

- Drilling Program, Volume 20: Washington (U.S. Government Printing Office), p. 857-869.
- Lawrence, J. M., Gieskes, J. M. and Broecker, W. S., 1975. Oxygen isotope and cation composition of DSDP pore waters and the alteration of layer II basalts: *E.P.S.L.*, 27, p. 1-10.
- Matter, A., Douglas, R. G. and Perch-Nielsen, K., 1975. Fossil preservation, geochemistry, and diagenesis of pelagic carbonates from Shatsky Rise, Northwest Pacific. *In* Larson, R.L., Moberly, R., et al., Initial Reports of the Deep Sea Drilling Project, Volume 32: Washington (U.S. Government Printing Office), p. 891-921.
- McCrea, J. M., 1950. The isotopic chemistry of carbonates and a paleotemperature scale: *J. Chem. Phys.*, 18, p. 849-857.
- O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969. Oxygen isotope fractionation in divalent metal carbonates: *J. Chem. Phys.*, 51, p. 5547-5558.

14.2. PHILLIPSITE CEMENTATION IN A FORAMINIFERAL SANDSTONE AT HOLE 373A AND "THE CASE OF THE VIOLATED FORAM"

Daniel Bernoulli, Geologisch-paläontologisches Institut der Universität Basel, Basel, Switzerland,
 Robert E. Garrison, Earth Sciences Board, University of California Santa Cruz, California, U.S.A.
 and

Frédéric Mélières, Laboratoire de Géologie Dynamique, Université de Paris, Paris, France

ABSTRACT

Pliocene foraminiferal sandstone at Site 373A contains about 35% phillipsite as pore-filling cement. The sediment originated as a well-sorted foram-rich sand which was redeposited from an adjacent area and which had very high initial porosity. Following compaction, precipitation of phillipsite in intergranular pore space cemented the sand. Phillipsite crystals also precipitated within foraminiferal chambers where, in places, they replaced micrite. Some zeolite crystals also breach shell walls by penetrating their pores. This precipitation of phillipsite appears to be the consequence of unusual pore water chemistry, the proximity to altered basalt, and the high porosity of the sand layer.

INTRODUCTION

Foraminiferal sandstone cemented by zeolites forms a thin interval between 81 and 87 centimeters in Section 1, Core 2 at Site 373A on the flanks of a seamount in the Tyrrhenian Basin of the Mediterranean Sea (Figure 1). This rock has unusual compositional and textural properties which shed light on sedimentological and diagenetic processes in zeolitic carbonate sediments.

The sandstone is of Pliocene age and occurs interbedded with soft foraminiferal nannofossil marls and thin, calcareous volcanic ash layers at a sub-bottom depth of about 269 meters. It appears to lie 60 to 100 centimeters above the contact between Pliocene soft sediment and basaltic breccias at the top of the underlying seamount (see Site Report, Chapter 4).

PETROLOGY AND MINERALOGY

The sandstone is somewhat friable and porous, very well laminated and, possibly, cross laminated. Color is light gray (5Y 7/1). Some laminae are very well sorted, but others appear to have discontinuous lenses

of micritic matrix. Upon close examination, these lenses turn out to be compactionally squeezed clasts of micritic limestone. The rock consists mainly of sand to coarse silt-size grains cemented in finely crystalline, clear zeolites. Grains in this sandstone comprise three major kinds of components: planktonic foraminiferal tests; coarse silt to fine sand size, very angular clasts of quartz and plagioclase; and irregular to rounded lithoclasts of micritic limestone. Many of the micritic lithoclasts are compactionally flattened, and some of them contain clasts of planktonic foraminifera. Present in small amounts are biotite, glauconite, muscovite, pyroxene, plant fragments, and both altered and fresh, pale brown, vesicular glass. Trace amounts of benthic foraminiferal shells, broken echinoid spines, and unidentified skeletal fragments also are present.

X-ray diffraction indicates the rock has an approximate mineralogical composition, by weight, as follows: 35% phillipsite, 30% plagioclase (labradorite to bytownite), 20% quartz, 10% calcite, 3% illite or muscovite, and 2% dolomite.

