

Kambaldaite—a new hydrated Ni–Na carbonate mineral from Kambalda, Western Australia

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Abstract

Kambaldaite has the ideal composition $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$. It is hexagonal, space group $P6_3$, with $a = 10.340\text{\AA}$ and $c = 6.097\text{\AA}$; $Z = 1$. Strongest X-ray powder diffraction lines are: 9.03(10)(10 $\bar{1}$ 0), 4.490(9)(20 $\bar{2}$ 0), 3.613(4)(20 $\bar{2}$ 1), 2.681(4)(30 $\bar{3}$ 1), 2.584(4)(22 $\bar{4}$ 0), 2.519(4)(20 $\bar{2}$ 2) and 2.263(4)(21 $\bar{3}$ 2). The mineral occurs as needles and prismatic crystals elongated along c , as well as cryptocrystalline masses. Uniaxial positive, with $\omega = 1.65$ and $\epsilon = 1.69$. Kambaldaite is emerald green in color, with a pale green streak; in transmitted light it is dichroic with E = emerald green and O = light green. Measured density = 3.18 g/cm³; calculated density of the ideal formula = 3.193 g/cm³. Kambaldaite is a secondary mineral that has been precipitated on fracture surfaces in oxidizing Ni–Fe sulfide ore.

Introduction

The Kambalda nickel sulfide deposits, 56 km south of Kalgoorlie in Western Australia, have been the source of a number of secondary nickel minerals, including gaspéite, takovite, reevesite, pecoraite, morenosite, retgersite, nickelhexahydrite, nickelblöndite and hydrohonesite. The last two were discovered as new minerals at Kambalda (Nickel and Bridge, 1977; Nickel and Wildman, 1981).

This paper describes another new mineral from the locality. It was initially observed by Mr. David Vaughan of Perth, Western Australia, in material collected by Mr. R. Harrison of Kambalda, from the No. 1 ventilation shaft of the Otter Shoot, one of the Kambalda nickel mines. Mr. Vaughan brought samples containing the mineral to the laboratories of the Division of Mineralogy, CSIRO, for identification, where it was determined to be a new mineral.

The mineral was named kambaldaite in reference to the locality of its discovery, and both mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. The holotype specimen is retained in the mineral collection of the Division of Mineralogy, CSIRO, in Perth, Western Australia; cotype specimens have been lodged with the Government Chemical Laboratories of Western Australia, the Australian Museum in Sydney, the British Museum of Natural History in London, and the Smithsonian Institution in Washington, D.C.

Occurrence and morphological description

The mineralogy of the primary and supergene sulfide assemblages in the Otter Shoot has been described by

Keele and Nickel (1974). The primary sulfides, which occur as assemblages of pentlandite–pyrrhotite–pyrite and pentlandite–millerite–pyrite, have been altered to supergene assemblages consisting largely of violarite and pyrite, which have decomposed on further oxidation to a goethitic residue in which the secondary nickel minerals have been deposited.

The samples in which the kambaldaite was found are from a depth of about 20 meters, and consist largely of goethite with some reevesite and residual pyrite. The kambaldaite, together with gaspéite and some aragonite, occurs on fracture surfaces in the goethite. The kambaldaite occurs in a variety of types: massive, crystalline, nodular and chalky.

The massive kambaldaite occurs as cryptocrystalline veins, layers and concretionary growths up to about 2 mm thick, commonly intergrown with gaspéite. Although both minerals are green, they have different shades of this color, gaspéite having an olive-green cast compared to the more emerald-green shade of the kambaldaite.

The crystalline kambaldaite occurs as encrustations on the more massive kambaldaite and on gaspéite. The encrustations are bright grass green to emerald-green in color, and generally consist of tiny hexagonal prisms (Fig. 1a). Most of the prisms are terminated by basal pinacoids, and a few are zoned, with a clear core and a translucent marginal zone; when viewed end-on, such crystals have a striking “fish-eye” appearance. A few crystals are terminated by second-order pyramids (Fig. 1b), together with small pinacoidal faces. These faces commonly contain fine pits, which may represent the openings of tiny solution channels along the c axis.

