

## Motukoreaite: A common alteration product in submarine basalts

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### ABSTRACT

Motukoreaite occurs in fractures and amygdules in hyaloclastite dredged from the western Mediterranean. Motukoreaite apparently forms as a low-temperature alteration product during seawater–basaltic glass interaction. We report microprobe chemical analyses and the complete X-ray powder-diffraction pattern of motukoreaite to enable unambiguous identification in future work on submarine alteration of basaltic glasses. Comparison of our X-ray data and analysis of motukoreaite and “unknown minerals” published by several authors suggests that motukoreaite is a common basaltic alteration mineral having a widespread occurrence.

### INTRODUCTION

Altered basaltic samples have been recovered from numerous submarine volcanic areas around the world. An aluminum-magnesium hydrosulfate mineral has been detected in some of these samples (Alexandersson, 1972; Rad, 1974; Bernoulli et al., 1978). A sulfate mineral identified as pickeringite has been reported by Robinson and Flower (1977). In only a few cases have similar minerals been identified as motukoreaite (Rius and Plana, 1986; Rodgers et al., 1977; Brindley, 1979; Alker et al., 1981; Ramanaidou and Noack, 1987). This work provides new microprobe chemical analyses and the complete X-ray powder-diffraction pattern of motukoreaite and emphasizes that it appears to be a common alteration product of submarine basalt.

### RESULTS AND DISCUSSION

#### Occurrence and morphology

In the summer of 1980, several olivine basalt hyaloclastite samples were dredged from Emile Baudot Bank in the western Mediterranean Sea (Zamarreño et al., 1985). Emile Baudot Bank is a Miocene seamount located between Cabrera Canyon and the steep, fault-defined Emile Baudot Escarpment (Fig. 1). This bank has been associated with the Miocene extensional displacement that produced both the dislocation of the Balearic margin into separate blocks and the present physiography and sub-bottom configuration of this margin (Mauffret, 1979).

Motukoreaite occurs as radiating, fibrous, crystalline rims (60  $\mu\text{m}$  thick) coating veinlets or as larger platelike hexagonal crystals (150  $\times$  15  $\mu\text{m}$ ) filling amygdules (Fig. 2). The macrocrystalline variety is also typical of open-cavity growth, and the crystal size increases toward the center of the void. Motukoreaite is a very soft and colorless mineral with high negative relief. It is uniaxial (+) and has birefringence of about 0.012. It is pale yellow, in

close proximity to the palagonite matrix. Motukoreaite is the earliest mineral to form during submarine alteration of these basalts. The complete precipitation sequence is motukoreaite, phillipsite, and calcite. The contacts between these three mineral phases are sharp and lack any gradational zone. Some “floating” motukoreaite crystals suggest a time lag between their crystallization and the formation of phillipsite and calcite. There is no petrographic evidence of alteration of the secondary minerals.

#### X-ray analysis

The motukoreaite used for X-ray analysis was obtained by hand-picking microcrystalline radiating fibers from a thick rim and macrocrystals filling large amygdules in the basaltic hyaloclastite from the Emile Baudot Bank. The X-ray spectrum was collected using a SIEMENS D-500 dif-

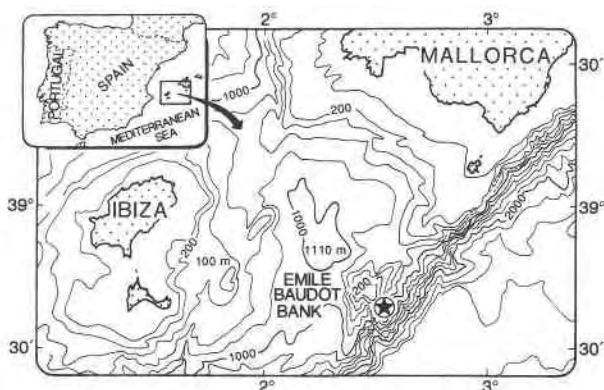


Fig. 1. Bathymetric chart of Emile Baudot Bank. The star symbol marks the location of the dredge sample containing motukoreaite. The bank is characterized by steep slopes with a complex surficial micromorphology and is devoid of sedimentary deposits.



Fig. 2. (a) Sketch of a vesicle filled by motukoreaite generalized from a scanning electron micrograph. The crystallization sequence is thin fibrous fringe (1), followed by macrocrystalline radiating bundles (2), and macrocrystalline booklike packages filling the remainder of vesicle space (3). (b) Enlarged view framed in (a) showing well-developed hexagonal motukoreaite crystals typical of open-cavity growth.

