

Occurrence of thaumasite in a seawater-basalt interaction, Mururoa atoll (French Polynesia, South Pacific)

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ABSTRACT. The first occurrence of thaumasite resulting from seawater-basalt interaction has been discovered in a drill hole on Mururoa atoll (French Polynesia, South Pacific). This sulphate-carbonate-silicate is associated with zeolites (phillipsite, chabazite, gmelinite), apophyllite, analcime, and gyrolite. In this environment thaumasite can be considered as the last mineral of an alteration sequence. It crystallized from a Ca-SO₃-CO₂-rich and Al-Na-K-poor fluid. The temperature of this solution is unknown, but was probably not greater than 100 °C.

THE Mururoa atoll (French Polynesia, South Pacific) consists of a volcano and a coral reef about 400 m thick. The volcano is formed of a succession of massive flows and volcanic breccias, with variable thickness, and from tholeiitic to alkaline composition. The volcanism essentially has a submarine origin with some subaerial lavas at the top. The present situation of the flows and breccias, and their submarine origin, has encouraged extensive argillaceous and zeolitic alteration. A complete study of the submarine alteration in two drill holes will be described in a further paper. However, in bore hole Echo II, some samples have revealed the existence of thaumasite, a rare mineral in the lavas and never previously observed in a submarine alteration sequence. In this paper we examine this mineral and the other associated secondary minerals.

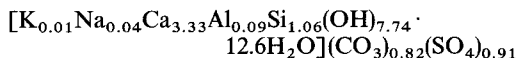
Primary mineralogy of the lavas

Olivine, plagioclase, and pyroxene are present as microlites or phenocrysts. Olivine is generally transformed to iddingsite, clays or carbonates. Plagioclase is sometimes replaced by clays and zeolites. Pyroxene is always fresh. In the hyaloclastites, volcanic glass is palagonitized.

Secondary mineralogy

Secondary minerals are developed in vugs, cracks and as cement of the breccias.

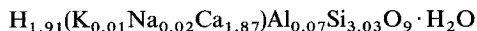
Thaumasite Ca₃Si(OH)₆ · 12H₂O(CO₃)(SO₄). This mineral has been found in seven samples as a cement in the breccias, between 550 and 700 m depth (fig. 1). It seems to be the last mineral to have crystallized. Macroscopically, it forms white compact masses. Electron scanning observations show that these masses are formed by fibres 3 μ wide and 70 to 120 μ long (fig. 2). The fibres are similar to those described by Wilson (1978). The nature of this mineral was confirmed by the XRD study; the X-ray spectrum is analogous with those of ASTM cards 25-128 (natural thaumasite) and 27-70 (synthetic thaumasite). In one sample (E II 27), the quantity of thaumasite was enough for a chemical analysis (Table I). The structural formula, calculated on the basis of ten oxygens, is as follows:



This formula shows greater Ca, Si, and H₂O, and lower CO₃ and SO₄ than the theoretical formula of thaumasite.

Zeolites, analcime and gyrolite. Zeolites are found in all the samples as fillings of cracks in the lavas or as cement in the breccias, associated with thaumasite. Phillipsite, chabazite and gmelinite were detected by X-ray diffraction and confirmed by electron microprobe analyses (Table II and fig. 3). Fig. 1 shows the distribution of the various zeolites in the zone where thaumasite is present. All three are not always found in the same sample. When this is the case, the order of crystallization is phillipsite-chabazite-gmelinite (samples 45 and 27). The gmelinite is relatively rare. Analcime was found only in sample E II 50 (Table II).

In sample E II 49 microprobe analyses revealed the presence of a calcium silicate hydrate similar to gyrolite (Table I), but this mineral was not detected by XRD. The structural formula calculated on the basis of 10(O,OH) is:



