

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

Jörg Hermann^{1,2*} and Shayne Lakey²

¹Institute of Geological Sciences, University of Bern, Baltzerstrasse 3, 3012 Bern, Switzerland

²Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia

ABSTRACT

Constraining deep-water recycling along subduction zones is a first-order problem to understand how Earth has maintained a hydrosphere over billions of years that created 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.

INTRODUCTION

Recycling of water to the deep layers of Earth along subduction zones impacts a number of key plate-tectonics 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 determine 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 Material¹), 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 parageneses. The arrangement of reactions is based on Schreinemaker’s analysis (Zen, 1966), with theoretical phase stoichiometries, abbreviations, and the according chemography presented in the Supplemental Material. For simplification, the reactions are shown as univariant lines in the (C)MASH system and are placed where the hydrous phases disappear rather than where the product first forms. Average phase compositions from the run products are given in Table S2.

*E-mail: joerg.hermann@geo.unibe.ch

¹Supplemental Material. Experimental and analytical methods, starting material, and characterization of experimental run products. Please visit <https://doi.org/10.1130/G48658.1> to access the supplemental material, and contact editing@geosociety.org with any questions.

CITATION: Hermann, J., and Lakey, S., 2021, Water transfer to the deep mantle through hydrous, Al-rich silicates in subduction zones: *Geology*, v. 49, p. 911–915, <https://doi.org/10.1130/G48658.1>

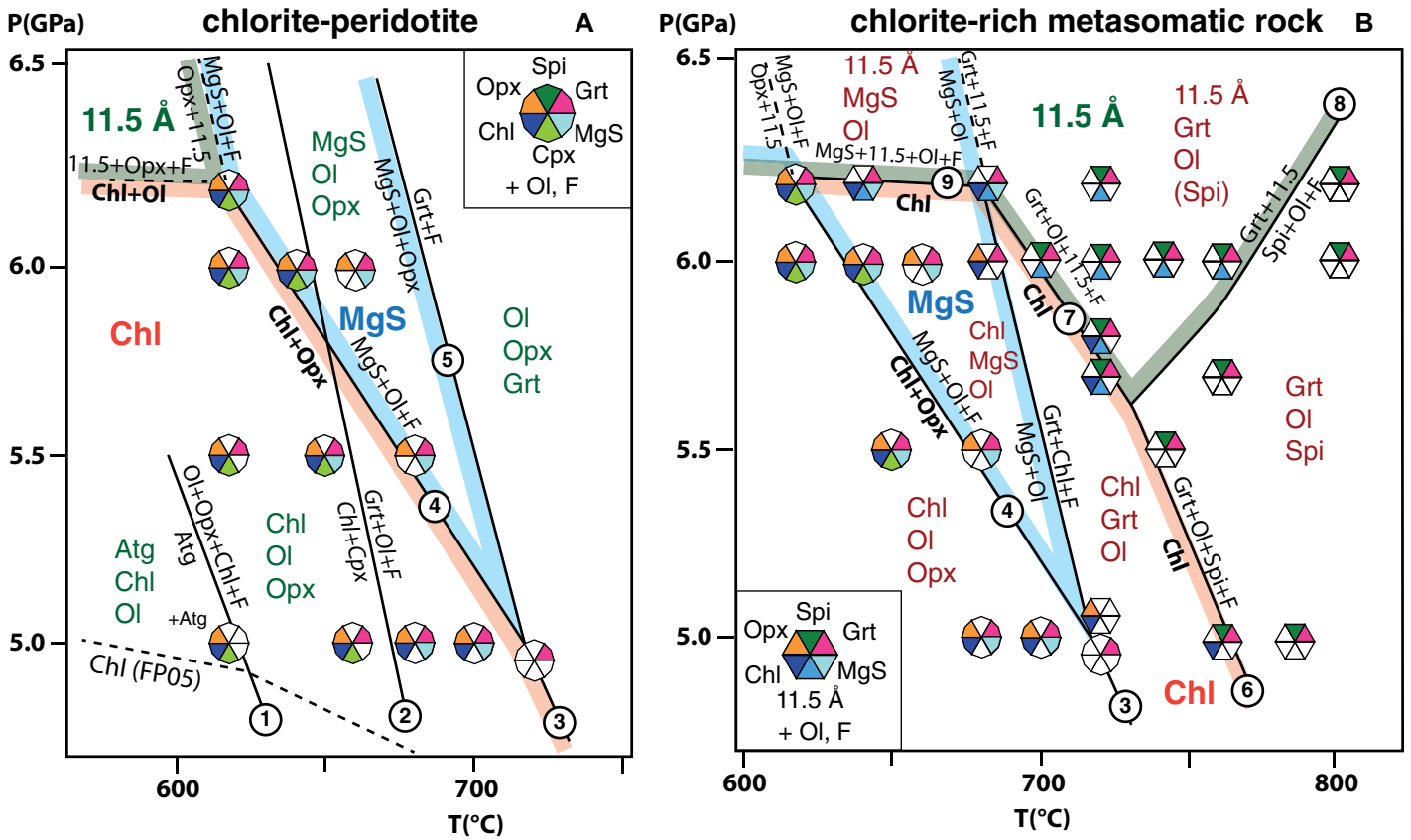
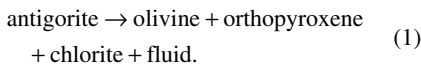


