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A high-pressure transformation in chlorite

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Sheet silicates provide an excellent opportunity to study the pressure responses of minerals as they have relatively simple modular layered topologies and varied interlayer structures (hydrogen bonding, Van der Waals, cations).

The high-pressure behaviour of synthetic end-member clinocllore, $Mg_3Al(Si_3Al)O_{10}(OH)_8$, has been studied by synchrotron X-ray powder diffraction and Raman spectroscopy to 27 GPa at 300 K. A non-quenchable, completely reversible transformation occurs between 9 and 10 GPa that is dominated by compression normal to the structural layering (Figure 1). An increase in the compressibility of chlorite and a small but significant shear of the β angle (97.2 to 96.3) are associated with the transformation. Diffraction patterns of the high-pressure chlorite are very similar from 10 to 27 GPa, indicating that it persists stably with little change up to very high pressures. Raman spectra indicate that large increases in the stretching frequencies ($\Delta\nu(OH) = +120-160 \text{ cm}^{-1}$) of hydrogen-bonded OH occur upon transformation to the high-pressure structure. In this presentation an interpretation of the transformation will be given in which arguments for and against a polytypic transformation will be assessed. The effects of high pressure upon hydrogen bonding in sheet minerals will be discussed in the light of these results.

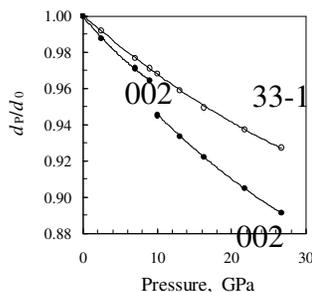


Figure 1. Variation of key d spacings with pressure.

Reference

[1] Dera et al., (2003) *Amer. Mineral.* **88**, 1428-1435.

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Metastable phase transitions and latent heat release

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Exothermic phase transitions, such as olivine to wadsleyite or ringwoodite, that take place under non-equilibrium conditions can release significant amounts of latent heat to their surroundings, causing large localized temperature increases. Such temperature changes taking place within the cold interiors of subducting slabs can significantly affect the amount of metastable olivine or the generation of deep earthquakes. However, these processes are often not well understood.

Calculating Gibbs free energies (G) at high pressures (P) and temperatures (T) requires integrating thermodynamic functions over both P and T from a reference state. Calculating enthalpy (H) and entropy (S) at T is straightforward. However, the pressure calculation typically combines both the H and S terms, as $(\partial H/\partial P)_T = V - \alpha VT$ and $(\partial S/\partial P)_T = -\alpha V$, where α is the volume coefficient of thermal expansion and V is volume. To calculate H by itself at P and T it is therefore necessary to account for the αVT term. This pressure dependence can be quite strong. For example, a theoretical FO_{100} olivine to ringwoodite transition at 1000 K and 15 GPa would have $\Delta H \approx -11.5 \text{ kJ/mol}$, whereas transitions at the same T but at 17.5 GPa would have $\Delta H \approx -19 \text{ kJ/mol}$ and -26 kJ/mol at 20 GPa.

As natural minerals do not typically have end-member compositions, solid solution effects must also be taken into account, through the enthalpies of non-ideal mixing. These effects result in even larger latent heat releases, especially at lower P and T . For example, ΔH for the olivine to ringwoodite transformation for a composition of FO_{90} ranges from -16 kJ/mol to -24 kJ/mol to -31 kJ/mol at 1000 K and 15, 17.5, and 20 GPa, respectively, increases of 39, 26, and 19% relative to FO_{100} . At 800 K, however, ΔH increases by 56, 30, and 23% at the same pressures. Such effects are therefore important in the modeling of cold subducting lithosphere, but often various simplifications are used in the calculation of ΔH . These can range from ignoring the T dependence of ΔH and using a P dependence of ΔP times a constant value of ΔV to proper treatment of the T dependence but a P dependence that neglects the αVT term. The former will systematically overestimate the enthalpy changes, translating into overestimates in ΔT of tens of degrees, whereas the latter results in small T differences, but not of any systematic nature.