

Eardleyite as a product of the supergene alteration of nickel sulfides in Western Australia¹

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Abstract

Eardleyite, a Ni-Al member of the pyroaurite group, has been found in the weathered crust overlying nickel sulfide deposits in four localities in Western Australia. Chemical analysis of material from the Perseverance deposit near Agnew indicates a composition corresponding to $\text{Ni}_{4.94}\text{Mg}_{0.10}\text{Ca}_{0.02}\text{Fe}_{0.13}\text{Al}_{2.81}(\text{CO}_3)_{2.27}(\text{OH})_{14.42} \cdot 5.42 \text{H}_2\text{O}$. Samples from other localities show a Ni-Al atomic ratio varying between 1.19 and 2.03, which is substantially below the 3:1 ratio expected in a pyroaurite-type mineral. The relatively high Al content is accompanied by a high carbonate content, which suggests a charge-balancing mechanism, as expressed by the general formula: $\text{Ni}_{6-x}\text{Al}_{2+x}(\text{OH})_{18-x-y}(\text{CO}_3)_{x+1/2y} \cdot n\text{H}_2\text{O}$. Thermal and mass spectrographic analyses indicate evolution of water at 260°C and of water and CO_2 at 370°C.

Introduction

The name "eardleyite" was given in an abstract by Anderson and Whelan (1962) to a mineral from Utah related to hydrotalcite and with a composition believed to be $(\text{Ni,Zn})_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. A description of the mineral is contained in an unpublished thesis (Anderson, 1959) in which it is referred to as "Mineral A", but the abstract cited above was all that was ever published. Nevertheless, the name eardleyite has been incorporated into mineralogical glossaries (e.g. Fleischer, 1975; Strunz,

1970; Hey, 1963), but no subsequent occurrences have heretofore been reported.

One reason for the apparent absence of other reports on eardleyite seems to be that the X-ray powder diffraction data for eardleyite are virtually identical to those of takovite, described as $\text{Ni}_5\text{Al}_4\text{O}_2(\text{OH})_{18} \cdot 6\text{H}_2\text{O}$ (Maksimovic, 1957). Since the X-ray data for takovite were published but those for eardleyite were not, subsequent occurrences of minerals giving that type of X-ray diffraction pattern (e.g. Bardossy and Mack, 1967; Coudray *et al.*, 1970) were identified as takovite, apparently without investigation for carbonate. Some of these occurrences may therefore actually have been of eardleyite.

Description of occurrences

Eardleyite has been found in four occurrences in Western Australia. All are in weathered near-surface

¹ Editor's note: This paper was in galley proof when the succeeding paper by David L. Bish and G. W. Brindley, describing the same mineral under the name takovite was being refereed. The nomenclatural problem was referred to the I.M.A. Commission on New Minerals and Mineral Names which has voted 12-3 to accept takovite and reject eardleyite as the name for this mineral.

material derived from nickel sulfide ore or from rock containing nickel sulfides. These occurrences are as follows:

- (1) Perseverance deposit, near Agnew; 27°49'S, 120°42'E;
- (2) Otter shoot, Kambalda; 31°10'S, 121°39'E;
- (3) Carr Boyd mine, Carr Boyd Rocks; 30°04'S, 121°37'E;
- (4) Dordie North deposit, 6 km southeast of Widgiemooltha; 31°32'S, 121°37'E.

In the Perseverance deposit, the eardleyite occurs as compact fracture fillings up to a millimeter thick in a silicified gossan between 20 and 23 meters below the surface, just above a thick layer of magnesite and about 10 meters above the present water table. The geological and mineralogical environment of this occurrence are discussed in detail by Nickel *et al.* (1976).

The other eardleyite occurrences have not been documented in equal detail. The samples were derived from a variety of sources, and their exact locations in the weathering profile were not recorded. In the Otter shoot and Dordie North deposits, eardleyite occurs in serpentinite as narrow fracture fillings and thin surface coatings. Associated minerals in the Otter shoot are glaukosphaerite (the nickel analogue of rosasite, described by Pryce and Just, 1974), paratacamite, nickeloan magnesite, gaspeite, gypsum and nepouite (the nickel analogue of lizardite). At Dordie North, the eardleyite is associated with glaukosphaerite, nickeloan magnesite, nickeloan glauconite, atacamite, paratacamite, malachite, azurite, chalcophyrite, and lithiophorite.