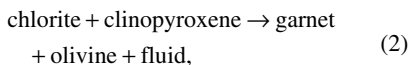
Figure 1. Experimental results: stability fields of parageneses for (A) chlorite-peridotite and (B) chlorite-rich metasomatic rock. Main reactions were deduced from phase analyses using Schreinemaker's rules (Zen, 1966), and numbers refer to reactions explained in the text. The stability fields of the hydrous Al-rich silicates chlorite (Chl), Mg-sursassite (MgS), and 11.5 Å phase are shown. FP05—chlorite breakdown after Fumagalli and Poli (2005). Atg—antigorite; Ol—olivine; Opx—orthopyroxene; Cpx—clinopyroxene; Grt—garnet; Spi—spinel; F—fluid.

PHASE RELATIONS IN CHLORITE-PERIDOTITE

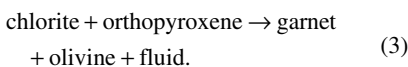
In the hydrous chlorite-peridotite system, three main dehydration reactions occur at 5 GPa (Fig. 1A). At 620 °C, antigorite breaks down, and minor new chlorite is formed along the reaction



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

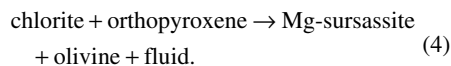


followed by the consumption of chlorite in zbruggite at 700 °C, by

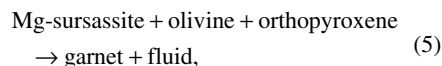


The presence of minor amounts of Fe (bulk Mg# = 0.94) and Cr transforms univariant lines into divariant or trivariant fields. For example, Fe is preferentially incorporated into garnet, leading to its appearance at ~20–30 °C lower

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



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

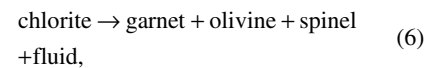


leading to a nominally anhydrous garnet peridotite. The position of this reaction is in excellent agreement with previous reversal experiments

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:



