

AUTHIGENIC SILICATES FORMED FROM BASALTIC
GLASS BY MORE THAN 60 MILLION YEARS' CONTACT
WITH SEA WATER, SYLVANIA GUYOT,
MARSHALL ISLANDS

by

R. W. REX

Chevron Research Company
La Habra, California

ABSTRACT

DREDGE haul MP43A, from a depth of 6180–10,860 ft on Sylvania Guyot, the companion seamount to Bikini Island, yielded large blocks of yellow buff-colored rock consisting of clay, opal, phillipsite, and veins of phosphatized foraminifera of basal Eocene age, suggesting more than 60 million years' exposure to sea water. These freshly broken blocks were partially covered with crusts of hydrated manganese and iron oxides. Occasional incompletely altered fragments indicate that the original volcanic rock was basaltic glass in a tuff breccia. The alteration products consist of: (1) water-clear phillipsite, (2) opal spherules which appear to have formed as linings of vesicles in the original glass, (3) a buff-colored, disordered, chloritic, mixed layer clay consisting of montmorillonite with interlayer ferric hydroxide.

The typical basaltic glass, weathered in the oceanic environment for much shorter periods of time, is converted to montmorillonite and phillipsite. The principal effect on the phillipsite of long exposure to sea water is etching of the crystal surfaces indicating non-equilibrium with sea water. The effect of the environment on montmorillonite is iron chloritization. Addition of iron occurs on a layer-by-layer basis, suggesting that hydroxy-iron polymers occur in sea water. Iron chloritization reduces the CEC of the MP43A montmorillonite by approximately one-third.

INTRODUCTION

THE role of silicates in buffering the composition of sea water has been a subject of major interest since Sillén (1961) called attention to the predominance of the silicate buffer over the carbonate–borate buffer. The literature on this subject has been reviewed recently by Mackenzie and Garrells (1966) and Hess (1966). A variety of chemical models has been postulated by various workers, and experimental work to delineate phase boundaries is underway at various laboratories. In order to test these models against nature, deep-sea dredge hauls are being studied for possible material useful for this purpose.

Ideally, a seamount in the open ocean is required, far from land, never exposed to subaerial weathering, of known minimum age, and containing a

suite of authigenic silicates crystallized from a gel or glass precursor of known composition. The ideal example has yet to be found, but a near approximation exists in dredge haul MP43A from Sylvania Guyot in the Pacific Ocean.

The work described in this paper is an outgrowth of several stimulating years spent with Professors Edward D. Goldberg and Gustaf Arrhenius at the Scripps Institution of Oceanography. Their interest and encouragement is sincerely appreciated.

GEOLOGICAL SETTING

The Scripps Institution of Oceanography—U.S. Navy Electronics Laboratory Mid-Pacific Expedition of 1950—collected a number of dredge hauls from the top of Sylvania Guyot, a seamount rising from a common base with Bikini atoll in the Marshall Islands. Sylvania has a very flat top at about 4230 ft and is connected to Bikini by a saddle at a depth of 4740 ft. The adjacent sea floor is deeper than 15,000 ft (Hamilton and Rex, 1959). The very flat top indicates that when the original seamount was at sea level, wave erosion stripped the terrain to sea level, removing any rock that might be subject to subaerial erosion.

Regional subsidence dropped Sylvania Guyot deeply enough and fast enough so that reef-producing organisms were unable to establish themselves. No *in situ* reef material was recovered from Sylvania (Emery *et al.*, 1954). Bikini, however, had enough relief or was younger and was able to establish reefs. Continued submergence of Sylvania is indicated by the continuous Recent to Oligocene succession of reef material on companion Bikini (Emery *et al.*, 1954). Consequently, the rocks of Sylvania have been continuously exposed to sea water without interruption.

Dredge haul MP43A was made on a north spur of Sylvania Guyot at depths from 6180 to 4860 ft, near the rounded edge of the flat top of the seamount. The rock recovered consisted mostly of yellow and brown basaltic tuff breccia (Macdonald *in* Emery *et al.*, 1954, p. 120) covered with crusts of manganese oxides. Detailed study of the largest block showed that the tuff breccia had altered to a mixture of phillipsite, a yellow-buff clay mineral, and opal. Cracks within the breccia had been filled with a planktonic foraminiferal ooze that had been altered to apatite.

