

Palagonites of the Red Sea: a new occurrence of hydroxysulphate

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Abstract

Palagonites from the Red Sea consist of two zones: an orange palagonite which is a mixture of Mg-Al double hydroxide, Al-hydroxide and an undetermined Si-K phase, and a white palagonite, similar to motukoreaite, a Mg-Al hydroxy-sulphate-carbonate. This mineral, frequent in experimental alteration of glass by seawater, is discovered for the first time in natural palagonite. Hydroxysulphates and hydroxides are the precursors of phyllosilicates, generally found in palagonites. The very young palagonites of the Red Sea are the first link between the natural and experimental observations.

KEYWORDS: palagonites, hydroxides, hydroxysulphates, Red Sea.

Introduction

NATURAL palagonites (alteration of basaltic glasses by water at low temperature) are generally described as a mixture of phyllosilicates (Hay and Iijima, 1968; Honnorez, 1972; Noack, 1981; Eggleton and Keller, 1982) often associated with zeolites and calcite. But, in experimental alteration of basaltic glasses by seawater at low temperature (between 25 °C and 90 °C), the first-formed mineral belongs to the hydroxycarbonate family (Crovisier *et al.*, 1983). To this day, such minerals have never been recognized in natural palagonites. In this paper, we describe an occurrence of hydroxy-sulphate in palagonites from the Red Sea.

Samples and methods

The specimens have been studied by optical microscopy, scanning electron microscopy (Philips SEM 505 with LINK Systems 860 Series 2), electron microprobe (CAMEBAX) and X-ray diffractometry (Philips PW 1730 diffractometer using Co-K α radiation with Fe filter). They were collected by a diving saucer in the axial rift of Red Sea at 18° N (Eissen, 1982). The specimens are composed of a lava crust with a glassy rim (1 cm thick) overlapped by carbonated sediments (5 mm thick) and a manganese crust (1 mm thick). The lava is a vuggy tholeiitic basalt with plagioclase and olivine

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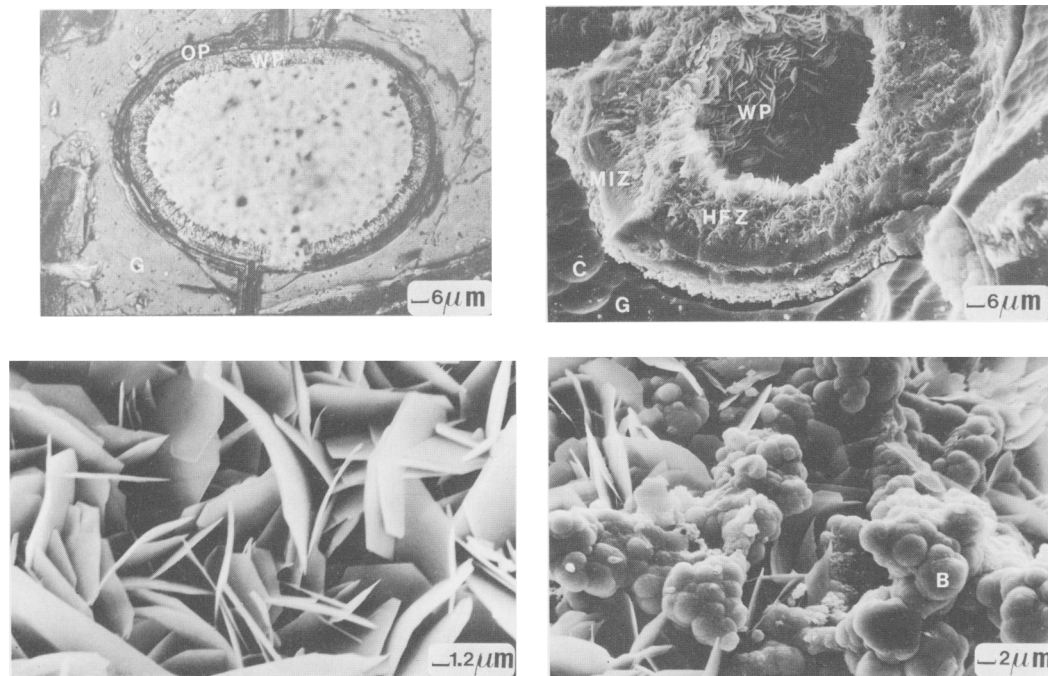
phenocrysts. An orange coloured layer occurs at the boundary between glass and sediment.

