Hydrothermal troctolite alteration at 300 and 400°C – Insights from flexible Au-reaction cell batch experimental investigations

Christian T. Hansen\textsuperscript{a,b}\textsuperscript{*}, C. Johan Lissenberg\textsuperscript{c}, Wolf-Achim Kahl\textsuperscript{a,d} and Wolfgang Bach\textsuperscript{a,b}

\textsuperscript{a} Geosciences Department, University of Bremen, Bremen, 28359, Germany
\textsuperscript{b} MARUM Center for Marine Environmental Sciences, Bremen, 28359, Germany
\textsuperscript{c} School of Earth and Ocean Sciences, Cardiff University, Cardiff CF10 3AT, United Kingdom
\textsuperscript{d} MAPEX Center for Materials and Processes, University of Bremen, Bremen, Germany

Abstract

Troctolites are increasingly recognized as a common rock found in association with oceanic core complexes. They are similar to komatiite in composition and troctolite alteration hence may provide insight into H\textsubscript{2} production on Early Earth. We investigated the hydrothermal alteration of olivine-rich troctolites in two batch experiments (300 °C, 400 °C and 40 MPa) by reacting forsteritic olivine and anorthite-rich plagioclase with salt solutions. The alteration process was evaluated based on concomitant fluid samples and solids retrieved upon termination of the experiments. In both experiments the initial rock powder was turned into a hard, compact mass through cementation by secondary phases. The heterogeneity of this mass was documented using \(\mu\)-computed tomography and electron microscopy. Thermodynamic computations were conducted to determine the equilibrium phase assemblages and fluid compositions with increasing reaction turnover. Mineral zonation developed between the fast reacting, fluid dominated top portion of the solids and the more isolated portions at the bottom of the reaction cell. At 300 °C, the total
reaction turnover after 1800 hrs was 77.5 %. Serpentinization of olivine controlled the fluid composition after plagioclase had reacted away in the top layers. In contrast, a Ca and Al-enriched assemblage of xonotlite and chlorite developed alongside unreacted plagioclase at the bottom. The porosity is very low in the top layers, but high (around 15%) in the bottom part of the cemented mass. At 400 °C, the reaction turnover was only 51% as olivine was stable after plagioclase had reacted away. Clinopyroxene, andradite ± chlorite had formed in the top layers, whereas xonotlite, grossular and chlorite had formed at the bottom. The permeability is more uniform and the mineral zonation less pronounced at 400 °C. These mineral zonations developed as a consequence of an increased mobility of Ca, Al, Mg and to a lesser extent of Fe in the experiment, which may be facilitated in the highly permeable granular materials when compared to a compact rock. Steady-state hydrogen concentrations were at least 20 mmol L^{-1} at 300 °C and <1 mmol L^{-1} at 400 °C. A lack of magnetite formation at the higher temperature is responsible for the low H₂ yields.

Keywords: Troctolite alteration, Experimental petrology/geochemistry, Hydrogen, Fluid-rock interaction

*Corresponding author: c.hansen@uni-bremen.de

INTRODUCTION

Oceanic core complexes (OCCs) are the result of extensive detachment faulting and exhumation along slow and ultraslow spreading ridges and provide a unique opportunity to study fluid-rock interactions between seawater and ultramafic lithologies (Blackman et al. 1998; Smith et al. 2008, 2012). These unique settings have attracted increasing interest, especially since hydrothermal systems hosted in OCCs produce some of the most
fascinating geochemical environments on earth (Charlou et al. 2002; Schmidt et al. 2007; German et al. 2010). The hydrothermal fluids originating from alteration of ultramafic rocks are often extremely enriched in H₂ and CH₄, which support chemolithoautotrophic microorganisms in core complex-hosted hydrothermal vent systems (Takai et al. 2004; Kelley et al., 2005). The production of H₂ and CH₄ in these systems is commonly related to serpentinization of mantle peridotite (Charlou et al. 2002; Sleep et al. 2004; Takai et al. 2004; Proskurowski et al. 2006; Konn et al. 2015), and hence most studies investigating the underlying reactions focused on ultramafic rocks (Seyfried et al. 2007; Klein et al. 2009, 2013; McCollom and Bach 2009; Cannat et al. 2010). However, other lithologies associated with OCCs reveal a high geochemical diversity of rocks in the crust-mantle transition zone facilitated by varied water-rock reactions during OCC exhumation such as rodingitization (Bach and Klein 2008; Frost et al. 2008) or melt impregnation of mantle peridotite (Jöns et al. 2010; Albers et al., 2019). These metasomatic reactions are driven by strong contrasts in chemical potential between major rock components, such as silica (Frost and Beard 2007; Klein et al. 2009, 2014). In this respect, troctolites provide an excellent example where enhanced compositional contrasts between forsterite-rich olivine and calcic plagioclase are key to the reactions observed during hydrothermal alteration (Frost et al. 2008). Troctolites are common in the lower crust and crust-mantle transition zone, and were long believed to represent magmatic cumulates. The origin of troctolites may be varied, however, and is subject to an ongoing discussion (Ildefonse et al. 2006; Dick et al. 2008; Suhr et al. 2008; Drouin et al. 2009, 2010; Blackman et al. 2011; Renna and Tribuzio 2011; Sanfilippo and Tribuzio 2013; Sanfilippo et al. 2013). Nakamura et al. (2009) investigated altered olivine-rich troctolites near the Kairei hydrothermal vent field and
highlighted the potential of troctolite-seawater reactions for producing strong enrichments of H$_2$. In this context, Kumagai et al. (2008) emphasized the significance of this H$_2$ production pathway for the early emergence of life as the geochemical character of troctolites resembles that of komatiites.

However, only few studies investigated the alteration of troctolitic rocks (Frost et al. 2008; Beard et al. 2009; Nakamura et al. 2009; Nozaka et al. 2017; McCaig et al. 2018). Frost et al. (2008) suggested that the troctolite alteration resembles a one-rock rodingitization, in which olivine represents the ultramafic and plagioclase the gabbroic component. The observed mineral assemblages include serpentine, magnetite, and brucite associated with olivine as well as prehnite, hydrogrossular and clinozoisite associated with plagioclase. Frost et al. (2008) further proposed an alteration temperature of <350 °C for serpentinized troctolites from Atlantis Massif. Similarly, Bach and Klein (2008) suggested that rodingitization can only proceed if olivine reacts to serpentine and brucite at temperatures <350 °C. At higher temperatures, serpenitization of olivine and rodingitization of plagioclase cannot take place. Nozaka and Fryer (2011) suggested that coronitic replacement of olivine and plagioclase by tremolite and chlorite represents troctolite alteration at $T > 450$ °C. Temperatures in the root zone of the troctolite-hosted Kairei hydrothermal vent field are believed to be about 400 °C (Nakamura et al. 2009).

The temperature dependency of troctolite alteration has not been explored experimentally. In this contribution, we present the results of two new batch experiments specifically designed to investigate the alteration of olivine-rich troctolites at conditions where olivine serpentinizes (300 °C) and where it does not serpentinize (400 °C).
EXPERIMENTAL DESIGN & ANALYTICAL METHODS

Experimental techniques

We used a modified version of a Dickson-type hydrothermal apparatus (Dickson et al. 1963; Seyfried et al. 1987) to conduct two hydrothermal troctolite alteration experiments at 300 and 400 °C (40 MPa). A mineral powder mix of forsteritic olivine (Fo91) and anorthite-rich plagioclase (An95) in mass ratio of 3.5:1, was reacted with a deoxygenated 3.2 wt.-% NaCl solution inside a flexible gold reaction cell. Fluid samples were taken repeatedly (initially prior to heating and after 10, 27, 49 and 76 days; final sample post premature cooling) from the reaction cell and analyzed for salinity, pH, and concentrations of dissolved ions as well as H₂ and CH₄. Solids were retrieved at the end of the experiment after approximately 76 days. Details on the experimental design are included in supplemental material M1.

Analytical techniques

Solute concentrations were measured by ICP OES (Agilent 720 – Si, Ca, Na) and ICP MS (Thermo Finnigan Element²™ – Mg, Al). Fluid aliquots for H₂ and CH₄ quantification were sampled into pre-weighed Hamilton® gastight glass syringes and analyzed within 1 hour using an Agilent® 7820A Gas Chromatograph.

Solids were retrieved as a cemented concretion from the reaction vessel. Untreated fragments were initially characterized via scanning electron microscopy (Zeiss SUPRA 40 FE-SEM equipped with a Bruker Modell XFlash 6 | 30 EDX) and the distribution of porosity and of mineralogical variability were assessed by μ-CT scanning. Cut slices of the encrusted solid reactants were prepared as polished, carbon coated epoxy mounts for additional SEM and EMPA work (Fig. 1). Detailed multi-element maps (Mg, Al, Fe, Ca)
of the mounts were prepared at Cardiff University on a Zeiss Sigma HD FEG-SEM equipped with dual Oxford Instruments X-max 150 mm² energy dispersive silicon drift detectors. EMPA analyses of mineral compositions were conducted with a CAMECA SX100. All of the remaining material was crushed, homogenized and subjected to further analysis including X-ray powder diffraction (XRD, Bruker D8 Advance). Bulk analysis of solids prior to and after reaction were conducted via ICP-OES following acid digestion. The fractions of alteration phases were estimated from phase characteristic dehydration during thermogravimetric analysis (TG) using a NETZSCH STA 449 F3 Jupiter® Thermal analyzer. The magnetite fraction was determined by magnetometric (AGFM) measurements with a Princeton MicroMag™ 2900 Alternating Gradient Magnetometer following the method described by Flanders (1988). Detailed specifications for all analytical techniques are provided in supplemental material M1.