The foraminiferal assemblage has been dated as latest Paleocene or basal Eocene (Hamilton and Rex, 1959). Using the absolute age (Kulp, 1961) of 58 million years for the Paleocene–Eocene boundary and assuming some passage of time for subsidence to a depth where planktonic foraminifera can accumulate, a minimum exposure to sea water for the altered basaltic tuff breccia of approximately 60 million years is obtained.

Detailed examination of the altered tuff discloses no evidence of secondary mineralization, suggestive of hydrothermal alteration. The extremely fragile nature of the altered tuff fabric makes subaerial formation prior to submergence through the surf zone unlikely. Consequently, this altered tuff

comes close to being nearly ideal material to study slow sea water-silicate interactions. The main shortcoming is a lack of information on the initial composition of the silicate glass.

AUTHIGENIC NONSILICATES

Hydrated Manganese-Iron Oxides

A black crust, approximately one centimeter thick, of hydrated oxides of manganese and iron encrusts the altered tuff breccia (Goldberg, 1954, p. 252). The iron is present as goethite and X-ray amorphous oxides, while manganese is present as δ -MnO₂ (Buser and Grütter, 1956, p. 51). The paragenetic relationships of these oxides to their substrate have been described previously (Hamilton and Rex, 1959).

Apatite

Apatite occurs as a replacement for calcitic fossils, as separate discrete platelets that lack apparent fossil morphology, and as dense vein-fillings (Hamilton and Rex, 1959).

AUTHIGENIC SILICATES

Opal

The original tuff breccia was highly vesicular, and the vesicles have been preserved as opal casts (Fig. 1). The first stage of glass alteration results in diffusion of silica to the vesicles. Thin shells of opal were deposited, which are still X-ray amorphous (Rex, 1958). This occurrence of opal is one of the oldest known examples of amorphous silica which has not ordered to cristobalite or quartz.

Phillipsite

Water-clear crystals of the zeolite phillipsite fill numerous cavities in the tuff breccia (Fig. 2). Their formation predates the basal Eocene foraminifera (Hamilton and Rex, 1959, plate 250, fig. 2) providing an unusual example of nearly perfect phillipsite crystals exposed to mid-ocean sea water for 60 million years or more. Electron micrographs of the surfaces of these crystals show that they are all undergoing re-solution (Fig. 3). Apparently phillipsite crystallized early in the history of tuff alteration and then has been slowly etched by sea water.

A separated fraction of pure phillipsite was analyzed chemically and by X-ray diffraction (Appendix 1). The chemical analyses, in addition to X-ray fluorescence checks for additional possible ions missed by wet chemical techniques, indicate that this phillipsite is essentially a potassium sodium aluminosilicate. The potassium-sodium atomic ratio is nearly 1:2 compared to 1:28 for sea water. This large difference suggests *either* an unusually large

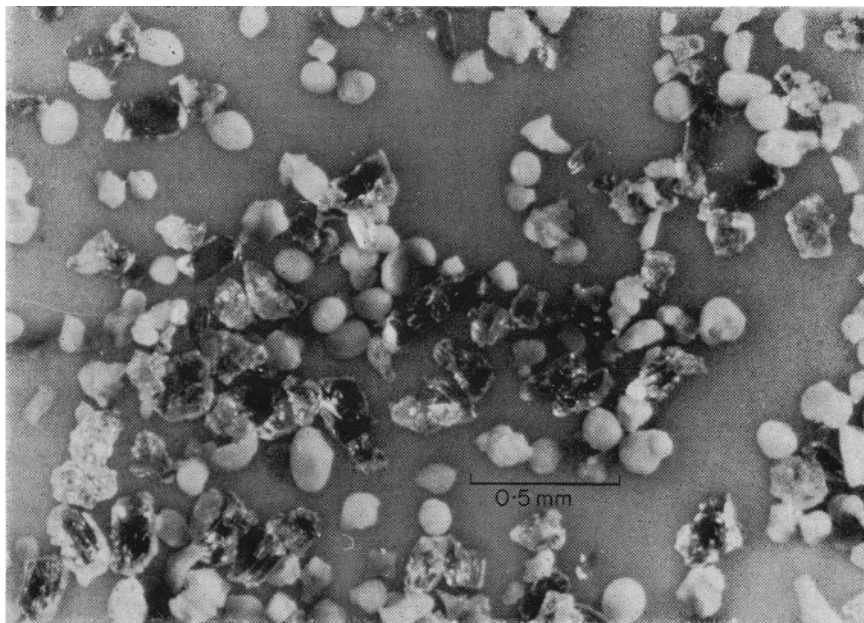


FIG. 1. Opal spherules originally formed as linings of gas vacuoles in the basaltic glass. Crystals are phillipsite.

