

Crystal chemistry of Ti-rich ferriallanite-(Ce) from Cape Ashizuri, Shikoku Island, Japan

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ABSTRACT

The crystal chemistry of Ti-rich ferriallanite-(Ce) in syenites from Cape Ashizuri, Shikoku Island, Japan, was studied using electron microprobe analysis (EMPA) and single-crystal X-ray diffraction methods. Our specimens (AS001 and AS304) are characterized by high-Ti (~3.6 wt% TiO₂) and Fe contents (~21.3 wt% FeO*; Fe²⁺/total Fe = 0.6–0.7). Structure refinements of two ferriallanite-(Ce) crystals converged to $R_1 = 1.50$ – 1.57% . In both specimens, the dominant cations at A1, A2, and M3 are Ca, Ce, and Fe²⁺, respectively. However, depending on Ti assignment, two different schemes of the cation distributions at M1 and M2 can be considered: (1) $(\text{Fe}_{0.72}\text{Ti}_{0.23}\text{Al}_{0.05})^{\text{M1}}(\text{Al}_{0.82}\text{Fe}_{0.18}^{3+})^{\text{M2}}$ and (2) $(\text{Fe}_{0.90}\text{Al}_{0.10})^{\text{M1}}(\text{Al}_{0.77}\text{Ti}_{0.23})^{\text{M2}}$ for AS001, and (1) $(\text{Fe}_{0.65}\text{Ti}_{0.29}\text{Al}_{0.06})^{\text{M1}}(\text{Al}_{0.89}\text{Fe}_{0.11}^{3+})^{\text{M2}}$ and (2) $(\text{Fe}_{0.76}\text{Ti}_{0.13}\text{Al}_{0.11})^{\text{M1}}(\text{Al}_{0.84}\text{Ti}_{0.16})^{\text{M2}}$ for AS304. The Si₂O₇ group is compressed along Si1-O9-Si2 direction because of the expansions of the M1O₆ and M3O₆ octahedra due to substitution of large octahedral cations for Al. This compression is monitored by the atom position of O9 that shifts away from the cation at A1 decreasing the Si1-O9-Si2 angle. In allanite-subgroup minerals, the A1-O9 distance is longer and the bridging angle is smaller than those of clinozoisite-subgroup minerals. Although the A1 polyhedron is generally described as a ninefold-coordinated site, it is appropriately described as sevenfold-coordinated in Ti-rich allanite-(Ce) because of the lengthened A1-O9 (×2) distance. The cation substitutions at M1 and M3 indirectly affect the topology of the A1 polyhedron.

Keywords: Ferriallanite, crystal structure, Cape Ashizuri, REE, Ti