

## **Titanium- and water-rich secondary olivine in HP metamorphosed serpentinites from the Voltri Massif (Ligurian Alps, Italy)**

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Large amounts of water are stored in the hydrated abyssal peridotites of slabs. During their subduction much of this water will be released at depths down to 240 km due to dehydration of serpentinite [1]. This dehydration is accompanied by the crystallisation of secondary olivine. It is typically very poor in water and fluid-mobile elements and assumed that the water and fluid-mobile elements are released to the overlying mantle wedge and to the Earth's surface through arc volcanism.

To evaluate the behaviour of elements in the mantle during the dehydration of serpentinites, we examined the compositions of secondary olivine grains from the high-pressure Erro-Tobbio unit (Voltri complex, Ligurian Alps) by ionprobe (SIMS), electron backscatter diffraction (EBSD) and electron microprobe. Secondary olivine (Fo86-88) is MnO-rich (0.26–0.43), has high NiO (0.23-0.34) and contains abundant inclusions of magnetite, which attest to its secondary origin. It has variable but very high water contents (up to 0.7 wt.%) which correlate with TiO<sub>2</sub> contents (up to 0.85 wt.%). These values are much higher than typical primary mantle olivine which contains up to 0.06 wt.% TiO<sub>2</sub> and 0.024 wt.% H<sub>2</sub>O [2,3]. Olivine grains with the highest H<sub>2</sub>O and TiO<sub>2</sub> contents show colourless to yellow pleochroism in thin section. They commonly occur as large porphyroblastic grains within the serpentine matrix but locally form rims around low-Ti olivine. Recrystallised fine-grained olivine is always Ti-poor. The sample also contains Ti-clinohumite ((Mg<sub>2</sub>SiO<sub>4</sub>)<sub>n</sub>.xTiO<sub>2</sub>.(1-x)Mg(OH)<sub>2</sub> with n=4 and x=0.34-0.46) and minor Ti-bearing humite (n=3) and chondrodite (n=2). Olivine closely associated with Ti-Chu contains low Ti contents, suggesting that Ti-rich olivine is not the breakdown product of Ti-Chu. Furthermore, detailed examination of olivine by EBSD shows no lamellae of Ti-Chu in Ti-rich olivine.

To further determine the origin of the high Ti and H<sub>2</sub>O contents of olivine, several grains were studied by FTIR absorption spectroscopy. The spectra show peaks of serpentine inclusions, Ti-Chu-like defects (MgTi[ ]O<sub>2</sub>(OH)<sub>2</sub>), Si vacancies (Mg<sub>2</sub>[ ](OH)<sub>4</sub>) plus an unidentified but prominent peak which could not be associated with any known water substitution mechanism in olivine. As serpentine contains little TiO<sub>2</sub>, it cannot contribute to high TiO<sub>2</sub> and H<sub>2</sub>O in olivine as measured by SIMS. The data also suggests that high TiO<sub>2</sub> and H<sub>2</sub>O contents of olivine are not related to submicroscopic Ti-Chu inclusions, as the atomic ratios of H/Ti of olivine (8-17) are higher than those of Ti-Chu grains in the sample (2.8-4.0). They are also much higher than the value of 2 expected for Ti-Chu defects in olivine crystals. Combining FTIR and SIMS data we conclude that TiO<sub>2</sub> and H<sub>2</sub>O are attributed to Ti-Chu-like defects in olivine structure that are more water-rich than co-existing Ti-Chu grains outside olivine. Hence, these defects may not necessarily have the ideal composition MgTi[ ]O<sub>2</sub>(OH)<sub>2</sub>. Irrespective of the incorporation mechanism of water, secondary olivine may serve as an efficient host for H<sub>2</sub>O to be transported beyond the stability field of antigorite in the mantle.

Previous work on the area established that B, Cl and Li are enriched in secondary olivine compared to mantle reservoirs and therefore subduction of oceanic mantle may introduce anomalies of light elements into the upper mantle [4]. We note that compared to serpentine from the same sample, secondary olivine is enriched in Li (2-60 ppm) and B (10-20 ppm) independent of its water and Ti content. In addition, Ti-rich olivine has high F contents (10-130 ppm) although less than serpentine (20-350 ppm). We thus confirm that secondary olivine may play a significant role during redistribution of fluid-mobile elements such as Li, B and F upon the dehydration of serpentinites in subduction zones.

References: [1] Hacker, 2008. G3, doi:10.1029/2007GC001707. [2] Bell et al., 2003. JGR 108, doi:10.1029/2001JB000679. [3] De Hoog et al., 2010. Chem. Geol. 270, 196-215. [4] Scambelluri et al., 2004. EPSL 222, 217-234.