fractionation factor for an ion exchange zeolite in favor of K^+ , or that the original pore water from which this phillipsite crystallized was greatly enriched in potassium. This latter probability is suggested by the wide variations in exchangeable cations in marine phillipsite reported by G. Arrhenius (personal communication).

The MP43A phillipsite has nearly the same powder pattern and a similar but more siliceous chemical composition as the crystals used by Steinfink (1962) for the analysis of the structure of phillipsite.

Mixed Layer Montmorillonite-Chlorite

There appears to be only one clay mineral present, a yellow-buff montmorillonite with interlayer iron partially converting it to a mixed layer iron chlorite. The clay now has a CEC of 0.71 meq/g, compared to an expected value of 1.10 meq/g for pure montmorillonite. The air-dried, K^+ saturated clay shows one broad line centering at 13.0 Å (Fig. 4). The glycerol-treated, K^+ -saturated clay (Fig. 4) shows a strong peak at 16.7 Å and a broad, very weak peak centered on 9.8 Å. Heating the K^+ -saturated clay to 300°C yielded one broad peak (Fig. 5) centered on 11.6 Å. Further heating to 550°C collapses the single broad peak to 10.2 Å (Fig. 5). Air-dried Mg^{++} saturated clay yielded



FIG. 2. Twinned water-clear phillipsite crystals. Delicate reticulated appearance of crystal surfaces suggests possibility of surface corrosion.

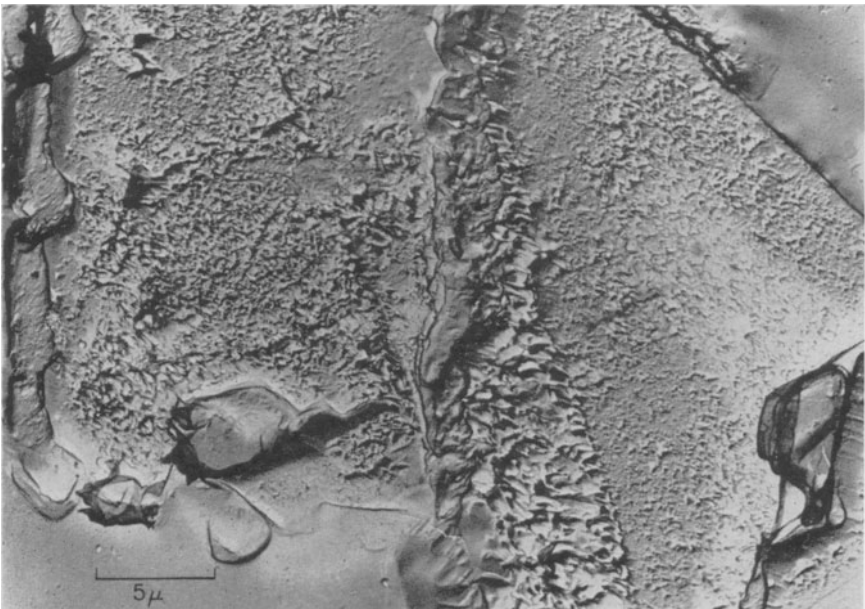


FIG. 3. Replica of phillipsite crystal surface showing deeply etched and pitted crystal surface. This etched morphology was observed on all the phillipsite crystal faces studied from MP43A.

one broad line at 15.5 \AA (Fig. 6). Heating this sample to 550°F collapsed this broad line to 10.0 \AA (Fig. 6).

The X-ray data are interpreted to indicate the presence of montmorillonite with some intercalation of hydroxy-iron polymers in the interlayer space, producing an iron chlorite-montmorillonite mixed layer clay.

