Reports

St. Peter and St. Paul Rocks: A High-Temperature, Mantle-Derived Intrusion

Abstract. *St. Paul's Rocks, often postulated to be an exposure of the suboceanic mantle, consists of a wider variety of rocks than previously recognized. These perhaps crystallized at different mantle levels, and were subsequently incorporated and mylonitized in a hot but solid intrusion.*

St. Peter and St. Paul Rocks (St. Paul's Rocks) are a tiny group of barren islets 80 km north of the equator and close to the axis of the mid-Atlantic Ridge (*1*). Charles Darwin (*2*) noted that unlike all other islands which rise from oceanic ridges or from the abyssal plains, St. Paul's Rocks are not volcanic, but rather consist of highly sheared (mylonitized) plutonic rocks. This has been repeatedly confirmed (*1*), and much additional interest has been stimulated by the suggestion that these islets are in fact an exposure of the suboceanic mantle (*3, 4*).

During cruise 20 of R.V. *Atlantis II* of the Woods Hole Oceanographic Institution, considerable work was done about St. Paul's Rocks, including the most detailed geological survey to date (*5*). During this survey and from two large dredge hauls taken from submarine talus slopes immediately south (dredge 7) or southeast (dredge 18) of the islets during cruise 35 of R.V. *Chain,* we collected mylonite samples of previously unrecorded compositional and mineralogic heterogeneity (*6*).

Descriptions follow based on the petrography of about 200 samples, on electron-beam microprobe analyses of mineral grains in many of these, and on the complete wet-chemical analysis of four samples. Table 1 summarizes the latter and gives an estimate of the average composition of the mylonites, based on the observed relative abundances of mylonites of various types, both in near-shore dredge hauls and exposed on the islets. Table 2 describes the mineralogy and locality of each sample in Table 1.

We have found it useful to classify the mylonites in two main mineralogic types: spinel peridotite mylonites (after Tilley, *3, 7*), and brown hornblende mylonites, characterized by abundant brown, alkali-rich hornblende. There is considerable variation among samples within each class. In addition, a third mineralogically distinct mylonite was found rarely on Southeast Islet; this type consists mainly of colorless to light-green clinopyroxene, plagioclase, and scapolite, with subordinate brown hornblende. We suspect that additional petrographic work will reveal other distinct rock types, but only as minority representatives.

Spinel periodite mylonites, as described by Tilley (*3, 7*) and others (*4, 8*) are the most abundant rocks on all the islands, and in near-shore dredge samples. Banding due to local concentration of amphibole is common on both Southwest and Southeast islets; amphibole may compose more than 50 percent of some of these bands. Enstatite and chromian spinel are always present. Diopside is commonly present when amphibole is scarce. Serpentine is restricted to joint surfaces and composes less than 10 percent by volume of most of these mylonites.

The second most abundant rock type, previously undescribed from the islets, we have found to be brown hornblende mylonites, characterized by abundant brown alkali-rich hornblende and a large and complex suite of associated minerals. These mylonites are minor constituents of both dredge hauls but occur *in situ* only on Southeast Islet; on this, the second largest islet, we estimate 20 to 30 percent of the surface consists of brown hornblende mylonite, interbanded with spinel peridotite mylonites petrographically identical to those of the other islets. The bands, a few millimeters (Fig. 1) to several meters thick, dip 60°E and strike about N10W, at right angles to the ridge from which the islets rise (*1*).

Particularly important features in unraveling the complex history of the mylonites are large single or multimineral sheared-out grains referred to here as augen (Fig. 2). The augen are thought to be relicts of the premylonitization (primary) assemblages (*3*). Recrystallization and formation of new minerals, particularly of hydrous or chlorine-rich phases, during and after mylonitization have obscured the primary assemblages of many samples. For this reason, the mineral assemblage of a mylonite matrix, although originally derived by granulation of the augen, is not always the same assemblage as that of the augen.

The spinel peridotite mylonites have been divided into two types by Tilley (*7*) on the basis of the primary assemblages: mylonites with abundant amphibole augen (the "amphibole type") and with abundant diopside and enstatite augen (the "pyroxene type"). We have found that: (i) the "amphibole type" is the most abundant type on all the islets; (ii) the amphibole augen are pargasite; (iii) augen of blue spinel (around $Sp_{80}He_{20}$), plagioclase, and phlogopite are common accessories in the "amphibole type"; (iv) augen of pargasite and diopside may coexist in the same thin section; and (v) the enstatite and diopside of the "pyroxene type" are aluminous.