As noted, compaction has squeezed some micritic limestone clasts between more resistant grains. It has

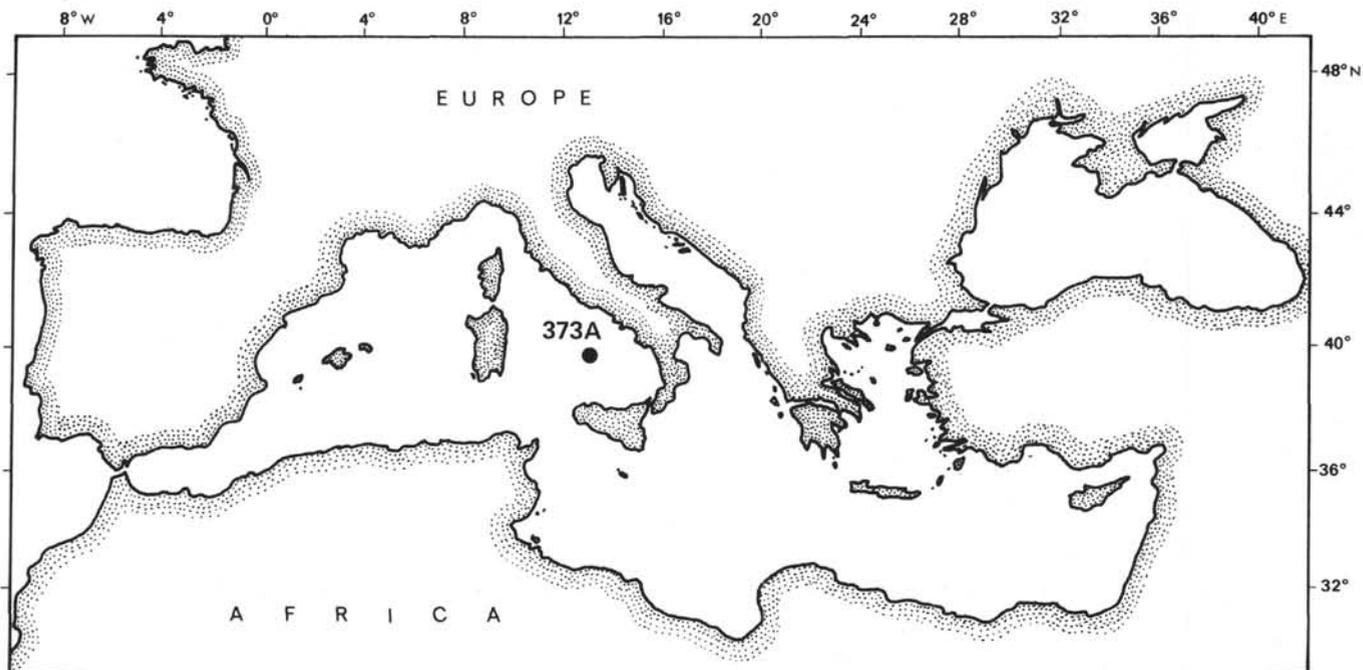


Figure 1. Map showing location of Site 373A.

also fractured some foraminiferal tests. Most foraminiferal shells are partly or wholly filled with euhedral phillipsite crystals (Figure 3[a]) or with brown micritic sediment like that in the lithoclasts (Figure 2) or with mixtures of the two (Figure 3[b]). A few foram chambers have geopetal floors of micrite which are overlain by void space or by euhedral zeolite crystals. However, in several chambers, the floors are at high angles to the laminations or even overturned, suggesting that lithification of the micrite on the floor of the shell chamber occurred before transport and deposition.

This kind of early diagenetic lithification on the sea floor probably accounts also for the lithoclasts of micritic limestone; some of the latter were apparently not fully lithified and thus were especially prone to compactional deformation. Early lithification of micrite in geopetal shell fillings would also explain another peculiar textural characteristic of this rock: the presence of grains which consist of about half or less of a foraminiferal shell chamber filled with micrite, with the other half missing (Figure 2). The explanation for these grains, which resemble half-moons, may be as follows: micritic sediment filled parts of the foraminiferal shell chambers and became lithified as geopetal floors; the upper parts of the chambers remained as voids; during erosion and reworking by currents, these unfilled upper parts became removed by abrasion. Reworking and shell abrasion during transportation might also explain the presence of scattered micritic internal molds of planktonic foraminifera without shells.

