

## Brindleyite, a nickel-rich aluminous serpentine mineral analogous to berthierine

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### Abstract

The nickel-rich aluminous serpentine mineral originally called nimesite has been renamed brindleyite in honor of Professor G. W. Brindley. Brindleyite is a green clay-like mineral occurring adjacent to the footwall limestone at the base of the Marmara karstic bauxite deposits in Greece.

The new mineral is closely related in structure and stacking sequence to berthierine; it occurs as mixtures of the group A and group C polytypes of Bailey (1969). Spectroscopic data indicate that both natural and synthetic samples have a disordered cation arrangement. As expected, the green color of the mineral is due to octahedrally-coordinated Ni<sup>2+</sup> ions. The structural formulae of brindleyites approximate to (Ni<sub>1.75</sub>Al<sub>1.0</sub>) (Si<sub>1.5</sub>Al<sub>0.5</sub>)O<sub>6</sub>(OH)<sub>4</sub>, and all analyzed samples showed a deficit in octahedral cations. Brindleyites exhibit a two-stage dehydroxylation process similar to that shown by amesite and other serpentine minerals.

### Introduction

A green clay-like material rich in nickel was discovered by Weisse (1967) in the Marmara bauxite deposit in Greece. Maksimovic later (1972) determined this mineral to be a new aluminous member of the serpentine group and proposed the name nimesite (Ni-amesite) for it. The I.M.A. Commission on New Minerals and Mineral Names subsequently did not accept the name because of its similarity to nimitite, a nickel chlorite.

This paper presents a detailed description of the new mineral, which the first author has renamed brindleyite in honor of Dr. George W. Brindley, Professor Emeritus of Mineral Sciences at The Pennsylvania State University. This name has been approved by the I.M.A. Commission on New Minerals and Mineral Names.

### Occurrence and paragenesis

The geological position and a description of the Marmara bauxite deposit were given by Weisse

(1967). A more detailed study of the mineralogy and geochemistry of the deposit will be published later by one of us (Z.M.).

Brindleyite occurs as green coatings a few millimeters thick, with sporadic thickening up to 12 mm, on the footwall limestone. It has a clayey appearance, but often is compact with a pronounced schistosity and lustrous surface. Brindleyite also forms thin veinlets and irregular accumulations in the red kaolinitic clay above the footwall limestone.

The mineralogical composition of the Marmara bauxite layer is rather simple: boehmite 60 percent, hematite 30 percent, kaolinite 6 percent, anatase 2.4 percent, and chromite 1.2 percent. In the lowermost part of the deposit near the footwall limestone kaolinite is the most abundant mineral, hematite occurs in very reduced amounts, and boehmite is present only in traces. Other minerals also appear, forming an unusual association: brindleyite, bastnaesite, malachite, bayerite, and calcite. The increased complexity of the mineralogy in the lowermost part of the deposit is a result of the genesis of the Marmara karstic bauxites.

Maksimovic and Roaldset (1976) found a progres-

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sive downward enrichment of all lanthanide elements (La–Lu) in the deposit, with maximum concentrations of about 6400 ppm total lanthanides in brindleyite. The same concentration trend “per descensum” was observed for Ni, Cu, Co, Mn, and Y. The enrichment of these elements is considered to be contemporaneous with the removal of silica, *i.e.* with the bauxitization process in a karstic environment (Maksimovic, 1973, 1976).

The enrichment of nickel and the formation of brindleyite were the result of several factors. The high initial nickel content of the clay material washed down into the karstic depression resulted from the weathering of ultramafic rocks. The strong downward migration of nickel was caused by percolating waters in a highly drained karstic environment. Finally, the footwall limestone acted as an effective alkaline barrier for descending solutions and caused the precipitation and concentration of nickel, REE (rare earth elements), and copper, and the formation of brindleyite, bastnaesite [(Ce,La)CO<sub>3</sub>F], and malachite.

The study of brindleyite by electron probe analysis revealed in all samples small amounts of bastnaesite and malachite. Bastnaesite forms veinlets and irregular accumulations up to 35  $\mu\text{m}$  thick. The study of brindleyite by X-ray diffraction revealed the presence of other impurities. In the purest brindleyite, traces of bayerite were detected by a very weak reflection at 4.72A, but in less pure samples the following reflections (in A) of bayerite and bastnaesite were recorded:

bayerite: 4.72(s), 4.35(ms), 3.20(m), 2.23(s), 1.72(m);  
bastnaesite: 4.87(m), 2.879(s), 2.058(m), 2.01(m).