The nodular kambaldaite occurs as partial spheres about 1 mm in diameter (Fig. 1c). Some of the nodules,

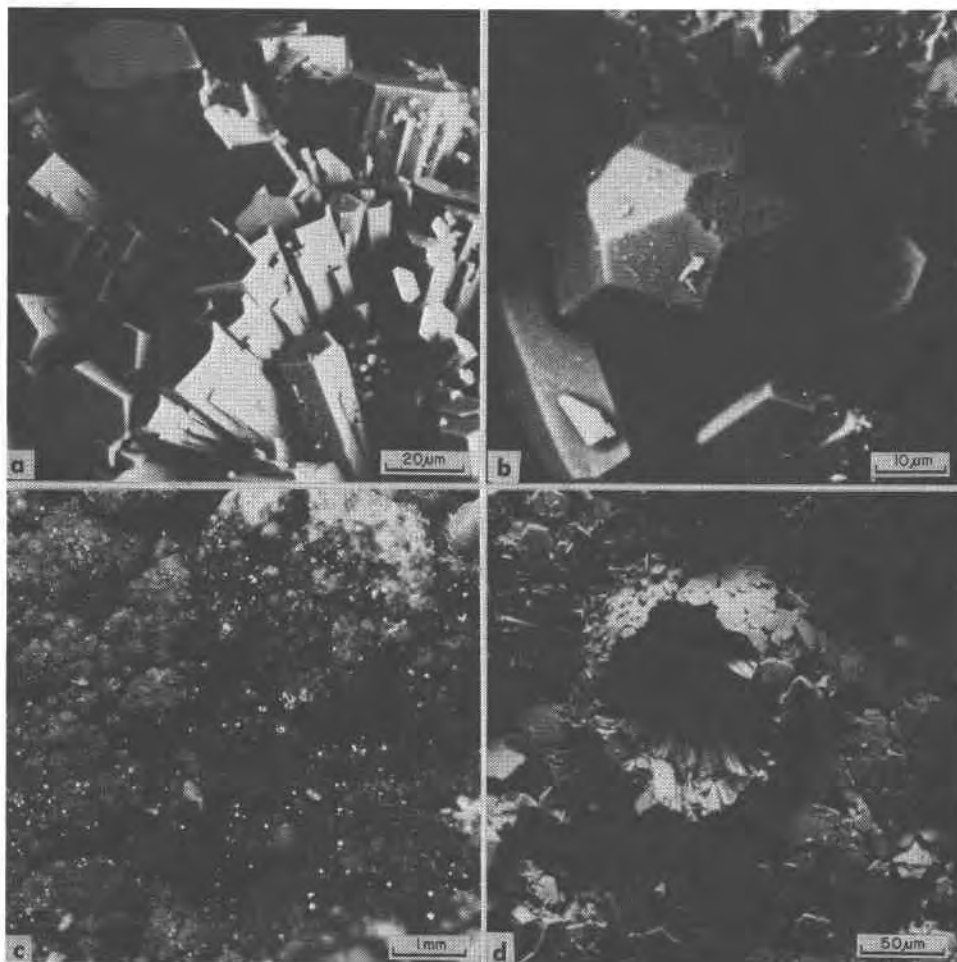


Fig. 1. (a) SEM micrograph of prismatic crystals; (b) SEM micrograph of a kambaldaite crystal with first order prism faces, second-order pyramid faces, and a pitted basal pinacoid; (c) Optical photograph showing sub-spherical nodules of kambaldaite. The white mineral is aragonite; (d) SEM micrograph of a broken sub-spherical nodule, showing that the spherical surface is composed of basal pinacoids of hexagonal prismatic crystals.

such as the ones shown in Figure 1c are very glossy and have a rich emerald-green color. When these spheres are broken, they are seen to consist of radiating hexagonal prisms, the pinacoidal faces of which comprise the spherical surfaces of the nodules (Fig. 1d). Other nodules, paler green in color, consist of fine radiating needles about 1 μm or less in diameter; when these nodules are broken open, they are pale green, with a silky luster.

