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Kalistrontite, its occurrence, structure, genesis, and significance for the evolution of potash deposits in North Yorkshire, U.K.

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Abstract

The rare mineral kalistrontite, $K_2Sr(SO_4)_2$, has been discovered in exceptional quantities in exploration boreholes targeting Permian polyhalite [$K_2Ca_2Mg(SO_4)_4 \cdot 2(H_2O)$]-bearing evaporite deposits in North Yorkshire, U.K. The kalistrontite is associated with anhydrite, polyhalite, halite, magnesite, and traces of celestine in the Fordon (Evaporite) Formation, English Zechstein 2 cycle, at depths of ~1.5 to 1.7 km below surface. It was first encountered here during quantitative X-ray diffraction assays of composited drill-core samples over an identified ~50 m interval in York Potash Ltd.'s boreholes SM6, SM9, and deflections SM9A and 9B.

X-ray diffraction including structural refinement, thermal analysis, Raman spectroscopy, petrographic examination, quantitative microanalysis, and Sr isotopic analysis have been employed to fully characterize the kalistrontite and determine its genesis to understand its distribution and significance for the polyhalite deposits.

Petrographic examination reveals that the kalistrontite is present in two general forms. First as irregularly shaped, poikilotopic millimeter-scale patches of subhedral, equant to elongate millimeter-scale crystals that enclose fine, rounded, irregular anhedral and rarely euhedral crystals of anhydrite, halite, and magnesite. Second as a vein-fill formed of an interlocking mosaic of elongate sub-millimeter scale, euhedral crystals that are compositionally zoned and again enclose fine rounded anhydrite and halite crystals at vein margins. Kalistrontite displays largely replacive contact relationships with both the earlier and generally simultaneously formed anhydrite and halite but before at least some of the polyhalite. Vein-fill kalistrontite was deposited by mineralizing fluids proceeding along fractures, patchily replacing the pre-existing low-porosity anhydrite and halite. EDX microanalysis of the North Yorkshire kalistrontite indicates a purer composition than previously reported but some (5–12% stoichiometric) substitution of Ca for Sr is identified and directly linked to petrographic textures identified during backscattered scanning electron imaging.

Improved resolution XRD data for the kalistrontite is comparable to that previously published, with similar unit-cell dimensions [$a = 5.45826(5)$ Å, $c = 20.8118(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 536.968(3)$ Å^3] and space group $R\bar{3}m$ (166), despite the limited Ca substitution for Sr. Thermal behavior, published for the first time, shows that kalistrontite is essentially stable from ambient to ~960 °C. Melting occurs from ~960 to 1430 °C with a resulting weight loss of 62.57%, accompanied by the evolution of SO_2. Minor endothermic features are tentatively ascribed to the boiling of K from surface sites.

The first published Raman spectrum for kalistrontite shows a major frequency shift at 968 cm^{-1} with minor features of decreasing intensity at 458, 617, 1095, 1152, 650, 170, and 127 cm^{-1}.

Consistent $^{87}Sr/^{86}Sr$ values for kalistrontite and anhydrite (mean, 0.707014 ± 0.000010, 2 S.E. and 0.707033 ± 0.000020, 2 S.E., respectively) along with very similar values obtained for the polyhalite are indicative of Late Permian seawater in an open environment with very limited evidence of basin constriction or Sr contribution from hydrothermal or meteoric source(s). When compared to the LOWESS global curve, the $^{87}Sr/^{86}Sr$ values suggest a consistent formation date of 255 ± 2 Ma (late Wuchiapingian), the first published date for the EZ2 deposits in North Yorkshire.

Diagenetic processes, particularly the late-stage supply of K- and Sr-rich fluid, must have proceeded extensively in the North Yorkshire deposits. However these show only limited spatial development, within the shelf zone on the margins of the main polyhalite deposit.

The K-rich nature (26.3 wt% K_2O) of kalistrontite, compared to other K-bearing evaporite minerals (e.g., kainite 18.9 wt% K_2O, carnallite 17.0 wt% K_2O, polyhalite 15.6 wt% K_2O), has a significant effect on borehole γ-ray response (303 compared to 229, 200, and 185 API units, respectively) and therefore considerable implications for evaporite deposit modeling and the determination of deposit-grade.

Understanding the character and distribution of kalistrontite is necessary for modeling the nature, extent, and grade of the world's richest-known deposit of polyhalite. York Potash Ltd. has recently commenced construction of the $3.0 bn Woodsmith Mine to support large-scale polyhalite production, promising the creation of thousands of jobs and a boost to both local and national economies. First production is scheduled for late 2021.

Keywords: Kalistrontite, North Yorkshire, evaporite, Permian, Zechstein, X-ray diffraction, petrography, Sr isotope

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