27. ALTERATION AND VEIN FORMATION IN SITE 321 BASALTS

W.E. Seyfried,¹ W.C. Shanks, and J.L. Bischoff,² Department of Geological Sciences, University of Southern California, Los Angeles, California

ABSTRACT

A smectite group mineral, mica, calcite, and pyrite are the dominant secondary minerals associated with the alteration of basalts cored at Site 321, DSDP Leg 34. The smectite has a partial trioctahedral character and is enriched in Fe₂O₃, MgO, and K₂O, while depleted in Al₂O₃, TiO₂, and CaO relative to the host basalt. The mica is dioctahedral and based on X-ray characteristics also appears to be rich in Fe₂O₃ and MgO, while low in Al₂O₃. Isotopic evidence, as well as the absence of anhydrite and presence of late Eocene coccoliths, strongly suggest that the secondary minerals formed in response to cold seawater circulating through veins and fractures.

INTRODUCTION

Alteration products of submarine basalts have become increasingly important as a possible key to understanding subsea-floor processes. Such processes may play an important role in the genesis of sea-floor metal deposits and perhaps a role in the geochemical balance of the oceans. The fundamental question is whether the aqueous fluids of the alteration process result from primary magmatic activity, or are simply seawater which has been drawn in along fractures in the basement rock.

The reported products of submarine alteration of basalts range from low temperature assemblages of clay minerals (Melson and Thompson, 1973) to greenschist facies assemblages including albite-actinolite (Hart, 1973), with gradations between. Other secondary minerals, such as calcite and pyrite, have also been reported (Bass et al., 1972).

This present study is concerned with characterizing a low temperature assemblage of alteration products associated with basalts drilled from DSDP Site 321 in the Nazca plate. Alteration products at this site occur most commonly in veins and fractures which are distributed throughout the 11 meters of basement penetration and which separate large chunks of relatively unaltered basalt.

The veins in 321-14-1 through 14-3 are composed of green to bluish-green smectite in association with minor pyrite, mica, and calcite. The vein thickness varies between 1 and 10 mm, and, although all of the above minerals are found together, there are areas of local concentrations of each mineral.

Pyrite generally occurs as small crystals (20 μ m) coating the edges of the large smectite-rich veins. Calcite is primarily located in holes within the smaller veins and is composed of small crystal aggregates. Mica also seems to be preferentially located in these smaller veins.

SAMPLING AND ANALYSIS

Two samples were taken from a large vein (Samples 321-14-3, 14-23 cm and 321-14-3, 70-77 cm). The samples were scraped from the veins, lightly ground in an agate mortar, and ultrasonically disaggregated to insure complete dispersion. The ultrasonic treatment was limited to 1 hr to maintain the crystallinity of the clay minerals. The dispersed material was then size separated by centrifugation, and each size fraction was X-rayed to determine the purity of the separation. Samples 321-14-3, 14-23 cm and 321-14-3, 70-77 cm contain almost pure smectite. Separates of the smectite were used for X-ray diffraction, isotope, and chemical analyses.

Mica was found in a vein (321-14-2, 104-114 cm) containing calcite and smectite as well. It was possible to separate enough mica for X-ray diffraction and isotope analysis, but not enough for chemical analysis.

Samples of bulk vein material (321-14-1, 120-125 cm) and of the holocrystalline basalt (321-14-3, 14-23 cm) were chemically analyzied for comparative purposes. Pyrite was sampled from veins at 321-14-2, 104-114 cm and 321-14-3, 100-103 cm for analysis of sulfur isotopes.

