

## The crystal structure of the new mineral devilliersite, $\text{Ca}_4\text{Ca}_2\text{Fe}^{3+}_{10}\text{O}_4[(\text{Fe}^{3+}_{10}\text{Si}_2)\text{O}_{36}]$

B. Krüger<sup>1</sup>, H. Krüger<sup>1</sup>, I.O. Galuskina<sup>2</sup>, E. Galuskin<sup>2</sup>, Ye. Vapnik<sup>3</sup>

<sup>1</sup>University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria,

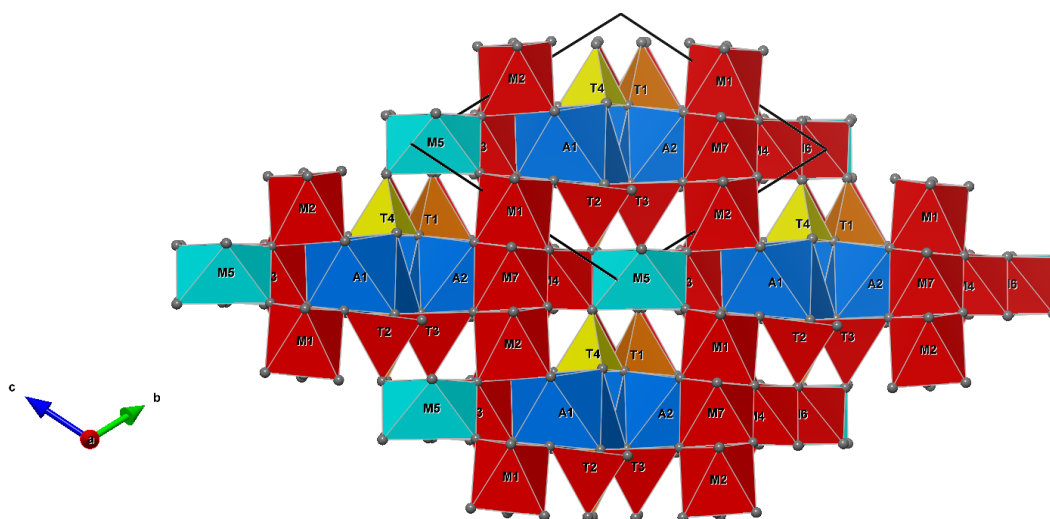
<sup>2</sup>Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland

<sup>3</sup>Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, Israel

*biljana.krueger@uibk.ac.at*

The crystal structure of the new mineral (IMA 2020-073) devilliersite  $\text{Ca}_4\text{Ca}_2\text{Fe}^{3+}_{10}\text{O}_4[(\text{Fe}^{3+}_{10}\text{Si}_2)\text{O}_{36}]$ , crystallizing in space group  $\overline{\text{P1}}$  with cell parameters  $a = 10.56619(10) \text{ \AA}$ ,  $b = 10.94969(11) \text{ \AA}$ ,  $c = 9.08459(7) \text{ \AA}$ ,  $\alpha = 106.4300(8)^\circ$ ,  $\beta = 95.7466(7)^\circ$ ,  $\gamma = 124.2978(11)^\circ$ ,  $V = 786.906(16) \text{ \AA}^3$ ,  $Z=1$ , was solved from single-crystal diffraction data, collected at PSI(SLS). Devilliersite, as well as khesinite,  $\text{Ca}_4\text{Mg}_2\text{Fe}^{3+}_{10}\text{O}_4[(\text{Fe}^{3+}_{10}\text{Si}_2)\text{O}_{36}]$  [1], is a  $\text{VI}\text{Fe}^{3+}$ -analog of dorrite,  $\text{Ca}_4\text{Mg}_2\text{Fe}^{3+}_{10}\text{O}_4[(\text{Al}_{10}\text{Si}_2)\text{O}_{36}]$  [2] and synthetic SFCA (Silico-Ferrite of Calcium and Aluminium) [3]. The structural formula of minerals of the dorrite–khesinite series can be written as  $\text{VII}(\text{A}_{12}\text{A}_{22})_{\Sigma 24} \text{VI}(\text{M}_1\text{M}_2\text{M}_3\text{M}_4\text{M}_5\text{M}_6\text{M}_7)_2 \text{O}_4[(\text{T}_1\text{T}_2\text{T}_3\text{T}_4\text{T}_5\text{T}_6)_2]_{\Sigma 12}\text{O}_{36}$ , where A are seven coordinated sites, M are octahedral sites and T are tetrahedral sites (Figure 1). The total scattering densities at the cation positions were determined using the atomic scattering factors combined with a refinement of the individual site occupancies and results of microprobe analysis.

In the structure of devilliersite all of the A-sites are fully occupied by calcium. However, chemical analyses show that additional 0.68 Ca atoms are present. For crystallochemical reasons this excess Ca has to be expected at the largest octahedral site M5, where it was placed and fixed for the refinement. The remaining scattering power at the M5 site is explained by Mg. The octahedral M1, M2, M3, M4 and M6 sites are dominated by  $\text{Fe}^{3+}$ , their scattering power was modelled with Fe and Mg, and converged for all sites to ~93% Fe. The M7 octahedra shows the smallest level of distortion, with bond lengths ranging from 1.999(2) to 2.75(19). In the Ti-rich minerals of the rhönite-group, titanium is found at the M7 site. Therefore, we fixed Ti at this site, according to the results of the chemical analysis, and the remaining occupancy was refined as Fe vs. Mg. Scattering power indicates that the T4 site in devilliersite is fully occupied by Si. Occupancy of all other tetrahedral sites was refined as Al vs Fe. The refined chemical formula is  $\text{VII}\text{Ca}_4\text{VI}(\text{Ca}_{1.36}\text{Mg}_{1.33}\text{Fe}_{9.07}\text{Ti}_{0.24})_{\Sigma 12}\text{O}_4\text{IV}(\text{Al}_{3.24}\text{Fe}_{6.76}\text{Si}_2)_{\Sigma 12}\text{O}_{36}$ .



**Figure 1.** The devilliersite structure, projection on (100): Fe-dominant polyhedra (M1, M2, M3, M4, M6, M7 octahedra and T2, T3, T5 and T6 tetrahedra) are in red. In blue are 6+1 coordinated pure Ca-polyhedra (A1 and A2-polyhedra). The octahedra M5, predominantly occupied by Ca (68%) is in light blue colour. A pure Si-tetrahedra T4 are in yellow. Al-dominant tetrahedra T1 have orange colour.

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