Water transfer to the deep mantle through hydrous, Al-rich silicates in subduction zones

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INTRODUCTION

Recycling of water to the deep layers of Earth along subduction zones impacts a number of key plate-tectonic processes such as arc volcanism and intermediate-depth earthquakes that are triggered by dehydration reactions (Schmidt and Poli, 1998; Hacker et al., 2003). Hydrated ultramafic rocks are considered to be the key lithology for this deep-water cycle (Ulmer and Trommsdorff, 1995; Rüpke et al., 2004). Previous investigations have shown that antigorite and chlorite are the main hydrous phases in serpentinites up to a pressure (P) of 5 GPa (Fumagalli and Poli, 2005; Till et al., 2012), corresponding to a depth of ~150 km. Experiments in simplified chemical systems, MgO-SiO2-H2O (MSH) or MgO-Al2O3-SiO2-H2O (MASH), provided evidence that there are many dense hydrous Mg-silicates that are stable at P > 6 GPa for very low geothermal gradients (<3.3 °C/km) that would be able to transport H2O to the lowermost upper mantle (Pawley and Wood, 1995a). However, the narrow region between 5 and 6 GPa (150–180 km depth) has not been well explored. The phase relations between chlorite and antigorite, the dense hydrous Mg-silicates, and the anhydrous minerals garnet, olivine, pyroxenes, and spinel in peridotite will determined how much H2O can reach the deep mantle through bypassing the “choke point” of Kawamoto et al. (1996). This point describes the lowest-temperature occurrence of an anhydrous garnet peridotite. Whether H2O is released or retained in the subducted slab thus depends on the position of this choke point in relation to the thermal structure of the subducted slab (Iwamori, 2004; Rüpke et al., 2004; Fumagalli and Poli, 2005).

H2O budgets at present are calculated mainly for typical peridotite compositions (Iwamori, 2004; Rüpke et al., 2004; van Keken et al., 2011; Magni et al., 2014). However, metasomatic chlorite schists can form at the slab-mantle interface by interaction of mafic and pelitic rocks with the mantle wedge (Spandler et al., 2008; Marschall and Schumacher, 2012). The phase relations of such rock types and their capability to transport H2O to the deep mantle are unclear and are the main focus of this study. The new experiments show that Al-rich hydrous silicates form at the expense of chlorite in the pressure range of 5–6 GPa and thus will influence garnet-forming reactions and impact the position of the choke point. The interplay between modeled slab temperatures and our newly determined experimental phase diagrams for different compositions provides a basis to assess how much H2O returns via arc magmatism in geologically short time scales and how much H2O is retained in the slab and subducted to the convecting mantle to be locked away for hundreds of million years.

APPROACH

Very few experimental results exist for the crucial conditions around the choke point in complex peridotite compositions (Fumagalli and Poli, 2005). In this study, we determined the phase relations and key reactions for a model hydrated peridotite composition enriched in chlorite as well as a metasomatic chlorite schist composition. The starting material consisted of mixes of natural chlorite with different amounts of serpentine and tremolite (see the Supplemental Material), ensuring H2O saturation at run conditions. In total, 29 experiments with run durations between 68 and 168 h were performed in a ultrahigh-pressure piston cylinder press (Hermann et al., 2016) at conditions between 620 °C and 800 °C and 5–6.2 GPa (see the Supplemental Material; the run products are listed in Table S1). Figure 1 displays the investigated pressure-temperature (P-T) range with the experimental conditions for a habitable planet. The pressure-temperature stability of hydrous phases in conjunction with slab geotherms determines how much H2O leaves the slab or is transported to the deep mantle. Chlorite-rich, metasomatic rocks that form at the slab-mantle interface at 50–100 km depth represent an unaccounted, H2O-rich reservoir in subduction processes. Through a series of high-pressure experiments, we investigated the fate of such chlorite-rich rocks at the most critical conditions for subduction water recycling (5–6.2 GPa, 620–800 °C) using two different natural ultramafic compositions. Up to 5.7 GPa, 740 °C, chlorite breaks down to an anhydrous peridotite assemblage, and H2O is released. However, at higher pressures and lower temperatures, a hydrous Al-rich silicate (11.5 Å phase) is an important carrier to enable water transfer to the deep mantle for cold subduction zones. Based on the new phase diagrams, it is suggested that the deep-water cycle might not be in secular equilibrium.
PHASE RELATIONS IN CHLORITE-PERIDOTITE

In the hydrous chlorite-peridotite system, three main dehydration reactions occur at 5 GPa (Fig. 1A). At 620 °C, antigorite breaks down, and minor new chlorite is formed along the reaction

\[
\text{antigorite} \rightarrow \text{olivine} + \text{orthopyroxene} + \text{chlorite} + \text{fluid.} \tag{1}
\]

