar in low weathered zoned have clayey altered twin lamellae with 3-5 μm width and 20 μm distance from each other at +20 °C, whereas at -20°C the feldspars are preserved only as strongly eroded crystal nuclei. The weathering at +20°C is characterized by "patchy weathering zone", at -20°C is characterized by "vesicular texture, destroying minerals along the fractures". Opposite to the sulfur-acid weathering, in the case of the aqueous weathering there are no strongly weathered zones, patches, and the rims of minerals are well preserved. Weathering was observed only in unique mineral grains by pure water (Table 1.).

At +20°C the H_2O weathered sample olivine shows etched surface, weak alteration along the fractures, whereas at -20°C (with H_2O ice) the olivine is strongly fractured and etched surfaces are coated by thin clay film. The feldspar at +20°C contains inclusion, whereas at -20° is characterized by fractures. The groundmass of basalts are not weathered at +20°C, but at -20°C diffuse alterational rims are observed near to mineral edges and fractures. Weathered features occur only at the outer 1/3 of the whole sample at +20 °C but across the whole sample in the case of -20 °C.

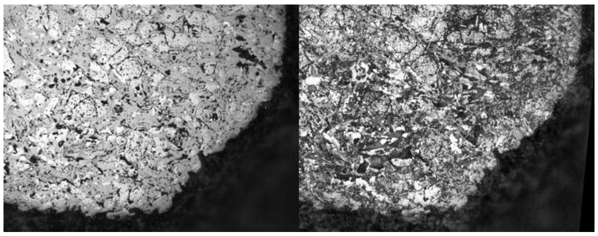

Fig. 2. Before (top) and after (bottom) images of the polished surface of the -20 C acid attack

Infrared spectral analysis: The original basalt and basalts after aqeous altearation both at +20°C and -20°C shows very similar infrared spectra containing plagioclase, diopside, olivine and less chlorite and montmorillonite, and amorphous glass too. The spectrum of sulfuric acid weathered basalt shows several clay minerals, such as kaolinite, montmorillonite, chlorite and less feldspar relatively to the water saltered and intact samples – but in it is dominated by the acid in the spectra (Fig.3).

Prliminary conclusions: Several observations are perspectivic to separate weathering features formed at different conditions, including more dense fracturing in the -20°C sample even where no clays are present, the pyroxene/glass ratio looks to be different at water and acid attack, the H_2SO_4 is very hygroscopic and covers several IR spectral peaks, despite the sample was dried, the freezing produced several fractures that supported the weathering as physical pathways for the agents, low temperature acid weathering produced inhomogeneous alterational product distribution, and acid attack is highly effective at the analyzed -20°C. In the future we continue the simulations toward lower temperature and the analysis of different factors in the process too, as such type of weathering might occur on Mars and could contribute in sulfate formation [5].

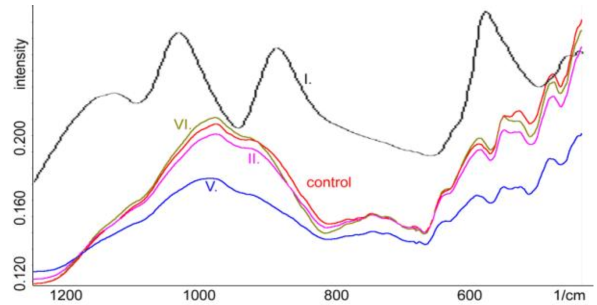

Figure 3. FTIR spectra of the powder samples

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References: [1] Tosca et al. (2008) *Science* 320, 1204. [2] Chevrier & Altheide (2008) *GRL* 35, L22101. [3] Tosca et al. 2004 *JGR* 109(E5) E05003. [4] Sági T., Harangi Sz. 2013. (in Hung.) IV. Kőzett. Geokém. Vándorgyűl, Orfű 49-50. [5] Golden et al. (2005) JGR 110(E12), E12S07.

Table 1. Comparison of microscopic analysis based differences between the rock slices

weathering medium	**H_2SO_4**		**H_2O**		**no (control)**
temperature	+ 20 °C	-20 °C	+20 °C	-20 °C	+20 °C
weathered area	20-70% starts form sample edge	50-70 %	<10%	10-15%	<5%
large, dark weathered dendritic xenocrysts	10%	continous vesicular weathering zones, which consists of etched minerals (50%) and clay (50%)	mostly relict grains, no weathering	mostly relict grains, no weathering patches	pre-test weathering, low-grade weathering
ratio of large, dark weathering patches	33%				
small weathered patches	50%				
dendritic crystals/clay ratio	50-50%				
size of weathered patches	100 - 500 μm				
olivine (30-200 μm, tabular)	iddingsited, etched inclus., FeO+clay in fractures.	iddingsitisation alteration along freezing pruduced fractures	etched surf. + inclus., aq. alter. at rims, iddingsite along the fractures.	clay films along the rims and freezing produced fractures	fractured olivine
feldspar (50-100 μm, lath shaped)	clayey filling along the twin lamellae	strongly weathered, only sendritic xenocrysts	inclusions	freezing produced fractures	not weathered
groundmass, melt	weathering, clayey alteration	weathering at freezing produced fractures	not weathered	diffuse rim and fractures	
characterization of weathering	patchy weathered zone	vesicular texture, destroying minerals along freezing fractures	small weathering only in weakness zones of minerals, inclusions	freezing produced fractures with clayey filling in larger grains	little, only along the fractures