In optical microscopy, cracks and vugs (up to 400 μm in diameter) were observed in the yellow, isotropic glass (Fig. 1). The orange, zoned layer (30 μm thick) is also present along the cracks and around the vesicles. This orange layer is rimmed by a layer of white-grey minerals (up to 40 μm thick). In the text, the orange layer will be called orange palagonite (OP) and the white-grey minerals white palagonite (WP). Under the scanning electron microscope, the surface of the glass at the contact with orange palagonite shows solution cusps (1 to 25 μm large and 1 to 4 μm deep). The orange palagonite is formed of two zones (Fig. 2): a massive inner zone (M.I.Z.), 18 μm thick; and a heterogeneous, fibrous zone (H.F.Z.), 12 μm thick.

The white palagonite is composed of a box-work of plate-like crystals with hexagonal forms (15 μm in diameter, 1 μm thick) (Fig. 3). In some places, these minerals are covered by small spherules (1 to 10 μm in diameter) (Fig. 4). The same succession can be seen in the vugs and in the cracks.

Mineralogy

It was not possible to separate orange and white palagonite. The diffractogram shows strong peaks at 11.1, 7.6, and 3.8 Å and many other minor peaks (Table 1). This diffractogram can be assigned to a mixture of three minerals: motukoreaite (Mg-Al hydroxy-carbonate-sulphate), Mg-Al double hydroxide and aragonite. Only a few peaks could



FIGS. 1-4. FIG. 1 (*top left*). Palagonitized vug and cracks in thin section. G = glass; OP = orange palagonite; WP = white palagonite. FIG. 2 (*top right*). Palagonitized vug (scanning electron microscope). G = glass; C = dissolution cusps; MIZ = massive inner zone; HFZ = heterogeneous fibrous zone; WP = white palagonite. FIG. 3 (*lower left*). Lamellae of white palagonite (scanning electron microscope). FIG. 4 (*lower right*). Lamellae of white palagonite (L) overlapped by Mn-spherules (B).

not be indexed. The peak at 4.59 \AA is probably a superlattice reflection of motukoreaita (Brindley, 1979). The other peaks can be identified as plagioclase (3.20 \AA) and Mg- or Fe-calcite (2.98 \AA). The unit-cell parameters calculated, using a least-squares refinement program (Tournarie, 1969), are very similar ($a = 3.045$ and $c = 22.68 \text{ \AA}$ for the Mg-Al hydroxide; $a = 3.065$ and $c = 33.47 \text{ \AA}$ for the motukoreaita) to those given by Mascolo and Marino (1980) and Brindley (1979).

Geochemistry

The fresh glass has the chemical composition of a normal tholeiitic glass (Table 2).

The low oxide totals of the average composition of orange palagonite (analysed with electron microprobe) is probably due to its H_2O content, porosity, and non-analysed elements (such as S and C). The large variation of each oxide content reflects the fact that orange palagonite consists of a mixture of different phases. In comparison with glass, the orange palagonite shows a deficiency of SiO_2 , CaO

and Na_2O and gains of TiO_2 , Al_2O_3 , MgO and K_2O . The gains of TiO_2 , Al_2O_3 and Fe_2O_3 can be attributed to a passive accumulation but part of the MgO and K_2O gains can have their origin in seawater. A treatment by factor analysis indicates, for the electron microprobe analysis of orange palagonite, two major phases (Si-K and Mg-Al) and four accessory phases (Ti, Fe, Ca, Na). The correlations obtained are:

$$\begin{aligned} \text{K}_2\text{O} &= 0.045 (\text{SiO}_2) - 0.695 & r &= +0.780 \\ \text{Al}_2\text{O}_3 &= -0.294 (\text{SiO}_2) + 29.761 & r &= -0.700 \\ \text{MgO} &= -0.898 (\text{SiO}_2) + 43.038 & r &= -0.906 \\ \text{MgO} &= 2.109 (\text{Al}_2\text{O}_3) - 27.020 & r &= +0.895. \end{aligned}$$