**Thermodynamic and kinetic modelling techniques**

Phase relations in the system MgO-CaO-SiO₂-Al₂O₃-H₂O were calculated with Geochemist’s Workbench® (GWB) (Bethke 2005), using a customized database (300, 400 °C – 50 MPa; attached as supplemental material M3.1). Activity-Activity diagrams showing the phase relations in the system CaO-MgO-SiO₂-H₂O as well as CaO-Al₂O₃-MgO-SiO₂-H₂O were prepared using ACT2 of the GWB® software package to evaluate the fluid data from the experiments and from reaction path model predictions. Additional phase relations for metastable anorthite-chlorite and forsterite-xonotlite reactions were derived from log K values calculated with SUPCRT92 (Johnson et al. 1992), complemented with thermodynamic data for xonotlite reported by Blanc et al. (2010).
Measured elemental concentrations and pH of fluid samples were used as input parameters for an EQ3NR speciation and subsequent heat-up to experimental conditions using EQ6 to obtain in-situ activities and pH. In-situ fluid pH and activities of Ca\(^{2+}\), Mg\(^{2+}\) and SiO\(_2\)(aq) were computed using EQ3/6 (Version 8.0) (Wolery, 1992) with a customized database.

For reaction path modelling, the EQ3/6 database from Klein et al. (2013) was complemented with log K values for xonotlite. The log K values were calculated using SUPCRT92 (Johnson et al., 1992) and thermodynamic data from Blanc et al. (2010) (provided as supplemental material M3.2). Following an initial speciation and heating of the 3.2 wt.-% NaCl solution, reaction path modeling was conducted using the titration mode. In these simulations, a total amount of olivine-plagioclase mixture equal to the average W/R and composition used in the experiments was added to the fluid phase in small aliquots. Reaction progress is expressed through the dimensionless parameter ξ, which varies between 0 and 1. Details regarding thermodynamic modelling are included in supplemental material M1.

RESULTS

Time series evolution of fluid compositions

Characterization of concomitant fluid samples provided ad hoc information on the on-going reaction within the flexible gold reaction cells (see Fig. 2 and Table 1). The last in-situ fluid samples were obtained after approximately 1200 hrs. The experiment continued for another 450 hrs, before a power failure occurred and the system cooled down. The solids were retrieved after another 48 hrs. Hence, the in-situ fluid chemistry to go with the final solids is not known. But as the fluid composition appeared to reach a steady state...
after 1200 hrs, it may not have been too dissimilar after 1750 hrs and can be reasonably assumed as representative of the fluid supernatant to the plug of cemented solids finally retrieved.

Incipient hydrolysis of olivine resulted in a sharp increase of Mg concentration (156 µmol/kg (µM)). Less pronounced were simultaneous increases of Si (32 µM), Ca (25 µM) and Al (7 µM), of which the latter two are due to incipient plagioclase dissolution. Major changes were observed after heating the experiments to 300 and 400 °C.

At 300 °C, Mg (to 15 µM) was rapidly depleted, while Si contents remained virtually unchanged (30 µM) and Ca concentrations increased to > 2 mmol/kg (mM) (see Fig. 2 A). All elements were subsequently depleted from the fluid. After 1200 hrs, Mg and Si levels were <10 µM, while Ca contents stayed well above 1 mM. Reactions at 300 °C involved a net consumption of H$^+$ ions that caused an increase in the fluid pH. Calculated in-situ pH increased from an initial 6.4 to a final value of 7.2 (pK$_W$ at these P T conditions is 11.086). Increasing amounts of H$_2$ indicated significant oxidation of Fe$^{2+}$ to Fe$^{3+}$, as is expected for serpentinization reactions. H$_2$ concentrations steadily increased to 20.5 mM after 1174 hrs. Small amounts of methane (< 40 µM) were also detected, which could have been produced through breakdown of organic contaminants or CO$_2$-reduction with H$_2$ (McCollom and Seewald, 2001).

In the 400 °C experiment Mg concentrations rapidly decreased, while Si concentrations continuously increased to about 0.8 mM after 1200 hrs (see Fig. 2 B). Calcium was initially enriched to more than 3.5 mM but decreased to a final level close to that observed in the 300 °C experimental run. Proton activity at 400 °C remained almost unchanged at near-neutral pH level around 6 (in-situ pK$_W$ is 11.356) throughout the experiment. Initially, H$_2$
concentration increased to 4 mM (after 238 hrs), before returning to only 200 µM after 1200 hrs. Methane contents at 400 °C are 5-fold increased (max. 250 µM) relative to the 300 °C run. The increase in methane contents cannot explain the drop in H₂ levels, as 250 µM of methane from DIC would require no more than 1 mM of H₂. Moreover, methane concentrations also drop in the later stages of the experiment A summary of all fluid data is given in Table 1.

**Fluid-mineral reactions**

The solids retrieved from the two experiments were not muds as is commonly the case in serpentinization studies. Instead, the retrieved material was a hard, compact concretion that had formed at the bottom of the reaction cells. Oriented fragments of the concretion were selected for detailed documentation. The concretions are zoned in terms of mineralogical composition and the boundaries between different zones (α to ε in Fig. 1) are parallel to the solid-fluid interface in the autoclave (see Fig. 3 F). The mineralogical variability and zonations were characterized on cut polished sections and on untreated crust surfaces (see Fig. 1).

**Fluid-mineral reaction in the 300 °C experiment.** Bulk sample powder-XRD characterization revealed the presence of serpentine, brucite, magnetite, chlorite, xonotlite and andradite, in addition to unreacted forsterite and anorthite. SEM and EMP work showed that these phases form different assemblages in five domains (Fig. 3 A+B and supplemental Fig. S1).

The domain closest to the fluid-rock interface (α) was dominated by a typical serpentinization product mineral assemblage (serpentine, brucite, and magnetite) with additional chlorite (see Fig. 3 A, B and D). Former grain boundaries of primary olivine are
traced by a thin band of fine-grained chlorite (< 1 µm), which is the sole Al-bearing phase in domain α. In some cases, remnants of olivine with distinct dissolution features are preserved in the center of the cavities bordered by these chlorite rims (see Fig. 3 D+E). The interstitial spaces between the proposed former grain boundaries were entirely cemented with fine-grained serpentine and patches of xenomorphic brucite (see Fig. 3 D). In contrast, the cavities left by apparently dissolved olivine or plagioclase are only partially filled with serpentine and the cavity walls are covered with abundant microcrystalline magnetite (< 2 µm) forming euhedral octahedrally shaped crystals. In contrast, some additional xenomorph iron (likely iron oxide or hydroxide) infrequently occurs in the completely cemented interstitial space (see Fig. 3 E and Fig. S1). Brucite disappears at the transition from domain α to domain β (see Fig. 3 A+B). Significantly larger portions of unreacted olivine are present in domain β and the chlorite rims around them are thicker. Like in α, serpentine is the dominant phyllosilicate. Microtomographic images of the intact concretion show low porosities for domains α (2 vol.-%) and β (4 vol.-%) (see supplemental Fig. S5.1). Hence, most of the chlorite-lined cavities seen in thin-section were filled with relict olivine crystals that have been plucked during the polishing of the mount. Such plucking is a common phenomenon due to the stark contrast in hardness between olivine and serpentine (±chlorite). We assume that this plucking was more limited in β as chlorite rims were thicker.

SEM work on an untreated crust fragment representing the interface of the top section of the concretion with the cell wall shows a mixture of serpentine and subordinate chlorite that covers almost the entire surface. But in contrast to the inner parts of domains α and β, hydroandradite (\(X_{Fe} = \frac{Fe}{Fe + Al} = 0.98\)), and not magnetite, is the dominant
Fe-phase. Idiomorphic, rhombic dodecahedron-shaped crystals (2-4 µm) of hydroandradite may cluster in dense aggregates (Fig. 3 C). This occurrence of andradite is entirely restricted to a thin layer representing the interface to the cell wall.

The transition between domains β and γ is marked by significant drop in magnetite abundance (see Fig. 3 A+B). Instead, domain γ contains major portions of unreacted olivine. Serpentine is less abundant and chlorite is the dominant phyllosilicate forming thick coronas around primary olivine. Interstitial void space makes up significant portions of this domain and we suspect that these voids were in part created by anorthite dissolution. Microtomography confirms a considerable porosity for domain ε (16 vol.-%), so significant plucking can be ruled out. In domain δ these voids are partly to completely filled by xonotlite (Fig. 3 A+B). Magnetite is rare and the fraction of unreacted olivine (max. 30 µm) is clearly subordinate to the alteration phases. The chlorite rims around the olivine relics are again notably thicker (up to 20 µm) than in domain γ (Fig. 3A). Where chlorite in the interstitial space occurs as less dense aggregates, it exhibits a characteristic edge-to-face arrangement of small individual flake-shaped crystals (see Fig. 4 H). In contrast to domain α – γ, the interstitial space in domain δ is almost completely cemented by acicular xonotlite crystals, up to 80 µm long (see Fig. 3 G+H). Domain ε shows abundant primary anorthite, which is completely absent in all other domains (Fig. 3 A+B). A close to original size and shape of anorthite crystals (up to 100 µm, recognizable crystal planes) indicates a very limited plagioclase dissolution in this domain. At the same time olivine is rare and leftover relics exhibit the thickest chlorite coatings of all domains. Interstitial space is partly cemented with xonotlite like in domain δ, but the overall xonotlite abundance is decreased in domain ε.
We summarize the most striking differences in the five domains (α – ε): (1) There is no Ca-bearing alteration phase in domains α – γ and anorthite is restricted to domain ε. (2) The abundance of chlorite as the sole Al-bearing mineral is low in domains α – β and much increased in the inner domains (δ and ε); the thickness of chlorite rims increased markedly from outside to the inside. These variations come with chemical differences between the inner domains that are Ca- and Al-rich and the outer domains of the concretion, which are Mg- and to a lesser extend Fe-rich.

