

Carlsonite, $(\text{NH}_4)_5\text{Fe}_3^{3+}\text{O}(\text{SO}_4)_6 \cdot 7\text{H}_2\text{O}$, and huizingite-(Al), $(\text{NH}_4)_9\text{Al}_3(\text{SO}_4)_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, two new minerals from a natural fire in an oil-bearing shale near Milan, Ohio

ANTHONY R. KAMPF^{1,*}, R. PETER RICHARDS², BARBARA P. NASH³, JAMES B. MUROWCHICK⁴, AND JOHN F. RAKOVAN⁵

¹Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.

²Geology Department, Oberlin College, Oberlin, Ohio 44074, U.S.A.

³Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah 84112, U.S.A.

⁴Department of Geosciences, University of Missouri-Kansas City, 420 Flarsheim Hall, 5110 Rockhill Road, Kansas City, Missouri 64110, U.S.A.

⁵Department of Geology and Environmental Earth Science, Miami University, Oxford, Ohio 45056, U.S.A.

ABSTRACT

The new minerals carlsonite (IMA2014-067), $(\text{NH}_4)_5\text{Fe}_3^{3+}\text{O}(\text{SO}_4)_6 \cdot 7\text{H}_2\text{O}$, and huizingite-(Al) (IMA2015-014), $(\text{NH}_4)_9\text{Al}_3(\text{SO}_4)_8(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, formed from a natural fire in an oil-bearing shale near Milan, Ohio. Carlsonite crystals are yellow to orange-brown thick tablets, flattened on {001}, or stout prisms, elongated on [110], up to about 0.5 mm in size. The mineral has a tan streak, vitreous luster, Mohs hardness of 2, brittle tenacity, irregular fracture, perfect {001} cleavage, calculated density of 2.167 g/cm³, and is easily soluble in H₂O. Carlsonite is optically biaxial (–), $\alpha = 1.576(1)$, $\beta = 1.585(1)$, and $\gamma = 1.591(1)$ (white light). Huizingite-(Al) crystals, typically intergrown in light greenish yellow drusy aggregates, are tabular to bladed, flattened on {100}, up to about 0.25 mm in maximum dimension. The mineral has a white streak, vitreous luster, Mohs hardness of 2½, brittle tenacity, irregular fracture, no cleavage, calculated density of 2.026 g/cm³, and is easily soluble in H₂O. Huizingite-(Al) is optically biaxial (+) with $\alpha = 1.543(1)$, $\beta = 1.545(1)$, and $\gamma = 1.563(1)$ (589.6 nm light). Raman and infrared spectroscopy was conducted on both minerals. Electron microprobe analyses provided the empirical formulas $[(\text{NH}_4)_{4.64}\text{Na}_{0.24}\text{K}_{0.12}]_{\Sigma 5.00}\text{Fe}_{3.05}^{3+}\text{O}(\text{SO}_4)_6 \cdot 6.93\text{H}_2\text{O}$ and $[(\text{NH}_4)_{8.76}\text{Na}_{0.22}\text{K}_{0.02}]_{\Sigma 9.00}(\text{Al}_{1.63}\text{Fe}_{1.34}^{3+})_{\Sigma 2.99}(\text{OH})_{1.98}(\text{H}_2\text{O})_{4.02}(\text{SO}_4)_{8.00}$ for carlsonite and huizingite-(Al), respectively. Huizingite compositions with Fe > Al were noted. Carlsonite is triclinic, $P\bar{1}$, $a = 9.5927(2)$, $b = 9.7679(3)$, $c = 18.3995(13)$ Å, $\alpha = 93.250(7)^\circ$, $\beta = 95.258(7)^\circ$, $\gamma = 117.993(8)^\circ$, $V = 1506.15(16)$ Å³, and $Z = 2$. Huizingite-(Al) is triclinic, $P\bar{1}$, $a = 9.7093(3)$, $b = 10.4341(3)$, $c = 10.7027(8)$ Å, $\alpha = 77.231(5)^\circ$, $\beta = 74.860(5)^\circ$, $\gamma = 66.104(5)^\circ$, $V = 948.73(9)$ Å³, and $Z = 1$. The five strongest lines in the X-ray powder diffraction pattern of carlsonite are [d_{obs} in Å(hkl): 9.23(100)(002); 8.26(40)(100,011); 7.57(43)($\bar{1}11, 1\bar{1}1, 011$); 4.93(23)($\bar{1}\bar{1}1, \bar{1}20$); and 3.144(41)(multiple)]. Those for huizingite-(Al) are: 8.82(60)(100); 5.04(69)(121); 3.427(100)($\bar{2}\bar{2}1$); 3.204(68)($\bar{2}11$); and 3.043(94)($2\bar{1}2, 312$).

The crystal structures of carlsonite ($R_1 = 0.030$) and huizingite ($R_1 = 0.040$) are bipartite, each consisting of a structural unit and an interstitial unit. For carlsonite, the structural unit is a $[\text{Fe}_3^{3+}\text{O}(\text{H}_2\text{O})_3(\text{SO}_4)_6]^{5-}$ cluster and the interstitial complex is $[(\text{NH}_4)_5(\text{H}_2\text{O})_4]^{5+}$. For huizingite-(Al), the structural unit is a $[(\text{Al}, \text{Fe}^{3+})_3(\text{OH})_2(\text{H}_2\text{O})_4(\text{SO}_4)_6]^{5-}$ cluster and the interstitial complex is $[(\text{NH}_4)_9(\text{SO}_4)_2]^{5+}$. In the carlsonite cluster, three FeO₆ octahedra share a common vertex, while in the huizingite-(Al) cluster, three (Al,Fe)O₆ octahedra form an abbreviated corner-linked chain. The cluster in carlsonite is the same as that in metavoltine, while the huizingite-(Al) cluster is unique. The range of Lewis basicity of the structural unit in carlsonite is 0.23–0.11 valence units (v.u.) and in huizingite-(Al) it is 0.20–0.12 v.u.; the corresponding Lewis acidities of the interstitial complexes in these structures are 0.13 and 0.14 v.u., respectively. A characteristic Lewis acid strength of 0.13 v.u. is suggested for NH₄⁺ when it is in its most typical coordinations of 7 to 8. The close structural relationship between carlsonite and metavoltine and the similarity of their powder diffraction patterns suggests that carlsonite may have misidentified as metavoltine in some NH₄-rich mineral assemblages. The new heteropolyhedral cluster in the structure of huizingite-(Al) is of interest because its existence may provide insights into the structural and paragenetic relations among hydrated ferric sulfate minerals. In particular, it may exist as a complex in aqueous solutions or in solid-state transformations involving the formation and/or breakdown of sideronatrite-style $[\text{Fe}^{3+}(\text{SO}_4)_3]^{3-}$ chains. We surmise that it may be a more commonly formed mineral than its abundance would indicate and that its rarity may reflect a narrow stability range, and so a transitory existence.

Keywords: Carlsonite, huizingite-(Al), new mineral, crystal structure, Raman spectroscopy, infrared spectroscopy, Lewis acidity-basicity, Huron Shale burn site, Milan, Ohio