

Nickeloan melanterite from Sudbury Basin

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Abstract

Locomotive heat discharge on nickel sulphide ore and slag northwest of Sudbury, Ontario has formed nickeloan melanterite. The uncommon Ni-Fe substitution is the result of the unusual "weathering" of an atypical source material. The existence of the septahydrate rather than the tetrahydrate is due to the elevated temperatures and humidities of the locomotive steam.

Introduction

A visually most striking "outcrop" of an efflorescent bloom was observed in 1978 at a railroad locomotive switching site on Rt. 144 in Leveck, 25 km northwest of Sudbury, Ontario. The material was identified as nickeloan melanterite $[(\text{Fe},\text{Ni})\text{SO}_4 \cdot 7\text{H}_2\text{O}]$ by X-ray diffraction and energy-dispersive spectra techniques.

This particular occurrence is notable for three reasons. The end-members melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and morenosite ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) are not uncommon weathering products of suitable protoliths, the latter especially in mines of the Sudbury, Ontario area (Hawley, 1963, Table 2). However, while Fe-Mg and Ni-Mg substitution have been documented, no natural occurrences of Fe-Ni solid solution in sulphates are noted in any of the standard descriptive mineralogy references. Second, the local climate is conducive to the formation of rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) rather than the septahydrate (Ehlers and Stiles, 1965). Third, the paragenesis brings into question whether or not the phase is "naturally occurring" and thus a mineral according to most common definitions. This note describes the composition and paragenesis of the material and suggests a modification of the definition.

Description

Bright green to blue-green concretionary and stalagmitic masses occur as individual and aggregate clusters up to 15-20 cm in diameter on gossan-like material. The iron gossan appears to have formed

from ore which dropped off trains as well as from weathering of slag fill. Clusters are most dense in the central portion of a railroad switching site where ore cars from mines to the northwest are shunted onto tracks to Sudbury. From the center of the site, cluster concentrations decrease to zero longitudinally within 25 m and laterally within 5 m. Sparser concentrations occur within track sets and between sets. The spacial limitation is not due to lack of adequate source material since the gossan-like material extends beyond the zone of accumulation.

Optical study of this material revealed the occasional presence of fine-grained disseminated silicate impurities in the sulphate. These iron-bearing silicate impurities did not yield a recognizable X-ray pattern because of their low concentration and amorphous nature.

The results of qualitative energy-dispersive spectra studies of the concretionary material are consistent with the identification from X-ray diffraction of $(\text{Fe},\text{Ni})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. The following elements were identified (with peak heights approximately normalized to S): S (100), Fe (75), P (25), Si (30), Ni (20), Al (15), Cu (5), K (tr), Ca (tr), Co (tr), Cr (tr). Since such intensities are only crude approximations of relative elemental abundances, spectra were also obtained for pure samples of hydrous iron and nickel sulphates. Assuming a linear relationship between metal/sulphur peak intensities and bulk composition, comparison of the spectra of the unknown sample with the pure end members yields a composition of 8 wt% nickel sulphate and 80 wt% iron sul-

phate. The lack of summation to 100% suggests that the intensity:composition relationship might not be linear, but instead might display a negative deviation. Evaluation of various slopes and consideration of analytical errors indicates a composition of 80–90% iron end members and 10–20% nickel end member.

The X-ray pattern of the slag matrix was identified as consisting mainly of a clinopyroxene-like phase. Energy-dispersive analysis of slag matrix material revealed the following elements (given with peak heights here approximately normalized to Si): Si(100), S(80), Fe(70), P(50), Al(45), Cl(30), K(15), Ca(10), Mg(5), Ni(tr), As(tr). The physical state of the phosphorus, probably added during smelting, could not be determined. The chlorine may be a residue from salts used to melt snow. Copper was not detected in the matrix, although the sulphate has an Fe–Cu energy dispersive intensity ratio of 15:1.

These data are consistent with the efflorescent bloom having formed from oxidative alteration and hydration of, and on, iron silicate slag in the intimate presence of Cu–Ni–Fe sulfide ore. Retgers as well as Wyrouboff (in Palache *et al.*, 1951, p. 517) reported that in experimental studies on Mg–Fe–Ni sulphate hydrates, “Fe substitutes for Mg up to at least Fe–Ni = 1:5.” The lack of such compositions in natural environments is due to the rarity of suitable protoliths for weathering. In this occurrence, the lack of Mg and the availability of Fe and Ni have produced this unusual solid solution.

Initially, the laboratory hydration–dehydration of the sulphate was readily reversible. However, after a few months of storage in a water-containing desiccator, the reversible reaction could no longer be demonstrated since the iron had oxidized and the sulphate was partially converted to limonite. Before this oxidation had started, the dehydrated material exhibited an X-ray diffraction pattern interpreted as due to a single phase similar to the tetrahydrate rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$). Thus, the conversion of this partial nickeliferous–ferrous solid solution suggests that a Ni tetrahydrate analogue to $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ may be possible. However, the natural occurrence of this as a pure phase has not yet been reported.

Discussion

Ehlers and Stiles (1965) conclude that the stability field of rozenite and melanterite is a simple function of temperature and relative humidity. Under drier conditions, the tetrahydrate is stable. The amount of Ni solid solution in the materials studied here is believed unlikely to have a pronounced effect on these

stability relations. Thus, it is unusual to observe the septahydrate in a mid-continental region of moderate humidity, where rozenite is more likely to form (see Jambor and Traill, 1963). On the other hand, a source for elevated relative humidity (and temperature to speed the reaction) is locally available. At the switching site, cooling motors discharge heated air laterally from the engines. Reaction with moderately humid air produces a steam which “weathers” the ore and slag rubble. This causative agent restricts the sulphate formation longitudinally and laterally along the right-of-way in the switching area. Thus, even though similar source material is available outside of the immediate area of bloom formation, the limited “artificial climate” localizes formation of the septahydrate. Further, in 1979 when the switching site was unused because of a labor strike, no bloom formation was observed.

The hydrated sulphate formed not as the result of man’s willful action, but as a by-product of or incidental to man’s direct and deliberate activities. The oft-quoted definition of Berry and Mason (1959, p. 3–4) notes that a mineral is “naturally occurring,” although exceptions are often made which tend to be largely dependent upon the degree of human *vs.* natural (non-human) activity involved. To accommodate anthropogenic phases, the following formalized redefinition is proposed: “a mineral . . . should have formed by natural processes which are not the result of man’s willful or deliberate actions . . .” Then, the nickeloan melanterite discussed herein is clearly not a synthetic analogue to a mineral, but is a mineral in the strict sense.

Note added in proof

By July 1980, the “outcrop” no longer exists, having been removed by bulldozing and the site covered with grass planted as part of a reforestation project.

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References

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