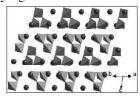
## MS6 – P7: Ca-walstromite and its relevance in understanding ring carbonates at deep mantle conditions

Sula Milani<sup>a</sup>, Davide Comboni<sup>a</sup>, Paolo Lotti<sup>a</sup>, Patrizia Fumagalli<sup>a</sup>, Juliette Maurice<sup>a</sup>, Marco Merlini<sup>a</sup>

<sup>a</sup>Dipartimento di Scienze della Terra 'Ardito Desio', Università degli Studi di Milano, Milano, Italy

CaSiO<sub>3</sub> walstromite is the triclinic ring-silicate polymorph of CaSiO<sub>3</sub> and is stable between 3 and 9 GPa at ambient temperature. In the studies of the Earth's interior, it is considered important for two main reasons. Firstly, it is one of the main Ca-bearing phases in the Earth's mantle transition zone [1]. This has been proved by both laboratory experiments at high pressure (P) and temperature (T) and by natural findings in diamonds [1, 2]. Despite this, its thermoelastic behaviour and its stability at high T are still poorly known. The only existing phase diagram has been determined through multi-anvil experiments, which shows that walstromite transforms to an assemblage of CaSi<sub>2</sub>O<sub>5</sub> + Ca<sub>2</sub>SiO<sub>4</sub> [3]. Secondly, the different CaSiO<sub>3</sub> polymorphs constitute a low-P analogue for the study of ultra-high-P carbonate structures at conditions of the lower mantle. Carbonate minerals are considered as one of the main carbon-host phases in the mantle. They are stable from crust to lower mantle conditions, as demonstrated by direct observation of carbonates inclusions in superdeep diamonds [e.g. 4]. To date, the different possible structures adopted by carbonates during their polymorphic phase transitions are still unclear [5], even if recent important experimental [e.g. 6, 7] and theoretical studies [e.g. 8, 9] have demonstrated the transition in complex tetrahedral ring or chain carbonate structures. However, ring-carbonates are unquenchable at ambient P and T conditions and is extremely difficult to perform extreme high-pressure single crystal diffraction with suitable quality of data for accurate structural details determination. Since CaSiO<sub>3</sub> polymorphs show the same ring-structure and are quenchable, they constitute evaluable analogue to understand the crystal chemistry of HPcarbonate structures. We performed in-situ high-pressure Diamond Anvil Cell experiments on a synthetic sample of the triclinic Ca-walstromite polymorph at the beamline ID15b at ESRF (Grenoble). The sample was synthesized at 6.5 GPa and 1500°C with a multi-anvil module. We report its phase transition towards a monoclinic structure walstromite-II, at 8.5 GPa, studied by single crystal X-ray diffraction. The monoclinic structure is topologically similar to the triclinic one, but the arrangement of 3-fold ring silicate groups determines a denser structure by about 3%. The walstromite-II structure is significantly denser if compared to wollastonite chain silicate structure. Since the Ca-walstromite is a low-P quenchable structural analogue to 3-fold ring high-P carbonates (Fig. 1), from this preliminar high-P experiment we can envisage that also higher P carbonates, like dolomite IV (Fig. 1), might have a phase transition to higher density structures at extremely high P.





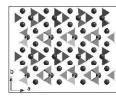


Figure 1. Left - crystal structure of the triclinic polymorph of the  $CaSiO_3$ ; centre - crystal structure of the monoclinic polymorph and right - crystal structure of dolomite IV, where it is evident the presence of corner-sharing tetrahedral  $CO_4$  units in threefold rings as in the Ca-walstromite structure (left and centre).

- [1] D. G. Pearson, F. E. Brenker, F. Nestola, J. McNeill, L. Nasdala, M. T. Hutchison, S. Matveev, K. Mather, G. Silversmit, S. Schmitz, B. Vekemans, L. Vincze *Nature*. **2014**, *507*, 221-224.
- [2] C. Anzolini, R. J. Angel, M. Merlini, M. Derszi, K. Tokár, S. Milani, M. Y. Krebs, F. E. Brenker, F. Nestola, J. W. Harris *Lithos.* 2016, 265, 138-147.
- [3] T. Gasparik, K. Wolf, C. M. Smith Am. Mineral. 1994, 79, 1219-1222.
- [4] A. R. Thomson, S. C. Kohn, G. P. Bulanova, C. B. Smith, D. Arujo, M. J. Walter Contrib. Mineral. Petrol. 2014, 168, 1081.
- [5] R. M. Hazen, R. J. Hemley, A. J. Mangum T. Am. Geophys. Union. 2012, 93, 17-28
- [6] M. Merlini, W. A. Crichton, M. Hanfland, M. Gemmi, H. Müller, I. Kupenko, L. Dubrovinsky *Proc. Natl. Acad. Sci. USA.* **2012**, *109*, 13509-13514.
- [7] V. Cerantola, E. Bykova, I. Kupenko, M. Merlini, L. Ismailova, C. McCammon, M. Bykov, A. I. Chumakov, S. Petitgirard, I. Kantor, V Svitlyk, J. Jacobs, M. Hanfland, M. Mezouar, C. Prescher, R. Rüffer, V. B. Prakapenka, L. Dubrovinsky *Nat. Commun.* **2017**, *8*, 15960.
- [8] A. R. Oganov, R. J. Hemley, R. M. Hazen, A. P. Jones Rev. Mineral. Geochem. 2013, 75, 47-77.
- [9] C. J. Pickard, R. J. Needs J. Phys. Condens. Matter. 2011, 23, 053201.