TABLE 1. Comparison of the cell dimensions of motukoreaite

Reference	$a = b$	$c$
This work	9.172(2) Å = 3 × 3.057 Å	33.51(1) Å = 3 × 11.170 Å
Rodgers et al. (1977)	9.336 Å = 3 × 3.112 Å	44.72 Å = 4 × 11.18 Å
Rad (1974)	9.36 Å = 3 × 3.12 Å	34.0 Å = 3 × 11.33 Å
Brindley (1979)	3.062 Å = 1 × 3.062 Å	33.51 Å = 3 × 11.170 Å
Alker et al. (1981)	---	11.216 Å = 1 × 11.216 Å
Ramanaidou and Noack (1987)	3.065 Å = 1 × 3.065 Å	33.47 Å = 3 × 11.157 Å

fractometer with  $\text{CuK}\alpha_1 = 1.5405 \text{ \AA}$  radiation, graphite monochromator, and scintillation counter. The X-ray powder pattern obtained was scanned from  $4^\circ$  to  $70^\circ 2\theta$  with 40 kV and 20 mA at 10 s per  $0.05^\circ$  steps, with quartz

as an internal standard. The pattern quality was improved by very gently grinding the sample. The diffractogram was indexed using an hexagonal cell according to the structural data of Rius and Plana (1986).

TABLE 2. X-ray powder-diffracton data for motukoreaite indexed according to the hexagonal space group  $R\bar{3}m$ 

This work				Rodgers et al. (1977)			Brindley (1979)			Alker et al. (1981)		Rad (1974)		Ramanaidou and Noack (1987)	
$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	(hkl)	$l/l_0$	$d_{\text{obs}}$ (Å)	$l$	(hkl)	$d_{\text{obs}}$ (Å)	$l_{\text{obs}}$	(hkl)	$d_{\text{obs}}$ (Å)	$l$	$d_{\text{obs}}$ (Å)	$l$	$d_{\text{obs}}$ (Å)	$l$
11.15	11.170	003	87	11.32	vvs	0004	11.26	10	003	11.22	100	11.5	100	11.10	s
8.48	—	—	12	—	—	—	—	—	—	—	—	—	—	—	—
7.57	—	—	15	7.61	vw	1.0.1.2	7.61	0.5	—	—	—	—	—	7.59	s
6.41	—	—	5	6.54	vw	1.0.1.4	—	—	—	—	—	—	—	—	—
5.58	5.585	006	59	5.58	s	0.0.0.8	5.59	4	006	5.609	45	5.56	65	5.57	mw
5.22	5.230	111	9	—	—	—	—	—	—	—	—	—	—	—	—
5.01	5.049	112	7	—	—	—	—	—	—	—	—	—	—	—	—
4.57	4.544	021	8	4.59	m	1.0.1.8	4.58	3	—	—	—	—	—	4.59	ms
4.24	4.244	107	2	4.24	w	1.0.1.9	4.22	1?	—	—	—	—	—	—	—
3.88	3.842	116	10	3.85	vw	—	—	—	—	—	—	—	—	—	—
3.72	3.723	009	100	3.72	vvs	0.0.0.12	3.72	7	009	3.786	80	3.77	70	3.73	s
3.51	3.467	120	4	3.55	mw	2.0.2.6	—	—	—	—	—	—	—	—	—
3.40	3.395	122	4	—	—	—	—	—	—	—	—	—	—	3.40	s
2.996	{ 3.044	031	—	3.03	vw	2.1.2.2	—	—	—	—	—	—	—	2.98	s
	{ 2.949	033	11	—	—	—	—	—	—	—	—	—	—	—	—
2.951	2.948	303	5	2.958	w	1.0.1.14	—	—	—	—	—	—	—	—	—
2.785	2.792	0.0.12	8	2.784	w	0.0.0.16	—	—	—	—	—	—	—	—	s
2.694	2.682	306	6	—	—	—	—	—	—	—	—	—	—	2.69	m
2.644	{ 2.671	128	1	2.650	mw	3.0.3.3	2.646	1	101	—	—	—	—	2.65	—
	{ 2.615	222	—	—	—	—	—	—	—	—	—	—	—	—	m
2.571	2.576	223	9	2.578	s	3.0.3.5	2.576	4	103	—	—	—	—	2.57	—
2.526	2.536	113	3	—	—	—	—	—	—	—	—	—	—	—	—
2.466	2.470	1.1.12	2	—	—	—	—	—	—	—	—	—	—	2.49	ms
2.444	2.434	134	1	—	—	—	—	—	—	—	—	—	—	—	—
2.391	2.392	226	8	2.386	mw	1.0.1.18	2.392	3	106	—	—	—	—	2.37	ms
2.345	2.362	309	8	2.34	vww	2.2.4.1	—	—	—	—	—	—	—	2.34	ms
2.274	2.272	042	4	2.268	vw	2.2.4.5	2.272	0.3	—	—	—	—	—	2.28	w
2.235	2.234	0.0.15	4	2.235	vw	0.0.0.20	—	—	—	—	—	—	—	2.25	w
2.159	2.158	229	6	2.158	mw	1.0.1.20	2.160	2	109	—	—	—	—	2.16	—
2.065	2.061	0.3.12	4	2.029	w	0.0.0.22	—	—	—	—	—	—	—	{ 2.11	w
														{ 0.06	w
1.972	1.970	143	3	1.983	w	—	—	—	—	—	—	—	—	1.98	w
1.922	1.921	2.2.12	9	1.921	ms	—	1.924	2.5	1.0.12	—	—	—	—	1.93	mw
1.859	1.861	0.0.18	4	1.870	vww	—	—	—	—	—	—	—	—	1.88	w
1.767	1.765	330	2	1.763	vww	—	—	—	—	—	—	—	—	—	—
1.725	1.731	241	3	—	—	—	—	—	—	—	—	—	—	1.74	w
1.709	1.707	2.2.15	5	1.709	m	—	1.710	3	1.0.15	—	—	—	—	1.72	w
1.597	1.596	0.0.21	1	—	vww	—	—	—	—	—	—	—	—	—	—
1.522	{ 1.528	060	4	1.528	m	—	1.529	1	110	—	—	—	—	1.52	ms
	{ 1.522	2.2.18	—	—	—	—	—	—	—	—	—	—	—	—	—
1.515	1.515	603	1	1.513	m	—	1.516	1	113	—	—	—	—	—	—
1.475	1.474	066	1	1.477	m	—	1.476	0.5	116	—	—	—	—	—	—
1.367	{ 1.367	2.2.21	2	1.367	vw	—	—	—	—	—	—	—	—	—	—
	{ 1.363	1.4.18	—	—	—	—	—	—	—	—	—	—	—	—	—