Eardleyite is abundant in the dumps from the glory hole at the Carr Boyd nickel mine, where it occurs mainly as millimeter-thick weathering crusts and joint fillings in gabbroic rock. The eardleyite has been deposited preferentially on aluminous minerals, particularly plagioclase, and to a lesser extent on prehnite and chlorite, leaving minerals such as actinolite virtually uncoated. The eardleyite also replaces feldspar; here, the eardleyite contains numerous tiny angular feldspar remnants and larger grains of unreplaced amphibole. Other associated minerals at Carr Boyd are glaukosphaerite, paratacamite, gypsum, brochantite, malachite, azurite, epsomite, nickeloan magnesite, chalconatronite, a new hydrated sulfate of nickel and aluminum, described elsewhere (Nickel and Clarke, 1976), and several minerals not yet identified.

Experimental procedure

Chemical analysis

Some eardleyite was scraped from the surface of one of the Perseverance samples, and from this about 100 mg of relatively pure material was hand-picked under a stereomicroscope. Three 10 mg portions of this material were heated with concentrated HCl, evaporated to dryness, taken up in 0.3 ml HCl, and made to 16.00 grams with distilled water. The undissolved residues were dissolved in 0.10 ml HF at room temperature, 5 ml of 5 percent boric acid was added to complex the HF, and they were made to 12.00 grams. Blanks were carried through all stages.

Portions of the solutions were taken for determining SiO₂ colorimetrically, and other oxides by atomic absorption. For determining NiO in the HCl fractions, weighed portions had to be diluted. All solutions and matching standards contained 2,000 ppm lanthanum to act as a radiation buffer and to minimize interferences. The instrument was a Varian Techtron AA-5 model, with digital indicator, and used in the integration mode. A nitrous oxide-acetylene flame was used for determining Al₂O₃ and CaO, and air-acetylene was used for the other oxides.

Carbon dioxide and water were determined on a 17 mg portion of the hand-picked sample. The sample was heated in a Pregl combustion train, and the evolved water was absorbed in a desiccant, and the CO₂ on an alkaline-based absorbent. Weight gains were determined gravimetrically. Details of the method are described by MacDonald (1974).

Electron-microprobe analyses were made of eardleyite samples from all four localities with the chief aim of determining the range of Ni:Al values. Elements were determined on an MAC instrument using crystal spectrometers and metal standards for Ni and Al. Corrections were made by the MAGIC IV computer program (Colby, 1971). Comparison of microprobe and wet-chemical analytical results on the same sample showed that the microprobe results were virtually identical for NiO and 4.5 percent higher for Al₂O₃.

X-ray diffraction

Room-temperature X-ray powder diffraction patterns were obtained by means of 57.3 and 114.6 mm Debye-Scherrer diffraction cameras using Ni-filtered Cu radiation. The principal diffraction lines were indexed according to the scheme proposed for hydro-talcite by Allmann (1968a), and unit-cell parameters

were calculated from the indexed pattern by a computer program adapted from "CELFIT", a cell-parameter refinement program developed by B. H. Bracher of the Atomic Energy Research Establishment, Harwell, England.

High-temperature diffraction patterns were obtained by means of an Enraf-Nonius Guinier-type camera in a normal laboratory atmosphere. Temperatures were increased in increments of 50°C, and held constant while each pattern was being recorded.

Thermal analysis

Thermogravimetry (TG) and Evolved-Gas Analysis (EGA) were carried out with a Stanton Thermobalance, model TR1, coupled to an EAI Quad 160 quadrupole mass spectrometer. Details of this system have been given by Kennedy and Twaddle (1975).

Differential Scanning Calorimetry (DSC) results were obtained with the DuPont 990 thermal analyzer system fitted with a DSC cell. In a typical DSC run, about 5 mg of the sample was weighed into an open aluminum sample pan and placed in the DSC cell. An open empty aluminum pan was used for reference purposes. The DSC cell was closed, and purged with nitrogen flowing at 200 cm³/min. The time base was set at 5 min/in, the Y¹ range scale to 1.0, and the Y scale to 100°C/in. Starting at 30°C, the sample was heated at 10°C/min to 550°C. A dynamic nitrogen atmosphere was maintained throughout the program.

