

Mass balance calculations

Multiple methods and considerations were combined to estimate the mineral proportions in the bulk solid retrieved from the two experimental runs. While the share of water-bearing and magnetic phases could be directly derived from TG and AGFM measurements, we emphasize that a certain error is introduced, as the pieces of cemented solids prepared for the SEM and μ -CT analysis (less than 15% of the material) were not included in the bulk crushed and homogenized material (TG, XRD, AGFM) and this might constitute an unequal contribution of the different domains.

Mass balance for the 300 °C run.

Two distinct dehydration events were identified for solids from the 300°C experiment during TG analyses. A water loss of 1.01 wt.-% between 180 and 410 °C could be assigned to brucite (Trittschack et al. 2014) and corresponds to 3.39 wt.-% of the retrieved bulk solid material. The second dehydration occurred between 415 and 880 °C and could not explicitly be assigned to chlorite or serpentine (Földvári 2011; Trittschack et al. 2014). It accounts for 8.23 wt.-%. As both of these phases exhibit an almost identical water fraction (about 13 wt.-%) the total corresponding mass fraction is, however, still well defined with about 64.7 wt.-% (± 1 wt.-%), regardless of which of the two phases comprises the major fraction. A potential water loss for xonotlite would be very small compared to that of brucite, serpentine and chlorite and would fall into an identical temperature range (Esteban et al. 2003). Hence the xonotlite fraction could not be determined via TG. The magnetite fraction derived from multiple AGFM analyses corresponds to 2.40 ± 0.3 wt.% of the total mass. The proportions of the remaining phases were reconstructed from stoichiometric considerations and balancing of elemental budgets. The absolute amounts of the major components Mg, Fe, Si, Ca, Al, Na and O in the system are given through the input amounts of olivine and plagioclase reactants. This input was balanced against the elemental budget defined by the known mineral fractions (serpentine, chlorite, brucite, magnetite). Fractions for unreacted olivine and plagioclase as

well as product andradite and xonotlite were then estimated based on their measured composition. This was done by finding the smallest sum of squared residuals between precursor composition and a mixing model of all identified phases. Being the major Al-bearing phase, the fraction of chlorite defines a minimal amount of reacted plagioclase, which in turn defines a minimal amount of xonotlite which was the single Ca-bearing phase produced in the 300 °C experiment. Andradite introduces some uncertainty in this regard, but the abundance of this phase was restricted to the solid-fluid interface at the gold cell contact and it is expected to contribute only a very small fraction of the bulk solid. As xonotlite has significant Al contents we decided not to directly couple the amount of reacted plagioclase to the chlorite fraction. The absolute number of moles of product xonotlite was directly calculated from the estimate of the destroyed moles of plagioclase minus the Ca fraction incorporated into an estimate of product andradite. We then used the generalized reduced gradient (GRG) method of the Excel solver to perform a multiple nonlinear least-squares regression to find the optimal mineral proportions that provide a minimal deviation between input and output elemental budgets. For this purpose, the algorithm was allowed to (1) freely adjust the amount of unreacted olivine and anorthite, (2) adjust the andradite fraction in a range between 0.15 and 1.5 wt.% and (3) to freely change the ratio of chlorite to serpentine while maintaining the quantified definitive mass fraction corresponding to 8.23 wt.% water. In this modification, the model consistently failed to achieve a good agreement regarding Mg. As it is likely that brucite was partially dissolved during solid phase retrieval, we implemented a correction to account for this loss. The following regression provided a very good agreement between initial and final elemental budgets ($\ll 1\%$ deviation) and the total mass of the modeled solid assemblage equaled 99.97 wt.-% of the retrieved mass (18.51 g). The results are given in Table 4.

Mass balance for the 400 °C run. For the 400°C experiment, thermogravimetric analysis produced only one distinct dehydration event between 350 and 880 °C corresponding

to combined serpentine and chlorite dehydration. The weight reduction of 4.75 wt.-% corresponds to 38.21 wt.-% of chlorite and serpentine. In the mass balance model for the 400°C experiment, we directly coupled the destroyed fraction of plagioclase to the amount of Al in chlorite plus Al in estimated fractions for the other phases except clinopyroxene. As no pure serpentine end member was observed among the 400°C solids and the mixed analyses revealed to be rather uniform composition, the system was less complex in this regard. The amount of clinopyroxene was subsequently derived from Ca balancing. For the following multiple nonlinear least-squares regression the algorithm was allowed to adjust the fractions of unreacted olivine reactant as well as the Ca-bearing phases xonotlite, andradite and grossular. Garnet abundances were limited to a range between 0.5 and 2 wt.-%. Whereas this mass balance is considered to have a larger error because the resulting garnet fractions tend to be quite low compared to its apparent fraction in the investigated sections, the deviation in the elemental budgets could be sufficiently minimized even without a correction like the one necessary for the 300 °C run. The results are provided in Table 4.