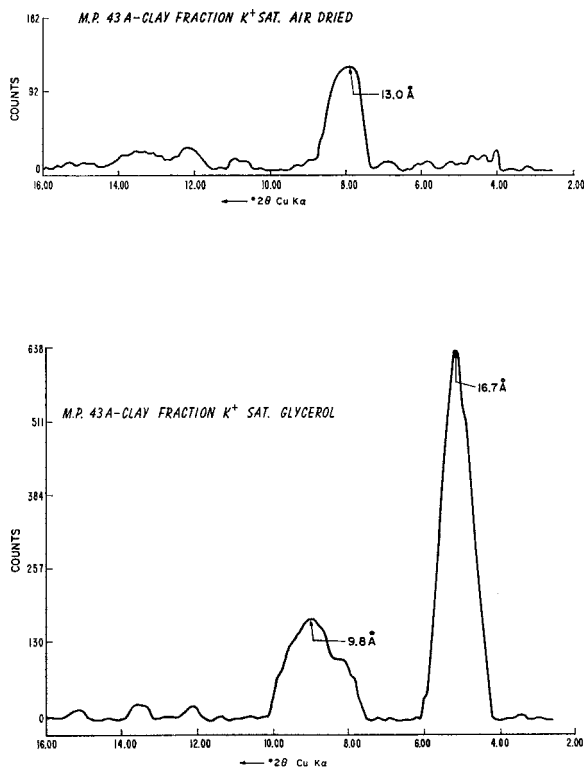


FIG. 4. X-ray diffraction patterns of potassium-saturated clay from MP43A. The glycerol-treated sample shows both a weak line, attributable to a 13.0 \AA mixed-layer component also seen in the air-dried clay and an overlapping second order of the 16.7 \AA line as well as the strong first-order 16.7 \AA reflection.

Analyses were run on fresh clays, dithionite-citrate buffer-treated clays, and by hydrazine-mixed acid and base ion exchange resin treated clays. These treatments show that removal of surface iron films from clay particles has little effect on the X-ray patterns other than enhancement of the intensity of the mixed layer $00l$ diffraction lines, probably by reduction of iron micro-absorption effects. The $00l$ lines are very broad, indicating small crystallite sizes. Electron micrographs of both shadowed and unshadowed crystallites

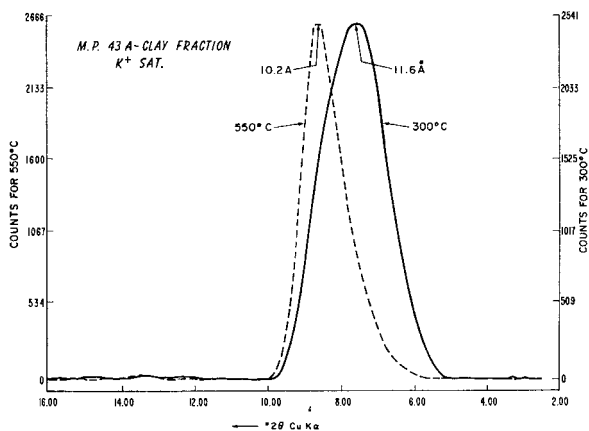


FIG. 5. Potassium-saturated clay fraction heated to 300°C and 550°C. At 300°C a normal montmorillonite should be fully collapsed. However, the chloritic layers keep the montmorillonite layers expanded to 11.6 Å. At 550°C iron chlorite has decomposed, and the structure collapsed to give an (001) spacing of 10.2 Å.

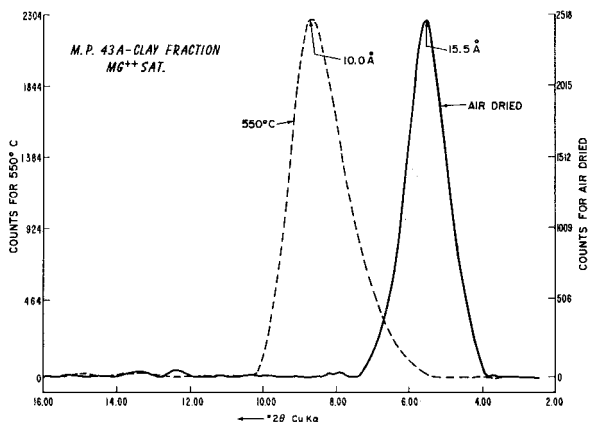


FIG. 6. Magnesium-saturated air-dried clay fraction yields a single peak at 15.5 Å compared to 13.0 Å for the potassium-treated clay. Collapse to 10 Å on heating to 550°C supports the montmorillonite-iron chlorite mixed-layer identification.

show that the iron is distributed heterogeneously within the clay microcrystals. Electron diffraction studies of single clay platelets with strong electron absorptivity (suggestive of high iron content) showed no evidence of random orientation of the iron hydroxide layers with respect to the pseudohexagonal silicate structure. The electron micrographs combined with the X-ray data are interpreted to mean that the iron hydroxide polymer mosaic elements

within the chlorite layer have their *c*-axes oriented approximately normal to the montmorillonite (00*l*). Ordering of the *a*- and *b*-axes is not established by these data.

