Zr-Ti disilicates from the Pian di Celle volcano, Umbria, Italy

VICTOR V. SHARYGIN\textsuperscript{a}, FRANCESCO STOPPA\textsuperscript{b, *}, & BORIS A. KOLESOV\textsuperscript{c}

\textsuperscript{a}Inst. of Mineralogy and Petrography, Universitetsky prospect 3, 630090 Novosibirsk, Russia
\textsuperscript{b}Dipartimento di Scienze della Terra, Piazza Università, 06123 Perugia, Italy
\textsuperscript{c}Inst. of Inorganic Chemistry, Lavrentiev prospect 3, 630090 Novosibirsk, Russia

Abstract: Phases of the cuspidine and götzzenite groups, in addition to khibinskite, are observed in melilitolite from the Pian di Celle volcano both as groundmass minerals and as trapped/daughter phases of melt inclusions hosted by melilite and olivine. The approximate crystallisation sequence, as inferred from their relationships in melilitolite, is thought to be as follows: Zr,Ti-rich cuspidine $\rightarrow$ Zr-rich cuspidine $\rightarrow$ götzzenite, khibinskite.

Zr-rich cuspidine shows notable variations in CaO (58.2-40.4 wt.%), ZrO$_2$ (0.2-11.2 wt.%), Na$_2$O (0.5-4.5 wt.%) and F (10.1-8.1 wt.%). These variations suggest partial solid solution between monoclinic cuspidine, $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$, and pseudo-monoclinic hiortdahlite-2, $\text{Na}_2\text{Ca}_2\text{Zr}_4\text{Si}_2\text{O}_7\text{F}_2$, due to possible combined substitution $2\text{Ca}^{2+} + \text{F}^-$ $\leftrightarrow$ $\text{Na}^+ + \text{Zr}^{4+} + \text{O}^2-$. The X-ray patterns of the Pian di Celle cuspidines, with a different abundance of ZrO$_2$, fall between those of pure cuspidine and hiortdahlite. Raman spectroscopy supports the hypothesis of the above solid solution and shows that the Pian di Celle cuspidine retains monoclinic symmetry with a maximum content of Zr+Ti (up to 0.5 a.f.u.).

Götzzenite, (Na,Ca)$_3$Ti$_5$Zr$_{0.5}$Si$_2$O$_7$(F,$\text{O}_2$)$_2$, generally varies in CaO, REE$_2$O$_3$, TiO$_2$, ZrO$_2$ and Na$_2$O, which may indicate two main cation substitutions: $2\text{Ca}^{2+} \leftrightarrow \text{REE}^{3+} + \text{Na}^+$ and $\text{Ti}^{4+} \leftrightarrow \text{Zr}^{4+} + \text{O}^2-$. The X-ray and spectroscopic data of Pian di Celle götzzenite show negligible differences from götzzenite from other localities. The Zr-Ti-cuspidine composition ranges from Na$_{0.7}$Ca$_{2.8}$Ti$_{0.5}$Si$_2$O$_7$F$_2$O$_{0.3}$ to Na$_{0.8}$Ca$_{2.4}$Zr$_{0.8}$Si$_2$O$_7$F$_2$O$_{0.8}$. Chemical, diffraction and Raman data suggest that the extreme Zr,Ti-rich composition approaches that of hiortdahlite (possibly, hiortdahlite-1).

Khibinskite differs from the ideal composition K$_4$Zr$_2$Si$_2$O$_{14}$ in having high Na (up to 0.25 a.f.u.) and Fe (up to 0.12 a.f.u.) contents.

Key-words: cuspidine, götzzenite, hiortdahlite, khibinskite, compositional data, Raman spectra.

Introduction

The mineralogy of rare Zr-Ti-disilicates representing the cuspidine-wöhlerite-lâvenite and götzzenite-rosenbuschite-seidozerite families has begun to be intensively studied in the last few years (e.g. Merlino & Perchiazzi, 1988). These minerals are fairly typical accessory phases in carbonatites and related rocks (e.g. Keller et al., 1995).

Cuspidine occurs in high-temperature contact metamorphic and metasomatic rocks, while the only reliable possible identification in a magmatic assemblage has been reported from the carbonatite tuffs of Fort Portal, Uganda (Hogarth, 1989).