X-ray diffraction was carried out on a Norelco X-ray diffractometer with a curved crystal monochromator employing CuK α radiation. The smectite and the mica were X-rayed in oriented mounts prepared by aspirating the clays to 0.45 μ m silver filters (Hathaway, 1972). Pretreatments such as glycolation and heating (550°C/1 hr) were employed to distinguish the various phases present. Oriented powders were prepared using a planchet accentuating the b-axis direction of the smectite (Carroll, 1970) to obtain the (060) reflection. Powder camera patterns of the randomly mounted smectite and mica were obtained using a 57.3-mm Debye-Sherrer camera with Mn-filtered FeK α radiation. Chemical analyses of the smectite, bulk vein, and basalt for Fe, Mg, Ca, Na, K, and Mn were carried out by atomic absorption spectroscopy, while Al, Ti, and FeO were analyzed colorimetrically (Shapiro and Brannock, 1962; Shapiro, 1960). Si was analyzed titrimetrically after McLaughlin and Biskupski, (1965). Ignition loss was determined by weight loss at 1000°C.

¹Present address: Department of Geology, Stanford University, Stanford, California.

²Present address: U.S. Geological Survey, Menlo Park, California.

Sulfur isotope composition of the pyrite was determined at UCLA by techniques described in Shanks et al. (1974). Isotopes of carbon, oxygen, and hydrogen were analyzed in the stable isotope laboratory at the California Institute of Technology. Carbon and oxygen isotopes from carbonate phases in bulk vein material (321-14-1, 120-125 cm) were determined on CO_2 liberated by phosphoric acid.

Isotopes of oxygen in the silicate structure of the smectite and mica samples were analyzed according to methods of Taylor and Epstein (1962). Isotopes of hydrogen in structural water in the smectite and mica samples were determined by techniques of Craig (1961a), Godfrey (1962), and Sheppard and Epstein (1970).

DATA

X-Ray Diffraction Analysis of the Clay Minerals

As shown by oriented diffraction patterns (Figure 1), the smectite behaves as do other smectite group minerals, expanding to 17Å upon glycolation, and contracting to 9.9-10Å upon heating at 550°C. The pattern of untreated smectite displays a (001) reflection at 14.48Å. Data given by randomly oriented mounts of the smectite X-rayed with the powder camera are given in Table 1. The (060) reflection was obtained by scanning the *b*-oriented planchets, and found to be 1.529Å.

The X-ray patterns of oriented mica are shown in Figure 2. The pattern of untreated mica shows a welldefined, although slightly asymmetric (001), reflection at 10.18Å and an (003) reflection at 3.34Å with an intensity equal to or slightly greater than the former. The (002) reflection is just visible. With glycolation there is no expansion of the basal spacings, indicating that there is little, if any, interlayered smectite. The low angle peak at $6.0^{\circ}2\theta$ shows a shift to lower angles after glycol treatment, indicating the presence of a small amount of smectite impurity (<15%). This impurity is also suggested by the increased intensity of the mica (003), which results from the reinforcement provided by the smectite (005). The d_{060} was determined from the powder camera data (Table 1) and found to be 1.514Å.

The X-ray diffraction pattern of the carbonate separated from 321-14-1, 120-125 cm was that of low-Mg calcite.

Chemical Analysis

The chemical analyses of the two smectite samples (Table 2) indicate that they are nearly identical, being rich in MgO, Fe_2O_3 , and K_2O , and low in Al₂O₃, TiO₂, CaO, SiO₂, and FeO relative to the host basalt.

The bulk vein sample contains considerable calcite, as indicated by the high value for calcium and the large ignition loss (Table 2). Coccoliths were observed in the large smectite vein (321-14-3, 70-77 cm); however, they comprise only a small fraction of the calcite in this sample. The bulk vein is also rich in K_2O and Fe_2O_3 relative to the unaltered rock.

The chemical analysis of the basalt (Table 2) shows it to be an oceanic tholeiite, with moderate TiO_2 and relatively high total iron contents. The potassium con-

tent (0.13%) and the loss on ignition (0.80%) confirm its relatively unaltered nature.

Isotope Analysis

Stable isotope analyses of the secondary minerals are listed in Table 3. The δs^{34} of the pyrite is very negative, typical of diagenetic sedimentary pyrite, while the oxygen and carbon ratios of the calcite are similar to those of normal marine calcites (Garlick, 1974).