Note: vvs = very very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, vww = very very weak, vvvw = very very very weak.

**TABLE 3.** Several analyses of the chemical composition of motukoreaite in percentages

	1	2	3	4	5	6	7	8	9	10
Na <sub>2</sub> O	8	5	0.71	1.10				1.83	3.41	3.56
MgO	28	30	22.98	31.43	27.2	26.46	24.26	26.34	27.7	27.8
Al <sub>2</sub> O <sub>3</sub>	36	19	17.87	23.13	23.2	21.33	18.63	16.64	17.5	17.5
SO <sub>3</sub>	14	15	10.00	13.33	10.5	11.51	11.18	9.17	18.0	18.2
SiO <sub>2</sub>			5.55	0.77	3.0			3.68	0.0	0.0
Fe <sub>2</sub> O <sub>3</sub>			0.73					2.14		
FeO				2.88					0.11	0.15
CaO			0.92	0.04				0.42	0.00	0.00
MnO			0.70	0.02				26.34	0.00	0.00
ZnO			0.56							
K <sub>2</sub> O			0.10	0.01				0.13	0.00	0.00
CO <sub>2</sub>			9.32							
P <sub>2</sub> O <sub>5</sub>				0.25					0.25	0.21
TiO <sub>2</sub>				0.01					0.01	0.00
BaO				0.28						
H <sub>2</sub> O <sup>-</sup>			19.62							
H <sub>2</sub> O <sup>+</sup>			10.35							
Residual					36.1	40.73	45.93	2.83		

Note: (1) and (2) Microprobe data from Rad (1974). (3) Chemical analysis from Rodgers et al. (1977). (4) Microprobe data (average of three analyses) from Robinson and Flower (1977). (5) Microprobe data from Alker et al. (1981). (6) and (7) Chemical analyses (uncorrected and corrected, respectively, for the calculated formula of motukoreaite) from Rius and Plana (1986). (8) Microprobe data from Ramanaidou and Noack (1987). (9) and (10) Microprobe data from this study.

The cell dimensions of motukoreaite are  $a = b = 9.172(2) = 3 \times 3.057 \text{ \AA}$ ,  $c = 33.51(1) = 3 \times 11.170 \text{ \AA}$ , and these values were used to index the X-ray spectrum. These parameters are different from the values presented by several authors who assumed other multiples in the brucite-like main layer ( $3.057 \text{ \AA}$ ) and the ordered sulfate- and cation-bearing interlayer ( $11.170 \text{ \AA}$ ). Table 1 shows the different cell dimensions used by various authors.