Garnet first appears in the resulting lherzolites at ~660 °C during the reaction

\[
\text{chlorite} + \text{clinopyroxene} \rightarrow \text{garnet} + \text{olivine} + \text{fluid,} \tag{2}
\]

followed by the consumption of chlorite in harzburgite at 700 °C, by

\[
\text{chlorite} + \text{orthopyroxene} \rightarrow \text{garnet} + \text{olivine} + \text{fluid.} \tag{3}
\]

The presence of minor amounts of Fe (bulk Mg# = 0.94) and Cr transforms univariant lines into divariant or trivariant fields. For example, Fe is preferentially incorporated into garnet, leading to its appearance at ~20–30 °C lower temperatures than indicated in the model reactions. The reaction sequence is in agreement with previous studies at lower pressures (Fumagalli and Poli, 2005). However, previous work suggested a strong back-bend of the reaction in Equation 3, so that chlorite stability crosses the antigorite stability field at 5 GPa, 630 °C (Fig. 1A). This was not observed in our study. Instead, a change in slope is related to the appearance of the Al-rich, hydrous phase Mg-sursassite (MgS; Fig. 2A) along the reaction

\[
\text{chlorite} + \text{orthopyroxene} \rightarrow \text{Mg-sursassite} + \text{olivine} + \text{fluid.} \tag{4}
\]

Mg-sursassite has been observed in the MASH system at similar conditions (Artioli et al., 1999; Bromiley and Pawley, 2002), but the reaction topologies in natural complex systems have not been determined so far. It then disappears above 700 °C during the reaction

\[
\text{Mg-sursassite} + \text{olivine} + \text{orthopyroxene} \rightarrow \text{garnet} + \text{fluid,} \tag{5}
\]

leading to a nominally anhydrous garnet peridotite. The position of this reaction is in excellent agreement with previous reversal experiments in the MASH system (Bromiley and Pawley, 2002).

PHASE RELATIONS IN CHLORITE-RICH METASOMATIC ULTRAMAFIC ROCKS

In ultramafic rocks dominated by chlorite (Fig. 1B), pyroxenes are fully exhausted before chlorite during the reactions in Equations 2 and 3. The terminal chlorite breakdown in chlorite-rich rocks therefore occurs at higher temperatures of 770 °C, 5 GPa:

\[
\text{chlorite} \rightarrow \text{garnet} + \text{olivine} + \text{spinel} + \text{fluid,} \tag{6}
\]

producing an anhydrous, garnet-rich assemblage. The terminal chlorite breakdown reaction changes slope at 5.7 GPa with the appearance of another hydrous Al-silicate—the 11.5 Å phase (Cai et al., 2015; Gemmi et al., 2016). This phase forms needles and laths in the run products (Fig. 2B) and has been characterized by Raman spectroscopy (Fig. S1) and confirmed by X-ray diffraction. The 11.5 Å phase forms through the reaction

\[
\text{chlorite} \rightarrow 11.5 \text{ Å} + \text{garnet} + \text{olivine} + \text{fluid.} \tag{7}
\]
At 6 GPa, the 11.5 Å phase is stable up to 760 °C, and it was found in another study up to 12 GPa, 1000 °C (Cai et al., 2015). It contains 12 wt% of H₂O and is thus an important carrier of water in Al-rich, ultramafic compositions (Gemmi et al., 2016). The dehydration reaction

\[
garnet + 11.5\text{Å} \rightarrow \text{spinel} + \text{olivine} + \text{fluid,} \tag{8}\]

has a positive slope. At 6.2 GPa, 680 °C, the chlorite stability has a dramatic back-bend related to a change in the chlorite breakdown reaction to

\[
\text{chlorite} \rightarrow \text{Mg-Sursassite} + 11.5\text{Å} + \text{olivine} + \text{fluid}. \tag{9}\]

The same assemblage has been previously observed as a breakdown product of Cr-rich chlorite in the CrMASH system at 6 GPa, 650 °C (Fumagalli et al., 2014), in excellent agreement with our study. The intersection of the reaction in Equation 9 with the reaction in Equation 4 leads to an invariant point that is also present in the chlorite-peridotite phase HAPY (hydrous Al-bearing pyroxene; Gemmi et al., 2011) were not observed in our experiments. For peridotite compositions, the choke point (green) is defined by the intersection of Mg-sursassite and phase A [Mg₂Si₂O₆(OH)₄] at ~6.8 GPa, 650 °C (geothermal gradient of 3.1 °C/km). The extended chlorite stability determined in our experiments in conjunction with the newly defined appearance of the 11.5 Å phase constrain a choke point (red) at a significantly higher geothermal gradient of 4.2 °C/km for metasomatic chlorite-rich rocks. We calculated H₂O contents for mineral assemblages for a harzburgite composition and a chlorite-rich metasomatic rock type, and these serve as a basis for H₂O recycling along different geotherms (Fig. 3). The efficiency to transport H₂O beyond 200 km depth depends on the position of the slab geotherms with respect to the extent of the anhydrous nose. The thermal models of Syraceuse et al. (2010) return the highest top slab temperatures, as exemplified by the Marianas and Tonga (Pacific Ocean) top slab subduction zone geotherms. Rüpeke et al. (2004) and Magni et al. (2014) both used cooler slab geotherms in their modeling of the deep-water cycle (Fig. 3).