The smectite and mica of this study are very rich in O^{18} (Figure 3), very nearly the same as authigenic clays of the sea floor, and are isotopically quite different from sea-floor basalts and other igneous and metamorphic rocks, as well as detrital clays. These data are in agreement with those of Muehlenbachs (1974) who studied oxygen isotopes in smectites from veins recovered from Sites 319 and 321.

DISCUSSION

Smectite

A smectite group clay mineral is the dominant secondary mineral in the basalts at Site 321. A structure formula for this clay is developed around the general montmorillonite formula $Y_{2-3}Z_4$ O₁₀(OH)₂ (MacEwan, 1961), where Y and Z refer to octahedrally and tetrahedrally coordinated cations, respectively, and is calculated from the data in Table 2 to be $(Ca_{0.02}Na_{0.39}K_{0.08})$ $(Fe^{+3}_{0.52}Fe^{+2}_{0.30}Mg_{1.94})_{2.76}$ $(Al_{0.46})$ Fe+30.11 Si3.43)4.0 O10(OH)2. All silicon and aluminum were assigned to the tetrahedral layer, and the remaining tetrahedral site deficiency was filled by ferric iron. The remaining ferric iron was then assigned to the octahedral layer, along with ferrous iron and magnesium. Potassium, calcium, and sodium were assigned to the interlayer positions in order to balance the net layer charge (-0.53).

The cation population in the octahedral layer (2.76) implies that this mineral is not a pure trioctahedral phase, and may be partially interstratified with dioctahedral layers (Weaver and Pollard, 1973). This partial trioctahedral character is supported by the d_{060} of 1.529Å.

The smectite contrasts with a smectite associated with altered basalts of the Mid-Atlantic Ridge described by Melson and Thompson (1973), in its anomalously low aluminum content (5% compared to 15% Al₂O₃). However, it is similar in chemistry to the saponite reported earlier by Melson et al. (1969). Iron-rich, aluminumpoor smectites have also been described from the metalliferous sediments which overlie the basalts in the Nazca plate (Dymond et al., 1972; Bischoff and Sayles, 1972; Sayles and Bischoff, 1974). The smectites from the metalliferous sediments, however, have significantly lower magnesium contents (< 2% compared to 16% MgO), and therefore appear to be genetically unrelated.

The oxygen and hydrogen isotopic compositions of the smectites are analogous to those of authigenic silicates of marine sediments (Figure 3), and differ markedly from those of hydrothermal and detrital smectites. These data suggest that the smectites formed by interaction of the basalt with seawater at low temperature



Figure 1. X-ray diffraction pattern of separated smectite (321-14-3, 70-77 cm) untreated; glycolated; heated 550°C/1 hr. Instrument settings as follows: CuK α radiation; 1°20/min scanning rate, 2000 counts/sec full vertical scale, rate meter 2, slits 1°, 1°, 0.006"; kv, 40 Ma, 20. Samples were oriented on microporous silver filters.

W. E. SEYFRIED, W. C. SHANKS, J. L. BISCHOFF



Figure 2. X-ray diffraction pattern of separated mica (321-14-1, 120-125 cm); untreated and glycolated. Instrument settings as follows: CuK α radiation; 1°20/min scanning rate, 2000 counts/sec full vertical scale, rate meter 2, slits 1°, 1°, 0.006", kv, 40, Ma, 20. Samples were oriented on microporous silver filters.