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



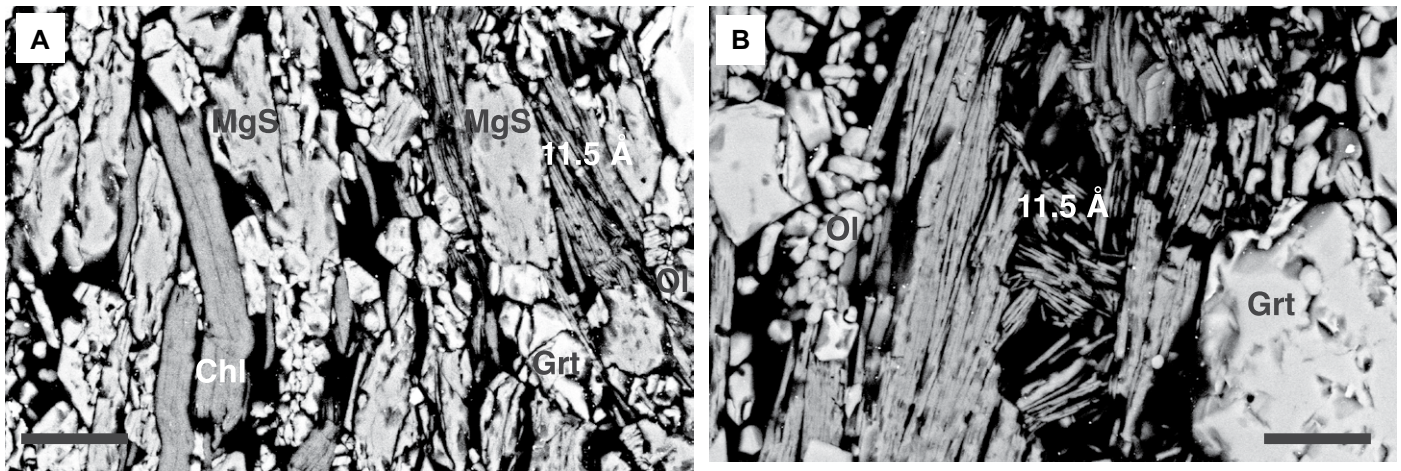
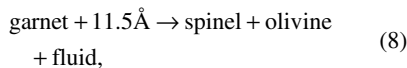
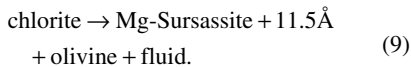


Figure 2. Textural relationships of run products. (A) Chlorite (Chl), Mg-sursassite (MgS), and the 11.5 Å phase are in textural equilibrium in run 341 at 6.2 GPa, 640 °C, documenting H₂O transfer between hydrous Al-rich phases. (B) The 11.5 Å phase coexists with garnet (Grt) and olivine (Ol) in run 335 at 6.0 GPa, 700 °C. Scale bar is 10 μm.

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



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



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 (Fig. 1A). Phase relations dictate that, at lower temperatures than this invariant point, chlorite reacts with olivine to produce the 11.5 Å phase and orthopyroxene. The 10 Å phase (Pawley and Wood, 1995b; Fumagalli et al., 2001) and phase HAPY (hydrous Al-bearing pyroxene; Gemmi et al., 2011) were not observed in our experiments. The terminal chlorite stability is ~70–100 °C higher at 5 GPa than what has been reported before (Fig. 1A; Pawley, 2003; Fumagalli and Poli, 2005; Till et al., 2012). Moreover, the chlorite stability extends to ~1 GP higher pressures than those reported in previous studies, with important consequences for H₂O recycling.

IMPLICATIONS FOR H₂O RECYCLING IN SUBDUCTION ZONES

The new phase relations and previous experimental results allow construction of a phase diagram for hydrous ultramafic rocks in complex systems (Fig. 3). The hydrous Al-rich silicates are stable to higher temperatures than the most important hydrous Mg-silicate antigorite, which shifts the position of the anhydrous nose (shown with the red fields). For peridotite compositions, the choke point (green) is defined by the intersection of Mg-sursassite and phase A [Mg₇Si₂O₈(OH)₆] 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 Syracuse et al. (2010) return the highest top slab temperatures, as exemplified by the Marianas and Tonga (Pacific Ocean) top slab subduction zone geotherms. Rüpke 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 Rüpke 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-

