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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, strontianite, barite, ancylite-(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 $(\mathrm{Ca}_{0.43-0.91}\mathrm{Sr}_{0.40-0.69}\mathrm{REE}_{0.18-0.59}\mathrm{Na}_{0.18-0.53}\mathrm{Ba}_{0-0.08})_{\Sigma 1.96-2.00}(\mathrm{CO}_3)_2$. Interelement correlations indicate that the examined crystals can be viewed as a solid solution between two hypothetical end-members, $\mathrm{CaSr(CO_3)_2}$ and $\mathrm{NaREE(CO_3)_2}$, 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 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 $[(\mathrm{Ca}_{0.57}\mathrm{Na}_{0.42})_{\Sigma 0.99}(\mathrm{Sr}_{0.50}\mathrm{REE}_{0.47}\mathrm{Ba}_{0.01})_{\Sigma 0.98}(\mathrm{CO}_3)_2]$ 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, $\gamma = 89.979(17)°$, $Z = 2$] 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 ancylite-group carbonates characterized by similar energy-dispersive spectra.

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