

Supplemental Material M: Contents

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Experimental and analytical techniques

Experimental design and preparation of reactants

In the modified Dickson-type hydrothermal apparatus (Dickson et al. 1963; Seyfried et al. 1987) used in this study the reactants reside within a flexible gold reaction cell ($V_{\text{total}} \approx 100$ ml), which is sealed through a titanium closure and itself encased in a stainless-steel pressure vessel filled with distilled water. The vessel is placed in an electric ceramic heater arrangement and connected to a hydraulic pump system; temperature (max. 400 °C) and isostatic pressure (max. 56.5 MPa) can be controlled independently. A titanium access tube connected to the titanium closure piece enables repeated fluid sampling during the experiment through an attached custom-fitted valve.

The forsteritic olivine (Fo91) and anorthite-rich plagioclase from Miyake-jima volcano (An95) were used to prepare a mixture of mineral reactants resembling the mode of an olivine-rich troctolite (see Table 2). Due to their gem-like quality, a pure olivine powder mineral separate (50 – 100 μm) could be obtained immediately via grinding and sieving a number of handpicked translucent crystals. As the anorthite occurred in close association

with small olivine grains and volcanic scoria, pre-processing required an additional step of moderate crushing and separation using a magnetic separator.

For each of the experiments, 12.96 g of olivine and 3.70 g of plagioclase (mass ratio of 3.5:1) were weighed into a separate glass vial and well homogenized prior to transfer of the powder mixture into the pre-conditioned gold reaction cells. To account for volume expansion at experimental conditions, a maximum of 54.12 g (53 ml) of the 3.2 wt.% NaCl-solution was added. Dissolved oxygen was largely removed by thorough bubbling with N₂ gas, prior to sealing and confining the bag inside the pressure vessel. The headspace in the reaction cells was replaced with N₂ and removed through the sampling valve prior to heating the two setups to 300 and 400 °C respectively, while pressure was maintained at a level of 40 MPa in both experiments. Fluid samples were taken into gas-tight glass syringes after flushing the sampling line with ~1.5 mL (dead volume). After a total runtime of approximately 1800 hours, both setups slowly cooled to room temperature after a power failure. Due to these circumstances, the last in-situ fluid sample was taken after 1200 hrs. The solids were repeatedly purged and centrifuged with ultrapure water, dried, and subjected to comprehensive geochemical and mineralogical analyses.

Fluid analytics via ICP-MS, ICP-OES and GC

Fluid sample chemistry was characterized via ICP OES (Agilent 720 – Si [251.611 nm], Ca [317.933 nm], [Na [589.592 nm]]) at the Sediment Geochemistry Division of MARUM Centre for Marine Environmental Sciences and ICP MS (Thermo Finnigan Element2™ – ²⁴Mg, ²⁷Al in medium resolution) in our own lab. Yttrium was used as internal standard for the ICP-MS analyses; precision (<1.1 RSD% for Mg and Al) and accuracy (<3.5% deviation of expected values for Na, Mg, Al, Si, Ca) were controlled through replicated measurements of

NASS-5 and an independently prepared standard solution. Signals for Ti, Cr, Mn, Fe and Ni consistently stayed below limits of quantification for both methods. Hydrogen and CH₄ were quantified on an Agilent® 7820A Gas Chromatograph equipped with a packed 60/80 Mol Sieve column following headspace extraction. N₂ was used as carrier (0-4 min - 10 mL min⁻¹; 4-7 min – 25 mL min⁻¹) and oven temperature was maintained at 40°C. Intensities were measured with a thermal conductivity (200 °C, H₂) and a flame ionization detector (350 °C, CH₄). The instrument was calibrated using a Scotty® certified gas standard mixture (1 mol-% CO₂, CO, H₂, CH₄, O₂ in N₂). Accuracy was consistently better than 4% deviation from the expected standard value.

Characterization of solids via XRD, SEM, EMP, AGFM and TG

X-ray powder diffraction measurements were conducted on a Bruker D8 Advance system, operating with a Cu anode at 40 kV and 40 nA, while a Ni foil screen was used to filter Fe fluorescence radiation. In addition to the multi-element SEM mappings conducted at Cardiff University, spot SEM work was carried out at the Geoscience Department in Bremen with a Zeiss SUPRA 40 FESEM equipped with a Bruker Modell XFlash 6 | 30 EDX system at 15 kV accelerating voltage and with 1 µm beam diameter. The CAMECA SX100 EMP analysis were carried out with 15 kV acceleration voltage, 15 nA beam current, and full beam focus, while counting times of 20-40 s on peak and 10-20 s on background. Plagioclase was measured with a slightly defocused beam. For the bulk analysis of the solids prior to and after reaction via ICP-OES the solids were subjected to acid digestion with a 2:1:2 mix of 48 wt.-% HF, 32 wt.-% HCl and 65 wt.-% HNO₃ at 150°C. Thermogravimetric analysis (TG) on the NETZSCH STA 449 F3 Jupiter® Thermal analyzer were carried out with a defined heating program (30 – 1440 – 30 °C) at a heating rate of 5°C/min, calibrated against a simultaneously

measured empty Al_2O_3 crucible. Following the magnetometric measurements with a Princeton MicroMag™ 2900 Alternating Gradient Magnetometer (AGFM), the saturation magnetization M_s was calibrated against a sample of identical weight consisting of pure magnetite (62.2 Am²/kg from Peters and Dekkers (2003)).

