

55. PRELIMINARY RESULTS ON THE MINERALOGY AND GEOCHEMISTRY OF BASALT ALTERATION, HOLE 794D¹

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ABSTRACT

The basaltic rocks of Hole 794D drilled during Leg 128 are strongly altered. Microprobe analyses and XRD spectra on small quantities of matter extracted from thin sections show that primary minerals and glassy zones of the groundmass are totally or partially replaced by clay minerals with chlorite/saponite mixed-layer composition whatever the rock sample considered. This mixed-layer was also identified in veins and vesicles where it crystallizes in spheroidal aggregates. The largest veins and vesicles are filled by a zoned deposit: the chlorite/saponite mixed-layer always occupies the central part and is rimmed by pure saponite. Calcite crystallizes in secondary fractures which crosscut the clayey veins and vesicles.

Chemographic analysis based on the $M^+4Si-3R^{2+}$ projection shows that the chemical composition of the saponite component in the mixed-layer is identical to that of the free saponite. This indicates that the clay mineral crystallization was controlled by the chemical composition of the alteration fluids. From petrographic evidence, it is suggested that both chlorite/saponite mixed-layer and free saponite belong to the same hydrothermal event and are produced by a temperature decrease. This is supported by the stable isotopic data.

The isotopic data show very little variation: $\delta^{18}O$ saponite ranges from 13.1 ‰ to 13.5 ‰, and δD saponite from -73.6 ‰ to -70.0 ‰. $\delta^{18}O$ calcite varies from +19.7 ‰ to +21.9 ‰ vs SMOW and $\delta^{13}C$ from -3.2 ‰ to +0.4 ‰ vs. PDB. These values are consistent with seawater alteration of the basalt. The formation of saponite took place at 150°-180°C and the formation of calcite at about 65°C.

INTRODUCTION

Hole 794D, drilled during Leg 128, is located in the Japan Sea in the northeastern part of the Yamato Basin. A total of 733.5 m of sediment and igneous rock was penetrated beneath 2807 m of water. Igneous rock was encountered at 573 m below seafloor. Nine hard-rock lithologic units were recognized (Ingle, Suyehiro, von Breyman, et al., 1990) and are summarized in Figure 1. Igneous rocks cored from Hole 794D have been highly altered and contain abundant secondary minerals which appear as vein and vesicle fillings or as primary mineral replacements. We selected 16 samples from 660 m to 710 m below the seafloor (units 6-8) in order to determine the nature of these secondary minerals and search for paragenetic sequence and timing of basalt alteration.

EXPERIMENTAL METHODS

The investigation procedure used for the present study was based on *in situ* identification (XRD and electron microanalysis) of each secondary mineral. Diamond-polished thin sections of each selected sample were made after hardening with epoxy resin impregnation to preserve the clay minerals observed in vein and vesicle fillings. The secondary minerals were first located on thin section and then analyzed *in situ* using a CAMECA SX 50 microprobe (W.D.S. analysis) at the "Laboratoire de Pétrographie," University of Paris VI. The analytical conditions were the following: accelerating voltage of 15

kV, beam size of 1 μ m, beam current of 5 nA, counting time of 10 s for each analyzed element. In order to simplify the presentation of the results, the microprobe analyses were plotted into the $M^+4Si-3R^{2+}$ ternary diagram where $M^+ = 2Ca + Na + K$, $4Si = Si/4$ and $3R^{2+} = (Fe^{2+} + Mg + Mn)/3$ (Meunier et al., 1991); the trioctahedral clay mineral species are distributed into separate chemical domains (Fig. 2A). The smectite domain is bounded by the four following end members:

High charge saponite: $[Si_{3.34}Al_{0.66}]O_{10}[R^{2+}_3](OH)_2M^{+0.66}$

Low charge saponite: $[Si_{3.70}Al_{0.30}]O_{10}[R^{2+}_3](OH)_2M^{+0.30}$

High charge stevensite: $[Si_4]O_{10}[R^{2+}_{2.34}Li_{0.66}](OH)_2M^{+0.66}$

Low charge stevensite: $[Si_4]O_{10}[R^{2+}_{2.70}Li_{0.30}](OH)_2M^{+0.30}$

Averaged chemical compositions of clay minerals are presented in Table 1.

The X-ray diffraction data reported here were obtained from natural or glycolated oriented preparations using a PHILIPS PW 1730 diffractometer (40 kV, 40 mA) with an iron-filtered cobalt source. The bulk samples were first crushed and ultrasonically dispersed in distilled water in order to identify the totality of the secondary minerals present in the sample; they were X-rayed using a proportional detector in continuous scanning mode. The secondary minerals analyzed on thin section with the microprobe were extracted from their microsites using the method of Beaufort et al. (1983) and X-rayed with an ELPHYSE position sensitive detector allowing identification of small quantities (10^{-3} mg) of crystallized mineral phases (Rassineux et al., 1988). Mixtures of clay minerals and interstratifications were identified after a mathematical treatment of diffractograms using the decomposition program Decomps5 (Champion and Lanson, 1991).