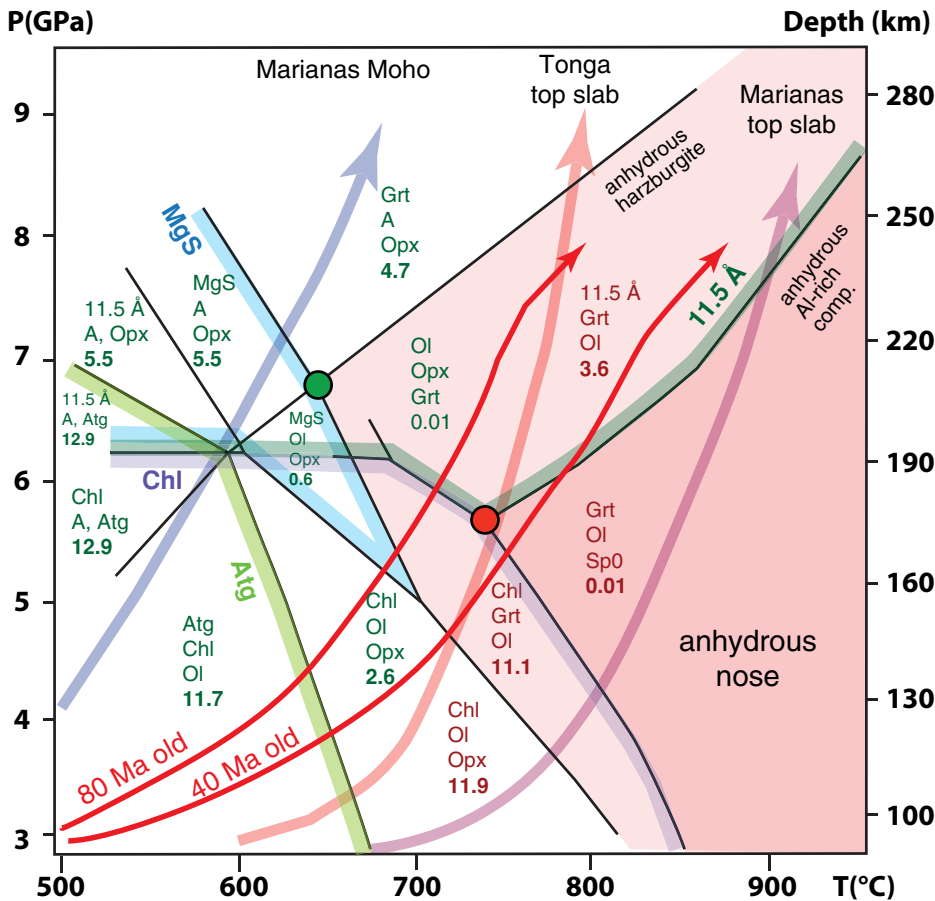


Figure 3. Phase diagram for hydrous ultramafic rocks in complex systems, based on this study and other experiments (Luth, 1995; Ulmer and Trommsdorff, 1999; Bromiley and Pawley, 2002; Fumagalli et al., 2014; Cai et al., 2015). The extent of the anhydrous nose for peridotite and for metasomatic rocks is shown with pink fields, and corresponding choke points are shown with a green circle (peridotite) and red circle (metasomatic rock). Calculated H_2O contents from assemblages with serpentinite starting composition (85% antigorite, 5% chlorite, 10% olivine) are shown in green, and those for chlorite-rich metasomatic composition (90% chlorite, 10% antigorite) are shown in red. Top slab geotherms for the Tonga and Marianas subduction zones (Pacific Ocean) are shown with orange and purple arrows, and geotherm at the interface between subducted oceanic crust and lithospheric mantle for Marianas is shown with the blue arrow (Syracuse et al., 2010). Red arrows refer to thermal model of Rüpke et al. (2004). Abbreviations are as in the Figure 1 caption. A—Phase A [$Mg_3Si_2O_8(OH)_6$].

ing to 1.65 Gg H_2O/km slab length/yr. This illustrates that chlorite-rich metasomatic rocks are the most effective rock type at the slab-mantle interface to transport H_2O to the deeper mantle in cold subduction zones.

Temperatures in the interior of the subducted slab are much colder than at the slab surface (Syracuse et al., 2010). Figure 3 displays the geotherm at 7 km slab depth for the Marianas subduction zone, which corresponds to the slab Moho in a fast-spreading environment. Serpentinized mantle rocks intruded by gabbroic dikes and bodies are common in the top 4 km of crust in slow-spreading ridges and at continental margins (Dilek and Furnes, 2014). Chlorite-rich rocks that formed at the contact of mafic to ultramafic rocks in such settings most likely bypass the anhydrous nose. So far, there are no quantifications for the volumes of chlorite-rich rocks that form in these environ-

ments, representing an unaccounted reservoir in the deep-water cycle.