TG results were obtained on 25 mg samples, contained in an open silica pan. The nitrogen flow rate was 200 cm³/min, the heating rate 10°C/min, and the temperature range 30–550°C. The exit-gas flow was monitored at 30-second intervals with the mass spectrometer during thermal events.

Infrared spectroscopy

The infrared absorption spectrum was obtained by Dr. L. H. Little of the Department of Chemistry, University of Western Australia, using a Perkin-Elmer model 521 infrared spectrophotometer equipped with an RIIC beam condenser. The sample was molded into a micropellet with KBr.

Synthesis

Eardleyite and related compounds were synthesized in the following way: Mixtures of nickel and aluminum sulfates, in different proportions, were added to stirred sodium bicarbonate and hydroxide solutions. The precipitates were filtered and washed to remove any free sulfates. X-ray examination

showed the precipitates to be poorly crystallized compounds with diffraction patterns similar to those of the pyroaurite type. Chemical analyses gave the cation ratios and confirmed the absence of sodium salts as residues in the precipitates.

The precipitates were then reacted hydrothermally with NaHCO₃-Na₂CO₃ solutions in gold capsules in small bombs, at 200°C and 15,000 psi for three weeks. This resulted in well-crystallized products, some of which gave X-ray diffraction patterns identical to the best naturally-occurring eardleyite specimens. Evolved-gas analysis of a sample giving the eardleyite diffraction pattern showed the evolution of CO₂, thereby confirming that the synthetic product contained this component.

Results of X-ray diffraction analysis

The X-ray powder diffraction data for the eardleyite from Perseverance, Western Australia, are given in Table 1, together with data for the Utah eardleyite, takovite, and reevesite. Since individual crystallites are much too small for single-crystal X-ray diffraction analysis, the powder data have been indexed using the indexing generally accepted for members of the pyroaurite group, and cell dimensions of the corresponding hexagonal unit cell were calculated. The cell parameters obtained are $a = 3.018 \text{ \AA}$ and $c = 22.58 \text{ \AA}$. Two weak lines in the pattern (4.47 Å and 3.935 Å) are close to possible superlattice positions, but indexing on this assumption gives poorer agreement for the rest of the lines. They could not be attributed to any known impurity, and lacking single-crystal diffraction data, it is not known whether these lines are essential to the eardleyite powder pattern.

The X-ray powder diffraction data for the type eardleyite from Utah, obtained from a sample kindly provided by Professor J. A. Whelan, show good agreement with the data obtained from the Australian sample except for several extra lines that can be attributed to a calcite impurity. Both sets of data are in excellent agreement with those of takovite (Maksimovic, 1957). The X-ray diffraction pattern of reevesite, by contrast, has appreciably larger d -values for equivalent lines, indicating larger cell parameters.

Chemical composition

The results of the chemical analysis of the Perseverance eardleyite are given in Table 2. Also included are the results of one of the spectrographic analyses made on the Utah eardleyite by Anderson (1959). Anderson's analyses of various samples dif-