Samples for isotopic analysis were prepared following conventional procedures. CO_2 gas was extracted from the carbonate samples by reaction with phosphoric acid at 25°C (McCrea, 1950). Oxygen was extracted from silicate samples by reaction with BrF_5 and converted to CO_2 by combustion with graphite (Clayton and Mayeda, 1963). Water was extracted from hydrous mineral phases by induction heating under vacuum at 1300°C and the released water was reduced to hydrogen gas by reacting with uranium at 800°C (Friedman, 1953). Gas samples were analyzed on a FINNIGAN MAT Delta E mass spectrometer. The values are reported in the usual delta notation (δ)

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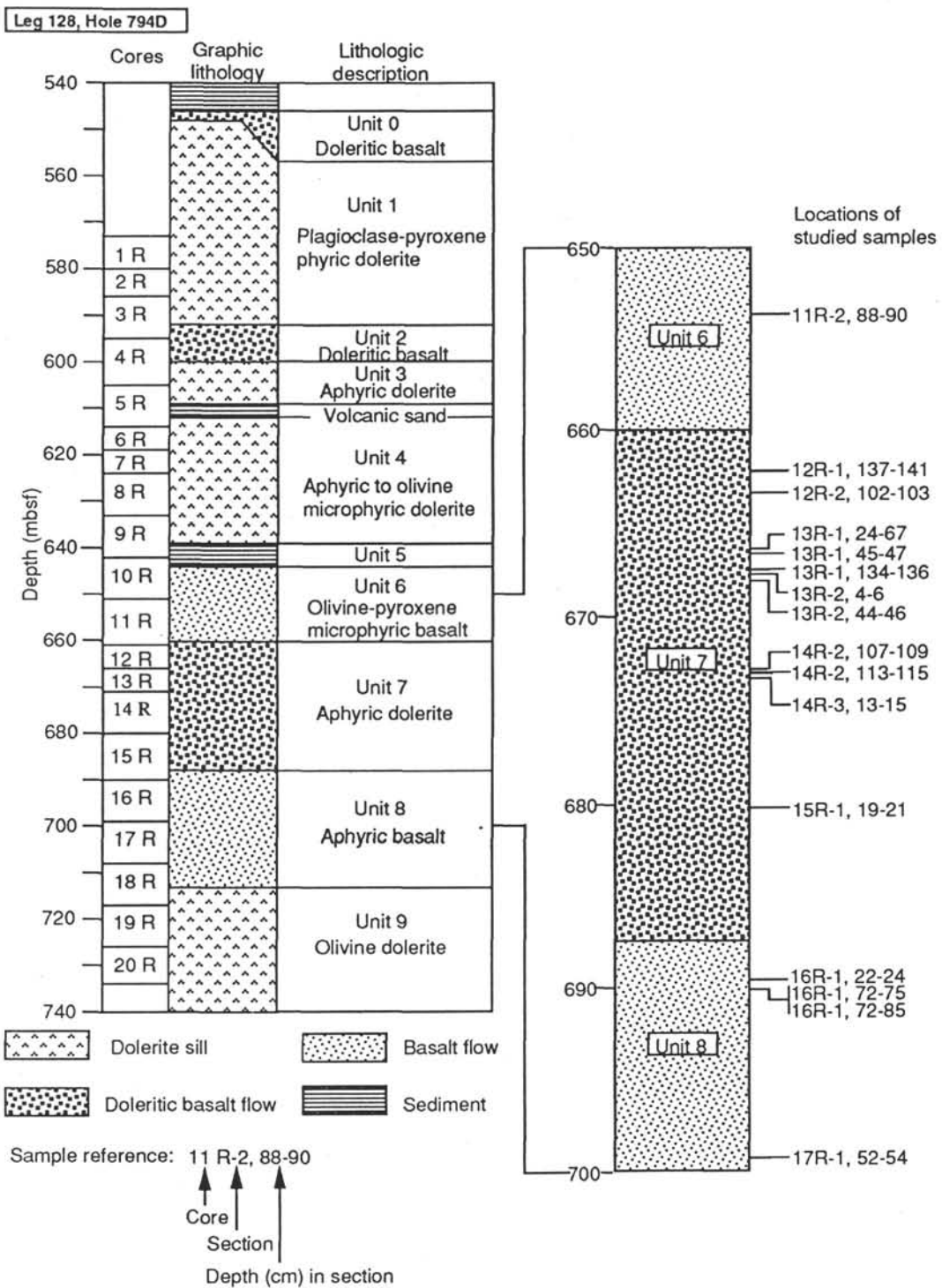


Figure 1. Core summary of igneous rocks at Hole 794D with location of the studied samples.

in per mil (‰) with $\delta^{13}\text{C}$ against PDB and $\delta^{18}\text{O}$ and δD against the SMOW standard.

RESULTS

Mineralogy

The petrographic investigation of all samples indicate that secondary minerals have developed (1) in the primary minerals (micropheno-

crysts and groundmass), (2) in the glassy zones of the groundmass, (3) in the veins and veinlets, and (4) in the vesicles.

