The structure of Mn-rich tuperssuatsiaite: A palygorskite-related mineral

FERNANDO CÁMARA,† LAURENCE A.J. GARVIE,‡ BERTRAND DEVOUARD,*, THOMAS L. GROY, and PETER R. BUSECK

1Department of Geological Sciences, Arizona State University, Tempe, Arizona 85287-1404, U.S.A.
2Department of Chemistry/Biochemistry, Arizona State University, Tempe, Arizona 85287, U.S.A.

ABSTRACT

The structure of tuperssuatsiaite from the Aris phonolite in central Namibia was refined to an R index of 0.075 for 905 observed reflections [I > 2σ(I)] obtained with a four-circle X-ray diffractometer. Tuperssuatsiaite is monoclinic, C2/m, with a = 14.034(7), b = 17.841(7), c = 5.265(2) Å, and β = 103.67(4)°. Microprobe analysis gave an average composition of Na1.87Fe2.14Mn0.48 Ti0.14Al0.03Mg0.02[Si8O20](OH)2·n(H2O), with five octahedral sites. The structure is closely related to that of palygorskite Mg5[Si10O23](OH)2·4H2O. Tuperssuatsiaite consists of ribbons of SiO4 tetrahedra linked by bands of octahedra running parallel to c. Channels occur that could be occupied by H2O as in palygorskite. The octahedral band contains three edge-sharing, six-coordinated sites labeled M1, M2, and M3. This band consists of alternating M3-M1-M3 and M2-M2 octahedra along [001]. The M1 and M2 sites both contain Fe and Mn, and M3 is occupied by Na. Bond-valence calculations indicate a formal charge of 2.48 for M1 and 2.67 for M2, i.e., a charge distribution of 2R2+1R3+. Octahedral angle variance and volume are similar for both sites, indicating disorder in the distribution of Fe and Mn atoms between the sites. Charge balance requirements agree with the presence of Fe3+ and Mn2+.

INTRODUCTION

Structure determinations of palygorskite and related species, such as tuperssuatsiaite, are limited due to a lack of suitable crystals for single-crystal X-ray diffraction. Understanding these minerals is important for calculating physical and chemical properties such as the number and behavior of channel and surface-molecular exchange sites. Most palygorskite-group minerals crystallize as fine-grained, hair-like aggregates with fiber widths of less than a few microns. Because of these crystallites, structural information has been inferred mostly from powder X-ray diffraction and transmission electron microscopy. As a result, numerous models have been produced regarding cell dimensions and indexing of powder patterns (Christ et al. 1969; Jones and Galan 1988) and polymorphs and structure models (Bradley 1940; Presinger 1963; Zyvagin et al. 1963; Gard and Follet 1968; Drits and Aleksandrova 1966; Drits and Sokolova 1971; Chisholm 1990, 1992).

Tuperssuatsiaite has a diffraction pattern similar to that of palygorskite, which implies that they have related structures. The palygorskite type minerals exhibit a range of structure variations as shown by yofortierite, the Mn-analogue of palygorskite (Perrault et al. 1975); interstitials (Na,K) Mn(Ti,Nb)Na8(0,OH)(OH)2[Si5O12](0,OH)2·4H2O (Egorov-Tismenko et al. 1996; Yamnova et al. 1996), a sepiolite-related mineral; and raite Na3Mn3Ti0.25[Si8O20](OH)2·10H2O (Pluth et al. 1997), with Na(H2O)6 octahedra along the channels. Kaliërsite (K,Na)3(Fe3+)2[Si8O20](OH)2·12H2O was described as a member of the palygorskite-sepiolite series (Ferraris et al. 1996, 1998; Ferraris 1997), with a and c lattice parameters similar to sepiolite and palygorskite and the b parameter intermediate between them.

Tuperssuatsiaite is common in some miarolitic cavities associated with alkaline intrusive and extrusive rocks from the Aris phonolite, Windhoek, Namibia (von Knorring et al. 1992). It was first described from the Ilímaussaq alkaline complex, South Greenland (Karup-Møller and Petersen 1984). We had access to high-quality specimens of tuperssuatsiaite from a new occurrence in the Aris phonolite and located a suitable crystal to perform a single-crystal X-ray diffraction study.

OCURRENCE

The phonolite intrusion is located about 25 km south of Windhoek. The samples were collected from a quarry being mined for road and railway ballast. The phonolite is highly vesicular, fine grained, aphyric, and consists of alkali feldspars, nepheline, and acmite with minute accessory apatite, zircon, and monazite (von Knorring and Franke 1987; Jahn et al. 2001). The vesicles range from ca. 1 mm to 10 cm in diameter. Many are filled with fluid and appear to burst when the rock is split. In addition to tuperssuatsiaite, the vesicles contain villiaumite, natrolite, aegerite, microcline, apophyllite, analcime, fluorite, kanemite, hydroxyapatite, galena, sphalerite, makatite, quartz, and other less well-characterized or new species. The occurrence and structure of kanemite from the Aris phonolite was recently described (Garvie et al. 1999).