The micrite in this rock shows variable alteration. In places, particularly within foraminiferal tests, it becomes replaced by a very fine-grained mineral or mineraloid which is pale brown, translucent, and

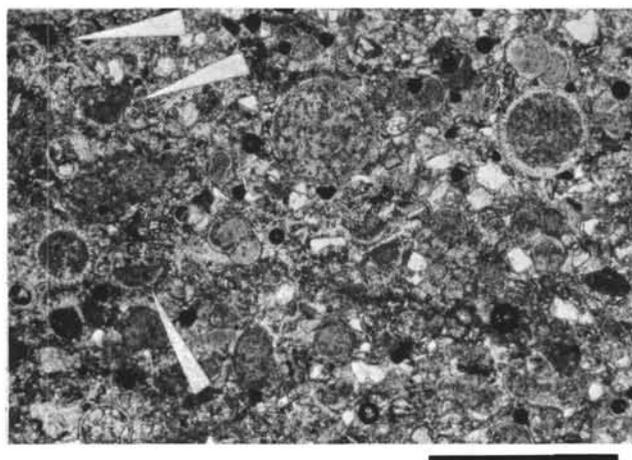


Figure 2. Zeolitic foraminiferal sandstone. Shells of planktonic foraminifera, detrital plagioclase grains, etc. cemented in finely crystalline phillipsite. Foraminiferal chambers are largely filled with micrite, some of which is partly replaced by zeolites. Small arrows point to "half-moon" micrite-filled foraminiferal tests whose origin is discussed in the text. Scale bar is 1 mm.

almost isotropic. We believe this material is very fine-grained phillipsite: The replacement varies from slight to complete.

SUMMARY OF SEDIMENTOLOGICAL AND EARLY DIAGENETIC HISTORY

The composition, textures, and structures in this rock indicate current redeposition of sediment that originally accumulated from diverse sources (volcanic, pelagic, with possible minor terrigenous admixtures) probably

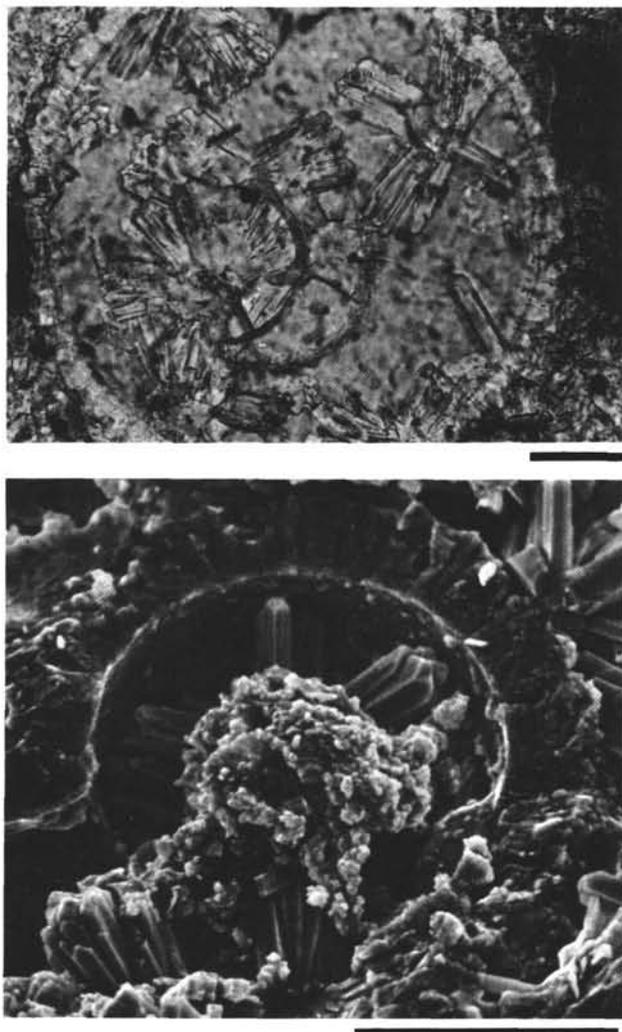


Figure 3. Pore-filling phillipsite crystals; scale bars are 50 microns. (A) Photomicrograph of micrograph of radiating phillipsite crystals within foraminiferal chamber. (B) Scanning electron euhedral phillipsite crystals in voids within and outside a foraminifer. Note that the phillipsite displaces and possibly replaces fine-grained sediment (micrite ?) at center.

on more elevated portions of this seamount. Prior to reworking, some lithification of a micritic foraminiferal sediment occurred, and clasts of this lithified carbonate were eroded and redeposited with the other components. Compaction of the sand altered the fabric and preceded the main phase of zeolitic cementation.

