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Carlsonite, $(NH_4)_5Fe^{3+}_3O(SO_4)_6\cdot 7H_2O$, and huizingite-(Al), $(NH_4)_9Al_3(SO_4)_8(OH)_2\cdot 4H_2O$, two new minerals from a natural fire in an oil-bearing shale near Milan, Ohio

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Abstract

The new minerals carlsonite (IMA2014-067), $(NH_4)_5Fe^{3+}_3O(SO_4)_6\cdot 7H_2O$, and huizingite-(Al) (IMA2015-014), $(NH_4)_9Al_3(SO_4)_8(OH)_2\cdot 4H_2O$, 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/cm^3, and is easily soluble in H_2O. Carlsonite is optically biaxial (–), α = 1.576(1), β = 1.585(1), and γ = 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/cm^3, and is easily soluble in H_2O. Huizingite-(Al) is optically biaxial (+) with α = 1.543(1), β = 1.545(1), and γ = 1.563(1) (589.6 nm light). Raman and infrared spectroscopy was conducted on both minerals. Electron microprobe analyses provided the empirical formulas $[(NH_4)_{4.64}Na_{0.24}K_{0.12}]_{\Sigma 5.00}Fe^{3+}_{3.05}O(SO_4)_6\cdot 6.93H_2O$ and $[(NH_4)_{8.76}Na_{0.22}K_{0.02}]_{\Sigma 9.00}(Al_{1.65}Fe^{3+}_{1.34})_{\Sigma 2.99}(OH)_{1.98}(H_2O)_{4.02}(SO_4)_{8.00}$ 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, α = 93.250(7)°, β = 95.258(7)°, γ = 117.993(8)°, V = 1506.15(16) Å^3, and Z = 2. Huizingite-(Al) is triclinic, $P\bar{1}$, a = 9.7093(3), b = 10.4341(3), c = 10.7027(8) Å, α = 77.231(5)°, β = 74.860(5)°, γ = 66.104(5)°, V = 948.73(9) Å^3, and Z = 1. The five strongest lines in the X-ray powder diffraction pattern of carlsonite are [d_{obs} in Å(I)(*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 $[Fe^{3+}_3O(H_2O)_3(SO_4)_6]^{5-}$ cluster and the interstitial complex is $[(NH_4)_5(H_2O)_4]^{5+}$. For huizingite-(Al), the structural unit is a $[(Al,Fe^{3+})_3(OH)_2(H_2O)_4(SO_4)_6]^{5-}$ cluster and the interstitial complex is $[(NH_4)_9(SO_4)_2]^{5+}$. In the carlsonite cluster, three FeO_6 octahedra share a common vertex, while in the huizingite-(Al) cluster, three $(Al,Fe)O_6$ 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 NH_4^+ 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 NH_4-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 $[Fe^{3+}(SO_4)_3]^{3-}$ 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