The chemical composition of the Mg-Al phase can be calculated with these equations, assuming that its silica content is zero (Table 2, column 2).

Analyses across the rim of a vug have been made by scanning microscope with Si-Li detector (Table 3 and Fig. 5). The inner rim of orange palagonite, near the glass, and the spherules overlapping the white palagonite have high MnO_2 contents. The composition of the white palagonite is essentially

Table 1. X-Ray data of Red Sea palagonite compared to motukoreaite, Mg-Al double hydroxide and aragonite.

SAMPLE		MOTUKOREAITE (Brindley, 1979)		Mg-AL DOUBLE HYDROXIDE (Mascolo & Marino, 1980)		ARAGONITE (ASTM 5-453)	
d	I	d	h,k,l	d	h,k,l	d	h,k,l
11.10	S	11.26	0,0,3				
7.59	S	7.61		7.60	0,0,3		
5.57	MW	5.59	0,0,6				
4.59	MS	4.58					
3.78	S			3.80	0,0,6		
3.73	S	3.72	0,0,9				
3.40	S					3.40	1,1,1
3.28	W					3.27	0,2,1
3.20	W						
2.98	S						
2.69	S					2.70	0,1,2
2.65	M	2.65	1,0,1	2.61	1,0,1		
2.57	MS	2.58	1,0,3	2.57	0,1,2		
2.49	MS					2.48	2,0,0
2.37	MS	2.39	1,0,6			2.37	1,1,2
2.34	MW					2.34	1,3,0
2.28	W	2.27		2.28	0,1,5		
2.25	W						
2.16	W	2.16	1,0,9				
2.11	W					2.11	2,2,0
2.06	W						
1.98	W					1.98	2,2,1
1.93	MW	1.92	1,0,12	1.94	0,1,8		
1.88	W					1.88	0,4,1
1.74	W					1.74	1,1,3
1.72	W	1.71	1,0,15	1.72	1,0,10		
1.52	MS			1.52	1,1,0		

Al_2O_3 , MgO and SO_3 . The obtained correlations are:

$$\begin{aligned} \text{SO}_3 &= -1.831 (\text{SiO}_2) + 31.234 & r &= -0.928 \\ \text{SO}_3 &= 0.963 (\text{MgO}) - 10.980 & r &= +0.753 \\ \text{SO}_3 &= 1.697 (\text{Al}_2\text{O}_3) - 16.974 & r &= +0.639 \\ \text{Al}_2\text{O}_3 &= 0.446 (\text{MgO}) + 7.116 & r &= +0.928. \end{aligned}$$

The SiO_2 -MgO and SiO_2 - Al_2O_3 correlations show high negative coefficients. The chemical composition of the white palagonite can be calculated with these equations, assuming that its silica content is zero (Table 2, column 5). The Mg/(Mg + Al) ratio is very similar to that of the Mg-Al phase in the orange palagonite. The average analysis, with SEM, of the massive inner zone shows a higher SiO_2 and K_2O content than the average analysis for the whole orange palagonite (Table 2, columns 2 and 4), which means that the Si-K phase is essentially in this zone. The Mg/(Mg + Al) ratio is 0.40 and there is no correlation between Al_2O_3 and MgO or SO_3 .

Discussion

The palagonites of the Red Sea are composed of two zones—an orange palagonite and a white

palagonite. The latter has the morphological, mineralogical and geochemical characteristics of motukoreaite, an Mg-Al hydroxy-sulphate-carbonate. Without data on the CO_2 content, it is not possible to give a structural formulae for this mineral. The orange palagonite consists of a mixture of Mg-Al phases, carbonates, iron and titanium oxides or hydroxides, and an undetermined Si-K phase.

