

Jamborite: A New Nickel Hydroxide Mineral From the Northern Apennines, Italy

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Abstract

Jamborite, $(\text{Ni}^{2+}, \text{Ni}^{3+}, \text{Co}, \text{Fe}^{2+}, \text{Fe}^{3+}) (\text{OH})_2 (\text{OH}, \text{S}, \text{H}_2\text{O})$, occurs as pseudomorphs after millerite in small cavities in ophiolites from three localities in the northern Apennines of Italy. The index of refraction for aggregates of microcrystals is about 1.60; for single lamellar microcrystals $n_e = 1.602 \pm 0.002$, $n_w = 1.607 \pm 0.002$. The specific gravity (obs) is 2.67. The mineral is insoluble in H_2O and only slowly soluble in cold dilute HCl. No carbonate or sulfate was detected. Analysis by electron microprobe gave (atomic wt percent) Ni 42.0-49.4, Co 1.9, Fe 0.9, S 3.5. Electron microprobe scans show a uniform distribution of sulfur in jamborite, indicating that the S content is not caused by included millerite. The X-ray powder pattern is similar to that for a synthetic nickel hydroxide (Glemser and Einerhand, 1950) and for some natural nickeliferous hydroxides and hydroxycarbonates. The cell parameters (hexagonal) are $a = 3.07 \text{ \AA}$ and $c = 23.3 \text{ \AA}$. The structure probably consists of positively-charged brucite-like layers $(\text{Ni}, \text{Co}, \text{Fe}) (\text{OH})_2$ in which Ni^{3+} partially replaces Ni^{2+} . The positive charge is balanced by an interlayer sheet containing OH^- and S^{2-} . The jamborite probably formed by low temperature hydrothermal alteration of millerite. The name is for John L. Jambor, mineralogist of the Geological Survey of Canada.

Introduction

A green mineral, here named jamborite, is associated with millerite (NiS) in small cavities in ophiolitic rocks near Bologna (Ca' de' ladri and Monteacuto Ragazza) and Modena (Castelluccio di Moscheda), northern Apennines, Italy. It occurs as a green coating on the walls of cavities lined by calcite, dolomite, and quartz crystals. At moderate magnifications, the coatings seem to consist of sheaves of transparent, single crystals (Fig. 1), pseudomorphous after millerite. The interior zones of some "crystals" contain unaltered millerite (Fig. 2). All gradations occur between pure millerite and jamborite.

Habit and Physical Properties

Under the microscope the green, apparently single crystals are seen to be aggregates of parallel fibers and lamellae. Some are bent and some are fractured perpendicularly (Fig. 2). There is considerable variety in the individual crystals. Lamellar or filiform ones show weak birefringence with parallel extinction. They are associated with isotropic microcrystal-line aggregates. For the latter, only the average index of refraction ($n = 1.60$) could be determined. The

birefringent lamellae are optically negative with $\epsilon = 1.602 \pm 0.002$ and $\omega = 1.607 \pm 0.002$ (Na light).

The specific gravity of jamborite for 2 milligrams of millerite-free material (suspension method) is $G_{\text{obs}} = 2.67$ and $G_{\text{calc}} = 2.69$.¹

Crystallography

The X-ray powder patterns from six samples of jamborite showed line broadening, but were sufficiently good to yield d -spacings, relative intensity values, and unit cell dimensions.

X-ray powder data are reported in Table 1 and are comparable with those for synthetic nickel hydroxide (Glemser and Einerhand, 1950); natural Ni hydroxide from British Columbia (Jambor and Boyle, 1964); nickeliferous magnesium hydroxide from Pennsylvania (Lapham, 1965); and reevesite from Wolf Creek (White, Henderson, and Mason, 1967). The d spacings and estimated intensities of all these materials are essentially similar; thus, the structures of these rather diverse compounds are closely related. The cell size of jamborite is closest

¹ The specific gravity calculated by us for the synthetic nickel hydroxide described by Glemser and Einerhand (1950) is 2.70.

