Carbocernaite from Bear Lodge, Wyoming: Crystal chemistry, paragenesis, and rare-earth fractionation on a microscale

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ABSTRACT

Zoned crystals of carbocernaite occur in hydrothermally reworked burbankite-fluorapatite-bearing calcite carbonatite at Bear Lodge, Wyoming. The mineral is paragenetically associated with pyrite, strombitane, barite, ancyelite-(Ce), and late-stage calcite, and is interpreted to have precipitated from sulfate-bearing fluids derived from an external source and enriched in Na, Ca, Sr, Ba, and rare-earth elements (REE) through dissolution of the primary calcite and burbankite. The crystals of carbocernaite show a complex juxtaposition of core-rim, sectoral, and oscillatory zoning patterns arising from significant variations in the content of all major cations, which can be expressed by the empirical formula \( \text{Ca}_{0.43-0.91}\text{Sr}_{0.40-0.69}\text{REE}_{0.18-0.59}\text{Na}_{0.18-0.53}\text{Ba}_{0-0.08} \). Interelement correlations indicate that the examined crystals can be viewed as a solid solution between two hypothetical end-members, \( \text{CaSr(CO}_3\text{)}_2 \) and \( \text{NaREE(CO}_3\text{)}_2 \), with the most Na-REE-rich areas in pyramidal (morphologically speaking) growth sectors representing a probable new mineral species. Although the Bear Lodge carbocernaite is consistently enriched in light REE relative to heavy REE and Y (chondrite-normalized \( \text{La/Er = 500–4200} \)), the pyramidal sectors exhibit a greater degree of fractionation between these two groups of elements relative to their associated prismatic sectors. A sample approaching the solid-solution midline \( \left[ \text{Ca}_{0.57}\text{Na}_{0.42}\text{Sr}_{0.09}\text{REE}_{0.10}\text{Ba}_{0.01}\text{CO}_3 \right] \) was studied by single-crystal X-ray diffraction and shown to have a monoclinic symmetry (space group \( P11m \), \( a = 6.434(4) \), \( b = 7.266(5) \), \( c = 5.220(3) \) Å, \( \gamma = 89.979(17)^\circ \), \( Z = 2 \)) as opposed to the orthorhombic symmetry (space group \( Pb2_1m \)) proposed in earlier studies. The symmetry reduction is due to partial cation order in sevenfold-coordinated sites occupied predominantly by Ca and Na, and in tenfold-coordinated sites hosting Sr, REE, and Ba. The ordering also causes splitting of carbonate vibrational modes at 690–740 and 1080–1100 cm\(^{-1}\) in Raman spectra. Using Raman micro-spectroscopy, carbocernaite can be readily distinguished from burbankite- and ancyelite-group carbonates characterized by similar energy-dispersive spectra.

Keywords: Carbocernaite, carbonatite, isotopic composition, rare earth elements, crystal structure, zoning, Bear Lodge, Wyoming

INTRODUCTION

Carbocernaite was discovered by Bulakh et al. (1961) in dolomite-calcite carbonatites and calcite veins at the Vuoriyarvi intrusive complex in northern Karelia, Russia. The name was chosen to reflect the presence of carbonate groups, cerium and sodium (Na) in its composition, which was initially given as (Ca,Na,REE,Sr,Ba)CO\(_3\) (REE = rare-earth elements). Subsequently, this mineral was reported also from carbonatites at Weishan (China), Phan Si Pan (Vietnam), Khanneshin (Afganistan), Sarnu-Dandali, Newania, Khamambettu, Kamthai (India), Swarthoosdrift, Kalkfeld, and Ondurakorume (Namibia), Araxá and Jacupiranga (Brazil), Rocky Boy (Montana, U.S.A.), Sturgeon Narrows (Canada), Korsnä (Finland), and Khibiny, Ozerny, and Biraya in Russia (Bulakh and Izokh 1967; Harris 1972; Eremenko and Vel’ko 1982; Wall et al. 1993; Zhang et al. 1995; Reguir and Mitchell 2000; Traversa et al. 2001; Orris and Grauch 2002; Pekov and Podlesnyi 2004; Wall and Zaitsev 2004; Drüppel et al. 2005; Costanzo et al. 2006; Mills et al. 2012; Bhushan and Kumar 2013; Burtseva et al. 2013). In addition, carbocernaite was described from metasomatized REE-rich dolomite in the West mine of the Bayan Obo deposit, China (Zhang et al. 1995) and from miarolitic cavities in alkaline igneous rocks at Mont Saint-Hilaire, Canada (Horváth and Gault 1990) and Khibiny, Russia (Pekov and Podlesnyi 2004). Notably, over one-half of these reports are not backed by any convincing analytical evidence. For example, Harris (1972), Traversa et al. (2001), and Bhushan and Kumar (2013) did not record any Na in their samples, which calls into question the validity of these identifications.

The current understanding of the crystal structure of carbocernaite is also inadequate. The structure was first determined by Voronkov and Pyatenko (1967), who used for this purpose a sample of unknown composition from an unspecified locality, although definitely not the type material of Bulakh et al. (1961). Voronkov and Pyatenko (1967) identified the symmetry as orthorhombic (space group \( Pb2_1m \), and recognized the presence of two symmetrically non-equivalent cation sites in the structure...