Primary Minerals

Plagioclase: The plagioclases observed in aphyric basalts and aphyric dolerites occur as euhedral microphenocrysts (500 μm –1 mm) or as microliths (100 μm –300 μm) in the groundmass. These crystals

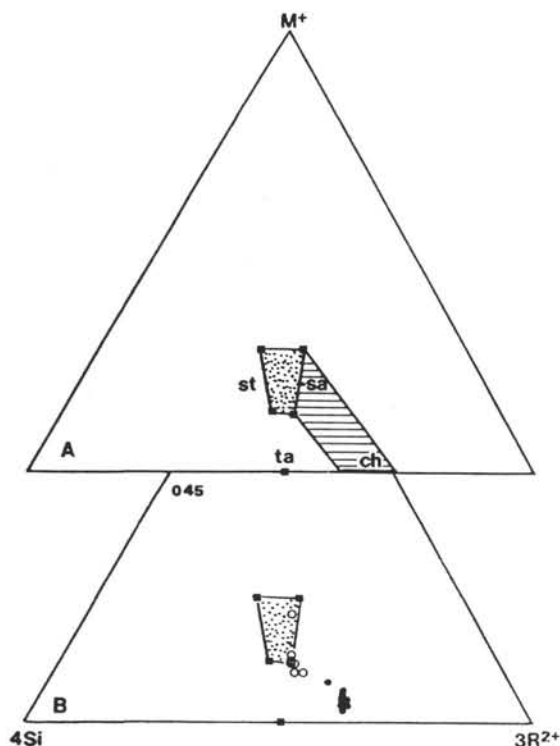


Figure 2. Projection of the chemical compositions of trioctahedral clay minerals in the $M^+-4Si-3R^{2+}$ coordinates. **A.** Theoretical compositions of high charge and low charge saponite (sa), high charge and low charge stevensite (st), talc (ta), chlorite (ch). The stippled area is the composition domain of trioctahedral smectites, the hachured area is the composition domain of chlorite/saponite mixed-layers. **B.** Circles and points represent the compositions of clay minerals crystallizing in two different plagioclases.

exhibit numerous etching cavities (200 μm –300 μm in phenocrysts) where colorless to light green sheaf-like secondary minerals crystallize (Fig. 3). The electron microprobe analyses of such clay minerals, when plotted into the $M^+-4Si-3R^{2+}$ ternary diagram of Figure 2B, fall in the compositional field of chlorite/saponite mixed-layers.

Olivine: The olivines occur as euhedral microphenocrysts (400 μm –1 mm) or subhedral crystals (200 μm –400 μm) arranged in intersertal texture with plagioclases. They are completely replaced by light green secondary clay minerals which preserve the initial shape of the mineral (pseudomorphosis). The electron microprobe analyses of such clay minerals plot in the compositional field of the chlorite/saponite mixed-layers of $M^+-4Si-3R^{2+}$ ternary diagram (Fig. 4A).

Pyroxene: The augitic clinopyroxenes occur as euhedral microphenocrysts (500 μm –1.5 mm) or as subhedral crystals (about 400 μm) which are often arranged in intersertal texture with plagioclase microphenocrysts. They are less altered than the olivine, but tiny lamellae of colorless to green clay minerals (20 μm) can be observed in the microcracks or along the cleavage planes of the pyroxene crystals. The chemical compositions of these lamellae are similar to the alteration minerals observed in the olivines and plot in the compositional field of the chlorite/saponite mixed-layers of $M^+-4Si-3R^{2+}$ ternary diagram (Fig. 4A).

Conclusion: The alteration products identified in dolerite and basalt from Hole 794D are similar regardless of the primary mineral precursor. The chemical compositions are those of chlorite/saponite mixed-layers, a result which is supported by the X-ray diffractogram obtained from microsampling in altered plagioclases (Fig. 5A): no expandable phase can be detected after ethylene glycol saturation (first-order reflection at 15.36 angströms, second-order reflection at

Table 1. Average chemical compositions of clay minerals from different origins.

	1	2	3	4	5	6	7
Oxides							
SiO ₂	42.14	35.25	37.63	39.08	41.64	35.69	39.77
Al ₂ O ₃	3.93	13.04	8.95	7.57	11.25	10.05	5.58
FeO	8.38	18.09	17.46	17.92	12.25	12.06	10.19
MgO	18.07	19.91	20.35	18.97	16.77	22.42	16.06
TiO ₂	0.01	0.07	0.05	0.04	0.07	0.04	0.04
MnO	0.03	0.13	0.11	0.14	0.13	0.05	0.05
CaO	1.50	0.33	0.37	0.48	1.46	0.63	1.07
Na ₂ O	0.37	0.26	0.36	0.57	1.53	0.22	0.98
K ₂ O	0.16	0.07	0.24	0.35	0.39	0.06	0.47
Total	74.59	87.15	85.52	85.12	85.49	81.22	74.21
Cations							
Si	3.64	3.54	3.84	1.02	4.11	3.74	4.48
Al	0.40	1.55	1.08	0.92	1.31	1.24	0.74
Fe ²⁺	0.61	1.52	1.49	1.54	1.01	1.06	0.96
Mg	2.33	2.98	3.10	2.90	2.47	3.50	2.69
Ti	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.01	0.01	0.01	0.01	0.00	0.00
Ca	0.14	0.04	0.04	0.05	0.15	0.07	0.13
Na	0.06	0.05	0.07	0.11	0.29	0.04	0.21
K	0.02	0.01	0.03	0.05	0.05	0.01	0.07

Note: 1 = vein saponite in large lamellae; 2 = chlorite/saponite mixed-layer from altered plagioclase; 3 = chlorite/saponite mixed-layer from altered olivine; 4 = chlorite/saponite mixed-layer from altered pyroxene; 5 = chlorite/saponite mixed-layer from altered glassy zones; 6 = chlorite/saponite mixed-layer from central vein deposit; 7 = chlorite/saponite mixed-layer from vesicles. Cationic proportions were calculated on an 11-oxygen basis for pure saponite and a 14-oxygen basis for chlorite/saponite mixed-layered minerals. Fe is assumed to be in the Fe²⁺ state.