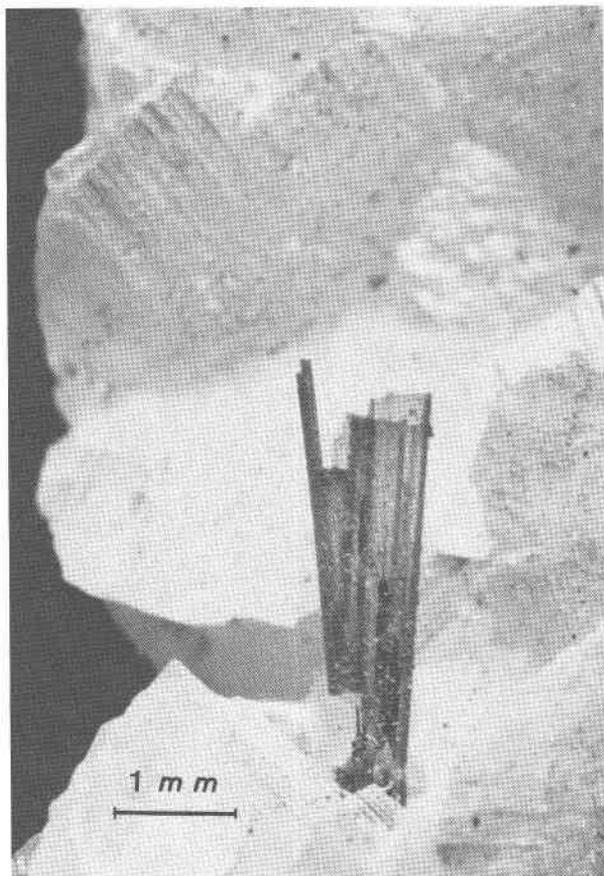


FIG. 1. Radiating aggregate of crystals of jaborite. White crystals are dolomite.

to the nickel hydroxide (II, III) of Glemser and Einerhand (1950).

An oscillation photograph obtained from an aggregate of lamellae oriented parallel to the oscillation axis yielded an ordinary powder photograph. Therefore the principal symmetry axis is not parallel to the elongation, and the refractive index perpendicular to the elongation is ϵ .

Chemical Composition

Qualitative, spectrophotometric analysis on a pure sample of jaborite shows Ni to be the main constituent, with minor amounts of Co and Fe. The amount of mineral collected was too small for either thermal analysis or conventional quantitative chemical analysis.

Jaborite is insoluble in water but slowly soluble in cold dilute HCl without any visible reaction. Addition of a few drops of barium chloride solution to the filtrate from this acid digestion does not produce

a white precipitate, and it is likely that acid-soluble sulfates are not present.

Electron microprobe (CAMECA) scans were made on jaborite and millerite. Fig. 3A shows an electron photomicrograph of one sample. The dark areas in the jaborite (I) are caused by cracks and cleavages. Figs. 3B, C, D are backscatter photographs showing the distributions of Ni, S and O in the millerite and surrounding jaborite. Ni is abundant in both millerite and jaborite, but is slightly more so in millerite (Fig. 3B). Sulfur occurs in both, but again is more abundant in millerite (Fig. 3C). The uniform distribution of sulfur in jaborite indicates that the S content is not caused by included millerite. Oxygen (Fig. 3D) occurs only in jaborite. Co and Fe occur in both jaborite and millerite but are more concentrated in jaborite.

Microprobe analysis of the millerite gives a composition close to that for ideal millerite. The millerite is very homogeneous.

The minor elements in jaborite are distributed fairly uniformly in the following percentages (atomic wt percent): 3.5 S, 1.9 Co, 0.9 Fe, < 0.2 Mg; Al and C not found. Ni is the only major metallic constituent; it ranges from 42.0 to 49.4 percent. At several points of incidence of the beam, the number of counts for oxygen during a fixed time varied inversely with the amount of Ni. The variable Ni content is common to the synthetic nickel hydroxide (II, III) of Glemser and Einerhand (1950) and the Italian jaborite.