X-Ray Powder Camera Reflections, Site 321					
Smectite (14-3, 70-77 cm)		Mica (14-1, 120-125 cm)			
hk Indices	dÅ	Ι	hkl Indices	dÅ	Ι
11; 02 13; 20 31; 15; 24 26; 40	4.55 2.62 1.73 1.68 1.31	MS M S W	001 020 021 112 003;022 112 023 130;131;200 132;201 040;221 005 311;241 060:331	14.50 10.04 4.54 4.17 3.66 3.34 3.11 2.69 2.59 2.43 2.27 1.99 1.72 1.51	M S M W W W W S W V W V W V W W

 TABLE 1

 X-Ray Powder Camera Reflections, Site 32

(Garlick and Dymond, 1970; Muchlenbachs and Clayton, 1972).

The chemical composition of the smectite compared to that of the basalt precludes a simple process of seafloor weathering. If such were the case, the aluminum and titanium contents of the alteration product would be preferentially increased relative to those of the other species, as is usual in weathering processes.

Our observations that aluminum and titanium are relatively low in the alteration product imply either that significant amounts of the other components came from seawater, or alternatively, that the smectite did not form as a simple replacement alteration, but precipitated from solution at a site removed from the source minerals of the dissolved constituents.

Considering the former possibility, the large content of magnesium in the smectite could have come from seawater. Uptake of Mg (as Mg [OH]₂) would make the aluminum-titanium content appear to decrease. However, this would not explain the increased ratios of silicon and iron to aluminum in the smectite, and it is unlikely that these components were derived from seawater.

This implies, therefore, that many of the components of the smectite were transported through an aqueous phase from another site in the rock. Aluminum and titanium are less soluble than iron, magnesium, and

Chemical Analyses of Selected Samples from DSD1 Site 521					
	(14-3, 70-77) Smectite	(14-3, 14-23) Smectite	(14-3, 14-23) Basalt	(14-1, 120-125) Bulk Vein	
SiO ₂	45.12	45.25	48.32	_	
$Al_2 \tilde{O}_3$	5.13	5.00	13.73	_	
TiÕ ₂	0.23	0.19	2.62	0.80	
Fe ₂ O ₃	11.14	11.19	6.34	18.02	
FeÕ	4.77	4.59	7.23	2.75	
MgO	17.06	16.22	6.16	4.93	
CaO	0.21	0.19	10.18	19.18	
Na ₂ O	2.68	2.24	2.52	2.72	
$\tilde{K_2O}$	0.85	1.18	0.13	2.32	
MnO	0.04	0.03	0.12	0.20	
Ignition loss ^c	13.60	13.60	0.80	21.90	
Total	100.83	99.68	98.26		

TABLE 2					
Chemical Analyses of Selected Samples from	DSDP	Site	321		

^aIgnition loss at 1000°C; includes loss of volatiles such as H_2O , CO_2 , and S with a correction for the added weight due to the oxidation of ferrous iron.

 TABLE 3

 Isotopic Analysis of Alteration Products from Site 321

Sample (Interval in cm)	Mineral	δS ³⁴	δO ¹⁸	δD	δC^{13}
14-3, 14-23	Smectite	_	+22.4	-56.1	_
14-3, 70-77	Smectite	_	+19.3	-50.3	
14-1, 120-125	Mica	-	+21.9	-73.0	-
	Calcite	-	+33.2	-	+2.09
14-2, 104-114	Pyrite	-30.14	-	_	_
14-3, 100-103	Pyrite	-27.53	-	_	-

silica, and therefore, would be relatively depleted in such an aqueous phase. The site of leaching would then be characterized by a residue enriched in aluminum and titanium.

Mica

Based on X-ray data, the mica is a 1M dioctahedral polytype rich in iron and moderately enriched in magnesium, as indicated by the relative intensities of the basal reflections and the d_{060} (Grim, 1968; Maxwell and Hower, 1968). Its 1M nature is indicated by the position of the (112) reflection (Table 1).

Oxygen and hydrogen isotopic compositions of the mica (Figure 3) plot close to those of authigenic minerals formed in marine sediments, specifically within the glauconite field. Although the mica contains a small amount of smectite impurity (Figure 2; Table 1), this would not greatly affect the δO^{18} and δD values of the sample considering its small amount and the fact that the oxygen isotopic value of the mica falls between those of the two pure smectites. We conclude, therefore, that the mica formed under the same conditions as the smectite.