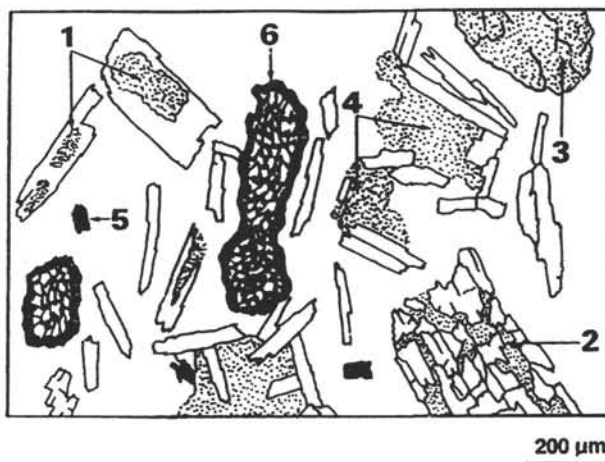


Figure 3. Alteration patterns observed in aphyric basalt. 1. Euhedral plagioclase microphenocrysts and microliths altered into chlorite/saponite mixed-layer. 2. Euhedral augite microphenocryst altered into chlorite/saponite mixed-layer. 3. Subhedral olivine microphenocryst altered into chlorite/saponite mixed-layer. 4. Glassy zone altered into chlorite/saponite mixed-layer. 5. Magnetite grains disseminated in the groundmass. 6. Vesicle with outer rim of saponite and central filling of chlorite/saponite mixed-layer.

7.53, with additional reflection at 9.67 angströms). No evolution of alteration with depth was detected.

Glassy Zones

The glass observed in aphyric basalt is generally devitrified and highly altered to brown, clayey anisotropic domains. The electron microprobe analyses of these clay minerals are distributed into two

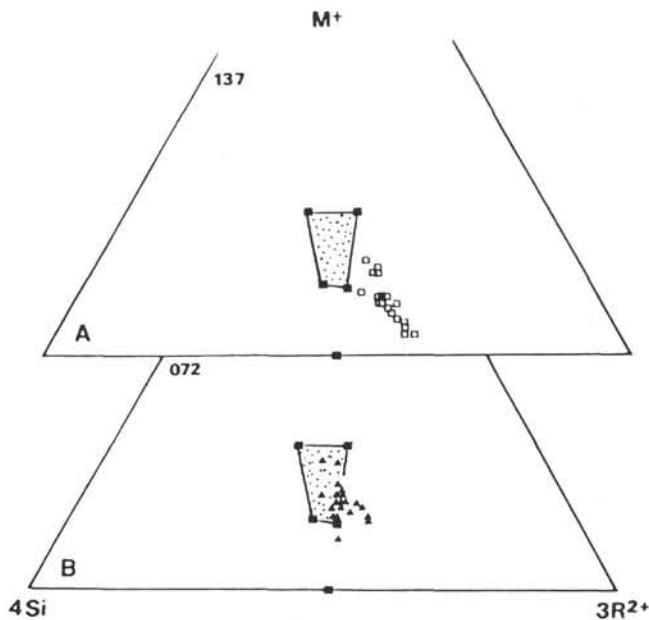


Figure 4. Chemical compositions of secondary clay minerals in the $M^+-4Si-3R^{2+}$ coordinates. **A.** Chlorite/saponite mixed-layers crystallizing in olivines and pyroxenes. **B.** Chlorite/saponite mixed-layers and saponites replacing the glassy zones.

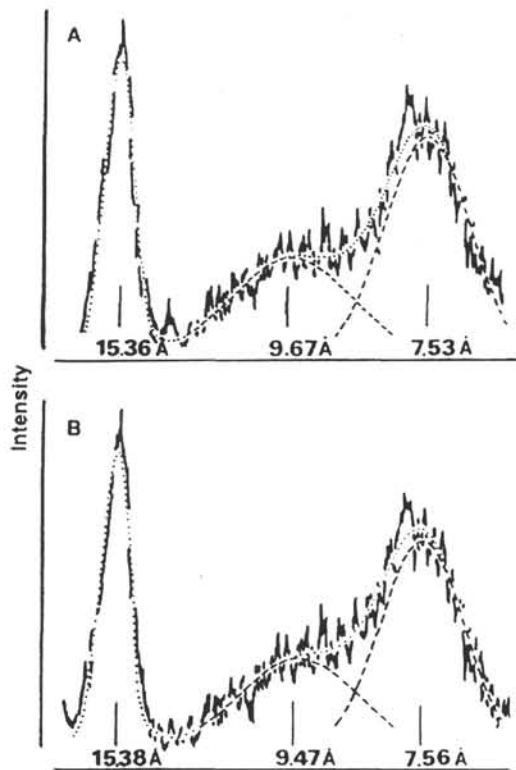


Figure 5. XRD spectra of chlorite/saponite mixed-layers from (A) altered plagioclase and (B) central deposit in a large vein. The decomposition calculation shows that they are composed of a mixture of several mixed-layers.

compositional domains in the $M^+-4Si-3R^{2+}$ ternary diagram (Fig. 4B): the chlorite/saponite mixed-layer and the saponite fields. The mixture of these two phases is supported by the X-ray diffraction study of the altered glass: an expandable saponite phase can be detected after ethylene glycol saturation; this saponite is mixed with small amounts of chlorite/saponite mixed-layer.

Veins

The veins observed in aphyric dolerite and basalt are millimeter-sized and can be classified in two types according to the nature of their fillings.