Reaction path modeling

In the comparative reaction path modeling with the EQ3/6 computer code, first, EQ3NR is used to speciate the 3.2 wt.-% NaCl fluid reactant at room temperature prior to heating it to the respective experimental temperature in a second step using EQ6. Input variables for the following titration model were chosen according to determined compositions and proportions of reactants olivine and plagioclase as well as the average time-weighted W/R in the reaction cell. Antigorite, monticellite, tremolite and amesite were suppressed in both runs. The first two phases are rarely observed in abyssal serpentinization environments. Tremolite occurred as a member of the equilibrium assemblage at both temperatures in initial model runs. However, it was suppressed in the final models since it was not observed as a reaction product. Amesite was suppressed as multiple WDS analyzes of the chlorite-

serpentine mixture didn't indicate a significant contribution of this component in either mineral (see Fig. 4). Suppressing amesite caused EQ6 to predict chlorite as part of the equilibrium assemblage which was clearly identified in both runs via XRD, EMPA and through its characteristic edge-to-face morphology. Uncertainty is introduced as the equilibrium model reacts olivines and plagioclase in equal rates.

Reaction path model at 300 °C and 50 MPa. Without any further modification, the model predicted serpentinization product minerals serpentine-ss (solid solution of chrysotile, greenalite and cronstedtite), brucite-ss, and magnetite, in addition to clinopyroxene-ss (solid solution of diopside and hedenbergite) and chlorite-ss (solid solution of clinocllore and daphnite) but no xonotlite. However, xonotlite was listed in the model output as a metastable phase and was predicted to form after diopside, garnet, akermanite, merwinite, wollastonite and portlandite were suppressed in the reaction path model (see Fig. 6 A). It should be noted that the available thermodynamic data for xonotlite is not very well constrained (Blanc et al. 2010). Also, the model xonotlite is Al-free, whereas the xonotlite formed in the experiment has elevated Al contents. The observed zonations do not support the assumption of a fully equilibrated bulk system, but local equilibrium conditions may have development in the different domains. Despite the implied limitations of the model, the proportions of different mineral phases that are indicated for the calculated reaction turnover (77.5% by weight corresponding to a ξ of 0.75; at this point the alteration products produced in the model contributed 77.5% of the solid phase weight) resemble the proportions derived from analyses and mass balancing (see Table 4). Accessory andradite is missing in the predicted assemblage, but as it is restricted to the concretion interface with the cell wall it cannot be expected to occur in the same equilibrium assemblage as the other minerals. Further, the model underpredicts the abundance of brucite, which makes sense as the markedly low Si activity assemblage in domain α (including brucite) appears to be a consequence of facilitated

mass transfer within the developed zonation. These chemical potential gradients cannot be captured in a bulk equilibrium model.

Reaction path model at 400°C and 50 MPa. In agreement with the mineral assemblage documented in the retrieved solids, the model predicted chlorite-ss, clinopyroxene-ss, serpentine-ss and large fractions of unreacted olivine. But it failed to reproduce the simultaneous formation of andradite-dominated garnet, unless magnetite, hematite, wuestite as well as the serpentine cronstedtite component were suppressed from the model. Furthermore, the model predicted a somewhat higher diopside fraction, which can be explained by the presence of metastable xonotlite and grossularian garnet in the actual reaction product retrieved from the experiments. Xonotlite and grossular were not predicted by the model and unlike in the 300 °C experiment, consecutive suppression of Ca bearing phases was not an option, as andradite-rich garnet and diopside clearly occurred in the characterized solids from the 400 °C run. But a major mismatch between model and observations is unsurprising considering that the model does not include dissolution kinetics and consequently leaves 32% plagioclase unreacted at 55.2% reaction turnover (versus 9% indicated by mass balance). The model predicts that plagioclase and olivine are coevally replaced by an invariable assemblage of chlorite, clinopyroxene, serpentine and andradite-rich garnet. This prediction matches the combined assemblages in domains α and β , but is in contrast to the mineralogical zonation and the appearance of additional Ca-bearing phases (xonotlite and grossularian garnet) in the two inner domains. A simple equilibrium thermodynamic titration path can clearly not explain the dissimilar mineral assemblages in the multiple domains that developed in the 400 °C experiment.

References cited

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