The compositions of the relict olivine (Mg$_{1.82}$Fe$_{0.18}$SiO$_4$; X$_{Mg} = 0.91$) and anorthite (X$_{Ca} = Ca / (Ca + Na) = 0.96$) from the 300 °C experiment are unchanged relative to the compositions of the reactants. Brucite (Mg$_{0.93}$Fe$_{0.07}$OH$_2$; X$_{Mg} = 0.93$) and especially serpentine (Mg$_{2.92}$Fe$_{0.08}$Si$_2$O$_5$(OH)$_4$; X$_{Mg} = 0.973$) found in domain α are enriched in Mg compared to olivine, which is in line with the abundant presence of magnetite. Chlorite compositions (Mg$_{4.54}$Fe$_{0.44}$Al$_{1.51}$Si$_{3.35}$O$_{10}$(OH)$_8$; X$_{Mg} = 0.91$) show no systematic differences between domains. Most analyses reveal a reduced fraction of Al and slightly increased Si, which may indicate minor but common intergrowth with serpentine or saponite (see Fig. 4). Chlorite has an X$_{Mg}$ of 0.91, similar to the olivine it replaced. This explains the lack of magnetite, which is not needed as Fe-host in the chlorite-rich inner domains (δ and ε). Xonotlite compositions are uniform (Ca$_{6.03}$Fe$_{0.06}$Al$_{0.30}$Si$_{5.65}$O$_{17}$(OH)$_2$) and indicate minor substitution of Si by Al. Average mineral compositions are provided in Table 2.

**Fluid-mineral reaction in the 400 °C experiment.** X-ray powder diffraction indicated relict olivine and plagioclase and secondary chlorite, serpentine, xonotlite as well as andradite, grossular and diopside. While all phases were observed in different domains
in the SEM/EMP surveys, unlike in the 300 °C experiment, these domains in the cemented solids do not simply follow a top-to-bottom layered sequence. The successive collapse of the gold cell following repeated fluid sampling has led to a certain degree of folding and compaction of the solid material but a differentiation of the different domains in terms of isolation and association between each other is still possible (Figs. 1 and S2). Domain α* contains large portions of unreacted olivine in addition to a mixture of chlorite ±serpentine as well as clinopyroxene (see Fig. 5 A+B). Domain α* is in itself very heterogeneous as the proportions of minerals change significantly towards the boundary to the adjacent domain β* (see supplemental Fig. S2). Towards this boundary olivine relics exhibit an increasingly thick chlorite coating. Next to the chlorite, large euhedral clinopyroxene crystals (up to 100 µm in length) grew as a cementitious phase in the intergranular void space. Euhedral isometric crystals (up to 10 µm in diameter) of andradite-rich hydrogarnet (X_{Fe} = 0.81) are commonly associated with clinopyroxene (see Fig. 5 C). The abundance of all three secondary phases increases towards the adjacent domain β* while unreacted olivine becomes less abundant. As in the 300 °C experiment, a particularly large discrepancy between the apparent (polished mount surface, Fig. 5 A) and actual porosity (µ-CT; Fig. S5.2) for domains α and β, as well as a similarity in cavity and olivine crystal shapes, indicates that the true share of unreacted olivine is much higher (see supplemental Tab. S1). Domain β* is comprised of pseudomorphic chlorite after olivine and cementing clinopyroxene as well as andradite (see Fig. 5 A+B). The boundary between domains β* and γ* is not gradual as clinopyroxene suddenly disappears and prismatic xonotlite crystals (up 90 µm in length) are instead developed as void fill (see Fig. 5 A+B). At the same time the hydrogarnet composition changes to hydrogrossular-rich (X_{Fe} = 0.23). Moreover, the
cementation appears much more compact than in domains α* and β* as xonotlite fills most voids and fine-grained chlorite almost completely fills the center of former olivine grains. Unreacted anorthite persists in domain δ*, (see Fig. 5 A+B) and the interstitial space is cemented by xonotlite (see Fig. 5 E).

Two distinguishable parts in the studied untreated fragment representing the contact to the cell wall resemble domains identified in the cut section (see Fig. 1 and Fig. 5 D). The upper part appears most similar to domain β* ± α*, as it is comprised of clinopyroxene, andradite and chlorite ± serpentine. But in contrast to domain β* ± α*, unreacted olivine is absent and this outer contact surface is almost exclusively comprised of massive clinopyroxene with minor andradite-rich hydrogarnet and accessory chlorite ± serpentine in between clinopyroxene crystals (see upper right of Fig. 5 D). The lower part resembles domain γ*, as it is exclusively comprised of chlorite, grossular and xonotlite. But again, there is a shift in the relative proportions of the minerals with abundant chlorite, common grossular-rich hydrogarnet and rare xonotlite (see Fig. 5 D).

In summary, the outside-to-inside variation in mineral abundance is as follows: (1) olivine is partly preserved on the outside, where chlorite and Ca-silicates are rare. (2) Clinopyroxene is very abundant in a zone that starts just underneath the top of the mineral pile. (3) Anorthite is partly preserved in the innermost zone; xonotlite bridges between clinopyroxene and anorthite. (4) Hydrogarnet is present throughout and is andraditic in the outside and grossularian in the inside parts of the concretion; it is the most abundant Fe-phase.

The compositions of unreacted olivine and anorthite also remained unchanged in the 400 °C experiment and the compositions of alteration phases did not deviate between
domains (see Table 3). Several chlorite analyses exhibit a reduced Al fraction, indicating
minor intergrowth with serpentine. Chlorite is somewhat more magnesian than the olivine
reactant \( \text{Mg}_{4.59}\text{Fe}_{0.42}\text{Al}_{1.49}\text{Si}_{3.36}\text{O}_{10}(\text{OH})_8; \ X_{\text{Mg}} = 0.92; \) see Fig. 4). In contrast, the
clinopyroxene composition \( \text{Ca}_{1.00}\text{Mg}_{0.86}\text{Fe}_{0.14}\text{Si}_2\text{O}_6 \) reveals a significant hedenbergite
component. Garnets could be subdivided into two groups. Those associated with
clinopyroxene were always dominated by andradite \( \text{Ca}_{2.99}\text{Al}_{0.37}\text{Fe}_{1.54}\text{Si}_{3.01}\text{O}_{12}; \ X_{\text{Fe}} = \text{Fe} / \text{(Fe + Al)} = 0.81 \). The zones in \( \beta^* \) and \( \alpha^* \) that are rich in clinopyroxene and andradite are
hence also somewhat enriched in Fe. The Al-rich garnet \( \text{Ca}_{2.98}\text{Al}_{1.58}\text{Fe}_{0.47}\text{Si}_{2.88}\text{O}_{12}; \ X_{\text{Fe}} = \text{Fe} / \text{(Fe + Al)} = 0.23 \) is exclusively associated with xonotlite. Totals of the garnets scatter
around 97 % indicating a small but noticeable katoite component \( \text{SiO}_4^+ \leftrightarrow 4(\text{OH})^- \) in
these hydrogarnets.

**Mass balancing of the overall reactions**

Mineral proportions in the bulk solid retrieved from the two experimental runs were
estimated via mass balancing. First, the absolute mass fractions of water-bearing phases
and magnetite contributions were quantified via TG and AGFM. The abundances of the
remaining identified phases were subsequently estimated from stoichiometric
considerations utilizing the measured compositions In the solid assemblage retrieved from
the 300 °C experiment, characteristic dehydration events in the thermogravimetric analysis
corresponded to 3.39 wt.-% of brucite and another 64.7 wt.-% of chlorite + serpentine
(Földvári 2011; Trittschack et al. 2014). The magnetite fraction derived from multiple
AGFM analyses corresponded 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 details of this procedure are provided in supplemental material M4.

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The results are given in Table 4 and match the observations made during the investigation of the cut sections. Reaction turnover based on this mass balance would be 77.5% by weight.

For the 400 °C experiment, thermogravimetric analysis yielded only one characteristic dehydration that corresponds to 38.21 wt.-% of chlorite and serpentine. Although magnetite was not observed during EMP and SEM surveys, AGFM analysis clearly indicated the presence of a ferrimagnetic component, yet the corresponding magnetite fraction would not contribute more than 0.03 wt.%. The share of the remaining phases was deduced following a balancing of elemental budgets similar to that used for the 300 °C experiment with details given in supplemental material M4. The results provided in Table 4 indeed appear quite reasonable as some parts of domain α* in the investigated section were almost exclusively comprised of unreacted olivine whereas overall lesser amounts of relict plagioclase were observed (see Fig. 5 and supplemental Fig. S2). Reaction turnover based on this mass balance is 52.2% by weight.

Implications from reaction path modeling

Reaction path modeling for both experimental runs was conducted using the EQ3/6 computer code to compare the experimental findings with equilibrium model predictions. Details of the exact parameterization of the model runs and all underlying assumptions are provided in supplemental material M4.

At 300 °C, the reaction path model predicted a typical serpentinization product mineral assemblage, including serpentine-ss (solid solution of chrysotile, greenalite and cironstedtite), brucite-ss, and magnetite, in addition to clinopyroxene-ss (solid solution of diopside and hedenbergite) and chlorite-ss (solid solution of clinochlore and daphnite). The
one major difference to the assemblage produced in the 300 °C experiment is that the model initially predicts diopside instead of xonotlite and several Ca bearing phases had to be suppressed in the model before apparently metastable xonotlite was predicted (see Fig. 6 A and supplement M4). But considering that the observed zonation is a clear sign of a not fully equilibrated system, the proportions of different mineral phases that are indicated for the calculated reaction turnover of 77.5% by weight resemble the proportions derived from analyses and mass balancing (see Table 4).