Iron-rich (Fe⁺³), aluminum-poor, dioctahedral micas can be of two varieties. The first is the mineral celadonite, commonly found in veins associated with altered igneous rocks. Bass et al. (1972) report diagenetic celadonite in volcanic rocks cored during DSDP Leg 17. The second type of iron-rich dioctahedral mica is glauconite, which forms authigenically in near-shore marine sediments (Weaver and Pollard, 1973).

Glauconites and celadonites have been extensively studied by Foster (1969) who concludes that the two minerals are indistinguishable chemically and structurally in many cases, and the fundamental difference appears to lie only in the environment of their formation.

Calcite and Pyrite

The isotopic compositions of the carbon and oxygen in the calcite are typical of those of low temperature sedimentary carbonates and are consistent with the compositions determined by Muehlenbachs and Clayton (1972) for carbonates from weathered submarine basalts. An isotopic temperature of 7.0°C can be computed using the data of Craig (1965), assuming isotopic equilibrium with seawater and assuming that seawater δO^{18} was the same as today back into the Eocene.

As cold seawater comes into contact with basaltic rock, Ca^{2+} is leached from the basalt and the pH is increased (Seyfried, unpublished experimental data). In the small vein this reaction could significantly supersaturate the system with respect to calcite, and hence lead to its precipitation. Bischoff and Ku (1970), and Thompson (1972) have called for such a mechanism to



Figure 3. Isotopic variation in silicates; igneous rock isotopic data from Taylor and Epstein (1962) and Sheppard and Epstein (1970); metamorphic rock isotopic data from Garlick and Epstein (1967) and Taylor and Epstein (1966); data on hydrothermal smectites (black dots) from Sheppard et al. (1969); data on glauconite and authigenic smectite (triangles) from Savin and Epstein (1970a); data on detrital illite and smectite from Savin and Epstein (1970b); samples from this study (+).

explain lithified carbonate sediments found associated with sea-floor basalts.

The isotopic composition of pyrite sulfur is consistent with an origin by bacterial reduction of seawater sulfate.

Conditions of Alteration

The isotopic compositions of the secondary minerals from Site 321 suggest that seawater interacted with basalt at low temperatures to form the observed alteration phases. The absence of anhydrite in Site 321 basalts, although carefully sought, also supports a low temperature environment of alteration. Anhydrite forms abundantly during seawater interaction with basalt at temperatures greater than 100°C. This has been demonstrated experimentally (Bischoff and Dickson, 1975) and has also been observed at the Reykjanes geothermal field, Iceland, Tomasson and Kristmannsdottir (1972) have carried out detailed sampling of drill cores penetrating different thermal zones through this active basalt-seawater system. Anhydrite is notably absent in the upper "cold" zone where the temperatures of the system are approximately 60°C and less. At the higher temperatures in the deeper zones, $SO_4 = is$ almost guantitatively removed from the aqueous phase, and anhydrite becomes a dominant alteration mineral phase.

Cold seawater circulation is further evidenced by the presence of upper Eocene coccolith tests in the vein material (Figure 4). The assemblage includes *Discoaster* saipanensis, *Reticulofenestra bisecta*, and *Discoaster bar*- badiensis, identified by J. McRaney (personal communication, 1974) and defines an age of about 40 m.y., which is discordant with the 22-m.y. age determined by K-Ar for these rocks (Corliss and Dymond, 1974). Although serious consideration was given to the possibility that the coccolith tests were contaminants, the fact that many were partially covered by the smectite, and that they represent a homogeneous age grouping, implies to us that they were introduced during the alteration process.

ACKNOWLEDGMENTS

We are grateful to S. Lambert and S. Epstein, of the California Institute of Technology, who carried out the isotopic analyses of carbon, oxygen, and hydrogen; to I. Kaplan, of UCLA, who provided the facilities for sulfur isotope analyses; and to J. McRaney, of USC, who identified the coccoliths.