Crystal Chemistry

A recently proposed structure may be a better representation than the one proposed by Glemser and Einerhand (1950). If we apply the structural scheme proposed by Brown and Gastuche (1967) for the synthetic Mg-Al hydroxycarbonates, jaborite can be considered to have a layer structure with layers 7.8 Å thick. The layers are composed of three sheets of anions. Two of these sheets of anions are close packed hydroxyls held together by octahedrally coordinated divalent and trivalent (Ni, Co, Fe) cations. The partial substitution of trivalent for divalent metal cations leads to a positive charge on this brucite-like layer. This is balanced by a third sheet of anions (OH^- , S^{2-}). An idealized structural formula is $(\text{Ni}, \text{Co}, \text{Fe})_{1-x}^{2+}(\text{Ni}, \text{Fe})_x^{3+}(\text{OH})_2[2(\text{OH}), \text{S}]_{0.5x}(1 - 0.5x)\text{H}_2\text{O}$.

This structural interpretation resolves some problems not satisfactorily explained by the Glemser and Einerhand model.

1) The variable Ni content is ascribed to different amounts of different states of oxidation of Ni. The presence of anionic S^{2-} in the structure is ascribed, moreover, to an incomplete oxidation of sulphur from primary millerite.

2) The cryptocrystalline and isotropic portions of the jamborite probably consist of stacking sequences of variably oxidized brucite-like layers and consequently of disordered arrangements of interlayer OH^- , S^{2-} , H_2O . Such material, characterized by weak interlayer bonds, would lack distinctive X-ray reflections. Moreover, line-broadening is characteristic of these materials (see Lapham, 1965) and further indicates an imperfect structure.

3) The more crystalline jamborite could be formed from slow oxidation and consequently more substitution of trivalent for divalent cations (Ni, Co, Fe). A more ordered stacking sequence of the brucite-like layers and sheets of anions would be obtained, with more distinctive X-ray reflections. The sheet of anions might contain small quantities of CO_3^{--} , SO_4^{--} or water molecules but this was impossible to verify.

4) The jamborite crystals are platy (Fig. 1) with the principal symmetry axis perpendicular to the lamellae, as would be expected for this structure and as has been reported (Jambor and Boyle, 1964; Lapham, 1965).

Related Compounds

The structural scheme shown by Brown and Gastuche (1967) also applies to some natural and synthetic materials such as minerals of the pyroaurite group, to the new nickeliferous magnesium hydroxide from Pennsylvania described by Lapham (1965), and to the synthetic compounds prepared by Glemser and Einerhand (1950). Jamborite is structurally similar to all these materials, including reevesite. However, with regard to chemical composition we can find close resemblance of the Italian specimens only with the synthetic nickel hydroxide of Glemser and Einerhand (1950) and with a natural Ni hydroxide from British Columbia (Jambor and Boyle, 1964). In addition, there are noticeable differences in the relative intensities of the X-ray reflections, perhaps indicative of compositional differences or differences in stacking of interlayer and layer packets. Therefore, the name 'jamborite' is intended to include the minerals both from Italy and from British Columbia.

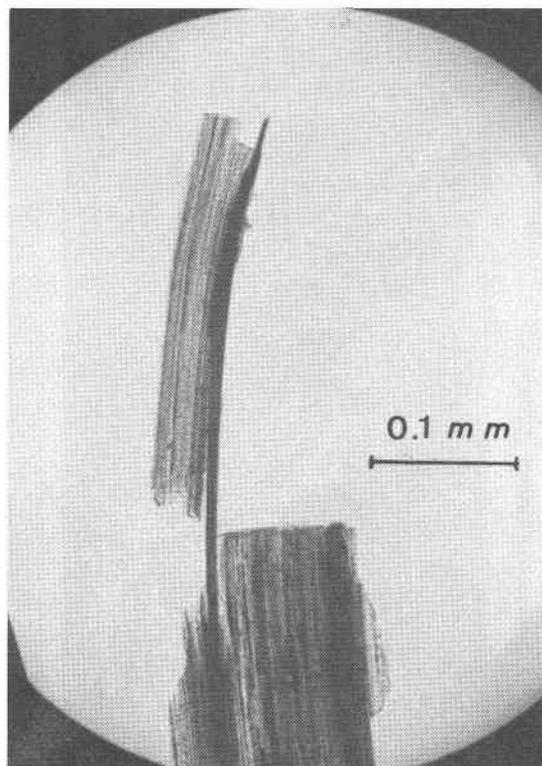


FIG. 2. Aggregate of fibrous and lamellar crystals of jamborite. Dark acicular crystal of the central zone is preserved millerite. Plane polarized light.

