American Mineralogist, Volume 99, pages 2008–2017, 2014

"Silicified" pyrochlore from nepheline syenite (mariupolite) of the Mariupol Massif, SE Ukraine: A new insight into the role of silicon in the pyrochlore structure

MAGDALENA DUMAŃSKA-SŁOWIK[1,*], ADAM PIECZKA[1], GIOACCHINO TEMPESTA[2], ZBIGNIEW OLEJNICZAK[3] AND WIESŁAW HEFLIK[1]

[1]Department of Mineralogy, Petrography, and Geochemistry, Faculty of Geology, Geophysics and Environmental Protection, AGH–University of Science and Technology, 30 Mickiewicza Avenue, Kraków 30-059, Poland
[2]Dipartimento Geomineralogico, Università degli Studi di Bari, Via Orabona, 4, I-70125, Bari, Italy
[3]Department of Magnetic Resonance Spectroscopy, The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, 152 Radzikowski Strasse, 31-342 Kraków, Poland

ABSTRACT

Pyrochlore-supergroup minerals containing relatively high Si concentration are quite common in various geochemical parageneses, e.g., carbonatites, alkaline syenites, pegmatites. However, the role of Si and the mechanism of its incorporation into the structure of these minerals, although widely discussed, have not been explained definitively. Our paper reports the results of comprehensive SEM, EPMA, XRD, TEM, and MAS-NMR studies performed for the first time on a natural pyrochlore, which is the late-magmatic to early hydrothermal accessory component of the nepheline syenite in the alkaline Mariupol massif in Ukraine. It represents partly metamict, patchy-zoned, *A*-cation depleted, REE-, U-, and Th-bearing fluornatropyrochlore, locally exceptionally rich in SiO_2 (up to 13.01 wt%) that underwent both primary and secondary alterations, leading to kenopyrochlore or hydropyrochlore species. The primary alteration was induced by high-temperature, Ca^{2+}- and Si^{4+}-rich, and F^- moderate fluids, which affected only some domains of the pyrochlore crystals and resulted in filling the *A* site vacancies mainly by Ca^{2+}, but also Mn^{2+}, Sr^{2+}, and K^+. The secondary alteration, induced by the exposure of the host rock to ground water driving fluid-mediated coupled dissolution-reprecipitation process, affected the whole pyrochlore crystals (both Si-enriched and Si-free domains) and caused, among others, the leaching of some *A*- and *Y*-site components. TEM investigations indicate that the selected-area electron diffraction patterns taken from Si-poor areas show strong and sharp diffraction spots related to well-crystalline pyrochlore, whereas the Si-rich areas show weaker spots with a diffuse diffraction halo that are typical of metamict material. Due to the fact that no intergrowth with other Si-bearing phases was observed in the TEM images even at very high magnification, it might be concluded that Si^{4+} can occupy severely α-decay damaged and chemically altered portions of this structure. The absence of Si in the sixfold-coordinated *B* site has been corroborated both by compositional relationships, and by the lack of any $^{[6]}Si^{4+}$ signal around –200 ppm in the MAS-NMR spectrum. A broad signal in the spectrum appearing at around –84 ppm, points to an amorphous species with tetrahedrally coordinated Si, close to $Q^{(2)}$ species defined as Si atom with two bridging O atoms, i.e., $[Si(OSi)_2(–)_2]$, in the form of finite-length chain-like structures, located in the damaged *A* and *B* sites of the primary structure.

Keywords: Si-rich pyrochlore, formula, geochemical alteration, metamictization, $Q^{(2)}$ species