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

MARIKO NAGASHIMA,1,* TERUYOSHI IMAOKA,1 AND KAZUO NAKASHIMA2

1Graduate School of Science and Engineering, Yamaguchi University, Yoshida 1677-1, Yamaguchi 753-8512, Japan
2Department of Earth and Environmental Sciences, Faculty of Science, Yamagata University, Yamagata 990-8560, Japan

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 \( R_i = 1.50–1.57\% \). In both specimens, the dominant cations at A1, A2, and M3 are Ca, Ce, and Fe\(^{2+}\), respectively. However, depending on Ti assignment, two different schemes of the cation distributions at M1 and M2 can be considered: (1) \((\text{Fe}_{0.76}\text{Ti}_{0.13}\text{Al}_{0.11})\text{M1}(\text{Al}_{0.84}\text{Ti}_{0.16})\text{M2}\) for AS001, and (1) \((\text{Fe}_{0.65}\text{Ti}_{0.26}\text{Al}_{0.09})\text{M1}(\text{Al}_{0.80}\text{Fe}_{0.11})\text{M2}\) and (2) \((\text{Fe}_{0.80}\text{Ti}_{0.14}\text{Al}_{0.06})\text{M1}(\text{Al}_{0.86}\text{Fe}_{0.14})\text{M2}\) 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

INTRODUCTION

Epidote-group minerals rich in rare earth elements (REE), in particular allanite, simplified as CaREE\(^{3+}\)AlFe\(^{2+}\)Si3O12(OH), are common accessory minerals in igneous, metamorphic, metasomatic, and sedimentary rocks (e.g., Gieré and Sorensen 2004). Monoclinic epidote-group minerals with the structural formula \(\text{A1}\text{A2M1M2M3Si3O12(OH)}\) belong to the soro/neso-silicate class. Their structure is based on a chain of edge-sharing M2 octahedra and a central chain of M1 octahedra with M3 octahedra attached on alternate sides along its length. Chains of octahedra run parallel to the \( b \)-axis, linked by SiO4 and Si2O7 groups (Ito et al. 1954; Dollase 1968). This structural arrangement gives rise to two types of highly coordinated sites: ninefold-coordinated A1 and tenfold-coordinated A2. In natural clinozoisite subgroup minerals, A1 and A2 are filled with Ca, and the octahedral M1, M2, and M3 sites are occupied by trivalent cations. The cations having large ionic radius such as REE, Sr, and Ba can locate at M1 and M2, and M3 sites are occupied by divalent cations. Although the smallest M2O6 octahedron is generally occupied by Al only in natural clinozoisite subgroup minerals, small amount of octahedral cations, such as Fe\(^{2+}\) can locate at M2 in allanite subgroup minerals (e.g., Holtstam et al. 2003). The key cation-sites M3 and A1 determine the root name, and for the dominant cation on A2 (other than Ca) the suffix designation is used. This paper follows the recommended nomenclature summarized by Armbruster et al. (2006).

The studied allanite-subgroup minerals found in syenites from Cape Ashizuri, Shikoku Island, Japan, are characterized by high Ti (~3.6 wt% TiO2) and Fe (~21.3 wt% FeO*; Fe2+/total Fe = 0.6–0.7). Subject of this study is to understand the crystal chemistry of this uncommon Ti-rich allanite-(Ce) type mineral, which can be classified as ferriallanite-(Ce). We investigated the cation assignments and the influence of the composition on the structural variation and flexibility of this complex Ti-rich allanite-(Ce) type mineral.

ANALYTICAL METHODS

Samples

The Ashizuri igneous complex is a small, semi-circular shape with about 7 km in diameter, and the southern part of the complex lies offshore. The igneous rocks of this complex yield K-Ar biotite age of 12.9 ± 0.6 Ma (Murakami et al. 1989) and U-Pb zircon ages of 12.95 ± 0.09 (Shinjoe et al. 2010), and are divided into three lithologic units (e.g., Murakami and Imaoka 1980, 1985; Imaoka et al. 1991). The major units are biotite granite in the northern part, hybrid rocks of gabbron and rapakivi granite in the central to eastern part, and syenite rocks in the southern part. Syenitic rocks consist of three stages of successive magma pulses, i.e., stage I: syenites (alkali-feldspar syenite, alkali-feldspar quartz syenite, and quartz syenite), stage II: alkali-feldspar granite, and stage II: peralkaline rhyolite. These