Saponite + chlorite/saponite mixed-layer + calcite veins (Fig. 6)

Two veins of this type were investigated in dolerite. The organization of the clay mineral fillings is similar in the two veins:

1. The external rim in contact with wallrock is made up of millimeter-sized lamellae of clay minerals, brown in plane light and second-order blue to yellow under crossed nicols. These lamellae are oriented perpendicularly to the wall. The electron microprobe analyses plot in the saponite chemical domain of the $M^+-4Si-3R^{2+}$ ternary diagram (Fig. 7A). This identification is well supported by the X-ray diffractogram obtained from microsampling in the vein (Fig. 8): a pure expandable phase can be detected after ethylene glycol saturation, with a first-order basal reflection at 17.10 angströms, and a second-order basal reflection at 8.45 angströms.

2. The central vein filling is made up of small size clay minerals (20–40 μm), colorless to light green under plane light and gray to pale yellow under crossed nicols. These clay minerals are arranged in spheroidal aggregates (150 μm in diameter). The electron microprobe analyses plot in the chlorite/saponite mixed-layer chemical domain of the $M^+-4Si-3R^{2+}$ ternary diagram (Fig. 7A). The X-ray diffractogram obtained from the microsampling in this central vein filling (Fig. 5B) identifies a chlorite/saponite mixed-layer: no expandable phase can be detected after ethylene glycol saturation (first-order reflection at 15.38 angströms, second-order reflection at 7.56 angströms, additional reflection at 9.47 angströms).



Figure 6. Millimeter-sized vein in aphyric dolerite showing a zoned deposit: 1. Millimeter-sized lamellae of saponite in contact with wall-rock. 2. Spheroidal chlorite/saponite mixed-layer as central filling of the vein. 3. Millimeter-sized crystals of calcite. 4. Calcitic veinlets crosscutting the saponite and chlorite/saponite mixed-layer deposits.

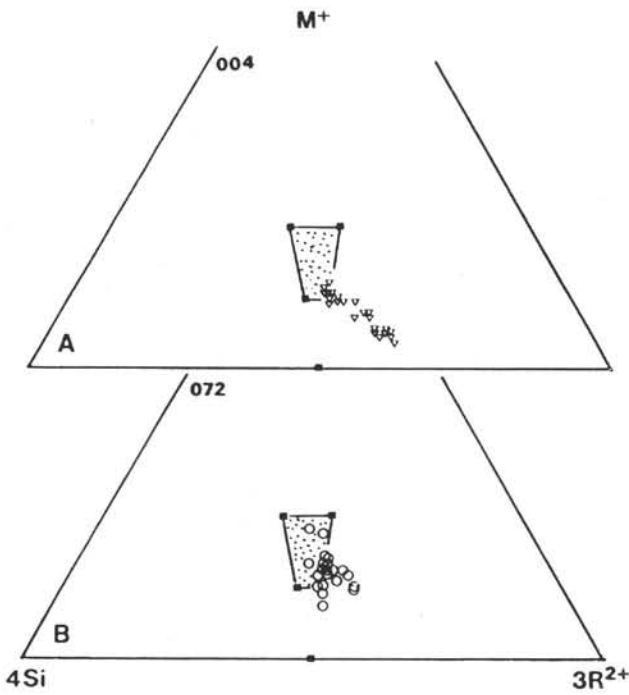


Figure 7. Chemical compositions of secondary clay minerals in the $M^+ - 4Si - 3R^{2+}$ coordinates. A. Saponite and chlorite/saponite mixed-layer in the central deposit of the vein described in Figure 6. B. Saponite from a vesicle.

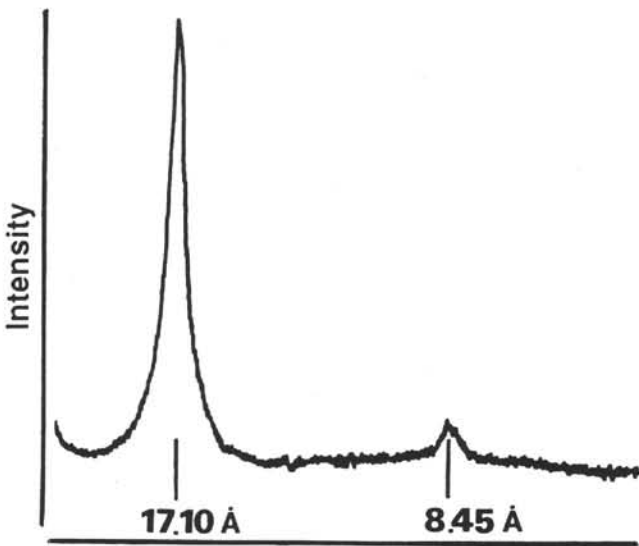


Figure 8. XRD pattern of large saponite lamellae from the millimeter-sized vein described in Figure 6.

3. Calcite is observed either as disseminated crystals ($400 \mu\text{m} - 1 \text{mm}$) in clayey vein fillings or as narrow vein fillings ($100 \mu\text{m}$ in width) crosscutting saponites and chlorite/saponite mixed-layers.

Chlorite/saponite mixed-layer veins (Fig. 9)

This vein filling is observed in only one sample. The optical properties of the clay minerals are similar to those occurring as central filling in the previous vein type: colorless to light green spheroidal aggregates, but they are not associated, in this site, with saponites.