Thermodynamic models with *GWB*, *SUPCRT92* and *EQ3/6*

In order to acquire meaningful results that could be compared to the characterized samples, the starting conditions of thermodynamic models were carefully adjusted based on reasonable assumptions. For the Activity-Activity diagrams showing phase relations in the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ as well as $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2\text{-H}_2\text{O}$ that were produced with Geochemist's Workbench® (*GWB*) (Bethke 2005), the mineral phases monticellite, wollastonite, tremolite, akermanite, merwinite and wairakite were suppressed in order to match the model mineral assemblage (representing meta-stable equilibria) to the mineral phases observed in the solids retrieved from the experimental runs. Likewise, diopside was also suppressed in the $\log (a_{\text{Ca}^{2+}}/a^2\text{H}^+) - \log (a_{\text{Mg}^{2+}}/a^2\text{H}^+)$ diagram for the 300 °C experiment.

Calculations performed with the *EQ3/6* computer code (Version 8.0) (Wolery, 1992) that was used to calculate in-situ fluid activities and comparative reaction path models are based on a set of $\log K$ values for the dissociation of different chemical components (e.g. minerals, aqueous species), various models describing corresponding activity coefficients (e.g. B-Dot, extended Debye-Hückel; Wolery and Jove-Colon, 2004), as well as a reference redox state for a defined range of pressures and temperatures. A customized *EQ3/6* database (0 — 400 °C in 25 °C increments at a constant pressure of 40 MPa) was used to

model in-situ fluid pH and speciation. Small variations in pressure (i.e., 50 vs. 40 MPa) between the GWB and EQ3/6 databases can be regarded as negligible.

As the leftover olivine in both experiments did not indicate any Fe-Mg exchange with the fluid phase, we added olivine with a fixed composition of 90 Mol.% forsterite (Fo90) as a unique phase in the reaction path model of the alteration process. All other olivine minerals and associated solid solutions were suppressed. Reaction progress in the resulting EQ3/6 model is expressed through the dimensionless parameter ξ , which varies between 0 and 1. For comparison of modelled and actually retrieved mineral proportions, the presented modelled proportions refer to a value of ξ corresponding to the reaction turnover calculated from mass balancing.

X-ray μ -CT imaging

The X-ray μ -CT scans were performed using the ProCon CT-ALPHA system of the Petrology of the Ocean Crust research group at the University of Bremen, Germany. After recovery from the gold cell experiment, the dried (but otherwise untreated) solid reaction products were imaged with a beam energy of 90 kV, an energy flux of 250 μ A, using a thin copper filter in 360° rotation scans conducted with a step size of 0.3°. The scans of the 300°C and 400°C experiment have been reconstructed with a voxel size of 8.4 μ m and 7.2 μ m per voxel, respectively. After an acquisition time of 7 hours for each sample, an image volume of 2000 x 2000 x 2000 voxels (or larger) was available. Correction of ring artefacts and reconstruction of the spatial information on the linear attenuation coefficient in the samples was done with the Fraunhofer software VOLEX. All subsequent processing of volume data (for example, rendering, filtering of the raw data, segmentation, surface generation et cetera) was done using Avizo 2020.2 (FEI).

In the reconstructed volume data of the run products, areas of very high to high attenuation phases (for example, diopside, olivine; see Figs. S5.1 and S5.2) are encoded in white or light gray values, whereas areas of low X-ray absorption are color-coded in dark gray (here chlorite, serpentine) or black (voids, cracks). To reduce noise and enhance segmentability, a combination of two digital image filters (Avizo modules *Recursive Exponential Filter 3D* and *Unsharp Masking 3D*) was applied successively to the reconstructed raw data. Thus, the resulting data volume comprises enhanced segmentability due to both smoothing of former noisy areas, and due to preserved edges at the grain boundaries facing the pore space. On the filtered data sets, a combination of global thresholding and the *Tophat black* tool was applied for the segmentation procedure of the pore space. The binarized voxels, containing only the pore space, were combined to a 3-D model. The porosity of the individual domains was determined by quantitative 3D image analysis of the volume fraction of the pore space model contained within the 3D model of the respective domain. Connected regions of voids (within the voxel size) were identified by applying the *Labeling* module on the segmented pore space.

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Figure Captions

Figure S5.1: Reconstructed images and volume renderings of the 300°C experiment (all with 8.4 μm per voxel). **(A)** Volume reconstruction of the run product shows the uneven distribution of minerals. The orange plane denotes the level of the image slice displayed in **(B)**, the semitransparent rendering of the particle shows the location of the volume of interest used for porosity determination **(C-E)**. **(B)** The domains exhibit a distinct distribution of pores and minerals. **(C)** Combined volume rendering of solid phases and the labeled pore space model. **(D)** Labeling of the pore space (shown as different colors) reveals the spread of connected voids. **(E)** Visualization of the unlabeled pore space and the 3D models of the different domains α , β , γ , δ , ϵ .

Figure S5.2: Reconstructed images and volume renderings of the 400°C experiment (all with 7.2 μm per voxel). **(A)** Volume reconstruction of the run product shows the uneven distribution of minerals. The orange plane denotes the level of the image slice displayed in **(B)**, the semitransparent rendering of the particle shows the location of the volume of

interest used for porosity determination (C-E). **(B)** The domains exhibit a distinct distribution of pores and minerals. **(C)** Combined volume rendering of solid phases and the labeled pore space model. **(D)** Labeling of the pore space reveals the spread of connected voids. **(E)** Visualization of the unlabeled pore space and the 3D models of the different domains α^* , β^* , γ^* , δ^* .