PHILLIPSITE CEMENT

The zeolitic cement in this sandstone consists of remarkably euhedral phillipsite crystals (Figures 3-7), most of which show pseudo-orthorhombic symmetry and two-sided "domal" terminations (Mumpton and Ormsby, 1976). Crystals range up to 3 or 4 microns wide and 30 microns long, although the length of most is 10 to 20 microns. Much of the phillipsite occurs as rosettes of crystals that radiate from a nucleation site

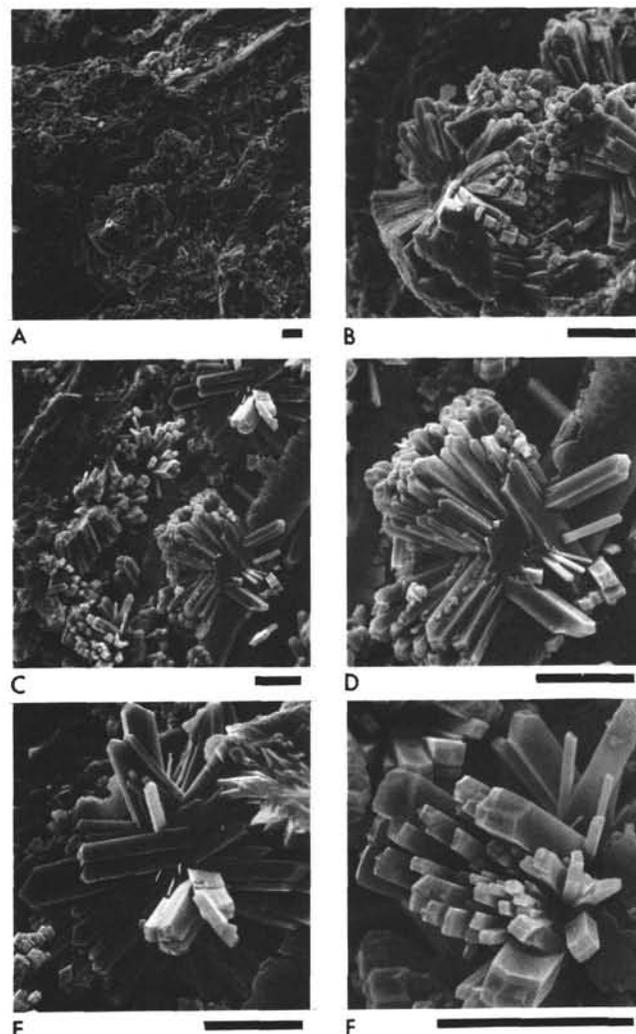


Figure 4. Scanning electron micrographs of pore filling phillipsite crystals. Scale bars are 10 microns. (A) is a low magnification view of a zeolite-filled foraminiferal test; (B) through (F) are enlarged views of clusters of phillipsite crystals within this test.

on the wall of a foraminiferal test or the edge of a clastic grain. Interlocking of these crystals in intergranular pore spaces has cemented the sand into a friable, moderately well lithified rock.

The most visible and spectacular of the zeolites are those crystals which grew unhindered into open void spaces within foraminiferal shells. Some zeolites, however, appear to replace the micritic fillings of these shells (Figures 3[b] and 6), although the foraminiferal shell walls themselves appear not to be replaced. This may be related to the stability of the carbonate phases present. Shells of planktonic foraminifers are composed of stable low-magnesium calcite that tends to resist alteration. The previously lithified micritic fillings of the shells, on the other hand, might be expected to be cemented by high-magnesium calcite (Bathurst, 1975, p. 452) which is more soluble and thus more prone to replacement.