The chalky kambaldaite consists of pale green pulverulent material which, at high magnifications under the scanning electron microscope (SEM), is seen to consist of masses of very fine acicular crystals up to ca. 10 μm long and up to 1 μm in diameter.

Composition

Crystals of kambaldaite were embedded in plastic resin, sectioned, polished, and then analyzed with an MAC electron microprobe analyzer operated at 15 kV,

and using an energy-dispersive procedure developed by N. G. Ware (Ware, 1981). Carbon and hydrogen were determined on a handpicked sample of massive kambaldaite by R. D. MacDonald of the Australian Microanalytical Service. The results of the analyses, converted to oxides, are shown in Table 1. The ideal composition of kambaldaite, $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$, is also given in Table 1.

The empirical formula for kambaldaite obtained from the analysis, using the measured density and unit-cell parameters (*vide infra*), and apportioning the H between OH^- and H_2O to preserve charge balance, is $\text{Na}_{1.05}(\text{Ni}_{7.81}\text{Mg}_{0.36})_{\Sigma=8.17}(\text{C}_{6.88}\text{Al}_{0.08}\text{Si}_{0.04}\text{S}_{0.03})_{\Sigma=7.03}\text{O}_{20.79}(\text{OH})_{3.97}5.67\text{H}_2\text{O}$. Ignoring the minor constituents, comparison with the ideal formula shows that Na and H_2O are lower, and C is higher. The low H_2O and high C values can be attributed to the presence of some gaspéite in the sample analyzed for H and C, since an X-ray powder

Table 1. Empirical and ideal composition of kambaldaite

| | Kambaldaite Wt % | $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$ Wt % |
|-------------------------|---------------------|----------------------------------------------------------------------------------------|
| Na_2O | 3.0 | 5.71 |
| NiO | 52.9 | 55.04 |
| MgO | 1.3 | — |
| CO_2 | 27.5 | 24.32 |
| Al_2O_3 | 0.4 | — |
| SiO_2 | 0.2 | — |
| SO_3 | 0.3 | — |
| H_2O | 12.5 | 14.93 |
| | 98.1 | 100.00 |

diffraction pattern of the analyzed concentrate contains the strongest gaspéite lines superimposed on the kambaldaite pattern. The low empirical Na content may be due to the loss of some of the Na under the electron beam during electron microprobe analysis, a phenomenon that has been reported by Autefage (1980), among others, and several microprobe experiments done on the kambaldaite support this suggestion. The apparent loss of Na is not surprising, since crystal-structure analysis (Engelhardt et al., 1985) has shown that the sodium ions, coordinated by water molecules, are located in relatively large c-axis channels, and can therefore be expected to be relatively mobile.

X-ray crystallography and physical properties

Single-crystal X-ray diffraction analysis of kambaldaite has shown that the mineral is hexagonal, with space group $P6_3$. The unit-cell parameters, obtained during the course of crystal-structure analysis (Engelhardt et al., 1985) are $a = 10.340(3)$ and $c = 6.097(2)\text{Å}$. The crystal-structure analysis showed that the structural formula is $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$, with $Z = 1$. The powder diffraction pattern, obtained with a Guinier camera, using thoria as internal standard, is given in Table 2.

Kambaldaite has a pale green streak. Its density, measured on single crystals by the sink-float method in heavy liquids, is 3.18 g/cm^3 . Calculated density of ideal $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$ is 3.193. The density calculated from the empirical composition, according to the Gladstone-Dale relationship, and using Mandarino's values for specific refractive energies of the oxide components (Mandarino, 1976) is 3.183. Hardness is approximately 3 on Mohs' scale. Cleavage is not discernible. The most common crystal form is a hexagonal prism with $\{10\bar{1}0\}$ and $\{0001\}$ terminations; less common are second-order pyramids, probably $\{11\bar{2}1\}$.

