

**Experimental studies on liquid and vapor phase alteration of basaltic glass: Implications for Earth and Mars.**

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**Introduction.** Hydrothermal alteration experiments on basaltic glass allow the study of factors influencing weathering and alteration of amorphous phases in various, controlled hydrous regimes. In the experiments materials have been located in vapor and liquid phases, with atmospheric composition of either air or CO<sub>2</sub> and temperatures of 120 and 200 °C. On Earth, basaltic glass is readily altered to clay minerals, zeolites and carbonates [1-3]. Comparable minerals have been detected on the Martian surface; often associated with impact craters and altered impact glass, probably a result past subsurface alteration [4, 5]. Here we perform experimental work to investigate the role of selected parameters; temperature, pH, O<sub>2</sub> and CO<sub>2</sub> fugacities.

**Sample and methods.** Basaltic glass of tholeiitic composition was used as analogue material. Prior to the experiments the glass was cleaned for contamination, crushed to a fine powder and analyzed for mineral content by X-ray diffraction analysis (XRD) and Near Infrared (NIR) spectroscopy; primarily of basaltic composition with a minor quantity of forsterite and pyroxene (Figure 1). Significant 1 and 2 μm absorptions are visible in its NIR spectrum (Figure 2), which is consistent with the presence of the olivine/pyroxene-bearing material.

The experiments were performed in 600 ml stainless steel Parr<sup>®</sup> reactors. An equal amount (10 gr.) of crushed material was located on the reactor floor and in a container elevated above the reactor floor, representing fluid and vapor phase alteration. A water/rock ratio (W/R) of 10 was applied, in experiments performed with a CO<sub>2</sub> atmosphere MilliQ-water was depleted of oxygen prior to mixing. After sealing the reactor, CO<sub>2</sub> experiments were purged with CO<sub>2</sub> gas before heating

to either 120 or 200 °C and kept constant for 3 weeks.

All products were examined for bulk and clay mineralogy (XRD and NIR analyses). Complementary studies were performed to attain high magnification images with Scanning Electron Microscopy (SEM) and element composition by Energy Dispersive Spectroscopy (EDS). Formation water pH was measured at the end of experiments along with element composition using ICP-MS.

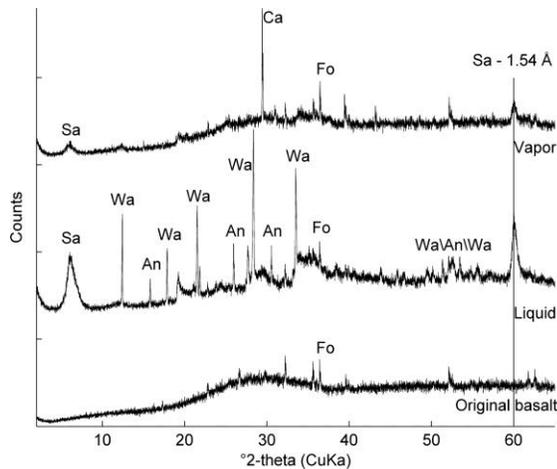
**Observations.** Table 1 shows the results of bulk and clay fraction XRD interpretations for all experiments. Examples of XRD runs (air atmosphere at 200 °C of liquid and vapor phase alteration) are shown in Figure 1. The general alteration mineral assemblage in experiments performed at 120 and 200 °C are comparable.

Saponite (smectite) was formed in all experiments, with largest abundances in liquid phase and CO<sub>2</sub> conditions (Table 1), based on position of the randomly oriented 060 XRD reflection (position 1.54 Å in Figure 1). NIR spectroscopy supports the identification; observed by absorption features around 1.9 μm and a plateau at 2.3 μm (Figure 2). Best developed crystallites were found in the liquid phase, as observed by better defined diffraction peaks (Figure 1) and supported by SEM studies. They commonly form grain coating honeycomb structures encircling unaltered basaltic grains, crystallites are commonly less than 0.5 μm in size.

Calcite is the second most abundant alteration phase, forming in the vapor phase regardless of atmospheric composition. It is a major phase under CO<sub>2</sub> conditions (Table 1). In the liquid phase it was only formed in CO<sub>2</sub> conditions. NIR analysis confirms the presence of carbonates, observed by absorption features at 3.35, 3.48 and 3.98 μm (Figure 2).

**Table 1.** Identified minerals in four different experimental setups for bulk and clay fraction using XRD analysis. +, ++ and +++ indicate relative abundance for each sample based on peak intensity relationship, respectively little, medium and abundant. ? indicates phases that might be present. Atm. – experimental atmosphere, L – liquid phase, V – vapor phase, Sap – saponite, Wa – wairakite, An – analcime, Ca – Calcite, Fo – forsterite, Am – amorphous phase, Chl – chlorite, Ka – kaolinite, Sr – serpentine, Mi – mica.