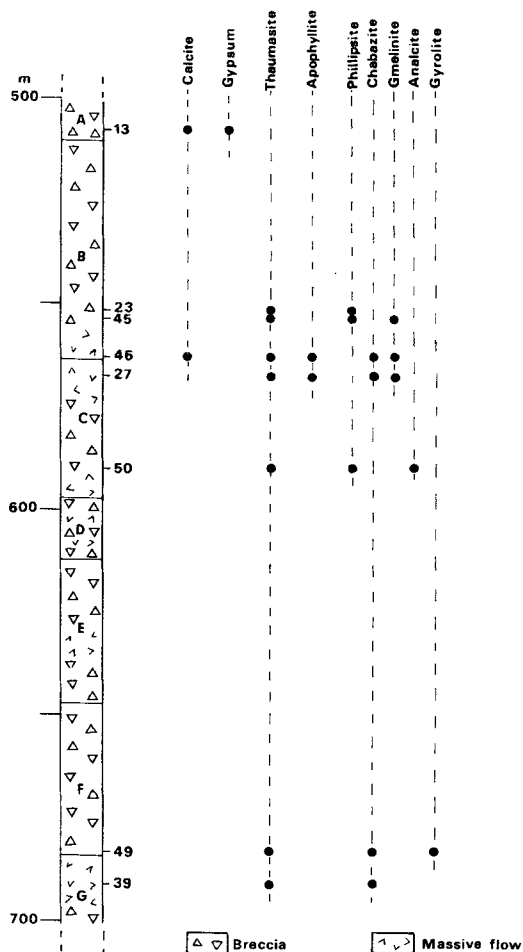


FIG. 1. Distribution of thaumasite and other associated secondary minerals in drill hole Echo II, Mururoa atoll. Petrographic types of the lavas: A = oceanite; B = PL-OL porphyric basalt and aphyric hawaite; C = aphyric hawaite, D = PL-OL porphyric alkali basalt; E = PL-PX porphyric basalt; F = polygenic breccia; G = PL-OL porphyric basalt.

This mineral is a little richer in Si and poorer in Ca than the theoretical formula of gyrolite [$H_2Ca_2Si_3O_9 \cdot H_2O$, Ford (1932)].

Apophyllite $KFCa_4[Si_8O_{20}]8H_2O$. Apophyllite has been found in several samples, sometimes with thaumasite. In sample E II 27, it was found as millimetric, bluish crystals, wedged between crystals of chabazite and thaumasite. In sample E II 46, together with calcite, it filled vugs. Electron microprobe analyses (fluorine was not analysed) showed slight substitution of Si by Al and a slightly low value for K_2O (Table I).

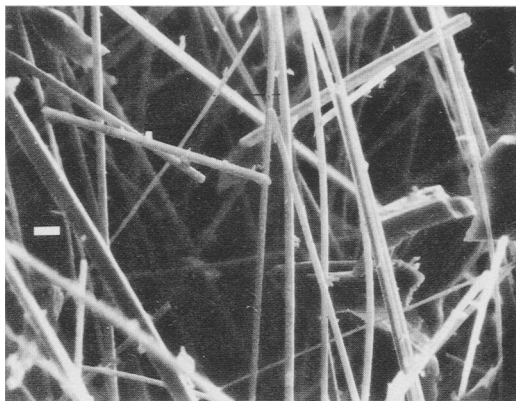


FIG. 2. Scanning electron micrograph of thaumasite. Scale bar = 8μ .

Origin of the thaumasite

A common mineral in concretes and cements, in which it induces expansion (Lachaud, 1979), thaumasite is rarely described in the geological literature. Discovered a hundred years ago, the number of known deposits is about ten. Two associations are recognized: with sulphides and hydrothermal minerals (Kirov and Pouliouff, 1968; Medici, 1972; Piskin and Delaloye, 1979)—thaumasite is the final product of a hydrothermal sulphidic fluid; and with low-temperature zeolites (phillipsite and chabazite) in a carbonated and sul-

TABLE I. Chemical analyses of thaumasite apophyllite and gyrolite

	1	2	3
SiO_2	9.60	50.73	55.68
TiO_2	0.00	0.00	0.00
Al_2O_3	0.65	1.40	1.04
$Fe_2O_3^*$	0.12	—	—
FeO^*	—	0.00	0.03
MnO	0.00	0.00	0.00
MgO	0.05	0.02	0.06
CaO	27.30	24.97	32.15
Na_2O	0.18	0.32	0.15
K_2O	0.03	3.44	0.09
CO_2	5.46	—	—
SO_3	11.00	—	—
H_2O	44.72	—	—
Total	99.11	80.88	89.20

* total iron.

1. Thaumasite: atomic absorption; sample 27.
2. Apophyllite: electron microprobe; sample 27.
3. Gyrolite: electron microprobe; sample 50.