Support for this research was provided by National Science Foundation Grant GA23495.

REFERENCES

- Bass, M.T., Moberly, R., Rhodes, M.J., and Shih, C., 1972.
 Volcanic rocks cored in the central Pacific, Leg 17, Deep Sea Drilling Project. *In* Winterer, E.L., Ewing, J.I., et al., Initial Reports of the Deep Sea Drilling Project, Volume 7: (U.S. Government Printing Office), Washington, p. 429-503.
- Bischoff, J.L. and Dickson, F.T., 1975. Sea water-basalt interaction at 200°C and 500 bars: implications as to the origin



Figure 4. Upper Eocene coccolith assemblage in vein (321-14-3, 70-77 cm) includes Discoaster saipanensis, Reticulofenestra bisecta, and Discoaster barbadiensis.

of sea floor heavy metal deposits and regulation of sea water chemistry: Earth planet. Sci. Lett., v. 25, p. 385.

- Bischoff, J.L. and Ku, T., 1970. Pore fluids of recent marine sediments 1. oxidizing sediments of 20°N continental rise to Mid-Atlantic Ridge: J. Sediment Petrol., v. 40, p. 960-972.
- Bischoff, J.L. and Sayles, F.L., 1972. Pore fluid and mineralogical studies of recent marine sediments; Bauer Depression region of East Pacific Rise: J. Sediment Petrol., v. 42, p. 711-724.
- Carroll, D., 1970. Clay minerals: a guide to their X-ray identification: Geol. Soc. Am. Spec. Paper, 126.
- Corliss, J.B. and Dymond, J., 1974. Major and trace element geochemistry, age and isotopic studies of Leg 34 basalts: Geol. Soc. Am. Abstract with Programs, v. 6, p. 694.
- Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide: Geochim. Cosmochim. Acta, v. 12, p. 133. _____, 1961a. Isotopic variation in meteoric waters:
 - Science, v. 133, p. 1702.

_____, 1961b. Standard for reporting concentrations of deuterium and oxygen 18 in natural water: Science, v. 133, p. 1833.

- _____, 1965. The measurement of oxygen isotope paleotemperatures: Spoleto Conf. Stable Isotopes in Oceanographic Studies and Paleotemperatures Proc., v. 3.
- Dymond, J., Corliss, J.B., Heath, G.R., Field, C.W., Dash, E.J., and Veeh, H.H., 1972. Origin of metalliferous sediments from the Pacific Ocean: Geol. Soc. Am. Bull., v. 84, p. 3355-3372.
- Foster, M.D., 1969. Studies of celadonite and glauconite: U.S. Geol. Survey Prof. Paper 614-F.
- Garlick, D., 1974. Stable isotopes of oxygen, carbon, and hydrogen. *In* Goldberg, E. (Ed.), The sea, v. 5: New York (John Wiley and Sons), p. 393-425.
- Garlick, G.D. and Dymond, J.R., 1970. Oxygen isotope exchange between volcanic materials and ocean water: Geol. Soc. Am. Bull., v. 81, p. 2137-2142.
- Godfrey, J.D., 1962. The deuterium content of hydrous minerals from the East-Central Sierra Nevada and Yosemite

National Park: Geochim. Cosmochim. Acta, v. 26, p. 1215-1245.