TABLE 1. X-ray powder diffraction data for eardleyite, takovite, and reevesite

hkl	Eardleyite, Perseverance, W.A.			Eardleyite, Oquirrh Mtns., Utah		Takovite, Takova. (Maksimovic, 1957)		Reevesite, Australia (White <i>et al.</i> , 1967)	
	d** (calc.)	d (obs.)	I (est.)	d (obs.)	I (est.)	d (obs.)	I	d (obs.)	I
0 0 3	7.53	7.52 4.47 3.935	10 1B 1	7.42 4.52 4.14	10 1B 1	7.566 — —	10 — —	7.63 — —	100 — —
0 0 6	3.763	3.770	8	3.778 3.062*	8 8	3.767	9	3.80	73
1 0 1	2.596	2.602	1	—	—	2.603	4	2.82 2.65	12 6
1 0 2	2.546	2.552	8	2.559 2.490*	9 1	2.552	9	2.60	81
1 0 4	2.372	2.375	2	2.375	1	2.375	5B	2.47 2.41	28 17
1 0 5	2.262	2.263	7	2.271 2.099*	8 2	2.264	8	2.30	61
1 0 7	2.031	2.028	1	—	—	2.031	2	2.06	8
1 0 8	1.918	1.916	7	1.918	6	1.917	9	1.946	48
0 0 12	1.882	1.873	1	1.873	3	—	—	1.924	6
1 0 10	1.709	1.709	3	1.706	3	1.708	7B	1.731	20
1 0 11	1.614	1.613	2	1.613	3B	1.613	6B	1.635 1.623	15 15
1 1 0	1.509	1.510	5	1.514	5	1.510	8	1.537	33
1 1 3	1.479	1.480	5	1.481	4	1.481	8	1.508 1.477	34 4
1 1 6	1.400	1.402 1.446	2 1	1.403 1.444	2 1	1.401	3vB	1.463 1.426	5 6
1 1 7	1.367	1.372	1	—	—	1.373	6	1.389 1.378	2 3
2 0 2	1.298	1.299	2B	1.300	2	—	—	1.325	4
2 0 5	1.255	1.258	2	1.258	2	1.256	5	1.280	6
2 0 6	1.234	1.240	2	1.239	2	1.241	1B	1.257	1
2 0 8	1.186	1.186	2B	1.181	2B	1.183	4B	1.236 1.208	1 1

* Calcite lines.

** Calculated on hexagonal unit cell, $a_0 = 3.018$, $c_0 = 22.58A$.

ferred considerably, presumably because of different contaminating minerals; the analysis shown in Table 2 was chosen for presentation here because it has the highest nickel content and is therefore probably the least contaminated. The analysis of the Utah eardleyite shows much higher Ca and Zn than the Perseverance sample. Anderson (1959) attributed the calcium to admixed calcite, but assumed that the zinc comprised an essential part of the mineral.

Both eardleyite analyses report substantial amounts of Si, an element that has no place in a pyroaurite-type formulation. Because of the wide variations in silica content of the Utah material, Anderson (1959) attributed its presence to impurities. In the Perseverance material, too, the silica content shows wide fluctuations, probe analyses giving SiO₂ analyses throughout the range from 4.8 to 16.6 percent SiO₂. Probe analyses of eardleyite from the other Western Australian deposits extend the range down-

ward to 1.0 percent. Since no silicate impurities were detected in any of the samples by X-ray diffraction analysis, it is assumed that the silica is due to admixed amorphous material, possibly silica itself. This is a reasonable assumption, since siliceous plates and flakes are a common impurity in layered minerals (Faust *et al.*, 1973). The analysis of the Perseverance material shown in Table 2 has therefore been recalculated to 100 percent on this assumption.

Dr. Charles Milton (personal communication) has suggested that the SiO₂ may be due to X-ray amorphous allophane or halloysite, thereby also accounting for the high Al₂O₃ content compared with the theoretical formula (Table 2). This is rather difficult to establish with any degree of certainty, but plotting Si against Al for the sixteen probe analyses done on Australian eardleyites failed to show an appreciable degree of correlation, as might be expected if the impurity were an aluminosilicate.

Attempts were also made to isolate an insoluble residue by selective chemical attack. In the most indicative test, the sample whose analysis is shown in Table 2 was subjected to 1M HCl attack at 60°C for two days. This left a small amount of residue which, upon analysis, was found to comprise 3.08 SiO₂, 2.26 Al₂O₃, 1.93 NiO, and 0.59 Fe₂O₃ (the figures represent percentages of the original sample). In terms of molecular ratios, these values are 100:43.2:50.4:7.2, respectively. The SiO₂:Al₂O₃ ratio is approximately what might be expected from allophane, but the relatively high nickel content, if attributed to unreacted eardleyite, suggests that about one-third of the alumina in the residue is due to eardleyite. If the remainder of the alumina in the residue (about 1.5% Al₂O₃) is attributed to allophane, this would leave about one-third of the silica in the residue unaccounted for, as well as the silica that appears to have gone into solution. It is therefore highly unlikely that all the silica is due to allophane.

Because of these uncertainties, and the difficulty of resolving them with any degree of confidence, it will be assumed that all the SiO₂ is due to silica, and all the Al₂O₃ is due to eardleyite. As will be shown later, the high CO₂ content relative to the theoretical formula may well correlate with the anomalously high Al₂O₃ content. Even so, the possibility that at least some of the "excess" alumina is due to impurities cannot be entirely dismissed.