The bending of the oceanic lithosphere when it enters the subduction zone can lead to partial serpentinization at 7–10 km depth (Ranero et al., 2003). The comparison between seismic velocities in such mantle rocks away from and near trenches indicates that serpentinization at the bending of plates may vary from <4% up to a maximum of 20% for the top few kilometers of mantle (Grevemeyer et al., 2018). Such serpentinites will undergo one major (antigorite out, ~7 wt% H_2O released) and one minor (MgS out, ~0.8 wt% H_2O released) dehydration reaction. H_2O contents will decrease from ~12 to 4.7 wt% that is incorporated into phase A and transported to the deeper mantle (Rüpke et al., 2004; Karlsen et al., 2019). Considering 2 km of mantle with 10% serpentinization, 5.3 Gg H_2O/km

slab length/yr are transported beyond 200 km depths for the Tonga 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 geotherms. 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 H_2O 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 (Rüpke 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.

ACKNOWLEDGMENTS

We thank D. Scott and D. Clark for assistance with the experiments, and the Centre for Advanced Microscopy (Australian National University, Canberra) for help with analyses. Discussions with H. O'Neill and G. Yaxley, and comments by D. Rubatto, F. Piccoli, and T. Pettke helped to improve the paper. We thank A. Pawley and two anonymous reviewers for constructive comments, and C. Clark for editorial handling. This work was financially supported by the Australian Research Council (grant DP14010622) and the Swiss National Science Foundation (grant 200021_169062).

REFERENCES CITED

- Artoli, G., Fumagalli, P., and Poli, S., 1999, The crystal structure of $Mg_3(Mg_2Al_2)Al_8Si_{12}(O,OH)_{56}$ pumpellyite and its relevance in ultramafic systems at high pressure: *The American Mineralogist*, v. 84, p. 1906–1914, <https://doi.org/10.2138/am-1999-11-1218>.
- Bromiley, G.D., and Pawley, A.R., 2002, The high-pressure stability of Mg-sursassite in a model hydrous peridotite: A possible mechanism for the deep subduction of significant volumes of H_2O : *Contributions to Mineralogy and Petrology*, v. 142, p. 714–723, <https://doi.org/10.1007/s00410-001-0318-5>.
- Brown, M., 2006, Duality of thermal regimes is the distinctive characteristic of plate tectonics since the Neoproterozoic: *Geology*, v. 34, p. 961–964, <https://doi.org/10.1130/G22853A.1>.
- Cai, N., Inoue, T., Fujino, K., Ohfuji, H., and Yurimoto, H., 2015, A possible new Al-bearing hydrous Mg-silicate (23 Å phase) in the deep upper mantle: *The American Mineralogist*, v. 100, p. 2330–2335, <https://doi.org/10.2138/am-2015-5148>.
- Dilek, Y., and Furnes, H., 2014, Ophiolites and their origins: *Elements*, v. 10, p. 93–100, <https://doi.org/10.2113/gselements.10.2.93>.
- Fumagalli, P., and Poli, S., 2005, Experimentally determined phase relations in hydrous peridotites to 6.5 GPa and their consequences on the dynamics of subduction zones: *Journal of Petrology*, v. 46, p. 555–578, <https://doi.org/10.1093/ptrology/egh088>.
- Fumagalli, P., Stixrude, L., Poli, S., and Snyder, D., 2001, The 10A phase: A high-pressure expandable sheet silicate stable during subduction of