#### Physical and optical properties

Brindleyite is massive with no observable cleavage and a Mohs hardness between 2.5 and 3. Relatively pure samples appear dark yellowish green (10GY4/4) (Rock Color Chart) in hand specimen. The density calculated from the observed chemistry and X-ray data is 3.16 g/cm<sup>3</sup>, in close agreement with the value determined using a hydrostatic balance, 3.17(1) g/cm<sup>3</sup>. The mean refractive index,  $n(\text{Na})$ , is 1.635(1). Because of the fine-grained nature of the material, no other optical properties could be determined. Electron micrographs of brindleyite were originally thought to indicate a fibrous morphology (Maksimovic, 1972), but further studies indicated that the material is platy with poorly developed crystals less than 1  $\mu\text{m}$  in diameter.

#### Optical and infrared spectroscopy

Optical absorption spectra obtained using a Beckman DK-2A spectrophotometer with a diffuse reflectance attachment confirm that the pronounced green color is due to Ni<sup>2+</sup> in octahedral coordination. Spin-allowed transitions for sample #1 occur at 8830 cm<sup>-1</sup>, 15,080 cm<sup>-1</sup>, and 26,320 cm<sup>-1</sup>. A spin-forbidden transition occurs at 13,570 cm<sup>-1</sup>. These absorptions give a value for  $Dq$  (crystal field splitting parameter) of 883 cm<sup>-1</sup>. Application of the curve constructed by Faye (1974) to this value of  $Dq$  gives an average Ni–O,OH distance of 2.04(2)A, in excellent agreement with the Mg–OH distance in amesite of 2.04(2)A (Steinfink and Brunton, 1956).

Infrared spectra obtained using a Perkin-Elmer 621 instrument are illustrated in Figure 1. Comparison with the spectra given by Serna *et al.* (1977) suggests that our samples of brindleyite possess a disordered cation arrangement.

#### X-ray study

All natural samples of brindleyite were examined with Ni-filtered CuK $\alpha$  radiation, using a Philips high-angle diffractometer and a 114.6 mm diameter powder camera. The synthetic sample was examined using only the diffractometer. Because brindleyite was first described as being analogous to amesite, an attempt was made to index the powder patterns according to group D of Bailey (1969), the common polytype group of amesite. Although the three strongest  $hkl$  lines of the patterns at first suggest group D, the patterns are adequately indexed only as a mixture of the group A and group C polytypes of Bailey. A number of the strongest calculated  $hkl$  reflections for group D are not present or are very weak in our patterns (111, 113, 115, 117 and 119 for the 2H<sub>2</sub>

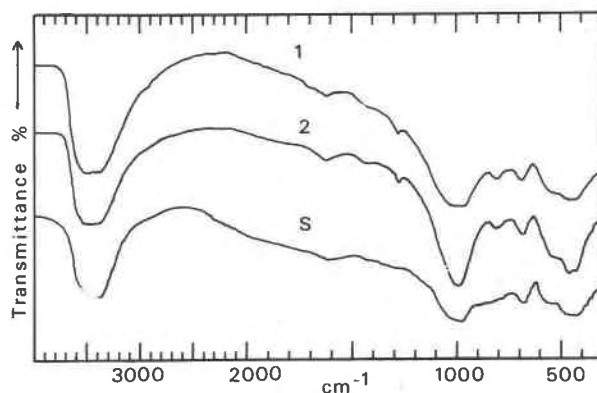


Fig. 1. Infrared absorption spectra for natural and synthetic brindleyite samples.

polytype). The indexed powder data for a natural sample are presented in Table 1, with cell parameters refined using the program of Appleman and Evans (1973). Data for a sample synthesized from a Ni-Al gel by hydrothermally heating in silica tubes at 225°C are also included. The 1M-3T and 1T polytypes are assumed only to facilitate indexing and calculation of cell parameters. Due to uncertainties in the indexing of weak lines and because of broadened reflections due to disorder and overlapping reflections, the cal-

culated standard errors stated for the cell parameters are somewhat optimistic. Also we could not differentiate between the three structures in each polytype group.