At 400 °C, the predicted mineral assemblage, mainly consisting of chlorite-ss, clinopyroxene-ss, serpentine-ss, as well as a large fraction of unreacted olivine is in good agreement with the documented solid reaction products (see Table 4). A mismatch between model and observation concerns magnetite, which was predicted to form instead of the ubiquitously disseminated andradite-dominated garnet observed in the studied section. The model run also produced a very iron-rich serpentine (large cronstedtite component), and the serpentine-chlorite mixture from the experiment was depleted in Fe. Then again, a complete absence of cronstedtite cannot be concluded as a very Mg-rich chlorite dominates in the serpentine-chlorite mixture and this could mask the presence of the Fe-serpentinite. If these Fe phases are suppressed, however, garnet is predicted and for a reaction turnover of 55.2% by weight (ξ of 0.69), predicted resemble the observed mineral proportions (see Fig. 6 B and Table 4), albeit the fraction of unreacted plagioclase is strongly overpredicted (32% versus 9% indicated by mass balance).

Differences between measured and modeled assemblages for both temperature levels highlight, how a simple equilibrium thermodynamic titration path can obviously not
fully explain the dissimilar mineral assemblages in the multiple domains that developed in
the experiments.

**DISCUSSION**

Interpretation of mineralogical observations, phase relations and fluid data

The temporal evolution of fluid composition reflects both the type and extent of
mineral-fluid reactions within the gold cell. Investigating corresponding phase relations is
most conveniently accomplished by plotting the *in-situ* activities of reactant solutes in
phase diagrams that also depict the stability fields of mineral assemblages in the fluid-rock
system under the relevant *p*-*T* conditions. Compositional trajectories of fluids predicted by
the comparative reaction path models can be complemented.

**Phase relations at 300 °C.** The initial fluid has low silica, coincidentally close to
the serpentine-brucite univariant line, and very low Ca\(^{2+}\) contents (see Fig. 7; Table 1:
T.1.1). Upon reaction with olivine and plagioclase, the measured composition evolves
towards higher Ca\(^{2+}\) activities, while silica activity remains close to the serpentine-brucite
univariant line. Olivine reacts to serpentine and brucite (rxn.1) and simultaneously the
dissolution of plagioclase provides sufficient Al for the formation of chlorite, from either
olivine (rxn.2) or serpentine (rxn.3).

\[
2 \text{Mg}_2\text{Si} \text{O}_4 + 3 \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}(\text{OH})_2 \quad \text{rxn. 1}
\]

\[
2 \text{CaAl}_2\text{Si}_2\text{O}_8 + 5 \text{Mg}_2\text{Si} \text{O}_4 + 6 \text{H}_2\text{O} + 4 \text{H}^+ \rightarrow 2 \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 3 \text{SiO}_2(\text{aq}) + 2 \text{Ca}^{2+} \quad \text{rxn. 2}
\]
Reactions of plagioclase release Ca and consume protons, which elevates log \(a\text{Ca}^{2+}/a\text{H}^+\). Silica is also released, but its activity is fixed by the reaction of brucite to serpentine (rxn. 4).

\[
3 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6 \text{H}^+ \\
\rightarrow 3 \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 7 \text{SiO}_2(\text{aq}) + 3 \text{Ca}^{2+} \quad \text{rxn. 3}
\]

\[
+ \text{H}_2\text{O}
\]

Such silica buffering can only be explained if olivine reacts in excess of plagioclase and mass balancing confirms that 7.4 moles olivine serpentinized while 1 mole of plagioclase reacted.

In contrast, the model had olivine and plagioclase react in exactly the initial proportions (ol/plg = 6.7) and the interacting model fluid initially showed an early spike to higher log \(a\text{SiO}_2(\text{aq})\) (see Fig. 7). But after less than 1 wt.% reaction turnover (\(\xi << 0.01\)), the model fluid composition meets the univariant serpentine-diopside line or, if diopside and garnet are suppressed, the xonotlite-in line (rxn. 5; see Fig. 7).

\[
6 \text{SiO}_2(\text{aq}) + 6 \text{Ca}^{2+} + 7 \text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2 + 12 \text{H}^+ \quad \text{rxn. 5}
\]

Further reaction will have compositions follow the univariant line towards an even higher log \(a\text{Ca}^{2+}/a\text{H}^+\) and a lower log \(a\text{SiO}_2(\text{aq})\) until they reach the intersection with the brucite–chrysotile phase boundary (see Fig. 7). After <20 wt.-% reaction turnover the fluid composition is buffered by serpentine, chlorite, magnetite, xonotlite and brucite. The formation of xonotlite alongside chlorite can also be written as a desilication of plagioclase.

As outlined before (rxn. 2 and 3), both serpentine or olivine can source Mg but the two
reactions (rxn. 6 and rxn. 7) are essentially linked through the serpentinization reaction (rxn. 1).

\[
6CaAl_2Si_2O_8 + 15 Mg_2SiO_4 + 25 H_2O \\
\rightarrow Ca_6Si_6O_{17}(OH)_2 + 6 Mg_5Al_2Si_3O_{10}(OH)_8 \quad \text{rxn. 6} \\
+ 3 SiO_2(aq)
\]

\[
6CaAl_2Si_2O_8 + 10 Mg_3Si_2O_5(OH)_4 + 5 H_2O \\
\rightarrow Ca_6Si_6O_{17}(OH)_2 + 6 Mg_5Al_2Si_3O_{10}(OH)_8 \quad \text{rxn. 7} \\
+ 8 SiO_2(aq)
\]

As long as log aSiO$_2$(aq) remains below -1.59, reactions 6 and 7 will be exergonic (see Fig. 7). Excess olivine in the s will sustain continuous brucite production, which buffers silica activity at sufficiently low levels (rxn. 4). Indeed, high amounts of brucite, serpentine and magnetite were observed in the experiment. This is due to the high olivine proportion in the starting material. The molar ratio of plagioclase to olivine required for reactions 2, 3, 6 and 7 are ≤ 1:2.5 compared to an actual reaction ratio of 1:7.4 indicated by mass balance. The olivine reactant also had a considerable fayalite component (X$_{Mg} = 0.91$), whereas serpentine and brucite from domain α were both depleted in Fe (X$_{Mg} = 0.96$ respectively 0.93). This observation is in line with the ubiquitous presence of additional magnetite in domain α and high H$_2$(aq) concentrations measured in the fluid samples. A serpentinization reaction for the 300°C experiment can be given as:

\[
2 Mg_{1.813}Fe_{0.187}SiO_4 + 2.84 H_2O \rightarrow Mg_{2.917}Fe_{0.083}Si_2O_5(OH)_4 \\
+ 0.76 Mg_{0.932}Fe_{0.068}(OH)_2 + 0.08 Fe_3O_4 \quad \text{rxn. 8} \\
+ 0.08 H_2(aq)
\]
The observed distribution of iron is also in agreement with bulk fluid composition and CaO-FeO-SiO$_2$-H$_2$O-H$_2$O phase relations at 300°C. The speciated fluid samples are likely most representative of the intergranular fluid in α and β and plot well within the magnetite stability field (see Fig. 7; T1.2 – T1.4). In contrast to the outermost domain α, serpentine also does not occur as a pure Mg-poor chrysotile-greenalite component but only in combination with chlorite in the inner domains (γ to ε). The mixture of both phases has an overall $X_{Mg}$ that is identical to that of the olivine reactant and hence ferrous iron (Fe$^{2+}$) was not available for oxidation and the formation of magnetite.

**Development of a mineral zonation at 300 °C.** Computational results confirm that the observed mineral phases can be expected at the experimental conditions. However, a bulk equilibrium model cannot reproduce the complex mineral zonation documented in the retrieved solids. Why are magnetite and brucite restricted to the outer domains (α and β), whereas xonotlite is only present in the inner domains (δ and ε)? We hypothesize that the zonation developed as different portions of the solids reacted at variable rates due to differences in the degree to which the bulk fluid could mix and homogenize with local intergranular fluid. As there is no temperature gradient throughout the reaction cell, there will be no fluid flow or convective mixing but only diffusive exchange between adjacent fluid volumes. As the water-rock reaction proceeds throughout the solid volume, the local intergranular fluid evolves towards saturation with respect to the local mineral assemblage. With the solid reactants at the bottom of the cell, the intergranular fluid in the uppermost portions of the reactants is in direct contact with the overlying bulk fluid (see Fig. 3 F). The fluid in this portion is quickly diluted through diffusive mixing. In contrast, the dilution of the intergranular fluid further towards the bottom of the cell can be expected to proceed
slower as there is an overlying batch of solid and fluid reactant separating it from the bulk fluid. Therefore, the intergranular fluid further towards the bottom would quickly become saturated with respect to the local assemblage slowing further reaction progress. In contrast, the reaction can be expected to proceed faster in the uppermost portions of the solid reactants. Regardless of this premise, plagioclase reacting next to serpentinizing olivine throughout the assemblage initially represented a source of Al for the formation of chlorite instead of serpentine (rxn. 2 and rxn. 3). Consequently, we observe thin chlorite coronas around relict olivine grains in domains α and β (see Fig. 7 A). This replacement of olivine by chlorite requires a certain fluid mobility of Al. And a similar initial chlorite formation can be assumed at the bottom of the cell, only somewhat slower due to the mechanism described above. This early cementation through the formation of chlorite would arguably further limit the exchange between the bulk fluid and the intergranular fluid in the lower portions of the solid reactants. As the much less abundant plagioclase reactant inevitably is exhausted in the faster-reacting outer domains, chlorite can no longer form and hence the chlorite coronas remain comparably thin. More importantly, this exhaustion of plagioclase also constitutes a major change with respect to the local buffering of the water-rock reaction. As the reaction proceeds, an increasing portion of the solids closer to the bulk fluid – solid interface will be exclusively buffered by unreacted olivine and this has manifold implications (see Fig. 3 F):

(1.) Further reaction of remaining olivine subsequently produces a pure serpentinization mineral assemblage of serpentine, brucite and magnetite in these domains (see Fig. 7 A; rxn. 8).
(2.) This serpentinization of olivine can be expected to proceed slower as there is no longer a local stark chemical contrast between the original reactants in which the serpentinization of olivine is fueled by the desilication of plagioclase. Taking into account that a major share of the cavities visible in domains α and β of the investigated mount were in fact filled with unreacted olivine (as indicated by μ-CT scans, see supplemental Fig. 5.1), we can conclude that olivine reaction in the outer domains α, β and γ ultimately was much less complete than in the innermost domains δ and ε (see Fig. 3 A+B).