- hydrated lithosphere: *Earth and Planetary Science Letters*, v. 186, p. 125–141, [https://doi.org/10.1016/S0012-821X\(01\)00238-2](https://doi.org/10.1016/S0012-821X(01)00238-2).
- Fumagalli, P., Poli, S., Fischer, J.K., Merlini, M., and Gemmi, M., 2014, The high-pressure stability of chlorite and other hydrates in subduction mélanges: Experiments in the system $\text{Cr}_2\text{O}_3\text{-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$: *Contributions to Mineralogy and Petrology*, v. 167, p. 979, <https://doi.org/10.1007/s00410-014-0979-5>.
- Gemmi, M., Fischer, J.K., Merlini, M., Poli, S., Fumagalli, P., Mugnaioli, E., and Kolb, U., 2011, A new hydrous Al-bearing pyroxene as a water carrier in subduction zones: *Earth and Planetary Science Letters*, v. 310, p. 422–428, <https://doi.org/10.1016/j.epsl.2011.08.019>.
- Gemmi, M., Merlini, M., Palatinus, L., Fumagalli, P., and Hanfland, M., 2016, Electron diffraction determination of 11.5 Å and HySo structures: Candidate water carriers to the upper mantle: *The American Mineralogist*, v. 101, p. 2645–2654, <https://doi.org/10.2138/am-2016-5722>.
- Grevemeyer, I., Ranero, C.R., and Ivandic, M., 2018, Structure of oceanic crust and serpentinization at subduction trenches: *Geosphere*, v. 14, p. 395–418, <https://doi.org/10.1130/GES01537.1>.
- Hacker, B.R., Peacock, S.M., Abers, G.A., and Holloway, S.D., 2003, Subduction factory 2. Are intermediate-depth earthquakes in subducting slabs linked to metamorphic dehydration reactions?: *Journal of Geophysical Research*, v. 108, 2030, <https://doi.org/10.1029/2001JB001129>.
- Hermann, J., Troitzsch, U., and Scott, D., 2016, Experimental subsolidus phase relations in the system $\text{CaCO}_3\text{-CaMg}(\text{CO}_3)_2$ up to 6.5 GPa and implications for subducted marbles: *Contributions to Mineralogy and Petrology*, v. 171, p. 1–17, <https://doi.org/10.1007/s00410-016-1296-y>.
- Hirschmann, M.M., 2006, Water, melting, and the deep Earth H_2O cycle: *Annual Review of Earth and Planetary Sciences*, v. 34, p. 629–653, <https://doi.org/10.1146/annurev.earth.34.031405.125211>.
- Iwamori, H., 2004, Phase relations of peridotites under H_2O -saturated conditions and ability of subducting plates for transportation of H_2O : *Earth and Planetary Science Letters*, v. 227, p. 57–71, <https://doi.org/10.1016/j.epsl.2004.08.013>.
- Karlsen, K.S., Conrad, C.P., and Magni, V., 2019, Deep water cycling and sea level change since the breakup of Pangea: *Geochemistry Geophysics Geosystems*, v. 20, p. 2919–2935, <https://doi.org/10.1029/2019GC008232>.
- Kawamoto, T., Hervig, R.L., and Holloway, J.R., 1996, Experimental evidence for a hydrous transition zone in the early Earth's mantle: *Earth and Planetary Science Letters*, v. 142, p. 587–592, [https://doi.org/10.1016/0012-821X\(96\)00113-6](https://doi.org/10.1016/0012-821X(96)00113-6).
- Luth, R.W., 1995, Is phase A relevant to the Earth's mantle?: *Geochimica et Cosmochimica Acta*, v. 59, p. 679–682, [https://doi.org/10.1016/0016-7037\(95\)00319-U](https://doi.org/10.1016/0016-7037(95)00319-U).
- Magni, V., Bouilhol, P., and van Hunen, J., 2014, Deep water recycling through time: *Geochemistry Geophysics Geosystems*, v. 15, p. 4203–4216, <https://doi.org/10.1002/2014GC005525>.
- Marschall, H.R., and Schumacher, J.C., 2012, Arc magmas sourced from mélange diapirs in subduction zones: *Nature Geoscience*, v. 5, p. 862–867, <https://doi.org/10.1038/ngeo1634>.
- Padrón-Navarta, J.A., and Hermann, J., 2017, A subsolidus olivine water solubility equation for the Earth's upper mantle: *Journal of Geophysical Research: Solid Earth*, v. 122, p. 9862–9880, <https://doi.org/10.1002/2017JB014510>.
