Occurrence and mineral chemistry of the titanian clinohumite from marble of Zorovac creek, Moslavačka Gora, Croatia

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OCCURRENCE AND MINERAL CHEMISTRY OF THE TITANIAN CLINOHUMITE FROM MARBLE OF ZOROVAC CREEK, MOSLAVAČKA GORA, CROATIA

POJAVA I MINERALNA KEMIJA TITANSKOG KLINOHUMITA IZ MRAMORA POTOKA ZOROVAC, MOSLAVAČKA GORA, HRVATSKA

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Clinohumite is a scarce mineral, but is the most abundant mineral of the humite group which is characterized by a general formula of nM2SiO4x*M1-xTix(OH, F)2-2xO2x, where M stays for octahedrally coordinated Mg, Fe, Mn, Ca and Zn cations in declining order of abundance, x < 1 with n=1, 2, 3, 4 for norbergite, chondrodite, humite and clinohumite (JONES *et al.*, 1969). The occurrence of clinohumite is in the nature limited to only five rock types: kimberlites, Archean ultramafics, Alpine peridotites, carbonatites and marbles. However, despite the rarity of its occurrence, clinohumite is essential in understanding hydration and dehydration processes in the petrogenesis of mantle derived ultramafic bodies found in polymetamorphic Archaean terranes (NISHIO *et al.*, 2019), but also in reconstruction of Ti mobility in the frame of crustal metamorphism linked to the clinohumite formation in forsterite marbles (KARMAKAR, 2021). Recently, the occurrence of humite-bearing marbles has been used for the reconstruction of the plate geometries during Neoproterozoic time, known as "humite epoch", characterized by very water-rich, fluorinated fluid activity coeval with the waning stages of Pan-African tectono-thermal event (PRADEEPKUMAR & KRISHNANATH, 2000; FERNANDES & CHAVES, 2014).

Clinohumite occurs in Croatia only in the grey marbles of Zorovac creek in the Moslavačka Gora and was described by BARIĆ (1972), GARAŠIĆ (1993) and BALEN *et al.* (2000). The Moslavačka gora is crystalline complex located in the SW part of the Pannonian Basin, in Croatia. It comprises metamorphic rocks of high-to medium-grade, predominately migmatites and gneisses and of medium grade, mostly metapelites and amphibolites, which intermittently surround granitoids of different kind (PAMIĆ, 1990). The Moslavačka Gora belongs to Sava zone (SCHMID *et al.*, 2008), located between Laurasia and Gondwana, and was recognised as high-heat flow zone causing Cretaceous igneous and metamorphic events (BALEN & PETRINEC, 2011). Zircon dating of two mica-granite gave Cretaceous age and Early Ordovician age for metagranite (the most of the metamorphic complex), whereas the Cretaceous age of low pressure-high temperature (LP/HT) metapelite was obtained by monazite dating (STARIJAŠ *et al.*, 2010).

The studied marbles occur as interlayers up to 50 cm thick in cordierite and diopside-amphibole schists. Mineral assemblages in marbles indicate three metamorphic events of different metamorphic grade. The highest grade mineral assemblage consists of forsterite+spinel+calcite+pargasite. The most important forsterite+clinohumite+calcite±phlogopite±tremolite assemblage occurred during LP/HT metamorphism, as result of replacement of fosterite by clinohumite. The textural relationships in the lowest grade mineral assemblage consisting of clinohumite+spinel+calcite+chlorite+dolomite suggest that chlorite and dolomite grew at the expense of clinohumite, spinel and calcite (Fig. 1). Also replacement of forsterite by talc and serpentine belongs to this retrograde lowest grade metamorphism.

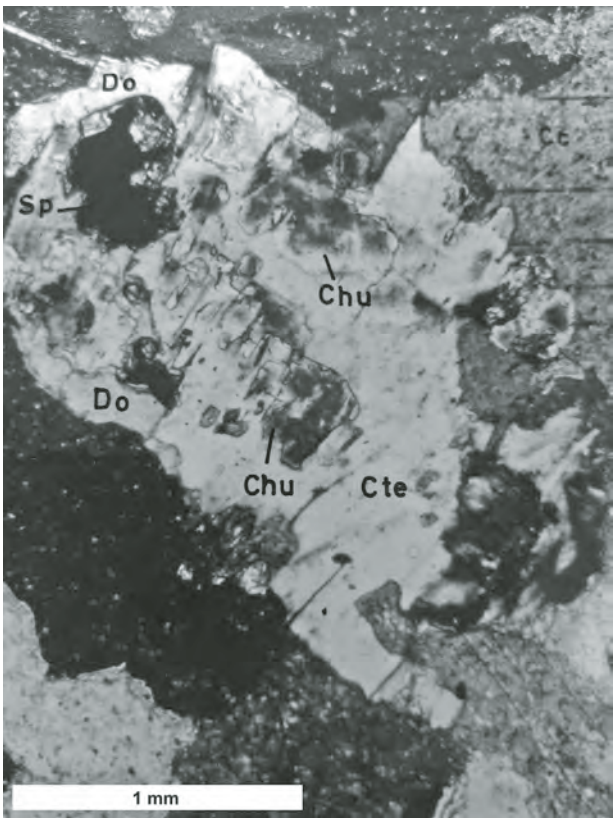

Figure 1. The lowest grade mineral assemblage in marbles of Moslavačka Gora consisting of clinohumite (Chu), spinel (Sp), calcite (Cc), chlorite (Chl) and dolomite (Do)

Microprobe analyses of clinohumite revelead that content of TiO_2 varies between 0.88 (in the mineral parageneses with phlogopite) and 4.04 wt.% (in the mineral parageneses with amphiboles). The fluorine concentration in Ti-clinohumite shows negative correlation with titanium, and ranges from 1.30 to 3.16 wt.%. This is in accordance with expected substitution (Mg,Fe)+2(OH,F) = Ti+2(O). The ratio of F/(F+OH) in clinohumite or $X_{F\text{-}Chu}$ is in the range between 0.32 (in the parageneses with amphiboles) and 0.57 (in the parageneses with phlogopite). Content of H_2O varies from 2.16 to 2.66 wt.%. The concentrations of MgO reach the values from 51.87 to 55.63 wt.% depending on the content of titanium and iron oxides, whereas FeO content ranges from 1.64 to 4.79 wt.%. The SiO_2 content shows slight variation (37.07 and 37.63 wt.%). Other cations in Ti-clinohumite are present in negligible amounts.

Textural relationships and microprobe analyses reveal that Ti-clinohumite grew at the expense of forsterite caused by infiltration of titanian and fluorinated H_2O-rich fluids. Such rare clinohumite marbles with remarkably similar mineral assemblages, textures and P-T-fluid metamorphic conditions and multiphase evolution are widespread in the dispersed Gondwana fragments (PRADEEPKUMAR & KRISHNANATH, 2000). Although the Cretaceous age of LP/HT metapelite was determinated in the Moslavačka Gora, because marbles are more sensitive than other rocks to the changes in fluid composition (FERRY, 1992), the LP/HT metamorphism in marbles is not necessarily comparable to the LP/HT metamorphism in the metapelites.

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