Comparison of the observed intensities with those calculated assuming ideal 1M-3T and 1T structures (Bailey, 1969) and the composition of sample #1 suggests that the group C polytype predominates in the synthetic sample. The proportions of the two polytypes are approximately equal in the natural samples

Table 1. Indexed X-ray diffraction data for brindleyite

Sample #1		Synthetic		hkl	1M-3T	d <sub>calc</sub> ***	hkl	1T	d <sub>calc</sub> ***
d*	I/I <sub>0</sub>	d	I/I <sub>0</sub>						
7.07	100	7.08	100	001		7.09	001		7.09
4.54	10	4.57	12b	020		4.57	100		4.57
3.85	4	3.87	6b	021		3.84	101		3.84
3.54	81	3.54	53	002		3.54	002		3.54
2.65	5			---			110		2.64
2.62	18	2.62	21	$\bar{2}01$ , $\bar{1}30$		2.62	---		
2.47	18	2.475	34	---			111		2.47
2.37	18	2.37	16	$\bar{2}02$ , $\bar{1}31$		2.37	---		
2.304	3b**	2.303	8b	$\bar{1}13$		2.302	---		
2.24	3b	2.24	6b	$\bar{1}32$ , $\bar{2}01$		2.24	---		
2.12	6b	2.12	10b	---			112		2.12
2.01	7b	1.99	6b	$\bar{2}03$ , $\bar{1}32$		2.00	---		
		1.87	3b	$\bar{1}33$ , $\bar{2}02$		1.87	---		
1.76	4b	1.762	8b	---			113		1.76
1.66	4b			$\bar{2}04$ , $\bar{1}33$		1.66			
1.60	2b			$\bar{2}41$ , $\bar{1}52$		1.60			
1.55	4b			$\bar{2}03$ , $\bar{1}34$		1.56	---		
1.524	17	1.525	25	$\bar{0}60$ , $\bar{3}31$		1.524	300		1.523
1.487	7	1.491	12	$\bar{0}61$ , $\bar{3}30$ , $\bar{3}32$		1.489	301		1.489
1.471	3b	1.469	5b	---			114		1.471
1.397	5b	1.400	9b	$\bar{0}62$ , $\bar{3}31$ , $\bar{3}33$		1.400	$\bar{3}02$ , $\bar{2}04$		1.400
1.318	3b	1.32	4b	$\bar{1}35$ , $\bar{4}01$ , $\bar{2}61$ , $\bar{2}04$		1.317	---		
1.297	3b	1.298	6b	---			221		1.297
1.281	3b			$\bar{3}32$ , $\bar{2}62$ , $\bar{4}00$ , $\bar{0}63$ , $\bar{3}34$		1.281	303		1.280
1.177	2b			$\bar{2}62$ , $\bar{0}06$		1.181	006		1.181
1.15	2b			---			223		1.15
1.099	2b			$\bar{2}63$ , $\bar{2}25$ , $\bar{4}05$		1.093	---		
1.036	2b			---			305		1.038
0.9875	2b			---			411		0.9876
0.9308	2b			---			306		0.9337
0.8795	2b			$\bar{3}91$ , $\bar{6}02$		0.8802	$\bar{3}30$ , $\bar{2}26$		0.8799

1M-3T

1M-3T

a = 5.286(5) Å

a = 5.283(4) Å

b = 9.133(3)

b = 9.149(2)

c = 7.31(1)

c = 7.29(1)

$\beta = 104^{\circ}9'(7)$

$\beta = 103^{\circ}49'(5)$

1T

1T

a = 5.277(1) Å

a = 5.283(2) Å

c = 7.09(1)

c = 7.08(1)

\*All d-spacings are in Å, powder camera data for sample #1, diffractometer data for the synthetic sample.

\*\*b = broad

\*\*\*Calculated using the refined cell parameters for sample #1. Where more than one value of hkl is given, d<sub>calc</sub> is an average for the given reflections, 1M-3T and 1T polytypes are assumed to facilitate indexing.

examined. These results are similar to those of Brindley (1951) for the mineral berthierine (7A chamosite). He found that natural samples were best indexed as mixtures of a monoclinic and a hexagonal polytype. In estimating the relative proportions of the two polytype groups, we used the relative intensities of the 1M-3T  $\bar{2}01$  and  $\bar{2}02$  reflections and the 1T 111 reflection. Calculated intensities are 27, 68, and 66 respectively. We have no explanation for the lack of agreement between experimental and calculated intensities, and emphasize that the relative proportions determined are approximate.