TABLE II. Chemical analyses of zeolites and analcime (by electron microprobe except sample 46)

Sample	45		46	27			50		49		39
Mineral	P	C	G	G	G	G	P	P	A	C	C
SiO ₂	56.74	50.81	53.47	64.08	54.57	51.39	58.97	60.05	54.74	53.73	57.02
TiO ₂	n.d.	n.d.	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	22.06	22.30	19.47	24.24	22.04	20.97	20.19	18.68	23.30	20.53	18.50
FeO	0.29	0.15	0.94	0.00	0.00	0.08	0.01	0.00	0.00	0.01	0.00
MnO	n.d.	n.d.	n.d.	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00
MgO	0.10	0.30	0.66	0.00	0.00	0.01	0.00	0.02	0.00	0.01	0.01
CaO	1.39	5.40	2.07	0.91	1.60	2.73	1.39	1.44	0.19	4.66	5.04
Na ₂ O	2.99	5.10	8.47	4.79	6.85	8.82	1.87	3.79	8.28	3.25	3.84
K ₂ O	2.66	2.10	0.70	0.26	0.80	0.64	8.62	7.42	0.03	4.95	1.12
H ₂ O ⁺	n.d.	n.d.	14.19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	86.23	86.16	99.99	94.28	85.86	84.64	91.09	91.40	85.64	87.14	85.53

Numbers of ions on the basis of 72(O)											
Si	25.72	23.82	25.00	26.10	24.38	24.37	26.14	26.56	24.81	24.98	26.22
Al	11.77	12.29	10.72	11.63	11.60	11.72	10.53	9.64	12.43	11.23	10.02
Fe + Mn	0.11	0.06	0.36	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.00
Mg	0.08	0.23	0.48	0.00	0.00	0.01	0.00	0.03	0.00	0.03	0.03
Ca	0.68	2.70	1.04	0.40	0.77	1.39	0.66	0.68	0.08	2.31	2.48
Na	2.61	4.64	7.66	3.78	5.93	8.11	1.60	3.21	7.26	2.93	3.42
K	1.55	1.27	0.42	0.13	0.46	0.39	4.87	4.16	0.03	2.93	0.66

P = phillipsite; C = chabazite; G = gmelinite; A = analcime.
n.d. = not determined; total iron as ferrous iron.

phated environment (Knill, 1960; Browne, 1973; Paulitsch, 1973; Jakob and Matoushek, 1979)—in this case, thaumasite results from the leaching of sulphates (gypsum and anhydrite) by a fluid which, under ordinary conditions, would precipitate zeolites (Knill, 1960).

In drill hole Echo II at Mururoa atoll, the

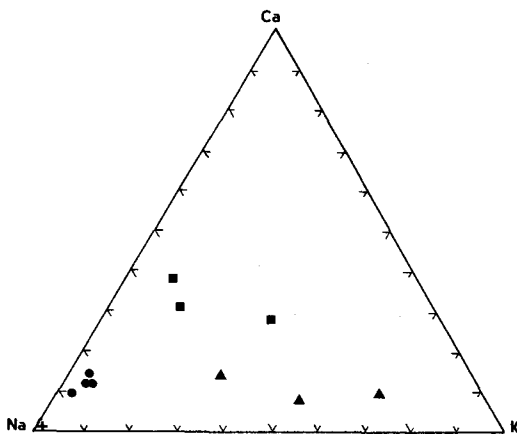


FIG. 3. Ca-Na-K compositions of zeolites and analcime: triangle = phillipsite; square = chabazite; circle = gmelinite; cross = analcime.

following facts must be considered: sulphides are absent; thaumasite is present in large cracks or in the cement of the breccias, never in the vesicles of the basalt; it was the last mineral to crystallize—when the alteration sequence is complete, the order is phillipsite-chabazite-gmelinite-thaumasite, sometimes with apophyllite between the zeolites and the thaumasite; gypsum (rare) and calcite are present in the upper part of the drill hole (above 600 m for the calcite, fig. 1)—these minerals could be a CO₂ and SO₃ source for thaumasite, particularly since calcite is abundant in the upper part of the hole and absent or in very small quantity when thaumasite is present; the circulating fluid (seawater) is naturally rich in sulphates and carbonates and is probably the source of calcite and gypsum; low-temperature alteration of basalt releases the constituent elements of the secondary minerals (Si, Al, and Ca).

At this locality, therefore, thaumasite is considered to be the final mineral in the alteration sequence. The fluids involved are rich in Ca, SO₄, and CO₃, and poor in Al, Na, and K. The enrichment in sulphate and carbonate can either result from leaching of gypsum and calcite (absolute enrichment), or from the precipitation of zeolites (relative enrichment).

Isotopic studies are planned to confirm the

temperature of formation of the thaumasite and other secondary minerals, but it is likely that this did not exceed 100 °C.

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