In the lower part of Table 2 are given the atomic proportions in the Australian and Utah eardleyites, calculated on the basis of 8 cations, in conformity with the hydrotalcite formula, Mg₆Al₂(OH)₁₆CO₃·4H₂O. The water in the Australian eardleyite has been distributed between OH and H₂O so as to balance the ionic charges.

The atomic Ni:Al ratio for the Perserverance eardleyite is 1.75:1, which is substantially below the ratio of 3:1 expected from a pyroaurite-related mineral. Even when the other metals possibly substituting for nickel (Zn, Mg, Ca, and Fe) are added to nickel, the ratio is increased only to 1.84.

Electron microprobe analyses of eardleyite from the Carr Boyd and Dordie North samples have quite divergent Ni:Al ratios ranging between 1.19 and 2.03. The synthetic product that gave an eardleyite X-ray diffraction pattern with no extraneous lines had Ni:Al = 1.45; preparations with Ni:Al ratios of 1.65 and higher gave mixed patterns of eardleyite and gaspeite.

These observations all point to the fact that eardleyite can have a wide range of Ni and Al values, but

TABLE 2. Chemical analysis of eardleyite

Perserverance, Western Australia		Oquirrh Mtns., Utah. (Anderson, 1959)*		Theoretical Ni ₆ Al ₂ (OH) ₁₆ CO ₃ ·4H ₂ O
Wt. %	Recalc. to 100% (less SiO ₂)	Wt. %	Wt. %	Wt. %
NiO	41.15	43.12	43.3	55.31
ZnO	0.03	0.03	22.4	-
MgO	0.45	0.47	0.2	-
CaO	0.11	0.12	14.0	-
Fe ₂ O ₃	1.16	1.22	1.0	-
Al ₂ O ₃	16.0	16.77	19.6	12.58
SiO ₂	6.2	-	4.3 - 17.1	-
CO ₂	11.14	11.67	-	5.43
H ₂ O	25.38	26.60	-	26.68
	101.62	100.00		100.00

Atomic Proportions					
Ni	4.936	} 8.00	3.072	} 8.00	6.000
Zn	0.003		1.461		-
Mg	0.100		0.022		-
Ca	0.018		1.324		-
Fe	0.130		0.076		-
Al	2.813		2.045		2.000
CO ₃	2.268			1.000	
OH	14.42				16.000
H ₂ O	5.42				4.000

* Recalculated as oxides from semi-quantitative spectrographic analysis for elements in Sample X.

that the Ni:Al ratio consistently falls below the expected 3:1 ratio. The implications of this for the generalized formula of eardleyite will be taken up more fully in the Discussion.

Optical and physical properties

Eardleyite varies in color from yellowish green (10GY 7/4; Munsell system) to pale bluish green (2.5BG 7/4). Birefringence is low to moderate, with $\epsilon = 1.600$ and ω slightly higher. The largest flakes give uniaxial negative interference figures.

The specific gravity of the Perserverance eardleyite, measured by the sink-float method in mixtures of bromoform and benzene, is 2.798. The calculated value, 2.947, is appreciably higher. The discrepancy is probably due to admixture of amorphous silica.

Eardleyite, if a member of the pyroaurite group, should have perfect basal cleavage. Because of the small size of the crystallites, and their generally felted intergrowth, it was not possible to determine if such cleavage exists.

The infrared spectrum of eardleyite (Fig. 1) shows a broad peak at 3400 cm⁻¹ that can be attributed to the H₂O stretching frequency, and which presumably swamps any OH vibrations that might be present. The weaker H₂O bending frequency is centered at about 1600 cm⁻¹, while a strong CO₃ absorption is in