TABLE 1. X-Ray Patterns for Jamborite*

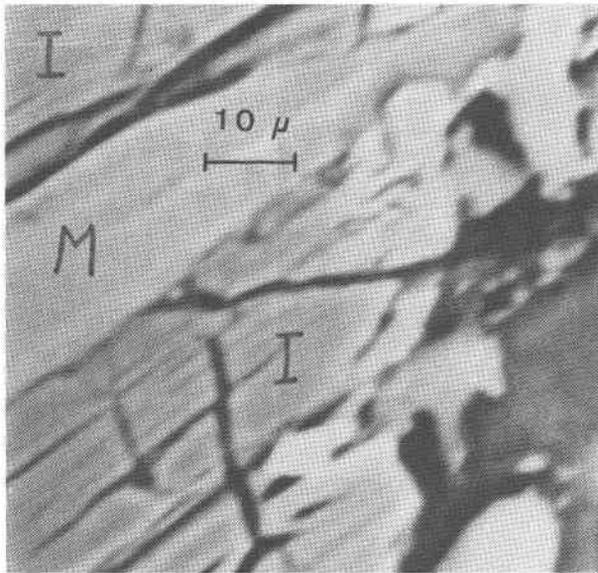
hkl	$d(\text{obs})$ Å	$d(\text{calc})$ Å	$I(\text{est})$
0003	7.78	7.78	10
0006	3.89	3.89	4
0112	2.592	2.592	6
$01\bar{1}5$	2.320	2.310	1
000.10			
$01\bar{1}8$	1.98	1.97	1/2
$11\bar{2}0$	1.530	1.535	5
$11\bar{2}1$			
$11\bar{2}3$	1.500	1.503	3
$11\bar{2}6$	1.42	1.43	1/2
2022	1.321	1.321	1
2025	1.28	1.28	1/2

* Values for d_{obs} and I_{est} represent averages from 6 samples. Indexing and d_{calc} are for a hexagonal cell: $a = 3.07\text{Å}$, $c = 23.3\text{Å}$. Filtered copper radiation and 57.3 mm diameter cameras.

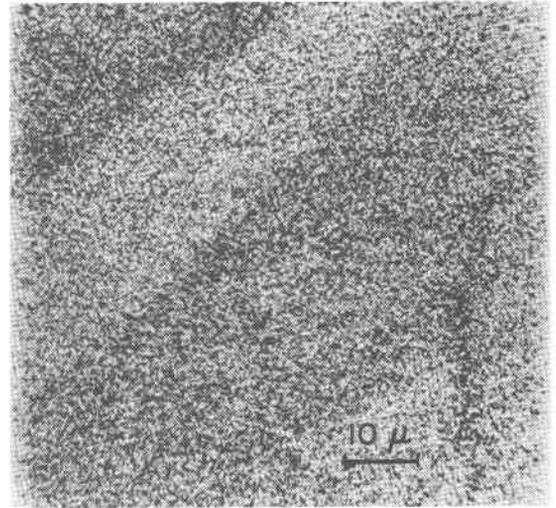
Genesis

Jamborite is pseudomorphous after millerite and is included within quartz and calcite in some places. Each aggregate of jamborite consists of microcrystalline individuals, either acicular or lamellar, and of crypto-crystalline or even isotropic patches that chiefly occur in the center of an aggregate. These facts indicate that it did not form by simple weathering