### Thermal data

DTA curves of brindleyite are compared in Figure 2 with that of amesite, and TGA curves are presented in Figure 3. Both minerals dehydroxylate in two steps and show a high-temperature exothermic reaction. However, the endothermic dehydroxylation reactions in brindleyite occur at lower temperatures than in amesite. The lower temperature of dehydroxylation for brindleyite is compatible with the fact that replacement of  $Mg^{2+}$  by  $Ni^{2+}$  in minerals of the serpentine group decreases the endothermic reaction temperature (Caillère and Hénin, 1957). Berthierine, the ferrous iron analogue of brindleyite, shows only one main endothermic peak at 520°C (Caillère and Hénin, 1963). It is peculiar that of the aluminous serpentine only brindleyite and amesite have the two-stage dehydroxylation.

The endotherm at about 114–140° is due to adsorbed water, and various small endotherms at 327–370° and 400–418°C are probably due to bayerite and malachite respectively. Natural bayerite shows an endothermic peak at 340° (Khorosheva, 1968), and malachite has an endothermic peak at about 390°C (Beck, 1950).

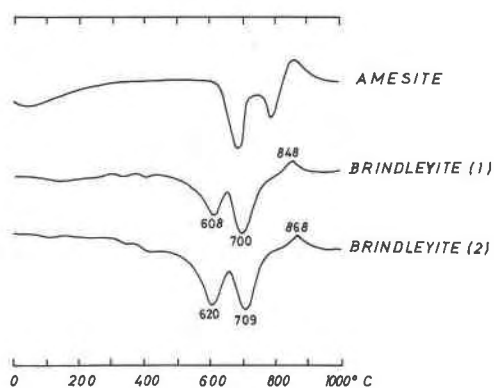


Fig. 2. DTA curves of brindleyite from Greece and amesite from Chester, Massachusetts (Phillips, 1963).

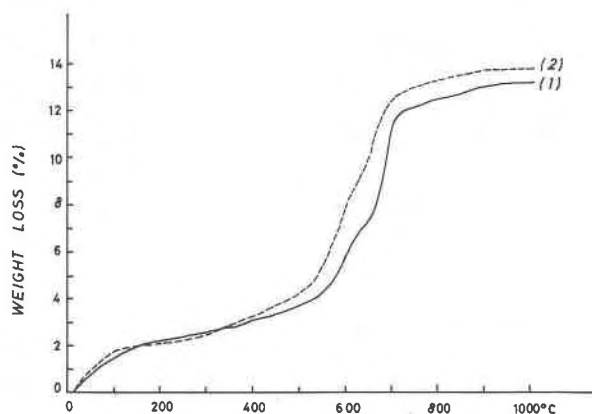


Fig. 3. TGA curves of natural brindleyite samples.

The two-stage dehydroxylation process in brindleyite involves the formation of an intermediate hydrous 14A phase. During static heating, a 14A reflection appears at  $\sim 500^\circ$  and increases in intensity up to 600°C. No higher orders are observed, and the original 7A reflection disappears at  $\sim 580^\circ$ . This behavior is similar to that shown by other serpentine minerals, for example lizardite–nepouite (Brindley and Wan, 1975).

### Chemical analyses and structural formulae

Chemical analyses, mainly by wet-chemical methods, (Table 2) indicate that only minor amounts of bastnaesite and malachite are present as impurities. In correcting the analytical results, all the REE and Cu with appropriate amounts of  $CO_2$  and (OH) were taken to form bastnaesite and malachite. The amount of water attributed to the decomposition of bayerite was estimated as the weight loss between 300° and 375°C in the TGA curves. In sample #2 this water loss was 0.6 percent, and with the appropriate amount of  $Al_2O_3$ , 2 percent of bayerite was subtracted. In sample #1 the water loss between 300° and 375°C was negligible.

The chemical analyses, after correction for impurities, were used to derive structural formulae of brindleyite based on a total cation valence of 14 (Table 2). An electron probe analysis of brindleyite and the calculated formula also are presented.

