

# Thermodynamic calculations of high-pressure phase relations in the systems $\text{Mg}_2\text{SiO}_4$ and $\text{MgSiO}_3$

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Since  $\text{Mg}_2\text{SiO}_4$  and  $\text{MgSiO}_3$  are the most abundant endmembers of the Earth's mantle constituent minerals, their high-pressure phase relations have been investigated in detail by high-pressure high-temperature experiments. On the other hand, the stability of phases in the systems has been also studied by thermodynamic approach in conjunction with the high-pressure experiments. In the thermodynamic calculation of phase equilibrium boundary, thermodynamic parameters such as enthalpy, entropy, heat capacity, thermal expansivity and bulk modulus reported by different researchers are used. Some thermodynamic parameters which have not been experimentally obtained are optimized using experimentally determined phase boundaries. From these reasons, the thermodynamic parameters for one material are sometimes not internally consistent. This causes large uncertainties in the calculated phase equilibrium boundaries.

Recently, more accurate enthalpy, heat capacity and entropy data and equations of state for high-pressure polymorphs in  $\text{Mg}_2\text{SiO}_4$  and  $\text{MgSiO}_3$  and their constituent oxides have been experimentally determined. In this study, the internally consistency among the thermodynamic parameters for each material was examined. For example, high-temperature isobaric heat capacity of a high-pressure phase which collapsed by heating at 1 atm was estimated by the following method. Isochoric heat capacity was calculated using a vibrational density of state model which reproduced experimentally determined low-temperature heat capacity. The contribution of anharmonic effect was, then, added to the isochoric heat capacity using the same thermal expansivity and bulk modulus as those applied to the equation of state of the high-pressure phase. In addition, formation enthalpies for all the phases in the systems  $\text{Mg}_2\text{SiO}_4$  and  $\text{MgSiO}_3$  considered in the present calculations were determined from the difference in drop-solution enthalpy between constituent oxides and them. This gives unified relative enthalpy relations among the materials. Finally, using the obtained thermodynamic data set, we calculated high-pressure phase relations in the  $\text{Mg}_2\text{SiO}_4$  and  $\text{MgSiO}_3$  systems up to 26 GPa and 2300 K in dry condition. In both the systems, calculated phase boundaries are consistent with those determined by high-pressure in situ experiments. It is noteworthy that, in the  $\text{Mg}_2\text{SiO}_4$  system, the calculation result predicts the existence of the stability field of  $\text{MgSiO}_3$  akimotoite + MgO between  $\text{Mg}_2\text{SiO}_4$  ringwoodite and  $\text{MgSiO}_3$  bridgmanite + MgO below about 1500 K. In subducted slabs whose temperature would be lower than that of surrounding mantle rocks, ringwoodite might first decompose to akimotoite + ferropericalse with increasing pressure and then transform to bridgmanite + ferropericalse.

Keywords: mantle minerals,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiO}_3$ , thermodynamic stability, high-pressure phase relation