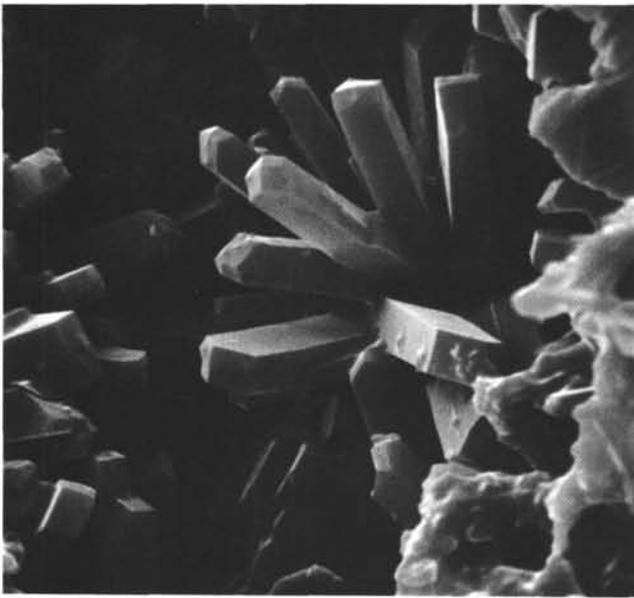


Figure 5. Scanning electron micrograph of a cluster of euhedral, pore-filling phillipsite crystals, with two-sided "domal" terminations. Scale bar is 10 microns.

Persistent zeolite growth, however, does manage to breach some of the shell walls, as shown in Figure 7. In this instance, phillipsite crystals which nucleated outside of a foraminiferal test, grew until they encountered the test wall where most were thwarted. But a few crystals penetrated pores in the shell wall and continued growing into empty chambers.

Much, if not most, of the growth of phillipsite crystals appears to have followed compaction of the sediment. The evidence for this is that phillipsite crystals have nucleated on foraminiferal shell walls that were broken by compactional crushing, yet the zeolite crystals were unaffected, indicating they post-date the fracturing.

ORIGIN OF PHILLIPSITE CEMENT

The phillipsite cement in this sample nucleated on a variety of substrates, including foraminiferal tests and clastic grains, and grew into void space. Textural evidence leaves no doubt that most of the crystals were precipitated from pore waters, and that much of this precipitation occurred following burial and compaction.

Comparison with other reports of deep sea phillipsites indicate this to be a somewhat unusual occurrence (see Bonatti, 1963, 1965; Arrhenius, 1963; Hay, 1966; Rex, 1967; Venkatarathnam and Biscaye, 1973; Cronan, 1974; Glaccum and Boström, 1976; Stonecipher, 1976). Kastner and Stonecipher (in press), in a review of occurrences of deep sea zeolites, find that phillipsite typically occurs at shallow burial depths (less than 100 m) and in slowly deposited, non-carbonate sediments, and that it forms through growth from or replacement of altered basaltic glass. Smectites are typically associ-

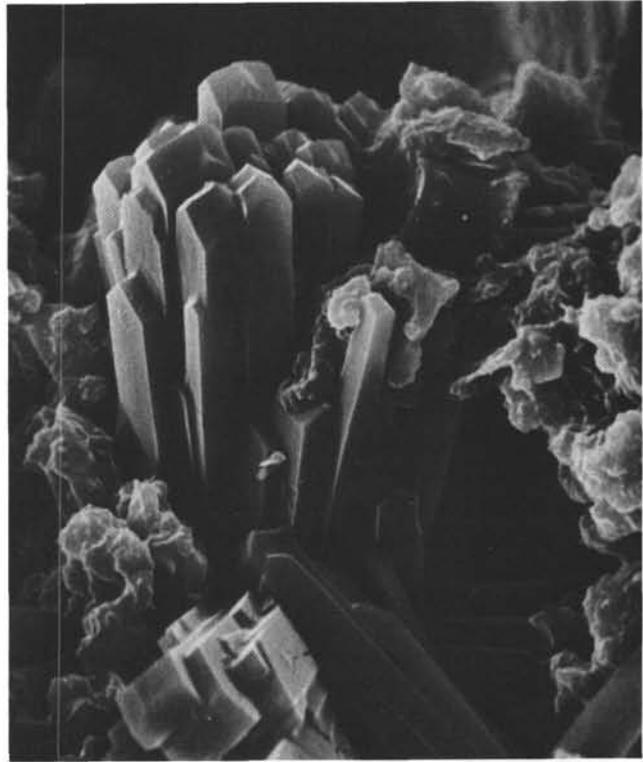


Figure 6. Scanning electron micrograph of phillipsite crystals replacing fine-grained sediment (micrite?) in interior of foraminiferal shell. Scale bar is 5 microns.

ated clay minerals. The phillipsite in this sample, however, formed in a calcareous sediment that was rapidly deposited, is now buried at 269 meters, is not directly growing on or replacing altered basaltic glass, and has no associated smectites.