The cation exchange capacity of brindleyite determined by an ammonium acetate treatment and Kjeldahl distillation method was 35.9 milliequivalents per 100 g.  $Ca^{2+}$ ,  $Na^+$ , and  $K^+$  with traces of  $Mg^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  were determined by atomic absorption spectrophotometry to be exchangeable cations, totaling 33.7 milliequivalents per 100 g. This exchange

Table 2. Chemical analyses and structural formulae of brindleyite

	1	2	3
SiO <sub>2</sub>	23.61	24.93	27.45
TiO <sub>2</sub>	0.99	1.10	0.99
Al <sub>2</sub> O <sub>3</sub>	23.39	24.39	24.09
Cr <sub>2</sub> O <sub>3</sub>	0.10*	0.05*	0.17
Fe <sub>2</sub> O <sub>3</sub>	0.45	0.24	
FeO	3.40	2.86	1.15
MnO	0.08	0.18*	
NiO	29.65	26.57	30.18
MgO	3.17	2.81	3.18
CaO	nd	0.39	0.07
ZnO	0.25*	0.24*	
CoO	0.18*	0.16*	
Na <sub>2</sub> O	0.10	0.10	
K <sub>2</sub> O	0.20	0.15	
H <sub>2</sub> O <sup>+</sup>	11.74	11.36	[12.37]
H <sub>2</sub> O <sup>-</sup>	0.70	1.29	
CO <sub>2</sub>	0.35	0.58	
CuO	0.70*	0.72*	
ΣLn	0.65*	1.56*	0.35
	99.71	99.68	100.00

## Formulae based on total cation valence +14

Si	1.35	} 2.00	1.44	} 2.00	1.49	} 2.00
Al	0.65		0.56		0.51	
Al	0.92	} 2.77	1.02	} 2.69	1.03	} 2.69
Ti	0.04		0.05		0.04	
Fe <sup>3+</sup>	0.02		0.01			
Fe <sup>2+</sup>	0.16		0.14		0.05	
Ni	1.36		1.23		1.31	
Mg	0.27	0.24	0.26			
H <sub>2</sub> O	O <sub>5</sub> (OH) <sub>4</sub> 0.23	O <sub>5</sub> (OH) <sub>4</sub> 0.07	O <sub>5</sub> (OH) <sub>4</sub> 0.23			

nd - not determined

\*determined by various analytical techniques (atomic absorption, emission spectrography, spark-source mass-spectrometry).

1. Dr. D. Nikolic, analyst. Formula derived after correction for 1.0% malachite and 0.7% bastnaesite.
2. Dr. D. Nikolic, analyst. Formula derived after correction for 2.0% bayerite, 1.9% bastnaesite and 1.2% malachite.
3. Electron probe analysis of sample No. 1. L. B. Eminhizer, analyst. Water added in brackets to 100%.

capacity is probably due to broken bonds in the extremely fine-grained mineral.

According to the X-ray data, chemical analyses, and derived structural formulae, brindleyite is a trioctahedral nickel-rich aluminous serpentine mineral with the formula (Ni,Mg,Fe<sup>2+</sup>,Al)<sub>2.7-2.8</sub>(Si,Al)<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. A deficit of cations in the octahedral layer was observed in all structural formulae, indicating possibly some defects in the structure. A similar deficit of cations in octahedral sites was found for berthierine by Brindley and Youell (1953).

The amount of water obtained between 110° and 1000°C after correction for impurities is higher than the amount corresponding to (OH)<sub>4</sub>. This excess is due to the presence of strongly adsorbed water, which according to the TGA curves is released above 110°C. Therefore, in the formulae of brindleyite the adsorbed water is presented separately in amounts varying from about 0.1 to 0.25 molecules per formula

unit. A higher amount of excess water was found in analyses #1 and #3, possibly due to the presence of small amounts of bayerite which were not corrected for in the analyses.

### Conclusions

Brindleyite is a Ni<sup>2+</sup>-rich aluminous member of the serpentine group. The brindleyite samples contain a mixture of group A and group C polytypes in about equal proportions. Compositionally, brindleyite is related more closely to berthierine than to amesite, having a deficit of octahedral cations. The structural formula approximates to (Ni<sub>1.75</sub>Al<sub>1.0</sub>)(Si<sub>1.5</sub>Al<sub>0.5</sub>)O<sub>5</sub>(OH)<sub>4</sub>. The mineral is somewhat disordered in its layer stacking, and crystalline development is poor. No evidence for cation ordering is found.

Type specimens of brindleyite are deposited in the Museum of the Department of Mineralogy, Crystallography, Petrology, and Geochemistry, University of Belgrade, Belgrade, Yugoslavia, and in the Smithsonian Institution, Washington, D.C.

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