(3.) At this stage considerable fractions of unreacted plagioclase were still present in the solids more towards the bottom of the reaction cell. As a consequence, a chemical potential gradient could have been established between the more isolated portions of the solids (buffered by olivine and plagioclase - chlorite) and the domains closer to the solid fluid interface (buffered by olivine – serpentine, brucite, magnetite ±chlorite) (see Fig. 3 F). To explore whether this proposed gradient resulted in a mass exchange between the inner and outer domains, an additional mass balance was prepared for the individual domains, based on SEM maps (see Fig. 3 A, supplementary Fig. S4.1-S4.3 and Table S1). This evaluation confirms that the different domains systematically differ with respect to individual elemental abundances and that a selective mass transfer must have occurred (see Fig. S4.2). While Si is distributed uniformly, Ca and Al are strongly depleted in the outer domains α and β, but very abundant in the inner domains δ and ε towards the bottom of the reaction cell. In contrast, Mg – and to a lesser extent Fe – are depleted in the interior but enriched in the outer domains α to β.

Plagioclase dissolution in the outer domains also released Ca, which was partially reflected in the initial spike in the fluids’ Ca concentration; however, the lack of any Ca-
bearing phase in domains α to γ indicates that most of the Ca was eventually transferred to
the inner domains. Possibly, the Ca concentration simply remained below the level
necessary for xonotlite formation in the uppermost layer of the solids by the time of
plagioclase exhaustion (see Fig. 3 A+B and Fig. 7, rxn. 5). Later, the local buffering by the
serpentine-brucite-magnetite assemblage and the absence of a precursor Ca mineral surface
could have actively prevented precipitation of a Ca-bearing mineral phase in the outer
domains. In the moderately isolated domain γ, a somewhat delayed incipient growth of
chlorite coronas is facilitated by Al supplied through limited diffusional equilibration with
the faster reacting domains α and β. As mass balancing indicates a faster reaction of olivine
compared to plagioclase, this externally sourced Al boosts the growth of chlorite. In
contrast to domains α and β, domain γ contains a considerable share of true porosity and
the shape of the pores more closely resembles the interstitial space which is filled with
xonotlite and plagioclase in the most isolated domains (see Fig. 3 A+F and supplemental
Fig. 5.1). Domain γ represents the connecting micro environment between the differently
buffered poles of the documented zonation, in which the plagioclase reactant ultimately
could completely dissolve but xonotlite formation might have been prevented through the
vicinity of the directly adjacent serpentine - brucite - magnetite buffered domain. At this
stage the comprehensive serpentine cementation in the outer domains and compaction
under high pressure resulted in further reduction of porosity to a degree where exchange
with the bulk fluid became very limited and a batch of intergranular fluid became locked-in
within the inner portions of the solids (see Fig. 3 B+F and supplemental Fig. S5.1). In
the inner domains δ and ε, a of time-integrated diffusive influx of Ca, further dissolution
of abundant plagioclase and a lack of fluid dilution eventually pushed the system to
supersaturation with respect to xonotlite. Xonotlite clearly precipitates in the intergranular space from a supersaturated solution and does not replace one of the primary phases (see Fig. 3 A+B and Fig. 7 B). Regarding the influx of Ca to domains δ and ε (see supplemental Table S1 and Fig. S4.2), one explanation for the directed mass transfer could be that once the high threshold for xonotlite crystal formation was breached in the innermost domains, further precipitation at existing crystal surfaces required much lower Ca levels and this would then constitute a sink for dissolved Ca. A pronounced inward directed flux of Ca\(^{2+}\) ions was apparently balanced by an outward directed flux of Mg\(^{2+}\) ions. In fact, mass balancing corroborates this hypothesis and the in-to-out flux of Mg\(^{2+}\) would facilitate the observed serpentine and brucite cementation in the outer domains (α + β) (see Fig. 3 A+D and suppl. Fig. S4.2). Similar to the explanation for Ca flux, the serpentine – brucite – magnetite buffered domains α and β provided conditions that allowed magnetite to crystallize and hence, these domains became a sink for Fe (see Fig. 3 D+E and supplemental Fig. S.4.2). On the opposite end, the diffusion-related surplus of Al and late reaction of plagioclase translates to ever thicker chlorite coronas around relict olivine in domains δ and ε. Serpentine did not precipitate in the intergranular space and is hence not part of the (meta) stable mineral assemblage in and around the pore space. In domain δ, where plagioclase is completely reacted, serpentine is limited to the space between thick chlorite coronas and relict olivine (see Fig. 3 H). In the innermost domain ε, olivine is closely armored by chlorite coronas indicating that as long as plagioclase provided an immediate source of Al, serpentine formation is effectively prohibited (see Fig. 3 I). Successive isolation through cementation increasingly decelerated the reaction progress so
that upon termination of the experiment, larger portions of anorthite remained unreacted in
the innermost domain \( \varepsilon \).

**Interpretation of phase relations, fluid data and zonation at 400 °C.** At 400
°C, forsterite is part of the equilibrium mineral assemblage instead of brucite and silica
activity is hence buffered at a higher level. Mass balancing indicates that \( \geq 90\% \) of
plagioclase reacted, while more than 60\% of olivine remained unreacted. The in-situ
speciated fluids are in equilibrium with a forsterite-chlorite assemblage (see Fig. 8). But
the reaction path model fluid quickly hits the univariant forsterite - diopside phase
boundary as plagioclase dissolves (see yellow path in Fig. 8). Silica released by plagioclase
dissolution facilitates some direct reaction of olivine to serpentine (rxn. 9), which is
intergrown with chlorite.

\[
3 \text{Mg}_2\text{Si}_4\text{O}_{10} + \text{SiO}_2(aq) + 4 \text{H}_2\text{O} \rightarrow 2 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4
\]

**rxn. 9**

However, the extent of olivine alteration in the outermost domain \( \alpha^* \) is very small
and limited to the formation of chlorite coronas (rxn. 2 and 3). This is in contrast to the
extensive replacement of olivine by serpentine-brucite in the 300 °C experiment and
suggests that the olivine reaction progress at 400 °C is strictly controlled by plagioclase
dissolution.

While the sampled fluid never reached diopside saturation, the model fluid does
reach the univariant forsterite - diopside line and precipitation of diopside in addition to
chlorite is predicted (see Fig. 8). A simplified overall hydration reaction can be defined:

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 3 \text{Mg}_2\text{Si}_4\text{O}_{10} + 4 \text{H}_2\text{O} \rightarrow \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + \text{CaMgSi}_2\text{O}_6
\]

**rxn. 10**
Texturally, chlorite replaces olivine and clinopyroxene precipitates in the void space created by plagioclase dissolution. The main observed Fe-phase in the outer domains was andradite. The position of the model fluids in Fig. 8 indicates that magnetite should be the stable Fe-phase. However, the univariant lines were constructed for unity activities of all reaction components. The andradite-magnetite boundary will shift downwards if lower H$_2$(aq) activities are assumed (Fig. 8; rxn. 11).

\[
2Fe_3O_4 + 9Ca^{++} + 9SiO_2(aq) + 10H_2O \rightarrow 3Ca_3Fe_2Si_3O_{12} + 18H^+ + H_2(aq) \tag{rxn. 11}
\]

Indeed, low H$_2$ contents were detected in the 400 °C fluids (Tab. 1), so the presence of andradite is not unexpected. Andradite can be an indicator for low temperature serpentinization environments (<220 °C), but it is stable at higher temperatures if brucite is not stable (Frost and Beard, 2008). Our results support the notion of possible andradite formation at T > 340 °C, the upper stability limit of brucite (McCollom and Bach, 2009).

The chlorite-clinopyroxene product mineral assemblage and the relative stability of the olivine reactant (bar some reaction to serpentine) in the outer domains α* and β* constitutes a major share of the reaction turnover in the 400 °C experiment. As in the 300 °C run, the reaction can be expected to proceed somewhat faster in the uppermost portion of solids (see Fig. 3 F). Likewise, it can be expected that the local buffering of the system within the uppermost layers shifted upon plagioclase exhaustion. But in contrast to the 300 °C experiment, olivine was stable after plagioclase had reacted away. The resulting conditions allowed for the Ca-phase diopside to crystalize (see Fig. 5 A+B). As supported evaluation of porosity, olivine stability also prevented a subsequent comprehensive cementation of domains α and β and the inner domains arguably did not become as isolated.
as in the 300 °C experiment (compare supplementary Fig. S5.1 and S5.2). Nonetheless the bipolar system of differently buffered water-rock reactions in the upper- and lowermost portions of the solids was also established at 400 °C. Mass balancing the elemental abundances in the individual domains confirms that Ca and Al were transferred inwards, while Mg abundance was overall increased in the outer domains (see supplemental Fig. 4.4 and Table S1). The Mg-free phases grossular, and xonotlite were observed in the inner domains γ* and δ*. As in the 300 °C experiment, we assume that Ca activities were elevated towards the inner domains due to limited dilution with the bulk fluid and active mass transfer from the outer domains. Reaction of plagioclase with the Ca enriched fluids in the inner domains resulted in the observed precipitation of xonotlite and grossular in the intergranular space (see Fig. 8 B; rxn. 12).

\[
CaAl_2Si_2O_8 + 8 Ca^{++} + 7 SiO_2(aq) + 9 H_2O \rightarrow Ca_3Al_2Si_3O_{12} + Ca_6Si_6O_{17}(OH)_{2} + 16 H^+ \text{ rxn. 12}
\]

Finally, a feature observed at both temperatures is the inward increase in the width of chlorite coronas around olivine.