Although it is not directly in contact with basaltic materials this zeolitic layer occurs less than a meter above basaltic rocks which show rather intense alteration to palagonite and other secondary products, including phillipsite (see Site Report, Chapter 4, Bernoulli et al., and Dietrich et al., this volume). We believe this alteration must have affected the chemistry of the pore waters which circulated through the sand layer and from which the zeolites precipitated. Rex (1967) suggested that deep sea phillipsite forms in the presence of a silica-rich solution with a high K/Na ratio, an interpretation apparently supported by the experimental results of Kühl (1969) and of Keene et al. (1976). Hart's (1970) data indicate that submarine alteration of basalt releases silica; additional silica might be derived from dissolution of siliceous microfossils in these and adjacent sediments, although we found no direct petrologic evidence of this. Potassium and sodium, however, both are elements which typically become enriched in basalt during submarine alteration (Hart, 1970). We may thus speculate that alteration of the basaltic rocks at Site 373A preferentially removed potassium and increased the K/Na ratio of circulating pore waters.

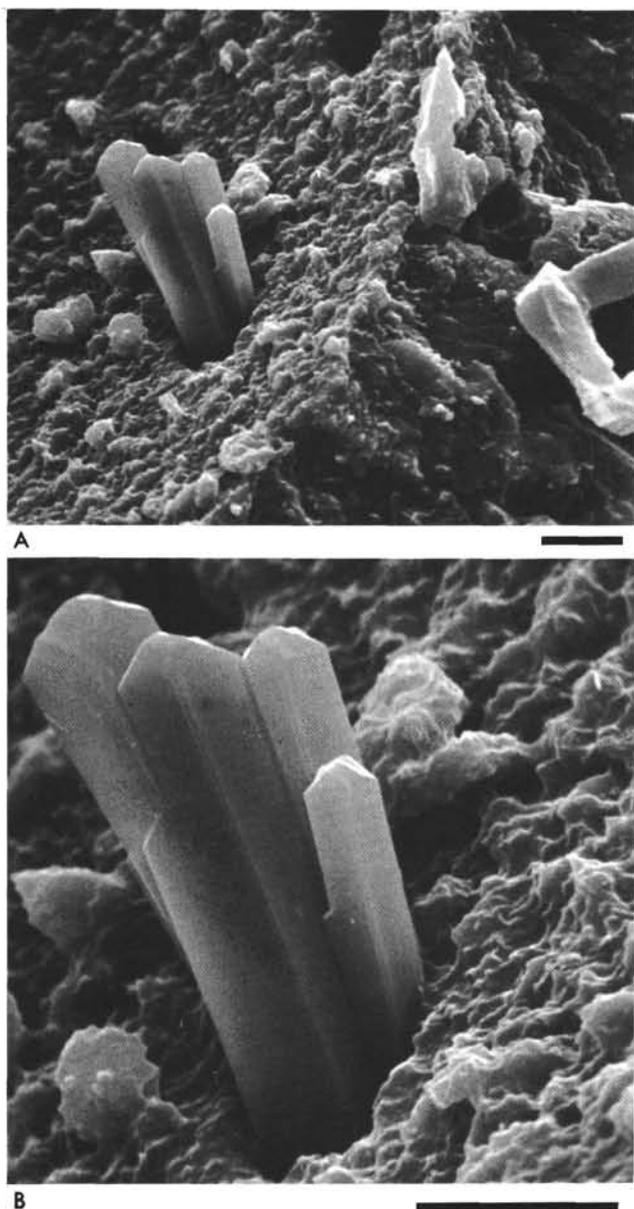


Figure 7. Scanning electron micrographs of the "violated foram," scale bars are 5 microns. Phillipsite crystals grew from the outside of a planktonic foraminiferal shell and penetrated into the interior of an empty chamber through pores in the shell wall.

