

Application of the hydrothermal diamond anvil cell for *in situ* observations of mineral nucleation and growth: a case study of tremolite synthesis

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Determinations of phase boundaries and thermochemical parameters using conventional hydrothermal techniques of analysing the 'quench' products often result in large uncertainties in experimental data. This problem is especially troublesome when the phases involved undergo compositional variation during crystal growth, and possibly during experimental quenching, producing deviations in the mineral compositions from the actual bulk composition of the experimental starting material. Such compositional offsets can be difficult, if not impossible, to distinguish from the presence of immiscibility regions within the compositional field. As a consequence, it is important to focus attention on the process of nucleation and mineral growth to better understand the physiochemical behaviour of mineral species. A point of recent discussion has been the true composition of tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) grown in hydrothermal experiments. It has been virtually impossible to synthesize an on-composition tremolite experimentally (Jenkins, 1991; Pawley *et al.*, 1993). This 'off-composition' behaviour has been explained as a result of a narrow miscibility region in compositional space, while several crystallographic studies have assigned it to numerous 'ordered and disordered' variations in the 'biopyribole' type structure (Maresch *et al.*, 1994).

In this study we conducted experiments in a Hydrothermal Diamond Anvil Cell (HDAC) for *in situ* observations of the process of tremolite nucleation and growth. We used a modified version of the HDAC (Shen *et al.*, 1992), which uses a pair of resistance heaters around the diamond anvils, capable of heating the cell to 1000°C. We used a decarbonated mixture of chemical oxides (MgO , CaCO_3 , SiO_2) in stoichiometric proportions for tremolite as the starting material for the water-saturated synthesis experiments. Additional silica (approx 6 wt.%) was added to ensure silica saturation

in the system. The experiments were set above the talc stability and below the tremolite breakdown curve (Jenkins, 1987) at temperatures of $820^\circ \pm 20^\circ\text{C}$ and pressure ranging between 2–6 kbar. A rhenium gasket was used as the sample chamber in which the oxide mixture and water was added leaving a visible air bubble. The bubble was used to determine the Th (homogenization temperature) of water, which was then used to estimate pressure at a given temperature following the corresponding water isochore. Initial pressure estimates were made using this technique during heating as well as quenching of the experiment. Differences in values between these determinations were primarily due to volume changes of the sample chamber.

The crystallizing phases were monitored *in-situ*, visually as well as using Raman spectroscopy.

The run products were first characterized using Raman spectra referenced to a natural Barrie Tremolite spectrum and later examined in a SEM to record the texture and estimate the synthesis yield. These 'time-series' show rapid crystallization in the form of radiating fibers surrounding the starting oxide mixture. With increasing duration of the experiment, the crystals were observed to grow from a fibrous form to an acicular form. *In-situ* laser Raman spectra obtained for the synthesized material indicated spectral peaks characteristic of amphibole at 400 cm^{-1} and 650 cm^{-1} . For short duration experiments, these peaks appeared as doublets, which closely correspond to the vibrational spectral peaks of a pyroxene (Fig. 1). For successively longer duration experiments, the 'twin-peak' pattern disappeared to produce a spectral pattern similar to the reference tremolite. These observations provide the physical evidence for a compositional (and structural) transformation of tremolite during nucleation and growth. Our results show that the reason for the 'off composition' behaviour of experimentally produced tremolite is the formation

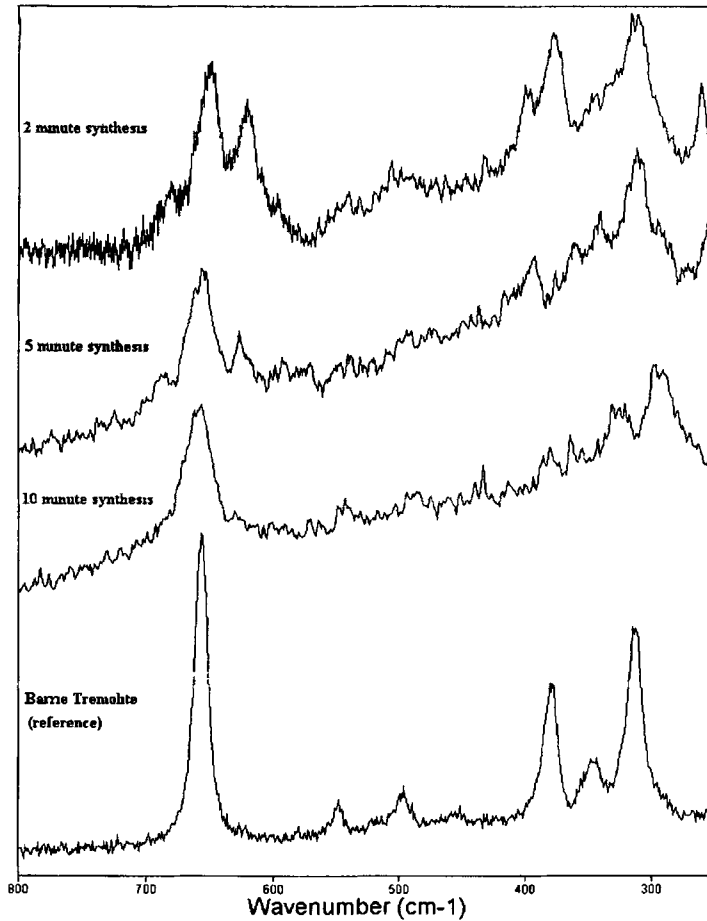


FIG. 1. Raman spectra for tremolite synthesis.

of a precursor amphibole with a pyroxene like structure. Formation of pyroxene as a precursor to tremolite has been suggested based on TEM studies on synthetic quench products (Bozhilov *et al.*, 1993), however in this study we have been able to record and monitor these changes during the nucleation.

References

- Bozhilov, K, Jenkins, D.M. and Veblen, D.R. (1993) AGU Spring meeting abstracts, p 166.
- Jenkins, D.M. (1987) *Amer. Mineral.*, **72**, 707–15.
- Jenkins, D. M., Holland, T.J.B. and Clare, A. K. (1991) *Amer. Mineral.*, **75**, 358–66.
- Maresch, W.V., Czank, M. and Schreyer, W (1994) *Contrib Min. Petrol.*, **118**, 297–313.
- Pawley, A. R., Graham, C.M. and Navrotsky, A. (1993) *Amer. Mineral.*, **78**, 23–35.
- Shen, A. H., Bassett, W. A. and Chou, I-Ming (1992) *High Pressure Research: Applications to earth and Planetary Sciences* (ed. Y Syono and M.H. Manghnani), AGU, Washington D.C.: 61–8.