For all thermal models, subducted serpentinites at the top of the slab pass through the anhydrous nose. Such serpentinites derive from exposed mantle either in slow-spreading ridges or at continental margins, or they were formed at the slab interface. H₂O stored in hydrous phases at the initiation of subduction is completely released through reactions in Equations 1–3 at forearc to subarc depths. Thus, H₂O release from ultramafic rocks situated at the surface of the slab is likely returned via forearc hydrothermal activity or arc magmatism toward the hydrosphere over short geological time scales. For such a case, H₂O transport to the deep mantle is limited to the storage capacity of nominally anhydrous minerals of ~100 ppm H₂O during breakdown reactions of hydrous phases (Padrón-Navarta and Hermann, 2017). This value is similar to that observed in the mantle source of mid-oceanic ridge basalt (MORB) (Hirschmann, 2006), suggesting that the H₂O in MORB might derive from H₂O replenishment of the mantle by ancient hot subduction.

Chlorite-rich metasomatic rocks form 10–100-m-thick layers at the slab-mantle interface (Spandler et al., 2008; Marschall and Schumacher, 2012). The coldest geotherm for Tonga (Syracuse et al., 2010) passes right through the choke point for this rock type. Using the thermal models of Rüpeke et al. (2004), oceanic lithosphere that is older than 80 Ma will bypass the anhydrous nose (Fig. 3). This highlights the sensitivity of the interplay between the choice of thermal models and H₂O transport to the deep mantle. For the case of Tonga, with convergence rates of 17 cm/yr, 100 m of chlorite schist would transport 5.1 Gg of H₂O per kilometer of slab length per year, whereas 70 m of sediments (Plank and Langmuir, 1998) with phengite as the H₂O carrier (bulk rock with 1 wt% H₂O) would only transport 0.35 Gg H₂O/km slab length/yr. An assumed 1 km of altered oceanic crust transformed into lawsonite-eclogites with 0.1 wt% H₂O (Schmidt and Poli, 1998) would transport 0.6 Gg H₂O/km slab length/yr, which will completely dehydrate with ongoing subduction. At the transition of chlorite to the 11.5 Å phase, a large amount of ~7.5 wt% H₂O is released at ~180 km depth. However, 3.6 wt% H₂O is retained in the 11.5 Å phase, correspond-
Chlorite-rich rocks that formed at the contact of the oceanic crust and the subducting slab are common in the top few kilometers of the slab (Grenville, 2001; The 10 Å phase: A high-pressure expandable sheet silicate stable during subduction of oceanic crust). The bending of the oceanic lithosphere away from the slab has led to the formation of serpentinites in the subduction zone, which corresponds to the slab-Moho interface. Serpentinites are characterized by the presence of serpentine minerals, such as lizardite and antigorite, which form as a result of the hydration of the dunite layer of the subducting oceanic crust.

The hydration of the dunite layer leads to the formation of serpentine minerals, which are more water-rich than the original dunite. This process can lead to the formation of serpentinites, which can be transported into the mantle and subducted back to the Earth's surface. The hydration process is sensitive to four key variables: ultramafic rock composition (influencing the position of the anhydrous nose), distribution of these rocks in the slab, degree of hydration with depth, and slab geometry. These variables can change in response to changes in the tectonic setting, and this can lead to changes in the distribution of serpentinites in the subduction zone.

CONCLUSIONS

Our study shows that deep-water recycling is sensitive to four key variables: ultramafic rock composition (influencing the position of the anhydrous nose), distribution of these rocks in the slab, degree of hydration with depth, and slab geometry. Indeed, changes in these variables need to be considered for the entire evolution of Earth to assess whether the deep-water cycle is in secular equilibrium. The initiation of cold subduction from ca. 620 Ma onward (Brown, 2006) coupled with H2O transport in metasomatic chlorite-rich rocks likely have resulted in an increased amount of water reaching the deep mantle. This process might have caused a lowering of sea level by hundreds of meters (Rüppke et al., 2004; Karlsen et al., 2019) in the past 500 m.y., and opens up the possibility that the deep-water cycle today is not in secular equilibrium.

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