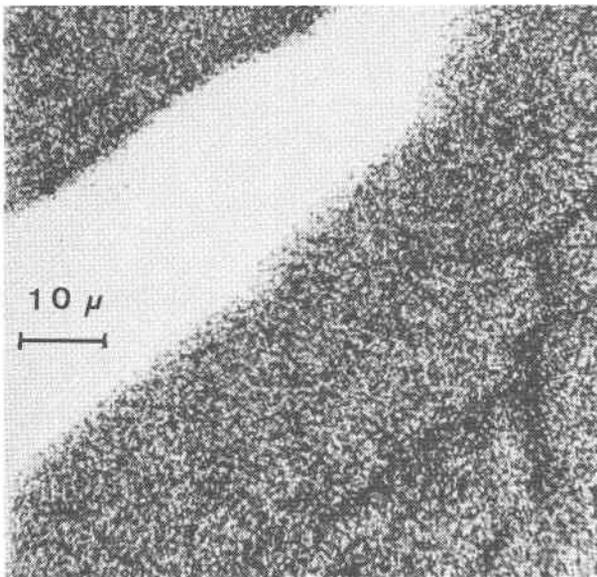
of millerite but by gradual, probably low-temperature, hydrothermal alteration. Millerite was formed in an early hydrothermal stage under reducing conditions. Later, more oxidizing alteration converted millerite into Ni hydroxide. The millerite underwent hydrolysis and then partial oxidation. The hydrolysis led to a partial replacement of S by OH, yielding an isotropic material whose remnants still



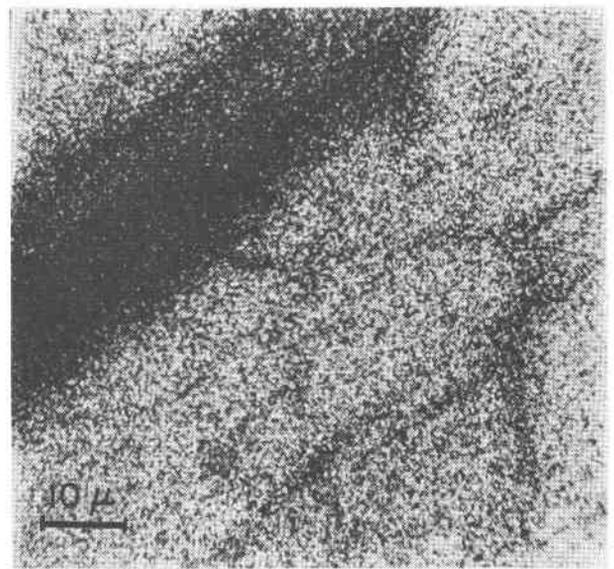
A



B



C



D

FIG. 3. Jamborite (I) associated with millerite (M). A. Electron photomicrograph. B, C, D. X-ray images. Light areas indicate presence of an elemental constituent: Ni in B, S in C, O in D.

can be seen within the crystalline jamborite. The more crystalline jamborite could have been produced by a slow oxidation inward from the surface, gradually producing an ordered crystalline structure.

The poor crystallinity of the new-formed mineral and the existence of various stages of millerite alteration indicate that one of the following occurred.

(1) The alteration occurred episodically or gradually; (2) the oxidation was not pervasive enough to produce well crystallized jamborite; (3) there was insufficient time in the oxidizing environment; (4) there was insufficient permeability for good ion mobility; or (5) the temperature was too low to permit a highly ordered arrangement.

The new mineral is named for John L. Jambor, mineralogist of the Geological Survey of Canada.

Type material is preserved at the University of Bologna, Italy.

The mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

Dr. Charles Milton (George Washington University) and Mr. R. B. Finkelman (U.S. Geological Survey) have informed us that they have found another occurrence of what may be jamborite. They have kindly permitted us to quote their unpublished data. The mineral occurs as an alteration product of capillary millerite in quartz-lined geodes from Hall's Gap, Kentucky. The mineral is pale green, $n \approx 1.58$ and has parallel extinction and positive elongation. Electron microprobe analyses show uniform distribution of Ni and S, but the quantities obtained are considered to be minimal because the mineral was

present in extremely thin plates. They found Ni 36.5, S 2.7, Fe ~ 1 , Co ~ 1 percent; carbon, although look for, was not found. X-ray powder diffraction, electron diffraction, and Gandolfi camera photographs showed only three diffuse lines at 7.75, 2.64 and 1.52 Å.

Acknowledgments

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