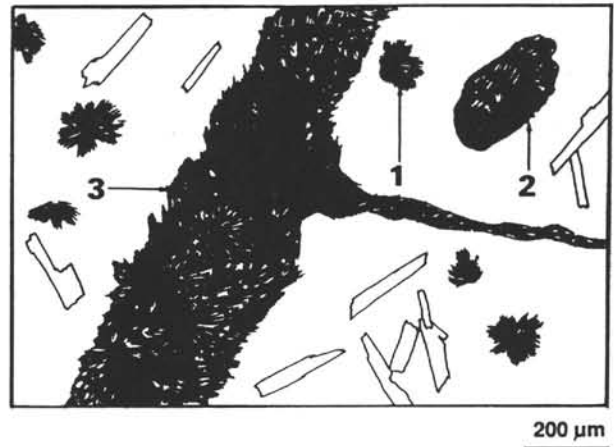


Figure 9. Alteration patterns in aphyric basalt. 1. Basaltic groundmass altered into spheroidal chlorite/saponite mixed-layers. 2. Vesicle with spheroidal chlorite/saponite mixed-layer filling. 3. Vein with spheroidal chlorite/saponite mixed-layer filling.

This millimeter-sized vein is crosscutting a basalt which is completely altered into a clayey plasma made up of similar spheroidal clay minerals aggregates.

Vesicles

Two types of vesicles were recognized in the dolerite and aphyric basalt:

1. Large-sized vesicles ($1 - 2 \text{mm}$) with the following organization from outer to central zone (Fig. 10):

- A. A dark-brown clayey rim ($150 - 200 \mu\text{m}$ in width) in contact with the basalt.
- B. An intermediate green clayey zone ($50 - 100 \mu\text{m}$ in width) with no preferential orientation of clay minerals.
- C. A central filling ($500 \mu\text{m} - 1 \text{mm}$) made up of radiating calcite fibers including small patches of green clay minerals (optically similar to the intermediate zone).

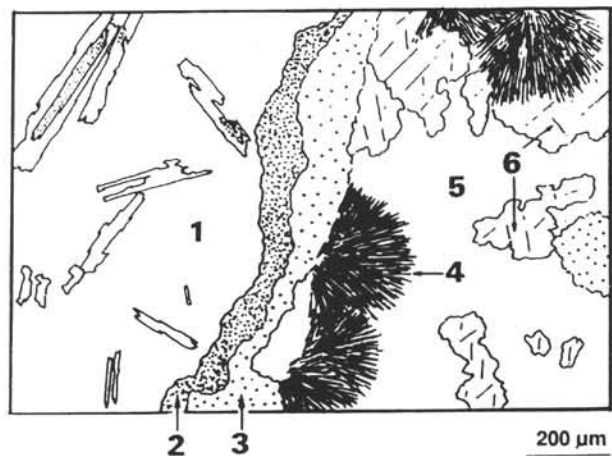


Figure 10. Millimeter-sized vesicle in aphyric basalt. 1. Groundmass of aphyric basalt altered into chlorite/saponite mixed-layer. 2. Outer rim of vesicle made up of saponite. 3. Intermediate zone made up of chlorite/saponite mixed-layer. 4. Radiating fibers of calcite. 5. Microcrystalline calcite. 6. Millimeter-sized crystals of calcite.

Electron microprobe analyses of the dark-brown and green clayey zones are similar and plot in the saponite domain of the $M^+-4Si-3R^{2+}$ ternary diagram (Fig. 7B).

2. Small-sized vesicles (200–400 μm) with the following organization from outer to central zone:

A. A light green clayey rim (50–100 μm in width) with clay minerals oriented perpendicularly to the wall of the vesicle.

B. A colorless central filling, gray under crossed nicols with clay minerals organized in spheroidal aggregates (100 μm in diameter).

Electron microprobe analyses of a transect along one of these vesicles were performed in order to verify the respective position of saponite and chlorite-saponite mixed layer. It appears that the outer rim is made up of saponite, whereas central filling has the chemical composition of chlorite/saponite mixed-layer.

ISOTOPIC DATA

A preliminary isotopic study of altered rocks from Hole 794D is presented here. Samples were collected from Cores 11R, 12R, 13R, and 14R, i.e., over a distance of 30 m. Carbon, oxygen, and hydrogen isotope data of clay mineral and secondary carbonate separates are given in Table 2.

Oxygen isotope compositions of saponite are very homogeneous, varying from 13.1 ‰ to 13.5 ‰. One of these samples is a mixture of saponite and of chlorite/saponite mixed-layer but its $\delta^{18}\text{O}$ value is no different from those of samples of pure saponite. This indicates that their isotopic compositions are at least very similar, possibly identical.

Hydrogen isotope compositions are also very homogeneous with a value of $-72 \text{‰} \pm 2 \text{‰}$.

Carbon and oxygen isotope compositions of secondary calcite range between -3.2‰ and $+0.4 \text{‰}$ and between $+19.7 \text{‰}$ and $+23.1 \text{‰}$, respectively. The $\delta^{13}\text{C}$ values are in the same range as those of marine limestones (which have $\delta^{13}\text{C}$ values of $0 \text{‰} \pm 4 \text{‰}$; Craig, 1953). The $\delta^{18}\text{O}$ values are close to, but overall slightly lower than, those of Tertiary marine carbonates (between $+25 \text{‰}$ and $+31 \text{‰}$; Hoefs, 1980).