Complex sediment fillings between clasts of the underlying basaltic breccias, described by Bernoulli et al. (this volume), attest to extensive circulation of water through the upper portions of the volcanic rocks of this seamount. These fluids probably also circulated through the superjacent sediments, including the zeolitic sand layer. The high porosity of this sand layer, relative to the fine-grained marls stratigraphically above and below it, may have also been important in that they allowed transmission of large quantities of pore fluids which nourished the euhedral phillipsite crystals.

ACKNOWLEDGMENTS

D. Bernoulli thanks the Swiss National Science Foundation for support during this project (Grant 2.125-0.74). R. Guggenheim provided facilities at the SEM-Laboratory at the Geological Institute of Basel University; Mrs. L. Luginbühl operated the microscope and prepared the photomicrographs.

R.E. Garrison thanks the Faculty Research Committee of the University of California, Santa Cruz, for a grant in support of this research, and Eugenio Gonzales and L. Horan for technical help. We are grateful to F.A. Mumpton for suggestions and review of the manuscript, and to Miriam Kastner for access to unpublished data.

REFERENCES

- Arrhenius, G., 1963. Pelagic sediments *In* Hill, M. N. (ed.) *The sea*, Vol. 3: New York, Wiley Interscience, p. 655-727.
- Bathurst, R. G. C., 1975. Carbonate sediments and their diagenesis (2nd ed.): Amsterdam, Elsevier Publishing Co., 658 pp.
- Bernoulli, D., Garrison, R. E., and McKenzie, J., 1977. Petrology, isotope geochemistry, and origin of dolomite and limestone associated with basaltic breccia, Site 373A, Tyrrhenian Basin: this volume.
- Bonatti, E., 1963. Zeolites in Pacific pelagic sediments: *Trans. N.Y. Acad. Sci.*, v. 25, p. 938-948.
- , 1965. Palagonite, hyaloclastites and alteration of volcanic glass in the ocean: *Bull. volcanol.*, v. 29, p. 257-269.
- Cronan, D. S., 1974. Authigenic minerals in deep-sea sediments, *In* Goldberg, E. D. (ed.) *The sea*, v. 5: New York, (Wiley Interscience), p. 491-525.
- Glaccum, R. and Boström, K., 1976. (Na, K)-phillipsite: its stability conditions and geochemical role in the deep sea: *Marine Geol.* v. 21, p. 47-58.
- Hart, R., 1970. Chemical exchange between seawater and deep ocean basalts: *Earth Planet. Sci. Lett.*, v. 9, p. 269-279.
- Hay, R. L., 1966. Zeolites and zeolitic reactions in sedimentary rocks: *Geol. Soc. Amer. Spec. Pap.* 85, 130 pp.
- Kastner, M. and Stonecipher, S.A., in press. Zeolites in pelagic sediments of the Atlantic, Pacific and Indian Oceans *In* special volume, *Zeolite '76*, Internat. Zeolite Conf., Tucson, Arizona, 1976.
- Keene, J. B., Clague, D. A., and Nishimori, R. K., 1976. Experimental hydrothermal alteration of tholeiitic basalt: resultant mineralogy and textures: *J. Sed. Pet.*, v. 46, p. 647-653.
- Kühl, G. H., 1969 Synthetic phillipsite: *Amer. Mineralogist*, v. 54, p. 1607-1612.
- Mumpton, F. A. and Ormsby, W. C., 1976. Morphology of zeolites in sedimentary rocks by scanning electron microscopy: *Clays and Clay Minerals*, v. 24, p. 1-23.
- Rex, R. W., 1967. Authigenic silicates formed from basaltic glass by more than 60 million years' contact with sea water, Sylvania Guyot, Marshall Islands: *Clays and Clay Minerals, Proc. Nat. Conf.*, v. 15, p. 195-203.
- Stonecipher, S. A., 1976. Distribution of deep-sea phillipsite and clinoptilolite: *Chem. Geol.*, v. 17, p. 307-318.
- Venkataratham, K. and Biscaye, P.E., 1973. Deep-sea zeolites: variations in space and time in sediments of the Indian Ocean: *Marine Geol.*, v. 15, p. 11-17.