**Experimental results compared to natural troctolite alteration**

Overall, the experimental results are in good agreement with the conclusion by Frost et al. (2008) that troctolite alteration is predominantly dictated by the contrasting interplay between the serpentinization of olivine and the alteration of plagioclase. Specifically, strong contrasts in buffering of the water-rock reaction in variably fast reacting portions of the solids appear to be key for generating driving force for the reaction and mass transfer. Close to the solid-fluid interface where the less abundant plagioclase is
eventually completely reacted, exclusive serpentinization of olivine to serpentine and brucite imposes locally extremely low silica activities and the intergranular fluid is buffered by the assemblage serpentine - brucite - magnetite. In natural olivine-rich rocks, this reaction dominates the composition of intergranular fluids and the alteration of plagioclase is desilication to prehnite and hydrogrossular. This is similar to what drives rodingitization reactions (e.g., Bach and Klein, 2008). Frost et al. (2008) and Nozaka and Fryer (2011) found two types of troctolite alteration: (1) the microrodingite type in which olivine is replaced by serpentine and plagioclase is altered to prehnite / hydrogrossular, and (2) a higher-grade type, in which coronas of chlorite (replacing plagioclase) and tremolite (after olivine) develop at the former plagioclase-olivine grain boundaries. Considering the estimated lower alteration temperature for the microrodingitized troctolites from the Atlantis Massif (<350 °C), they likely provide a better analogue for the 300 °C experiment. The 400 °C experiment did not produce tremolite. In both experiments the alteration produced significant amounts of serpentine, chlorite and magnetite, however, xonotlite and clinopyroxene (at 400 °C) were the most abundant Ca-silicates formed in the experiments, while in the Atlantis Massif samples serpentinization yielded prehnite and grossular. It should be noted that an early chlorite-tremolite assemblage after olivine and plagioclase was documented for both Atlantis Massive troctolite alteration types, including the microrodingites. As the prehnite and grossular assemblage overprinted this earlier assemblage, its existence may well have been a necessary condition for the formation of the observed alumosilicates. But Nozaka and Fryer (2011) also deduced formation temperatures between 400 and 650 °C for the early chlorite-tremolite assemblage and this would exclude a similar alteration sequence for our experiments. Another explanation for
this discrepancy might be that a powder sample was used in the experiment, whereas a compact rock reacted in the natural system. Prehnite (Ca/Si = 0.67) and grossular (Ca/Si = 1) are proposed to result from a 1st and 2nd step of consecutive desilication of plagioclase (Ca/Si = 0.5), which is driven by low silica activities imposed by serpentinization of olivine (Frost et al. 2008). Aluminum and Ca mobility in the compact rock was limited, which only allowed for limited formation of chlorite from nearby serpentine (rxn. 3). Consequently, released Al predominantly had to be incorporated into the Ca bearing phases, ultimately favoring the formation of grossular and prehnite. Then again, the powder sample used in our experiments initially had an open pore space facilitating a significant increase of elemental mobility. This would enable ubiquitous formation of chlorite in association with olivine, and the Al fraction released upon desilication of plagioclase did not necessarily have to be incorporated in the forming Ca-bearing mineral phases. Xonotlite formed instead of prehnite or grossular, but it can equally be seen as a product of desilication of anorthite exhibiting an increased Ca/Si ratio of 1 (rxn. 5, 6, 7 and 12). Xonotlite was repeatedly reported in rodingitization associated mineral assemblages (O’Brien 1973; Esteban et al. 2003) and even in context of an altered troctolite (Capedri et al. 1980). The fact that no Ca-bearing phase exhibiting an intermediate Ca/Si ratio was observed among the solids retrieved form the 300 °C experiment might be attributable to the separation into domains of very high (δ and ε) and distinctly low Ca activities (α and β) through the pronounced mass transfer of Ca after a chemical potential gradient established between very differently buffered portions of the solids. In addition, comprehensive cementation of the outer portions limited dilution of the inner intergranular fluid and further plagioclase reaction eventually pushed local saturation over the threshold.
for xonotlite formation. Once the first crystals had formed in the inner domains, they enabled further xonotlite precipitation even at lower Ca levels. This made domains δ and ε a sink for Ca and would arguably have facilitated further inward directed mass transfer of Ca\(^{2+}\) ions counterbalanced by an outflux of Mg\(^{2+}\) ions (see supplemental Fig. S4.2).

A major difference between the two experiments is the lack of brucite and the stability of olivine at 400 °C. Silica activity set by the serpentine-brucite buffer at 300 °C is much lower than that of the forsterite-serpentine assemblage at 400 °C (compare Figs. 7 and 8). If silica activity is sufficiently high, talc is expected to form like in altered troctolites exposed near the Kairei hydrothermal field (Nakamura et al. 2009), but not in our 400 °C experiment. In contrast to the compact rock in the natural system, increased Ca availability was not restricted to the immediate vicinity of reacting plagioclase in the experiment, and at higher log (aCa\(^{2+}\)/aH\(^{2+}\)) values diopside is the stable high silica mineral phase. A similar explanation can account for the absence of tremolite. Also, similar to the troctolites investigated by Nakamura et al. (2009), grossular was confirmed as a product mineral, indicating low silica activities. Solids retrieved from the 400 °C experiment revealed that strong chemical contrasts prevailed between portions of the reactants where plagioclase was fully reacted and more isolated portions with unreacted plagioclase. This facilitated inward directed mass transfer of Ca and Al, counterbalanced by Mg and resulted in the development of chemically extremely variable microenvironments. Grossular and even xonotlite could form in context of further desilication of plagioclase in one space, while simultaneously clinopyroxene formed elsewhere. The exact formation mechanism of andradite in association with clinopyroxene remains unclear; however, the co-occurrence
of the two phases in context of high temperature serpentinization was reported before (Frost 1985).

Another peculiarity in the 400 °C experiment is the massive occurrence of almost pure clinopyroxene ±andradite at the fluid-rock interface (see Fig. 5 D). Similar occurrences of diopsidite were previously reported as an unusual type of dyke lithology in the mantle section of the Oman ophiolite (Python and Ceuleneer 2003; Python et al. 2007). These authors suggested a formation hypothesis in which seawater penetrated into the upper mantle through cracks and fissures in the crust. The recharging fluids supposedly reacted with plagioclase-rich lithologies in the crust and became enriched in Ca before they penetrated into the mantle, where they caused diopsidite formation at extremely high temperatures (>800 °C). The paragenetic association also included forsterite and anorthite. The high temperature estimate was based on the co-occurrence of plagioclase, anorthite and olivine and the anhydrous nature of this assemblage. The dykes always occurred close to the former crust mantle transition zone and in particular in mantle sections that where intensely percolated by hot primitive melts. Moreover, it was suggested that the heat required for initiating and maintaining fluid circulation is provided by the crystallization of nearby troctolites. Considering this close association with troctolites and an alteration texture typical for rodingitization, massive occurrence of clinopyroxene in the 400 °C experiment might provide an alternative low T formation hypothesis for this unique dyke lithology. Secondary clinopyroxene in association with altered troctolites has been reported before at Hess Deep where it was interpreted as a late high-grade (>360 °C) hydrothermal overprint of a preceding chlorite-prehnite alteration that occurred lower temperatures (200 °C - Gillis et al. 2014; McCaig et al. 2018).
Potential for H\textsubscript{2} production

Following an early complete reaction of plagioclase, further olivine reaction in the outer domains \( \alpha \) and \( \beta \) produced predominantly Mg-rich serpentine and brucite (only \( \alpha \)) in the 300 \(^\circ\)C experiment. The Fe component of olivine reactant was oxidized to magnetite by water, releasing fairly large amounts of H\textsubscript{2} (up to 20 mM). The total extends of magnetite, and hence H\textsubscript{2} formation, were likely increased through additional Mg and Fe sourced from other portions of the solids. Andradite observed at the solid-fluid interface (gold cell contact) served as an additional, likely subordinate source of H\textsubscript{2}. This observation could be seen as an analogue for massive andradite in veins associated with Ca-metasomatic alteration in lherzolite rocks described by Plümper et al. (2014) as an elevated W/R can be assumed for both environments. Plümper et al. (2014) proposed a reaction mechanism, in which the principle serpentinization related Fe-component magnetite was destabilized through the addition of Ca (rxn. 13).

\[
4.5 \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 9 \text{Ca}^{2+} + 14 \text{H}_2\text{O} + 2 \text{Fe}_3\text{O}_4 \rightarrow 3 \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 13.5 \text{Mg(OH)}_2 + 18 \text{H}^+ + \text{H}_2(\text{aq})
\]

As the final H\textsubscript{2} concentration could not be measured due to the premature cooling of the system, we calculated a hypothetical value based on the quantified amount of magnetite and andradite in the 300 \(^\circ\)C experiment (45 mmol L\textsuperscript{-1}; according to rxn. 8 and 11) and compared it with an extrapolation based on the trend set through the previous fluid samples (30 mmol L\textsuperscript{-1}). The deviation could in part be subjected to a considerable error of the AGFM based quantification of magnetite. Additional CH\textsubscript{4} detected within the fluids is negligible in comparisson and a Sabatier type reaction does not provide a satisfying
explanation for the observed difference (McCollom and Seewald 2007; Bradley and Summons 2010). Both $H_2$ estimates demonstrated a great potential for $H_2$ production in context of alteration of olivine-rich troctolite.