- Pawley, A.R., 2003, Chlorite stability in mantle peridotite: The reaction $\text{clinocllore} + \text{enstatite} = \text{forsterite} + \text{pyrope} + \text{H}_2\text{O}$: *Contributions to Mineralogy and Petrology*, v. 144, p. 449–456, <https://doi.org/10.1007/s00410-002-0409-y>.
- Pawley, A.R., and Wood, B.J., 1995a, The low pressure stability of phase A $\text{Mg}_7\text{Si}_2\text{O}_8(\text{OH})_6$: *Contributions to Mineralogy and Petrology*, v. 124, p. 90–97, <https://doi.org/10.1007/s004100050176>.
- Pawley, A.R., and Wood, B.J., 1995b, The high-pressure stability of talc and 10 Å phase: Potential storage sites for H_2O in subduction zones: *The American Mineralogist*, v. 80, p. 998–1003, <https://doi.org/10.2138/am-1995-9-1015>.
- Plank, T., and Langmuir, C.H., 1998, The chemical composition of subducting sediment and its consequences for the crust and mantle: *Chemical Geology*, v. 145, p. 325–394, [https://doi.org/10.1016/S0009-2541\(97\)00150-2](https://doi.org/10.1016/S0009-2541(97)00150-2).
- Ranero, C.R., Phipps Morgan, J., McIntosh, K., and Relchert, C., 2003, Bending-related faulting and mantle serpentinization at the Middle America Trench: *Nature*, v. 425, p. 367–373, <https://doi.org/10.1038/nature01961>.
- Rüpke, L., Morgan, J.P., Hort, M., and Connolly, J.A.D., 2004, Serpentine and the subduction zone water cycle: *Earth and Planetary Science Letters*, v. 223, p. 17–34, <https://doi.org/10.1016/j.epsl.2004.04.018>.
- Schmidt, M.W., and Poli, S., 1998, Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation: *Earth and Planetary Science Letters*, v. 163, p. 361–379, [https://doi.org/10.1016/S0012-821X\(98\)00142-3](https://doi.org/10.1016/S0012-821X(98)00142-3).
- Spandler, C.J., Hermann, J., Faure, K., Mavrogenes, J.A., and Arculus, R.J., 2008, The importance of talc and chlorite “hybrid” rocks for volatile recycling through subduction zones: Evidence from the high-pressure subduction mélange of New Caledonia: *Contributions to Mineralogy and Petrology*, v. 155, p. 181–198, <https://doi.org/10.1007/s00410-007-0236-2>.
- Syracuse, E.M., van Keken, P.E., and Abers, G.A., 2010, The global range of subduction zone thermal models: *Physics of the Earth and Planetary Interiors*, v. 183, p. 73–90, <https://doi.org/10.1016/j.pepi.2010.02.004>.
- Till, C.B., Grove, T.L., and Withers, A.C., 2012, The beginnings of hydrous mantle wedge melting: *Contributions to Mineralogy and Petrology*, v. 163, p. 669–688, <https://doi.org/10.1007/s00410-011-0692-6>.
- Ulmer, P., and Trommsdorff, V., 1995, Serpentine stability to mantle depths and subduction-related magmatism: *Science*, v. 268, p. 858–861, <https://doi.org/10.1126/science.268.5212.858>.
- Ulmer, P., and Trommsdorff, V., 1999, Phase relations of hydrous mantle subducting to 300 km, *in* Fei, Y., Bertka, C.M., and Mysen, B.O., eds., *Mantle Petrology: Field Observations and High Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd*: Houston, Texas, The Geochemical Society, p. 259–281.
- van Keken, P.E., Hacker, B.R., Syracuse, E.M., and Abers, G.A., 2011, Subduction factory: 4. Depth-dependent flux of H_2O from subducting slabs worldwide: *Journal of Geophysical Research*, v. 116, B01401, <https://doi.org/10.1029/2010JB007922>.
- Zen, E.-A., 1966, Construction of Pressure-Temperature Diagrams for Multicomponent Systems after the Method of Schreinemakers—A Geometric Approach; *U.S. Geological Survey Bulletin*, v. 1225, 56 p.

Printed in USA