T (°C)	Atm.	L/V	Identified minerals											
			Bulk XRD						Clay fraction					
			Sap	Wa	An	Ca	Fo	Am	Sap	Chl	Ka/Sr	Mi	Am	
120	Air	V	+				+	++	+++					+++
		L						++	+++					+++
120	CO <sub>2</sub>	V	+				+++	+	+++					++
		L	++	++	+	+++	+	++					+++	
200	Air	V	+				+++	++	+++			?		+++
		L	+++	++	+		+	++				+	+++	
200	CO <sub>2</sub>	V	++	+			++	++	++					+++
		L	+++	++	++	++	+	++				+	++	



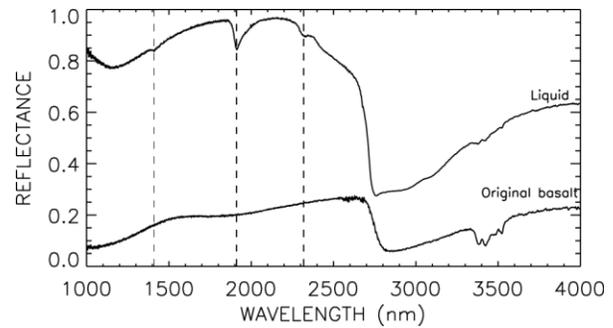
**Figure 1.** Whole rock diffractograms of alteration experiment performed at 200 °C with air atmosphere, from the bottom: original basalt; liquid - and vapor phase alteration. Sa = saponite, Ca = calcite, Fo = Forsterite, Wa = wairakite

The zeolites wairakite and analcime were observed, the former being a major constituent in the liquid phase mineral assemblage regardless of atmospheric composition (Table 1) and a minor component in vapor phase under CO<sub>2</sub> conditions. Analcime was only observed in the liquid phase (Table 1, Figure 1). The wairakite/analcime ratio reflects the atmospheric composition, lowest in CO<sub>2</sub> experiments.

The final pH-values of the water were 10 and 6, for air and CO<sub>2</sub> experiments, respectively.

XRD and NIR spectroscopical analyses showed similar mineralogy for the most abundant phases. The zeolite phases were easily detected in XRD (Figure 1), but were not observed in NIR analyses. Other minerals are present in quantities at or just above the XRD detection limit but somewhat easier identified during NIR spectroscopy. Thus, these two methods are complementary near the detection limits.

**Discussion.** Wairakite (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>•2H<sub>2</sub>O) is the Ca-analogue of analcime (NaAlSi<sub>2</sub>O<sub>6</sub>•H<sub>2</sub>O). On Earth it commonly forms by hydrothermal alteration of basalt, preferably at temperatures of 150-200 °C and higher, analcime, on the other hand, is not constrained to specific temperature conditions [6, 7]. In the current experiments wairakite was formed at lower temperatures, 120 °C. The wairakite/analcime ratio seems governed by the atmospheric composition; low values in CO<sub>2</sub> conditions. This can be explained by the solid solution series of the zeolites [8], the increased formation of calcite in these conditions consumes more Ca<sup>2+</sup> and pushes the series towards analcime. Wairakite is the only zeolite observed in the vapor phase. It may be a precursor to analcime or more stable at lower W/R ratios, but only analcime has been observed on Mars. Zeolites have been reported to have a strong link to craters on Mars [9]. In impact settings hydrothermal



**Figure 2.** NIR spectroscopy of alteration experiments performed at 200 °C with air atmosphere, from the bottom and up: original basalt and liquid phase alteration.

conditions with subsequent wairakite formation could appear at relatively low temperatures and W/R ratios. Identifying this phases in NIR spectroscopy is problematical and may explain the lack on Mars.

Saponite is the principal clay mineral forming regardless of experimental setup, both in liquid and vapor phase alteration (Table 1). The saponite formation in the vapor phase in spite of low W/R ratio demonstrates the low water concentrations required for smectite formation and it seems independent on atmospheric composition. This may explain why smectites are abundant on Mars and observed in a variety of geological settings [4].

Atmospheric composition seems to control the formation of calcite in liquid phase experiments; only appearing under CO<sub>2</sub> conditions (Table 1). A possible result of liquid CO<sub>2</sub> dissolution, increasing the carbon and oxygen content, and promoting calcite precipitation. The liquid dissolution of CO<sub>2</sub> is also reflected in decrease of formation water pH during CO<sub>2</sub> experiments.

**Conclusion.** Here we provide basalt glass alteration pathways for various environmental conditions on the Earth and Mars.

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