Table 2 shows our X-ray data indexed according to space group  $R\bar{3}m$ , and these data are compared with the X-ray data on this mineral from other works (Rodgers et al., 1977; Brindley, 1979; Ramanaidou and Noack, 1987; and the "unknown mineral" in Rad, 1974). The presence of several lines ( $8.48$ ,  $7.57$ , and  $6.41 \text{ \AA}$ ) in the X-ray spectrum that are not consistent with the ideal structure suggests the partial transformation of motukoreaite, probably due to partial dehydration during the grinding process in a low-humidity atmosphere. Similar basal lines ( $7.61$  and  $6.54 \text{ \AA}$ ) were reported by Brindley (1979). Analogous grinding effects have also been described in a  $11\text{-\AA}$  structure by Rius and Allmann (1984).

### Chemical considerations

Microprobe analysis of our samples (Table 3) shows SO<sub>3</sub> content considerably higher than that reported by Rodgers et al. (1977) and Rius and Plana (1986). The small amount of P<sub>2</sub>O<sub>5</sub> probably substitutes at the SO<sub>4</sub>-CO<sub>3</sub> site. Presumably this sample has lower CO<sub>3</sub> to balance the high SO<sub>4</sub> in that site. Dehydration (Brindley, 1979; Rius and Plana, 1986) and contamination by other phases (Brindley, 1979) can explain the variations in the minor-element values shown in Table 3. Differences between our chemical data and those reported by Rodgers et al. (1977) are due to the impurities of quartz, calcite, and goethite present in their sample. Data from Robinson

and Flower (1977) may be influenced by smectite that lines vesicles.

The genesis of motukoreaite as a basaltic submarine alteration product is poorly understood. Recently, the alteration of ocean-floor basalts by sea-water has been studied in detail in the Deep Sea Drilling Project. The results reported indicate that complementary studies are needed to fully document this process, particularly for the conditions under which it operates: water-rock ratio, pore-water composition, and temperature. In an extensive review on low-temperature alteration of oceanic basalts, Honnorez (1981) reported that basaltic glass alters differently and at different rates than crystalline basalts. He concluded that the initial stage of basaltic glass alteration is characterized by hydration and oxidation of the bulk glass. Chamley and Millot (1972) suggested that Al is released during volcanic glass hydrolysis, a process experimentally confirmed by Furnes (1975). Therefore, the Al needed for motukoreaite formation may be derived from the hydrolysis of the basaltic glass. Sea-water provides SO<sub>3</sub> and Mg, although Mg may also be derived from the alteration of the glass. Therefore, the chemical composition of basaltic glass may exert a strong effect on the composition and distribution of the secondary minerals, and mineral phases rich in the less-mobile elements, such as Al can precipitate.

Similar occurrences of motukoreaite have been reported in the literature, although in certain cases they have not been recognized as motukoreaite. Rad (1974) described a very common "mineral x," infilling mainly vesicles, voids, and veinlets in basalt and forming a rim 1–5 mm thick of radiating fibers that surrounds the palagonitic clasts in volcanic rocks from the Great Meteor and Josephine Seamounts (eastern North Atlantic). This "mineral x" has the same chemical composition as mo-

tukoreaite (Rad, 1974, p. 40). Bernoulli and his coworkers (1978) described an "unidentified material" with abundant Mg, Al, Si, and S in basaltic breccias cored at Hole 373A (Tyrrhenian Basin). It occurs as rosettes with a platy or fibrous habit and forms cement rims around basaltic clasts, particularly in the most palagonitized ones. Petrographic fabric, microprobe analysis, and X-ray data suggest that this "unknown mineral" is motukoreaite. Motukoreaite mostly occurs as cement in hyaloclastite or volcanic breccias (Alexandersson, 1972; Rodgers et al., 1977; Alker et al., 1981, Ramanaidou and Noack, 1987). The magnesium-aluminum sulfate reported by Robinson and Flower (1977) occurs as vesicle fillings lined with smectite.

### CONCLUSIONS

The present study allows us to conclude that motukoreaite can be a common mineral, formed during submarine basaltic glass alteration, and it can be accurately identified by using the complete X-ray diffraction pattern provided in this article. The alteration to form motukoreaite must have taken place at relatively low temperature conditions as the mineral assemblage does not include any minerals that form at temperatures near or higher than 150 °C. We encourage future studies to look for motukoreaite as a low-temperature alteration product of basalt in the oceans of the world.

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