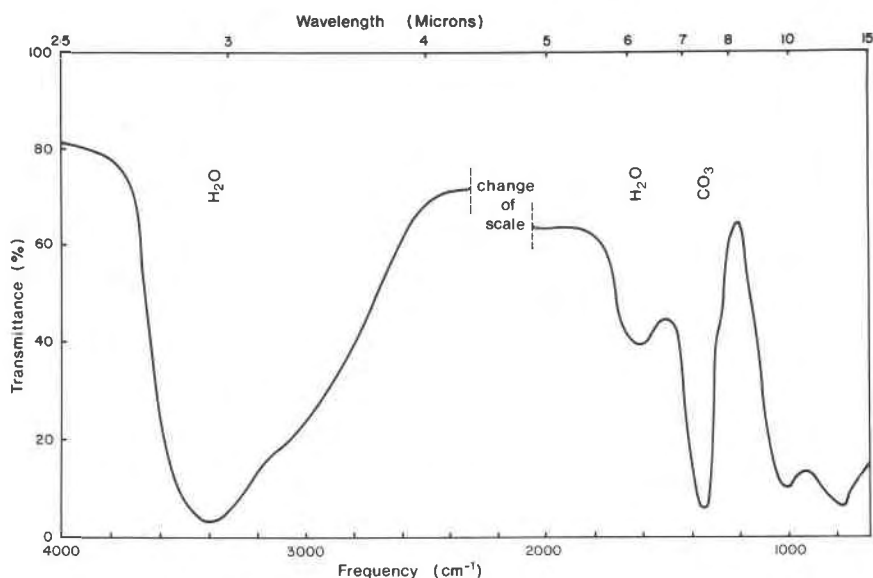


FIG. 1. Infrared absorption spectrum of eardleyite from the Perseverance deposit, Western Australia.

evidence at 1350 cm^{-1} . This carbonate band is at a slightly lower frequency than those exhibited by most hydrated carbonates of the transition metals (White, 1974). Absorption bands at lower frequencies are probably due to various cation-OH vibrations. On the whole, the IR spectrum is quite similar to that given by Anderson (1959), except for a relatively weak feature at 1270 cm^{-1} (Table 3), which is probably due to sulfate. IR spectra of eardleyite from the other Western Australian occurrences, namely Otter shoot, Carr Boyd mine, and Dordie North deposit, are also similar to the one obtained from the Perseverance sample.

The IR spectrum of takovite from Takova (Maksimovic, 1970) lacks the absorption band due to carbonate (Table 3), which indicates rather conclusively that takovite lacks this constituent.

Thermogravimetric and differential-thermal analy-

ses show substantial weight losses and endothermic effects peaking at 260°C and 370°C (Figs. 2a,b). The eardleyite from Utah and the takovite from Takova also give two endothermic peaks, although at slightly different temperatures (Table 3).

Quadrupole mass spectrographic analysis of the gases evolved during the thermogravimetric analyses show that water and CO_2 are evolved. Water evolution occurs at two temperatures, 280°C and 390°C , the latter coinciding approximately with the CO_2 evolution at 380°C (Figs. 2c,d).

High-temperature X-ray diffraction patterns of eardleyite show that at the first thermal event, recorded at about 150°C , the structure changes to one with a basal spacing of 6.7 \AA . After the second event, recorded between 250 and 300°C , the pattern disappears entirely, indicating disruption of the structure. The X-ray temperatures are substantially below the endothermic peaks charted by the DTA and TGA experiments, and probably represent the actual transformation temperatures more accurately, since the temperatures were held constant for several hours during exposure of the film, in contrast to the DTA and TGA runs which were made at continuously increasing temperature. The onset of the endothermic effect is, of course, a more accurate measure of the temperature.

Discussion

Structural formula

The close similarity of the X-ray diffraction patterns of eardleyite, takovite, and reevesite sug-

TABLE 3. Comparison of infrared and thermal analyses on eardleyite and takovite

	Eardleyite, Perseverance, W.A.	Eardleyite, Oquirrh Mtns., Utah	Takovite, Takova, Serbia
DTA	260°C 370	300°C 410	$160\text{--}250^\circ\text{C}$ $350\text{--}415$
IR	3400 cm^{-1} — 1600 1350 — 1000	3400 cm^{-1} — 1610 1350 1270 1000	3510 cm^{-1} 2330 1640 — 1240 1020
References	This paper	Anderson, (1959)	Maksimovic, (1970)

