Partitioning of trace elements between wadsleyite and ringwoodite, their solution mechanisms and predicted effects on the mantle transformation
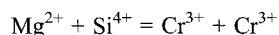
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We have conducted multianvil experiments at 16.5–18.5GPa pressure, at temperatures of 1400 and 1600°C, to determine the partitioning of Ti, Al, Cr and Ni between coexisting wadsleyite [β-$(Mg,Fe)_2SiO_4$] and ringwoodite [γ-$(Mg,Fe)_2SiO_4$]. Five different starting mixtures were used in the experiments, two Fo_{90} compositions and two Fo_{85} compositions with either 1% TiO_2 + 1% Al_2O_3 or 1% Cr_2O_3 + 1% NiO added. The fifth starting mixture was a peridotite composition, MPY-90. The experimental set-up allows up to 6 different samples to be run simultaneously, and to gauge the pressures of the experiments a trace-element free Fo_{90} starting mixture was included in some of the runs. Chemical analyses of the products of runs containing coexisting wadsleyite and ringwoodite were acquired by means of electron microprobe.

All the trace elements tested have weight partition coefficients closer to unity than comparable coefficients for partitioning between olivine and wadsleyite (Gudfinnsson and Wood, submitted). At the $P-T$ conditions of the experiments both Ti and Ni prefer ringwoodite to wadsleyite, approximately in the ratios 4:1 and 3:2, respectively, whereas Al and Cr are preferentially incorporated into wadsleyite, in the ratios 3:1 and 2:1, respectively. No Ni-rich accessory phase was found in the run products, and consequently the observed maximum solubility of NiO in both phases, over 1 wt.%, is limited only by the total abundance of this element in the starting compositions. Runs with olivine starting compositions with Al and Ti added always have accessory garnet and ilmenite among the run products, while Cr-bearing olivine compositions reacted to form small amounts of a Cr-rich phase as a part of the phase assemblage. The observed maximum solubilities of TiO_2, Al_2O_3 and Cr_2O_3 in wadsleyite are in good agreement with earlier determinations (Gudfinnsson and Wood, submitted) of 0.6, 0.4 and 2 wt.%, respectively. The maximum amounts of TiO_2, Al_2O_3 and Cr_2O_3 in ringwoodite were found to be about 1, 0.15 and 0.6 wt.%, respectively. In runs with the peridotite starting mixture garnet was also a major phase, and this greatly affects the abundances of the trace elements in wadsleyite and ringwoodite because Ti, Al and Cr all prefer garnet to wadsleyite and ringwoodite. Runs with the peridotite starting mixture, which contains approximately the expected mantle concentrations of the trace elements, indicate that the partitioning of Cr between garnet and wadsleyite is on the order of 3:1 and correspondingly larger between garnet and ringwoodite. The preference of Ti and Al for garnet is significantly stronger so that the amount of TiO_2 in ringwoodite and wadsleyite is always <0.1 wt.%.

From the stoichometry of the wadsleyite and ringwoodite crystals in the experiments, we are able to infer likely solution mechanisms for the trace elements in these phases. The data give evidence to suggest that the solution mechanisms of Ti, Al, Cr and Ni are the same in ringwoodite and wadsleyite. As expected, Ni appears to enter octahedral sites only, whereas Ti appears to replace Si on tetrahedral sites. The apparent incorporation mechanism of Cr in ringwoodite and wadsleyite is a coupled substitution of the form:

$$Mg^{2+} + Si^{4+} = Cr^{3+} + Cr^{3+}$$

As discussed by Gudfinnsson and Wood (submitted), however, it is most likely that Cr is actually incorporated under spinel stoichiometry and site occupancy and that the formal solution mechanism is:

$$2^{[6]}Mg^{2+} + {}^{[4]}Si^{4+} = {}^{[4]}Mg^{2+} + 2^{[6]}Cr^{3+}$$
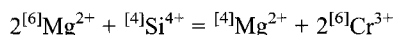
That is, both Cr^{3+} ions replace Mg^{2+} ions on octahedral sites and, in turn, one of the Mg^{2+} replaces the Si^{4+} ion on the tetrahedral site. The solution mechanism for Al appears to be identical to that of Cr.

If the trace elements enter wadsleyite and ringwoodite by these solution mechanisms and are randomly distributed on the cation sites, they

increase the partial molar entropies of the Mg_2SiO_4 and Fe_2SiO_4 components of the two phases, and thus have the potential to affect the width of the wadsleyite-ringwoodite transformation in the mantle. Because of the relatively weak differential partitioning between wadsleyite and ringwoodite and the small concentrations of the trace elements, however, preliminary calculations indicate that the effect of trace elements on the width of the transformation are insignificant.

References

Gudfinnsson, G.H. and Wood, B.J. (1998) *Amer. Mineral.*, submitted.