At 400 °C, serpentinization of thermodynamically stable olivine was limited and clinopyroxene formed in context of higher silica activities. Serpentine presence was limited and abundant chlorite had similar Fe fractions as primary olivine. With Fe-rich clinopyroxene and chlorite (±serpentine) there was little excess Fe available for the formation of additional magnetite. However, chlorite always co-occurred with serpentine and given that the thermodynamic model predicted a relatively large cronstedtite component at 400 °C, considerable portions of the Fe-serpentine could be present in the serpentine-chlorite mixture. Trivalent Fe incorporated in cronstedtite offers another $H_2$ formation pathway (Klein et al. 2013). Magnetite was barely observed, yet a significant contribution of andradite (less Fe-rich than at 300 °C) represents a potential source for $H_2$ production (see rxn. 11 and 13). Balancing the amount of $H_2$ produced though andradite and magnetite formation yields a potential concentration of 9 mM. However, subsequent to the measured initial increase, $H_2$ was depleted from the reaction fluid at 400 °C. Methane levels where somewhat higher than in the 300 °C experiment, but methane also became depleted with progressing reaction. Falling $H_2$ and $CH_4$ concentrations after an initial increase imply a yet unidentified process that consumes the two components.

**IMPLICATIONS**

The results presented herein provide an initial experimental perspective on the alteration mechanisms controlling the alteration of olivine-rich troctolites. The observations confirm that first-order controls on the alteration process are defined by the
combined effects of olivine serpentinization and plagioclase desilication reactions (Frost et al., 2008). Secondly, silica activity is key in determining the actual product mineral assemblage and it is set either to a relatively low (serpentine-brucite) or high (serpentine-forsterite) level depending on alteration temperature. The experiments also highlight how variable reaction rates in portions of a reacting rock that are closer or further away from a solid-fluid interface can produce stark contrasts in local buffering of the water-rock reaction and that this can entail pronounced selective mass transfer along chemical potential gradients. Progressive pervasive cementation by secondary phases like serpentine, chlorite, acicular clinopyroxene and xonotlite can increase partial isolation of certain rock portions, further increasing the tension between differently buffered portions of the solids. A selective diffusional mass transfer (Ca + Al counterbalanced by Mg and, to a lesser extent, Fe) enables the development of chemically extreme microenvironments that allow for the abundant formation of phases like magnetite, andradite, grossular or xonotlite that would not form in entirely equilibrated systems. The magnetite and andradite formation associated oxidation of iron mediates a significant H\textsubscript{2} production that can sustain chemosynthesis based microbial communities, especially at temperatures where brucite is stable (<315-340 °C). As the composition of troctolites closely resembles the chemistry of komatiites, their alteration could also be a good analogue for komatiite serpentinization processes that might have played a crucial role as an energy source for early life on earth (Kumagai et al. 2008; Nakamura et al. 2009). While H\textsubscript{2} production is limited at the higher temperature level, the observation that more CH\textsubscript{4} is formed and both compounds are eventually depleted from the fluid implies a further conversion to different, possibly organic components that should be further investigated. The described massive occurrence
of clinopyroxene association with minor andradite along a fluid-solid interface at the higher
temperature level resembles a massive diopsidite in dykes found in the Oman ophiolite
(Python et al., 2007). The serpentinization of olivine-rich troctolite might provide an
alternative formation scenario for these peculiar lithologies that does not require nearly as
high temperatures as previously suggested.

Whereas this study focuses on olivine-rich troctolites, more plagioclase-rich
troctolites are also a common rock type, both in the oceanic lower crust of fast- (e.g., Gillis
et al., 2014) and slow-spreading ridges (e.g., Dick et al., 2008) as well as in association
with anorthosite intrusions (Drüppel 2003). Considering the documented strong
interdependence of the olivine and plagioclase reactions, a shift towards a more
plagioclase-rich lithology would certainly have a profound impact on the alteration
process. In particular at elevated temperatures (>350 °C), a more prominent plagioclase
reaction could facilitate an increased co-reaction of otherwise stable olivine including the
oxidation of its fayalite component and thereby increase the potential for H\textsubscript{2} formation.
This could be further explored in future experimental studies. In addition, more emphasis
should be put on investigating the impact of variable element mobility during rock
alteration as the experiments demonstrated how major deviations in this regard can arise
from reacting a compact rock compared to powder sample.

Acknowledgements

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References cited


Dickson, F.W., Blount, C.W., and Tunell, G. (1963) Use of hydrothermal solution equipment to determine the solubility of anhydrate in water from 100 °C to 275 °C and from 1 bar to 1000 bars pressure. American Journal of Science, 261, 61–78.


Suhr, G., Hellebrand, E., Johnson, K., and Brunelli, D. (2008) Stacked gabbro units and intervening mantle: A detailed look at a section of IODP Leg 305, Hole U1309D. Geochemistry, Geophysics, Geosystems, 9, n/a-n/a.


Wolery, T.J. (1992) EQ3/6 - A Software Package for Geochemical Modeling of Aqueous
Figure captions

Figure 1: Summary of solid phase alteration modes retrieved from the conducted experiments. Formation of alteration phases like serpentine, chlorite, clinopyroxene and xonotlite facilitated a pervasive cementation. As a result of variable degrees of isolation distinct mineral assemblages occur in different microenvironments. Five domains (α, β, γ, δ, ε) could be distinguished in the solids retrieved from the 300 °C run, whereas 4 distinct assemblages (α*, β*, γ*, δ*) where identified in the concretion produced in the 400 °C run. References given in rectangular brackets for the investigated gold cell contacts indicate the domains which can be associated with these contact surface assemblages. The ranking position of olivine attributed with an asterisk takes into account that the mineral was in part plucked out from the respective domains during mount preparation. Details complementing this summary of different mineral phases are provided in the text and in Fig. 3 and 5, which cover a close up of profile sections S and S*.

Figure 2: Measured evolving fluid composition in the experiments. (A) in the 300 °C run and (B) in the 400 °C experiment.
**Figure 3:** Retrieved mineral assemblage from the 300 °C experiment I. (A+B) SEM element mapping (Mg, Al, Fe, Ca) of profile section S (see Fig. 1) and a corresponding false color image contrasting identified mineral phases. From top to bottom section S covers 5 (α, β, γ, δ, ε) domains in a zonation of distinct mineral assemblages distinguished in the 300 °C run. (C) BSE image of upper part of the cemented mass comprised of a fine serpentine-chlorite mixture, andradite crystals and relict olivine. (D) BSE image of the mineral assemblage in domain α. Patches of brucite intergrown with a fine serpentine-chlorite mixture. Chlorite is concentrated in a thin rim marking the boundary to cavities in the texture. Relict olivine with dissolution features that probably filled most of the cavities in the unpolished mount, is visible in the center of some cavities. (E) BSE image showing the occurrence of magnetite in domain α and β. (F) Schematic drawing of the solid reactants within the gold reaction cell. Arrows indicate elemental transfer between the top and bottom domains. (G) BSE image of the lower part of the cemented mass, which is mostly comprised of a chlorite-serpentine mixture and xonotlite. (H) BSE image of xonotlite void fill and thick chlorite coronas around dissolved crystals of olivine in domain δ. (I) Large portions of unreacted anorthite in domain ε. Remnants of unreacted olivine with thick chlorite rims and xonotlite in the interstitials.

**Figure 4:** Compositional variability in serpentine and serpentine-chlorite mixtures. Serpentine from the outermost domain α (300 °C) exhibits an almost pure magnesian end-member composition with minor additions of Fe. While serpentine contributions to chlorite (300 and 400 °C experiment) are not identifiable by optical measures, reduced Al fractions clearly indicate its additional presence. A significant amesite component is not indicated.
Figure 5: Retrieved mineral assemblage from the 400 °C experiment. (A+B) SEM element mapping (Al, Fe, Ca) of profile section S* (see Fig. 1) and a corresponding false color image contrasting identified mineral phases. From top to bottom section S* covers 4 (α*, β*, γ*, δ*) domains in a zonation of distinct mineral assemblages distinguished for the 400 °C run. The elemental transfer between the top and bottom domains within the cell is indicated. (C) BSE image of void clinopyroxene in domain α* and β*. Andradite-rich garnet occurs in a typical dense aggregation of small isometric crystals associated with clinopyroxene. (D) BSE images of the crust surface that represents the solid-gold cell contact. The upper part of the crust consists of massive clinopyroxene and associated andradite crystals. The lower part of the crust is almost exclusively comprised of chlorite, with some grossular-rich garnet and minor xonotlite. (E) BSE image of the transition between domains γ* and δ*. Thick, fine-grained chlorite completely replaced primary olivine, whereas the interstitials are filled with fibrous xonotlite and grossular-rich garnet. Larger fractions of anorthite remained unreacted in domain δ*.