Kambaldaite is uniaxial positive, with refractive indices $\omega = 1.65$ and $\epsilon = 1.69$; prismatic crystals are therefore

length-slow. Kambaldaite is dichroic in transmitted light, with E = emerald green, and O = light green.

The mineral is not readily soluble in cold 1:1 HCl or 1:1 HNO_3 .

Discussion

A search of the mineralogical literature has failed to reveal any minerals with composition or structure similar to those of kambaldaite, and no mineral analogues have been discovered. Neither have close relatives been found in tabulations of inorganic substances. It therefore appears that kambaldaite is a unique mineral species with no known relatives.

The mineral occurs near the base of the oxide zone in the supergene weathering profile, where the activity of nickel species in solution is particularly high due to the dissolution of violarite. Carbonate and sodium activities must also have been high for kambaldaite to form. Carbonates are common in the wallrock and ore, and their dissolution should create a high level of carbonate activity. Although there are no appreciable amounts of

Table 2. X-ray powder diffraction pattern of kambaldaite

| I | hki | d obs. | d calc* |
|----|---------------|-----------|------------|
| 10 | 10 $\bar{1}0$ | 9.03 | 8.955 |
| 2 | 10 $\bar{1}1$ | 5.053 | 5.040 |
| 9 | 20 $\bar{2}0$ | 4.490 | 4.477 |
| 4 | 20 $\bar{2}1$ | 3.613 | 3.609 |
| 1 | 0002 | 3.049 | 3.048 |
| 2 | 3030 | 2.985 | 2.985 |
| 4 | 30 $\bar{3}1$ | 2.681 | 2.681 |
| 4 | 2240 | 2.584 | 2.585 |
| 4 | 20 $\bar{2}2$ | 2.519 | 2.520 |
| 2 | 1340 | 2.485 | 2.484 |
| 1 | 2241 | 2.380 | 2.380 |
| 1 | 3141 | 2.300 | 2.300 |
| 4 | 21 $\bar{3}2$ | 2.263 | 2.265 |
| 1 | 4040 | 2.237 | 2.239 |
| 1 | 4041 | 2.096 | 2.101 |
| 1 | 3250 | 2.053 | 2.054 |
| 3 | 2242 | 1.970 | 1.972 |
| 1 | {4150} | 1.948 | {1.954} |
| | {3251} | | {1.947} |
| 2 | 3142 | 1.924 | 1.925 |
| 1 | 1123 | 1.889 | 1.891 |
| 1 | 4151 | 1.857 | 1.861 |
| 3 | 4042 | 1.802 | 1.804 |
| 1 | 2133 | 1.739 | 1.742 |
| 1 | 3252 | 1.701 | 1.704 |
| 2 | 4260 | 1.690 | 1.692 |
| 1 | 5161 | 1.553 | 1.555 |
| 1 | {4043} | 1.500 | {1.505} |
| | {1014} | | {1.503} |
| 2 | 6060 | 1.489 | 1.492 |
| 3 | 4262 | 1.478 | 1.480 |
| 2 | 1124 | 1.459 | 1.462 |
| 2 | {3253} | 1.441 | {1.445} |
| | {2024} | | {1.443} |
| 1 | 6062 | 1.338 | 1.340 |
| 1 | 6171 | 1.330 | 1.333 |

Powder data obtained using
80 mm Guinier camera with
 $\text{CuK}\alpha$ radiation. ThO_2
internal standard.

$$* a = 10.340\text{Å}, c = 6.097\text{Å}$$

sodium minerals in the primary rock, the groundwater in the region is very saline, values of up to 5.9% Na having been reported (Nickel et al., 1974). This high sodium content is probably due to seepage from salt lakes in the vicinity. It therefore seems likely that kambaldaite owes its origin to an unusual combination of elements in the groundwater. Significantly, the only other secondary Na-Ni mineral found to date, namely nickelblödite (Nickel and Bridge, 1977) was also found at Kambalda.

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