Table 2. Chemical analyses of glass and palagonite

	Microprobe analyses			Scanning analyses	
	Fresh glass	Orange (2) Palagonite	Mg-Al (3) phase	Orange (4) Palagonite	White (5) Palagonite
SiO_2	51.98	26.20 ± 5.17	0	36.65 ± 6.68	0
TiO_2	1.06	2.68 ± 0.51	0	1.89 ± 0.55	0
Al_2O_3	14.61	22.05 ± 2.18	29.76	18.74 ± 1.98	27.37
$\text{Fe}_2\text{O}_3^{(1)}$		26.62 ± 3.19	0	23.24 ± 5.18	
$\text{FeO}^{(1)}$	11.28				
MnO	0.39	0.10 ± 0.03	0	0.14 ± 0.08	
MgO	6.95	19.50 ± 5.13	43.04	9.47 ± 1.82	42.41
CaO	11.66	1.28 ± 0.36	0	0.99 ± 1.23	
Na_2O	2.07	1.07 ± 0.58	0	4.23 ± 0.89	
K_2O	0.11	0.50 ± 0.30	0	1.54 ± 0.33	
SO_3	ND	ND	ND	2.49 ± 1.66	30.22
H_2O	ND	ND	ND	ND	ND
Cl				0.62 ± 0.27	
TOTAL	100.11	100.00	72.80	100.00	100.00
Mg/Mg+Al ⁽⁶⁾		0.53	0.65	0.40	0.66

- (1) Total iron
- (2) Average of 29 analyses, recalculated at 100 %
- (3) Chemical composition obtained from correlations between oxides for 29 analyses, recalculated at 100 %
- (4) Average of 12 analyses, recalculated at 100 %
- (5) Chemical composition obtained from correlations between oxides for 18 analyses, recalculated at 100 %
- (6) Molar ratio

This is the first time that hydroxysulphate has been described occurring by the natural alteration of basaltic glasses by seawater at low temperature. Hydroxycarbonates and hydroxysulphates are generally found in sulphide deposits (Nickel and Clarke, 1976; Nickel and Wildmann, 1981; Bish and

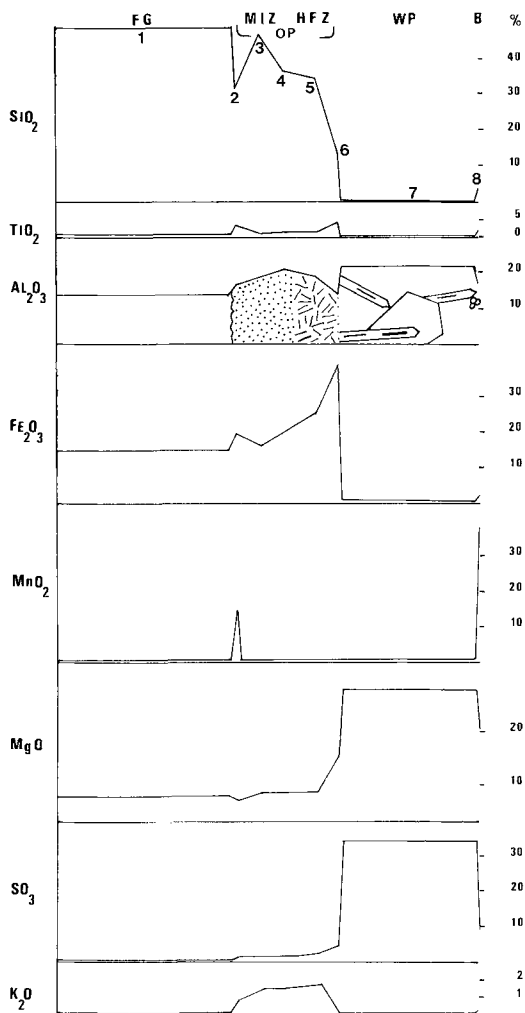


FIG. 5. Chemical zonation of palagonite: FG = fresh glass; OP = orange palagonite; MIZ = massive inner zone; HFZ = heterogeneous fibrous zone; WP = white palagonite; B = spherules. 1 to 8: see Table 3.