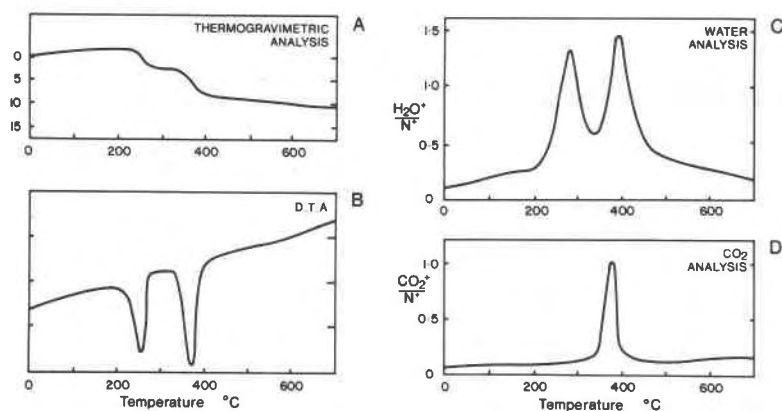


FIG. 2. Results of thermal analyses of eardleyite from Perseverance, Western Australia. (a) Thermogravimetric analysis, made on a 46.2 mg sample. (b) Differential thermal analysis of eardleyite from the same sample shown in (a). (c) Quadrupole mass spectrographic analysis of water evolved during the thermogravimetric analysis shown in (a). (d) Quadrupole mass spectrographic analysis of CO_2 evolved during the same thermogravimetric analysis.

gests that they have similar structures. Since reevesite is a member of the pyroaurite group (White *et al.*, 1967) which is characterized by the formula $\text{A}_6^{2+}\text{B}_3^{3+}(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, the other two minerals also belong to this group, or are closely related to it. The apparent absence of carbonate in takovite seems to be anomalous, but it is conceivable that $2(\text{OH})^-$ ions could substitute for CO_3^{2-} , as has been suggested for meixnerite (Koritnig and Süsse, 1975).

The structure of pyroaurite is regarded as consisting of positively-charged brucite layers of composition $[\text{Mg}_6^{2+}\text{Fe}_3^{3+}(\text{OH})_{16}]^{2+}$ alternating with negatively-charged interlayers $[\text{CO}_3 \cdot 4\text{H}_2\text{O}]^{2-}$ (Allmann, 1968b). If an analogous structure is assumed for eardleyite, then the ideal eardleyite formula should be $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. However, analyses of naturally-occurring eardleyite show less Ni and OH, but more Al and CO_3 . This suggests that some of the Ni^{2+} is replaced by Al^{3+} , and that charge balance is maintained by substitution of CO_3^{2-} for OH^- or H_2O . There are various structural possibilities for incorporating the carbonate ions: (a) they could be accommodated in the interlayer part of the structure, displacing some of the water if necessary; in this case each extra CO_3^{2-} ion would balance the substitution of two Ni^{2+} by two Al^{3+} ions; (b) they could be accommodated in the brucite layer, with one of their three oxygens occupying the structural position of an OH^- ion and the other two projecting into the interlayer region; in this case such a CO_3^{2-} ion would balance the substitution of one Ni^{2+} by one Al^{3+} ion; or (c) they could be accommodated in the brucite layer in such a way that two of the three carbonate

oxygens replace two OH^- ions, leaving the third to project into the interlayer region; in this case there would be no charge-balancing effect since the net result would be to have two OH^- ions replaced by one CO_3^{2-} ion. Possibility (c) does not have a charge-balancing effect, but it does provide a mechanism for additional substitution of OH^- by CO_3^{2-} , thereby accounting for an apparent excess of CO_3^{2-} in the Perseverance eardleyite.

The thermal and associated mass-spectrographic analyses show that the volatiles in naturally-occurring eardleyite are expelled at two different temperatures. The lower temperature (260°C) probably represents the loss of the interlayer water, and it is of interest to note that there is no evidence of CO_2 being liberated at that stage. The carbonate all appears to be released at the higher temperature (370°C) which presumably represents the decomposition of the brucite layer. This suggests that the carbonate ions are restricted to the brucite layer, as replacements for OH^- . On the other hand, the synthetic eardleyite gives up a small proportion of its CO_2 at the lower temperature, indicating the presence of some interlayer carbonate as well.

The results of the high-temperature diffraction experiments show that heating above about 200°C causes the structure to collapse, not to the brucite basal spacing of 4.7 \AA , but to the larger spacing of 6.7 \AA . This suggests that the brucite layers continue to be held apart, although to a reduced extent, even after loss of the interlayer water. This function can be attributed to the carbonate ions attached to, and presumably extending out from, the brucite layers.