- Grim, R.E., 1968. Clay mineralogy, 2nd ed.: New York (McGraw-Hill).
- Hart, R.A., 1973. A model for chemical exchange in the basalt-seawater system of oceanic layer II: Canadian J. Earth Sci., v. 10, p. 799-815.
- Hathaway, J.C., 1972. Regional clay mineral facies in estuaries and continental margin of the United States east coast: Geol. Soc. Am. Mem. 133, p. 293-316.
- McLaughin, J.W. and Biskupski, V.S., 1965. The rapid determination of silica in rocks and minerals: Anal. Chim. Acta, v. 32, p. 165-169.
- MacEwan, D.C.M., 1961. Montmorillonite minerals. In Brown, G. (Ed.), The X-ray identification and crystal structure of clay minerals: London (Mineral. Soc.), p. 143-208.
- Maxwell, D.T. and Hower, J., 1968. High grade diagenesis and low grade metamorphism in the precambrian belt series: Am. Mineralogist, v. 52, p. 843-857.
- Melson, W.G., and Thompson, G., 1973. Electron probe mineralogy of glassy basalt and its alteration products from the sea floor near St. Pauls Rocks, equatorial Atlantic: Geol. Soc. Am. Bull., v. 84, p. 703-716.
- Melson, W.G., Thompson, G., and van Andel, T.H., 1969. Volcanism and metamorphism in the Mid-Atlantic Ridge, 22°N latitude: J. Geophys. Res., v. 73, p. 5925-5941.
- Muehlenbachs, K., 1974. Oxygen isotope geochemistry of DSDP Leg 34 basalts: Geol. Soc. Am. Abstract with Programs, v. 6, p. 881-882.
- Muehlenbachs, K. and Clayton, R.N., 1972. Oxygen isotope studies of fresh and weathered submarine basalts: Canadian J. Earth Sci., v. 9, p. 172-182.
- Savin, S.M. and Epstein, S., 1970a. The oxygen and hydrogen isotope geochemistry of clay minerals: Geochim. Cosmochim. Acta, v. 34, p. 24-42.

_____, 1970b. The oxygen and hydrogen isotope geochemistry of ocean sediments and shales: Geochim. Cosmochim. Acta, v. 34, p. 42-63.

- Sayles, F.L. and Bischoff, J.L., 1974. Ferromanganoan sediments in the equatorial East Pacific: Earth Planet. Sci. Lett., v. 19, p. 330-336.
- Shanks, W.C., Bischoff, J.L., and Kaplan, I.R., 1974. Sulfur isotope studies of evaporites and shales from Site 225, 227, and 228 in the Red Sea. *In* Whitmarsh, R.B., Ross, D.H., et al., Initial Reports of the Deep Sea Drilling Project 23: Washington (U.S. Government Printing Office), p. 947-950.
- Shapiro, L., 1960. A spectrophotometric method for the determination of FeO in rocks: U.S. Geol. Survey Prof. Paper 400-B, p. 496-497.
- Shapiro, L. and Brannock, W.W., 1962. Rapid analysis of silicate, carbonate and phosphate rocks: U.S. Geol. Survey Bull. 1144-A.
- Sheppard, S.M.F. and Epstein, S., 1970. D/H and O¹⁸/O¹⁶ ratios of minerals of possible mantle or lower crustal origin: Earth Planet. Sci. Lett., v. 9, p. 232.
- Sheppard, S.M.F., Nielsen, R.L., and Taylor, H.P., 1971. Hydrogen and oxygen isotope ratios in minerals from parphyry copper deposits: Econ. Geol., v. 66, p. 515-542.
- Taylor, H.P. and Epstein, S., 1962. Relationship between O¹⁸/O¹⁶ ratios in coexisting minerals of igneous and metamorphic rocks. Part I. Principles and experimental results: Geol. Soc. Am. Bull., v. 73, p. 461-480.
- Thompson, G., 1972. A geochemical study of some lithified carbonate sediments from the deep sea: Geochim. Cosmochim. Acta, v. 36, p. 1237-1253.
- Tomasson, J. and Kristmannsdottir, H., 1972. High temperature alteration minerals and thermal brines, Reykjanes, Iceland: Contrib. Mineral. Petrol., v. 36, p. 123-134.
- Weaver, C.E. and Pollard, L.D., 1973. The chemistry of clay minerals: New York (Elsievier).