TRICLINIC "PHILLIPSITE" IN A Ca-RICH XENOLITH FROM THE BELLERBERG, EIFEL, GERMANY: REDUCTION OF SYMMETRY DUE TO NEARLY COMPLETE AI-SI ORDERING - EVIDENCE FOR AN UNUSUAL COOLING HISTORY?

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The crystal symmetry of zeolites often depends on the degree of cationic ordering on the tetrahedrally coordinated (Si,Al) sites. Chabazite, for example, has disordered tetrahedral sites and rhombohedral symmetry, whereas its dimorph willhendersonite is triclinic due to complete Si-Al ordering (TILLMANNS et al., 1984). A find of a distinctly triclinic zeolite with the phillipsite topology in a Ca-rich xenolith at the Bellerberg volcano, Eifel, Germany provides evidence for a new example of such ordering-induced symmetry reduction.

The new triclinic variant forms small aggregates of tabular, colourless glassy crystals, and is accompanied by willhendersonite and other, presently unidentified species. The crystal structure has been determined from single-crystal X-ray intensity data (Mo- $K\alpha$, CCD area detector, R(F) = 4.4 %). The crystals have space group $P\bar{1}$ (no. 2), with a = 8.702(2), b = 14.271(3), c = 16.573(3) Å, $\alpha = 91.36(3)$, $\beta = 99.61(3)$, $\gamma = 91.64(3)^\circ$, V = 2027.6(7) Å³, and Z = 2. The structure refinement and semiquantitative SEM-EDS analyses yield the chemical formula (K,Ca,Na)_{5,9}[Al₈Si₈O₃₂]·14.1H₂O, i.e., a 'normal', K-dominant chemistry of the non-framework sites and an Al:Si ratio of 1:1. The crystal structure can be described as a triclinically distorted variant of the idealised orthorhombic topology of phillipsite (STEINFINK, 1962; RINALDI et al., 1974).

The nearly complete Si-Al ordering is reflected by the average Si-O bond lengths for the eight non-equivalent Si sites (1.615 to 1.630 Å, mean 1.621 Å) and the distinctly different eight average Al-O bond lengths (1.732 to 1.741 Å, mean 1.738 Å). As in phillipsite, the three-dimensional framework of SiO₄ tetrahedra sharing corners with AlO₄ tetrahedra contains channels (limited by four- and eight-membered rings), hosting the non-framework cations and water molecules, most of which are located on partially occupied and/or positionally disordered sites. The observed Si-Al order may be attributed to an unusual cooling history of the crystals within the Ca-rich xenolith, as is also indicated by the association with willhendersonite. A more thorough characterisation of this interesting zeolite variant is currently underway.

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References

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