The results of studies of submarine hydrothermal systems are now available and provide information on conditions of formation of clay minerals in this context (Javoy and Fouillac, 1979; Lawrence and Drever, 1981; Stakes and O'Neil, 1982; Alt et al., 1986).

In particular, similar δD and $\delta^{18}\text{O}$ values of smectites are reported by Stakes and O'Neil (1982) for hydrothermally altered oceanic rocks from the Mid-Atlantic Ridge and the East Pacific Rise ($\delta^{18}\text{O}$ of saponite separates varies from 8.7 ‰ to 11.4 ‰ and δD from -79‰ to -49‰). Separates of calcite associated with the separated saponite have $\delta^{18}\text{O}$ values of 18.4 ‰ and 20.9 ‰ and $\delta^{13}\text{C}$ values of -0.9‰ and $+0.3 \text{‰}$. Alt et al. (1986) observed similar values for samples from DSDP Hole 504B ($\delta^{18}\text{O}$ of saponites between 11.4 ‰ and 13.4 ‰).

Stakes and O'Neil (1982) have shown that their results are consistent with alteration of fresh basalt to smectite minerals by seawater.

This type of alteration seems to occur under conditions of relatively high water/rock ratios. Thus, a change in $\delta^{18}\text{O}$ water value is unlikely. Assuming a $\delta^{18}\text{O}$ seawater of 0 ‰, and using the thermometric curve of Noack et al. (1986), a temperature of $155^\circ \pm 10^\circ\text{C}$ is obtained for the formation of saponite.

However a small contribution from deep-seated water can be suspected because of the lower $\delta^{13}\text{C}$ values of carbonates (-3‰ PDB), which could correspond to a mixing of carbon from marine carbonate (around 0 ‰) and from mantle CO_2 (around -7‰), and because of the low δD of saponites. The deep-seated water comes from hydrothermal exchange between seawater and subsolidus rocks in conditions of high temperature ($>400^\circ\text{C}$) and low water/rock ratio values, at depth, up to several kilometers within the crust (Gregory and Taylor, 1981) or near major heat source (Mid-Ocean Ridge) (Corliss et al., 1979; Spiess et al., 1980). In such cases, $\delta^{18}\text{O}$ enriched fluids evolve and then migrate upward and contribute to alter shallower rocks.

If a value of 2 ‰ is used for water in equilibrium with saponite, the corresponding calculated temperature will be around 180°C .

Carbon isotope compositions of carbonates here are similar to those of carbonates from other DSDP and ODP basalts and are consistent with formation from normal or slightly evolved seawater.

Oxygen isotope compositions of carbonates are lower than marine limestones of the same age, implying higher temperatures of deposition.

Using the thermometric curve of O'Neil et al. (1969) and assuming equilibrium with normal seawater (0 ‰ SMOW), temperatures of formation of the carbonates were calculated, giving values between 54° and 78°C . These temperatures are lower than those calculated for saponite. This is in agreement with the mineralogy. Carbonate deposition always postdates deposition of saponite.

DISCUSSION AND CONCLUSION

Petrographic investigation of Hole 794D has demonstrated that vein and vesicle fillings always occur as follows: (1) external rim with saponite crystallization, (2) internal filling with chlorite/saponite mixed-layer.

The existence of pure chlorite/saponite mixed-layers as vein and vesicle fillings or as groundmass alteration seems to indicate that they are the early formed clay minerals, prior to the saponites which corrode them along their interface with the wall-rock.

The successive crystallization of chlorite/saponite mixed-layers and saponites has been previously observed in hydrothermal alteration of basalts. The formation of the chlorite/saponite mixed-layers usually takes place at 200° – 230°C , but highly expandable mixed-layers (i.e., saponite-rich mixed-layers) can appear at about 150°C (Haymon and Kastner, 1986). The temperatures reported by Stakes and O'Neil (1982) for saponite formation in hydrothermally altered oceanic rocks are between 130° and 170°C .

The chemical compositions of chlorite/saponite mixed-layers as well as those of saponites appear to be homogeneous regardless of

Table 2. Mineralogy and carbon, oxygen, and hydrogen isotope data for secondary mineral samples from cored igneous rocks from Hole 794D.

Sample number	Sample description	Carbonates			Clay minerals	
		$\delta^{18}\text{O}$ SMOW	$\delta^{18}\text{O}$ PDB	$\delta^{13}\text{C}$ PDB	$\delta^{18}\text{O}$ SMOW	δD SMOW
794D-11R-2, 88–90 cm	Calcite vein	+21.9	-8.7	+0.4	----	----
794D-12R-1, 137–141 cm	Saponite in groundmass	----	----	----	13.5	-70.0
794D-13R-1, 45–47 cm	Calcite and saponite veins	+23.1	-7.6	-3.0	13.2	n.d.
794D-13R-2, 4–6 cm	Saponite in vein	----	----	----	13.1	-73.6
794D-14R-2, 113–115 cm	Calcite, saponite, and chlorite in veins	+19.7	-10.9	-3.2	13.5	-71.6

the site of crystallization. This indicates that the alteration of the rock was not controlled by the chemical composition of the primary minerals but rather by the composition of the alteration solutions.

These petrographic data are well supported by the isotopic study which shows that (1) there is no difference in isotopic composition between saponite in the groundmass and that in veinlets and (2) the formation of saponite takes place between 150° and 180°C, due to the interaction of seawater-dominated hydrothermal fluids with the basalt, followed by formation of calcite, during cooling of the system, at 65° ± 10°C.