Figure 6: Predicted equilibrium phase assemblages as plagioclase and olivine are successively added to water. $\xi = 1$ represents the proportions of fluid to solids used in the experiment. The vertical lines represent the observed reaction turnover. See text for details on the calculations. (A) Reaction path model for the 300 °C experiment. Antigorite, monticellite, tremolite, amesite, diopside, garnet, akermanite, merwinite, wollastonite and portlandite were suppressed from the model. (B) Reaction path model for the 400 °C experiment. Antigorite, monticellite, tremolite, amesite, magnetite, hematite, wuestite and cronstedtite were suppressed from the model.
**Figure 7:** Activity-activity diagrams showing the phase relations in the system MgO-SiO$_2$-H$_2$O (blue dashed lines) speciated over the phase relations in the system MgO-SiO$_2$-CaO-Al$_2$O$_3$-H$_2$O (red solid lines) at 300 °C and 50 MPa. Only minerals identified in the solids retrieved from the experiment were considered. Changing in-situ activity characteristics of the taken fluid samples (green stars) as well as the evolution of the corresponding titration model fluid (yellow path) are plotted for comparison. Phase relations of iron bearing phases that are key to potential H$_2$ production (green, pink and light blue dashed lines for H$_2$ activity of unity, 20 and 5 mmol L$^{-1}$) confirm that magnetite can be expected to form in the outer low Ca domains.

**Figure 8:** Activity-activity diagrams showing the phase relations in the system MgO-SiO$_2$-H$_2$O (blue dashed lines) speciated over the phase relations in the system MgO-SiO$_2$-CaO-Al$_2$O$_3$-H$_2$O (red solid lines) at 400 °C and 50 MPa. Only minerals identified in the solids retrieved from the experiment were considered. Changing in-situ activity characteristics of the taken fluid samples (green stars) as well as the evolution of the corresponding titration model fluid (yellow path) are plotted for comparison. Phase relations of iron bearing phases that are key to potential H$_2$ production (green and white dashed lines for H$_2$ activity of unity and 0.2 mmol L$^{-1}$) confirm that andradite instead of magnetite is the thermodynamically stable phase at moderately elevated Ca activities. Rxn. 10 is not shown as it would proceed throughout the depicted space.
Table 1: Summary of fluid data and related modelling results. Concentrations of dissolved elements and gases are given in µmol/kg.

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<th>$V_{\text{left}}$ [ml]</th>
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<th>Al</th>
<th>Si</th>
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Experimental Run at 300°C and 40 MPa

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Experimental Run at 400°C and 40 MPa

*Values were modelled analogue to those for samples taken at elevated temperatures for visual comparison.
Table 2: Mineral chemistry for reactants and phases retrieved from the 300 °C experiment determined via EMP analyses.

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<th>Plagioclase²</th>
<th>Serpentine¹</th>
<th>Chlorite¹</th>
<th>Brucite¹</th>
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<td>0.91</td>
<td>0.96</td>
<td>0.97</td>
<td>0.91</td>
<td>0.93</td>
<td>0.91</td>
<td>0.91</td>
<td>0.96</td>
</tr>
</tbody>
</table>

¹XMg = Mg / (Mg + Fe)  
²XCa = Ca / (Ca + Na)  
*Initial characterization of the reactants
Table 3: Mineral chemistry for phases retrieved from the 400 °C experiment determined via EMP analyses.

<table>
<thead>
<tr>
<th>Component</th>
<th>Olivine $^1$</th>
<th>Plagioclase $^2$</th>
<th>Chlorite $^1$</th>
<th>Clinopyroxene $^1$</th>
<th>Xonotlite</th>
<th>Andradite $^3$</th>
<th>Grossular $^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis</td>
<td>(12)</td>
<td>(5)</td>
<td>(28)</td>
<td>(14)</td>
<td>(2)</td>
<td>(6)</td>
<td>(11)</td>
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<tr>
<td>SiO$_2$</td>
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<td>44.64</td>
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<td>53.18</td>
<td>50.66</td>
<td>36.11</td>
<td>36.57</td>
</tr>
<tr>
<td>TiO$_2$</td>
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<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.07</td>
<td>0.35</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.06</td>
<td>36.53</td>
<td>13.42</td>
<td>1.76</td>
<td>0.39</td>
<td>3.81</td>
<td>17.04</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
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<tr>
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<tr>
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<td>1.17</td>
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<tr>
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<td>0.18</td>
<td>0.20</td>
<td>0.08</td>
<td>0.16</td>
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<td>46.33</td>
<td>33.59</td>
<td>35.38</td>
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<tr>
<td>Na$_2$O</td>
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<td>0.52</td>
<td>0.05</td>
<td>0.08</td>
<td>0.00</td>
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<td>0.02</td>
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<tr>
<td>K$_2$O</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Al</td>
<td>0.00</td>
<td>1.96</td>
<td>1.49</td>
<td>0.08</td>
<td>0.05</td>
<td>0.37</td>
<td>1.58</td>
</tr>
<tr>
<td>Cr</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
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<td>0.02</td>
<td>0.42</td>
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<td>0.14</td>
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<tr>
<td>Ca</td>
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<td>0.01</td>
<td>0.01</td>
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<td>0.00</td>
</tr>
<tr>
<td>K</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>12.00</td>
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<tr>
<td>$^1$X$_{Mg}$</td>
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<td>0.92</td>
<td>0.86</td>
<td>0.81</td>
<td>0.23</td>
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</tbody>
</table>

*Iron for andradite-grossular solid solutions was calculated as ferric Fe$^{3+}$

$^1$X$_{Mg} = \frac{Mg}{(Mg + Fe)}$  $^2$X$_{Ca} = \frac{Ca}{(Ca + Na)}$  $^3$X$_{Fe} = \frac{Fe}{(Fe + Al)}$
Table 4: Mineral proportions derived from TG, AGFM and regression modelling. Total mass percentage is based on a ratio of modelled total vs retrieved total mass.

<table>
<thead>
<tr>
<th>Components</th>
<th>Idealized formula*</th>
<th>M* [g/mol]</th>
<th>m [g]</th>
<th>X [wt.-%]</th>
<th>n [mol]</th>
<th>RP X [wt.-%]**</th>
<th>RP n [mol]**</th>
<th>M [g/mol]</th>
<th>m [g]</th>
<th>X [wt.-%]</th>
<th>n [mol]</th>
<th>RP X [wt.-%]**</th>
<th>RP n [mol]**</th>
</tr>
</thead>
<tbody>
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<td><strong>Initial</strong></td>
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<td></td>
</tr>
<tr>
<td>Olivine</td>
<td>Mg$_2$SiO$_4$</td>
<td>146.55</td>
<td>12.96</td>
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<td>8.84E-02</td>
<td>77.79</td>
<td>8.84E-02</td>
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<td>12.96</td>
<td>77.78</td>
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<td>77.78</td>
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<td>CaAl$_2$Si$_2$O$_8$</td>
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<td>1.33E-02</td>
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<td>278.39</td>
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<tr>
<td>Olivine</td>
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<td>146.51</td>
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<td>16.25</td>
<td>2.05E-02</td>
<td>17.48</td>
<td>2.21E-02</td>
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<tr>
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<td>6.26</td>
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<td>6.26</td>
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<td>5.03</td>
<td>3.34E-03</td>
</tr>
<tr>
<td>Andradite</td>
<td>Ca$_3$Fe$_2$Si$_3$O$_12$</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Xonotlite</td>
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<td>0.57</td>
<td>2.02E-04</td>
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<td>3.51E-05</td>
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<tr>
<td>Chlorite</td>
<td>Mg$_5$Al$_2$Si$_2$O$_10$(OH)$_8$</td>
<td>568.19</td>
<td>5.61</td>
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<td>Brucite</td>
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<tr>
<td>Magnetite</td>
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<td>0.01</td>
<td>0.06</td>
<td>4.32E-05</td>
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<tr>
<td>Grossular</td>
<td>Ca$_3$Al$_2$Si$_3$O$_12$</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
<td></td>
</tr>
<tr>
<td>Diopside</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>9.28</td>
<td>7.41E-03</td>
<td>10.94</td>
<td>8.74E-03</td>
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</tbody>
</table>

**Total** 18.51 99.98 17.68 98.42

*Exact compositions derived from EMP based WDS analyses were used in the regression algorithm

**Resulting mineral proportions for a reaction turnover of 77.49% (300 °C) and 52.23% (400 °C) by weight – model at 50 MPa

1Sum of serpentine and chlorite equals the fraction derived by TG

2Molar weight from the 300 °C run was used to calculate the mole equivalent for the model run

3Brucite fraction equals the amount derived by TG plus 1 wt.% dissolved fraction

4Magnetite determined via AGFM

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Gold reaction cell

Sections

Experiment at 300 °C
Srp/Chl, Adr, ±Brc ±Ol [α - β]
Chl/Srp, Xon ±Ol ±Mag [γ - δ]

Experiment at 400 °C
Di, Adr ±Chl ±Xon [α* - β*] → Fig. 5D
Chl/Srp, Grs ±Xon [γ*]
Srp, Ol*, Brc, Mag ±Chl
Srp/Chl, Ol, Mag
Chl/Srp, Ol ±Mag
Chl/Srp, Xon, Ol
Chl, An, Xon, Ol ±Srp

Di, Chl/Srp, Di ±Adr
Chl/Srp, Di, Ol*, Adr
Chl/Srp, Xon, Ol*, Grs
Chl/Srp, An, Xon, Ol*, Grs

Figure 1

Post experimental look into the Au cell (400 °C)
Figure 2

(A) 300 °C 40 MPa

(B) 400 °C 40 MPa
Figure 3

Top

Bottom

Diffusive fluid mixing

- titanium cap
- gold cell
- bulk fluid
- solids
- well mixed
- isolated
- max. isolation
Figure 4

+ $\text{H}_2\text{O}$
+ $\text{CaO}$

- Chlorite 400 °C experiment
- Serpentine 300 °C experiment
- Chlorite 300 °C experiment

- $\text{SiO}_2$
- $\text{MgO}$ + $\text{FeO}$
- $\text{Al}_2\text{O}_3$

- Forsterite
- Chrysotile
- Diopside
- Tremolite
- Saponite
- Amesite
- Clinochlor