Since the evidence supports the substitution of OH^- by CO_3^{2-} in the brucite layer, the composition of eardleyite can be expressed in a general formula applying to the pyroaurite-related hydroxy-carbonates as follows: $\text{Ni}_{6-x}\text{Al}_{2+x}(\text{OH})_{18-x-y}(\text{CO}_3)_{x+1/2y} \cdot n\text{H}_2\text{O}$.

In this formulation, x accounts for the Ni-Al substitution and the charge-balancing effect of CO_3^{2-} replacing OH^- , according to possibility (b), above; y represents replacement of 2OH^- by one CO_3^{2-} , with no charge-balancing effect, as in possibility (c).

If $x = 0$ and $y = 2$, we get $\text{Ni}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot n\text{H}_2\text{O}$, which is analogous to pyroaurite.

If $x = 0$ and $y = 0$, we get $\text{Ni}_6\text{Al}_2(\text{OH})_{18} \cdot n\text{H}_2\text{O}$, which is analogous to meixnerite.

If $x = 1$ and $y = 2.58$, we get $\text{Ni}_5\text{Al}_3(\text{OH})_{14.42}(\text{CO}_3)_{2.29} \cdot n\text{H}_2\text{O}$, which corresponds to the formula of the Perseverance eardleyite.

The published composition of takovite (Maksimovic, 1957, 1970) does not fit into this formulation because it has a relatively low Ni:Al ratio (5:4), but apparently no charge-balancing carbonate. However, this discrepancy could be due to a high alumina analysis due to the presence of allophane in the analyzed material. Maksimovic reported that the takovite occurs with allophane, but ascribed all of the 10.5 percent SiO_2 in the analysis to the presence of quartz.

Conditions of formation of eardleyite

Eardleyite is clearly a secondary mineral, precipitated from surface waters at ambient temperatures.

High pH appears to be a prerequisite for its formation, since it tends to be found in association with other carbonate minerals, indicating a pH on the high side of neutrality. The laboratory experiments also showed that the eardleyite precursor phase (recrystallizes to give eardleyite) can easily be precipitated from acid sulfate solutions by the addition of NaOH. It may be speculated that the composition is controlled by the activity of carbonate species in solution. If the carbonate-ion activity is high, the mineral might contain more carbonate and, in consequence, have a higher Al:Ni ratio than when the carbonate-ion activity is low.

In nature, both nickel and aluminum can be carried in solution if the pH is sufficiently low; increasing pH, such as contact with carbonates, can be expected to cause eardleyite to precipitate. On the other hand, if the pH of the groundwater solutions is too high to maintain Al^{3+} in solution, yet low enough to retain Ni^{2+} , then the nickel-bearing solutions will tend to react with aluminous minerals with which they come into contact. This explains why, in the Carr Boyd

samples, aluminous minerals are preferentially coated, or replaced, by eardleyite.

If the composition of eardleyite is indeed controlled by carbonate-ion activity, the stability relationships between eardleyite and takovite need to be clarified. Since takovite appears to be carbonate-free, a particularly low carbonate-ion activity might be suspected, and consequently a high Ni:Al ratio. However, Maksimovic (1970) reports that takovite is always found associated with limestone, and the analyses indicate a particularly low Ni:Al ratio (1.25:1). Clearly, more work needs to be done on the interesting relationship between the two minerals.

Distinguishing features

The X-ray diffraction patterns of eardleyite and takovite are virtually indistinguishable, and both are quite similar to jaborite, a hydrated sulfate of nickel (Morandi and Dalrio, 1973) that can probably also be assigned to the pyroaurite group (C. Milton, personal communication). From published reports, all three minerals have a similar green color, and their refractive indices are all in the near neighbourhood of 1.60. Optical properties and X-ray diffraction analysis alone are therefore not sufficient to enable a distinction to be made. Electron microprobe analyses will distinguish jaborite from the other two because of its lack of aluminum, but will not serve to discriminate between eardleyite and takovite. For this to be done, it appears to be necessary to determine the presence of carbonate, either directly by analysis, or indirectly by infrared spectroscopy.

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