Mixed layer clay was digested in 10% HCl for 64 hr, deionized, charged with Na⁺, and solvated with glycerol. The clay surviving this treatment gave a normal montmorillonite diffraction 001 line, expanding to 18 Å on solvation and collapsing to 10 Å on heating. These data are interpreted to mean that montmorillonite formed originally from the alteration of the basaltic tuff. This montmorillonite then scavenged iron hydroxide polymer cations from sea water, intercalating them into interlayer positions, thereby forming an iron chlorite, mosaic element by mosaic element.

The acid-leached montmorillonite still retained some of its yellowish-buff color, suggesting that the original montmorillonite might have been a nontronite.

INTERPRETATION

The altered basaltic tuff from Sylvania Guyot provides an opportunity for observing the effects on glass of an unusually long period of exposure to open-ocean sea water. The paragenetic sequence observed gives a number of clues to the equilibrium relations between phillipsite, montmorillonite, and sea water.

Phillipsite appears to form as a product of devitrification of volcanic glass in the marine environment, and, as might be expected, it is absent from Pacific Basin red clays wherever large quantities of pyroclastic sediments are absent (Rex, 1958). The present data indicate that it is a diagenetic mineral not directly precipitated from normal ocean water. Therefore, sea water composition probably should not be used directly to define the phase boundaries of phillipsite as Hess (1966) has done. The present data suggest that phillipsite forms in silica-rich solutions in equilibrium with opal and probably at a high K⁺/Na⁺ ratio compared to that of sea water. Phillipsite exposed to normal sea water appears to be undergoing solution. The very small amount of zeolite removed from the MP43A material in at least 60 million years amounts to an average rate of solution of one silicate monolayer in several thousand years. This suggests that phillipsite dissolution contributes little to buffering sea water.

Montmorillonite appears to be a "stable" aluminosilicate in sea water for periods of 60 million years and more. It forms from devitrifying volcanic glass and occurs in association with opal, which, however, is known to be unstable in sea water. Montmorillonite may owe its apparent stability to surface coatings of ferric hydroxides or it may be stabilized by the presence of excess silica from the opal in sediments. Consequently the hypothesis that montmorillonite is in thermodynamic equilibrium with sea water is not proved by this study.

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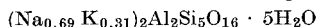
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APPENDIX 1.—CHEMICAL COMPOSITION OF PHILLIPSITE MP43A

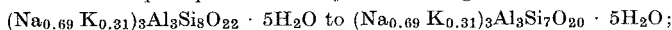
Major constituents	Wt. per cent
K ₂ O	6.0
Na ₂ O	7.4
SiO ₂	53.2
Al ₂ O ₃	16.8
CaO	0.3
MgO	0.3
H ₂ O	15.7
	<u>99.7</u>
Minor constituents	Wt. per cent
Fe ₂ O ₃	0.05
TiO ₂	0.03
P ₂ O ₅	0.02

The chemical analytical methods used were the U.S. Geological Survey standard rapid rock analysis procedure.

Consideration of the alkali to aluminum proportions suggests that the aluminum values are low or that the alkalis are high by a relative amount of 15%. Assuming equal distribution of the analytical error, the formula for this phillipsite is:



This compares with Steinfink's (1962) $(K_x Na_{1-x})_5 Al_5 Si_{11} \cdot 10H_2O$, but the MP43A zeolite is more siliceous. No reasonable reassignment of analytical errors can change the formula for the MP43A phillipsite much beyond the range from



consequently, these data support the data of G. Arrhenius (personal communication) suggesting that marine phillipsite has a variable range of silica-alumina ratios.

Water was measured by the weight loss between zeolite equilibrated at 25°C, 50% relative humidity, and heated to 110°C.