If one considers that alteration was induced by the interaction of seawater-dominated hydrothermal fluids with the basalt, the question of the timing of alteration remains unsolved. In other words, are the chlorite/saponite mixed-layer and saponite crystallizations two disconnected alteration episodes or two stages of a unique alteration episode?

A part of the answer can be found considering the $M^{+}4Si-3R^{2}$ chemographic representation where saponite and chlorite/saponite mixed-layer compositions are strictly aligned between saponite and chlorite poles. This fact argues strongly for a chemical control of clay mineral crystallizations, i.e., chemical compositions of rock-fluids do not change enough to induce drastic modification of the clay mineral compositions. Thus, we may infer that the clay mineral crystallization sequence is not principally induced by changes in rock-fluid composition, but rather by basaltic-rock cooling. In this case, chlorite/saponite mixed-layer and saponite crystallizations would be part of a unique alteration episode with decreasing temperature from chlorite/saponite mixed-layer to saponite crystallization, followed by crystallization of calcite in veins.

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REFERENCES

- Alt, J. C., Muehlenbachs, K., and Honnorez, J., 1986. An oxygen isotopic profile through the upper kilometer of the oceanic crust, DSDP Hole 504B. *Earth Planet. Sci. Lett.*, 80:217-229.
- Beaufort, D., Dudoignon, P., Parneix, J. C., Proust, D., and Meunier, A., 1983. Microdrilling in thin section: a useful method for the identification of clay minerals in situ. *Clay Mineral.*, 18:219-222.
- Champion, D., and Lanson, B., in press. *IS* to illite transformation in diagenesis. *Am. J. Sci.*
- Clayton, R. N., and Mayeda, T. K., 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta*, 27:43-52.
- Corliss, J. B., Dymond, J., Gordon, L. I., Edward, J. M., Von Herzen, R. P., Ballard, R. D., Green, K., Williams, D., Bainbridge, A., Crane, K., and Van Andel, T. H., 1979. Submarine thermal springs on the Galapagos Rifts. *Science*, 203:1073-1083.
- Craig, H., 1953. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta*, 3:53-92.
- Friedman, I., 1953. Deuterium content of natural waters and other substances. *Geochim. Cosmochim. Acta*, 4:89-103.
- Gregory, R. T., and Taylor, H. P., Jr., 1981. An oxygen isotope profile in a section of cretaceous oceanic crust, Samail ophiolite, Oman: evidence for ^{18}O -buffering of the oceans by deep (>5 km) seawater-hydrothermal circulation at mid-ocean-ridges. *J. Geophys. Res.*, 86:2737-2755.
- Haymon, R. M., and Kastner, M., 1986. The formation of high temperature clay minerals from basalts alteration during hydrothermal discharge on the East Pacific Rise axis 21°N. *Geochim. Cosmochim. Acta*, 50:272-292.
- Hoefs, J., 1980. *Stable Isotope Geochemistry*: New York (Springer-Verlag).
- Javoy, M., and Fouillac, A. M., 1979. Stable isotope ratios in Deep Sea Drilling Project, Leg 51 Basalts. In Donnelly, T., Francheteau, J., Bryan, W., Robinson, P., Flower, M., Salisbury, M., et al., *Init. Repts. DSDP*, 51, 52, 53: Washington (U.S. Govt. Printing Office), 1153-1157.
- Lawrence, J. R., and Drever, J. I., 1981. Evidence for cold water circulation at DSDP site 395: isotope and chemistry of alteration products. *J. Geophys. Res.*, 86:5125-5133.
- McCrea, J. M., 1950. The isotopic chemistry of carbonates and a paleo-temperature scale. *J. Chem. Phys.*, 18:849-857.
- Meunier, A., Inoue, A., and Beaufort, D., in press. Chemiographic analysis of trioctahedral smectite to chlorite conversion series from the Okyu Caldera, Japan. *Clays Clay Miner.*
- Noack, Y., Decarreau, A., and Manceau, A., 1986. Spectroscopic and oxygen isotopic evidence for low and high temperature origin of talc. *Bull. Mineral.*, 109:253-263.
- O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969. Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.*, 51:5547-5548.
- Rassineux, F., Beaufort, D., Bouchet, A., Merceron, T., and Meunier, A., 1988. Use of a linear localization detector for X-Ray diffraction of very small quantities of clay minerals. *Clays Clay Miner.*, 36:187-189.
- Shipboard Scientific Party, 1990. Introduction, background, and principal results of Leg 128 of the Ocean Drilling Program, Japan Sea. In Ingle, J. C., Jr., Suyehiro, K., von Breyman, M. T., et al., *Proc. ODP, Init. Repts.*, 128: College Station, TX (Ocean Drilling Program), 5-38.
- Spiess, F. N., MacDonald, K. C., Atwater, T., Ballard, R., Carranza, A., Cordoba, D., Cox, C., Diaz-Garcia, V. M., Francheteau, J., Guerro, J., Hawkins, J., Haymon, R., Hessler, R., Juteau, T., Kastner, M., Larson, R., Luyendyk, B., MacDougall, J. D., Miller, S., Normak, W., Orcutt, J., and Rangin, C., 1980. East Pacific Rise: hot springs and geophysical experiments. *Science*, 207:1421-1433.
- Stakes, D. S., and O'Neil, J. R., 1982. Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. *Earth Planet. Sci. Lett.*, 57:285-304.

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