American Mineralogist, Volume 98, pages 1302–1309, 2013

Rapidcreekite in the sulfuric acid weathering environment of Diana Cave, Romania

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Abstract

The Diana Cave in SW Romania develops along a fault line and hosts a spring of hot (T_{avg} = 51 °C), sulfate-rich, sodium-calcium-chloride bearing water of near-neutral pH. Abundant steam and H_2S rises from the thermal water to condensate on the walls and ceiling of the cave. The sulfuric acid produced by H_2S oxidation/hydrolysis causes a strong acid-sulfate weathering of the cave bedrock generating a sulfate-dominated mineral assemblage that includes rapidcreekite, $Ca_2(SO_4)(CO_3)\cdot 4H_2O$ closely associated with gypsum and halotrichite group minerals. Rapidcreekite forms bundles of colorless tabular orthorhombic crystals elongated along [001] and reaching up to 1.5 mm in length. For verifying the hydrogen bond scheme and obtaining crystal-chemical details of the carbonate group a single-crystal structure refinement of rapidcreekite was performed. Its unit-cell parameters are: a = 15.524(2), b = 19.218(3), c = 6.161(1) Å; V = 1838.1(5) Å^3, Z = 8, space group *Pcnb*. Chemical composition (wt%): CaO 35.65, SO_3 24.97, CO_2 13.7, H_2O 23.9, Na_2O 0.291, MgO 0.173, Al_2O_3 0.07, total 98.75%. The empirical formula, based on 7 non-water O atoms pfu, is: $Ca_{1.98}Na_{0.029}Mg_{0.013}Al_{0.004}(S_{0.971}O_4)(C_{0.97}O_3)\cdot 4.13H_2O$. The $\delta^{34}S$ and $\delta^{18}O$ values of rapidcreekite and other cave sulfates range from 18 to 19.5‰ CDT and from –9.7 to 7.8‰ SMOW, respectively, indicating that the source of sulfur is a marine evaporite and that during hydration of the minerals it has been an abundant ^{18}O exchange with percolating water but almost no oxygen is derived from $O_{2(aq)}$. This is the first description of rapidcreekite from a cave environment and one of the very few natural occurrences worldwide. We also report on the mineral stability and solubility, parameters considered critical to understand the co-precipitation of carbonates and sulfates, a process that has wide applications in cement industry and scaling prevention.

Keywords: Rapidcreekite, acid-sulfate weathering, hydrogen bond scheme, carbonate group, $\delta^{34}S$-$\delta^{18}O$ values, Diana Cave, Romania