Livingstone, 1981); in ultramafic rocks (Mumpton and Thompson, 1975; Hudson and Bussell, 1981; Noack and Nahon, 1982; Bernardelli *et al.*, 1983); or associated with serpentines in oceanic sediments (Schmitz *et al.*, 1982). Motukoreaite has been found in volcanic basaltic tuffs and beach-rocks in New Zealand by Rodgers *et al.* (1977).

In experimental alteration of basaltic glasses by seawater between 25 °C and 90 °C, the hydroxycarbonates (hydrotalcite and pyroaurite) are almost always found (Crovisier *et al.*, 1983; Thomassin, 1984). During the alteration process, the hydroxy-

carbonates are replaced by phyllosilicates. In experiments at 3 °C, hydroxycarbonates do not appear and a Si-Al-K phyllosilicate similar to illite is formed (Crovisier *et al.*, 1983).

By analogy with experimental work, the Si-K phase formed in orange palagonite can perhaps be interpreted as a precursor of phyllosilicate. The Si-K phase is also found in the first stage of palagonitisation in basaltic glasses of the Atlantic Ocean (Noack, 1979). Mg-Al hydroxides have never been described, to our knowledge, in natural or synthetic palagonites. The orange palagonite shows two zones: a massive zone near the glass and a fibrous outer zone. By examination with scanning electron microscope, this fibrous zone can be perhaps compared to altered lamellae of hydroxysulphate. The double hydroxides have the same basic structure (Mascolo and Marino, 1980) and the same Mg/Al molar ratio as the hydroxysulphate. The fibrous zone is probably the first stage of the transformation of the hydroxysulphate, with an exchange of SO_4^{2-} by OH^- . The massive inner zone is a second stage of this transformation. In this zone, the low Mg/(Mg+Al) ratio (0.40) and the X-ray data ($c = 22.68 \text{ \AA}$) suggest, after Mascolo and Marino (1980), a mixture of a Mg-Al double hydroxide and an Al-hydroxide. In further stages, we can imagine that the hydroxides and the Si-K phase would form phyllosilicates. This succession is not very far from the observed evolution in experimental alterations.

Palagonites of the Red Sea are the first link between natural palagonites and the experimental alteration of basic glasses by seawater.

Acknowledgements

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Table 3. Chemical analyses across a vug, recalculated at 100% (see fig. 5).

Point	1	2	3	4	5	6	7	8
Zone	FRESH	ORANGE PALAGONITE				WHITE PALAGONITE		BALLS
	GLASS	Massive	inner zone		Heterogeneous fibrous zone			
SiO ₂	49.40	32.23	47.42	37.22	35.34	14.40	0.35	3.68
TiO ₂	1.08	3.48	1.13	1.51	1.99	3.89	0.11	2.07
Al ₂ O ₃	13.86	16.53	19.03	21.50	19.57	14.46	22.06	16.64
Fe ₂ O ₃	13.64	19.30	16.34	20.16	24.77	39.03	0.63	2.14
MnO ₂	0.43	14.57	0.09	0.19	0.10	0.03	0.09	36.81
MgO	7.11	6.13	8.55	8.57	7.18	18.47	36.61	26.34
CaO	12.29	1.66	1.21	1.46	0.88	0.94	0.02	0.42
Na ₂ O	1.61	2.47	2.48	5.35	5.61	1.87	3.36	1.83
K ₂ O	0.17	0.94	1.66	1.49	1.73	0.16	0.06	0.13
SO ₃	0.36	1.65	1.80	1.83	2.25	4.64	34.47	9.17
Cl	0.04	1.05	0.31	0.72	0.87	2.07	2.22	0.76

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