The primary assemblages of the mylonites may have crystallized in markedly different pressure-temperature environments. The olivine + aluminous enstatite + aluminous diopside + chromian spinel assemblage of the "pyroxene type" corresponds to the assemblages of most olivine nodules of alkali olivine basalts, and is thought to be a stable assemblage at depths between about 30 and about 140 km in the oceanic mantle (*9*). At greater depths, pyrope probably appears (*9*); this mineral has not so far been noted in samples from St. Paul's, although searched for in every petrographic examination.

The olivine + pargasite + enstatite + chromian spinel primary assemblage of the "amphibole type" and the pargasite + olivine recrystallized assemblage are stable at much shallower mantle depths, according to Clark and Ringwood (*10*), who argue that such pargasite + olivine ("ampholite") assemblages occur only down to about 30 km in the suboceanic mantle. It appears, then, that the primary assemblages of the "pyroxene type" and "amphibole type" spinel peridotite mylonites equilibrated at, and thus were derived from, different mantle levels. As Ringwood notes (*9*), should P_{H_2O} in the mantle be inhomogeneous, and locally equal the load pressure, this could significantly increase the depth of the stability field of the hydrous assemblage, "amphibole-type" minerals. At sufficiently high partial pressures of H_2O, this assemblage might even have equilibrated at the same temperatures and total pressures as the "pyroxene type"; the two assemblages could, in this case, both have originated from the same depths, considerably greater than 30 km. Viewed in either of these ways, the mineralogy suggests that St. Paul's Rocks represent an intrusion of mantle material from below 30 km, and one which was intruded too rapidly to permit reequilibration at any shallower depth.

Table 1. Bulk analyses of spinel peridotite and brown hornblende mylonites, St. Paul's Rocks, and weighted average composition of mylonites (90 percent average of 7-327 and 7-479, 5 percent 18-900, and 5 percent SE 13, recalculated to 100 percent).

Component	Spinel peridotite mylonites			Brown hornblende mylonite SE-13	Weighted average mylonite
	7-327	7-479	18-900		
SiO_2	44.35	43.80	42.22	36.64	43.55
Al_2O_3	3.41	2.40	4.42	17.20	3.69
TiO_2	0.08	0.07	0.30	3.99	0.28
Fe_2O_3	1.19	1.41	2.86	2.78	1.45
FeO	7.07	6.22	4.45	8.88	6.64
MgO	38.88	42.13	34.61	6.48	38.45
CaO	2.77	1.13	3.92	13.30*	2.61
Na_2O	0.17	0.14	0.43	3.85	0.33
K_2O	.05	.07	.11	0.80	.10
H_2O^+	1.16	1.54	5.73	1.88	1.59
H_2O^-	0.13	0.10	0.19	0.12	0.12
MnO	.15	.14	.13	.13	.14
P_2O_5	< .05	< .05	.05	2.64	.13
Cr_2O_3	.53	.54	.50	< 0.02	.51
NiO	.25	.32	.27		.27
Cl	.09	.05	.20	1.47†	.14
CO_2				0.08	< .01
Summation	100.28	100.06	100.39	100.24	100.00
Summation (Cl = O)	100.26	100.05	100.34	99.91	100.00
Density	3.28	3.24	2.99	2.97	
(Cl, water soluble)	0.02	0.03	0.03	0.07	
(Cl, acid soluble)				.65	

* Includes 0.67 percent Sr (*34*). † Contains less than 0.05 percent F.

The pargasite augen of the spinel peridotite mylonites are similar to the dominant amphiboles of the banded parts of the spinel peridotite bodies near Lizard, England (*11*), and near Tinaquillo, Venezuela (*12*), which are postulated to be high-temperature, mantle-derived intrusions (*13*). The pargasite augen from St. Paul's Rocks typically have SiO_2 = 43 to 47 percent, Al_2O_3 = 10 to 12 percent, MgO = 17 to 20 percent, Fe = 2.8 to 6.0 percent, CaO = 11 to 13 percent, Na_2O = 2.0 to 3.3 percent, K_2O = 0.4 to 0.9 percent, and TiO_2 = 0.2 to 0.5 percent.

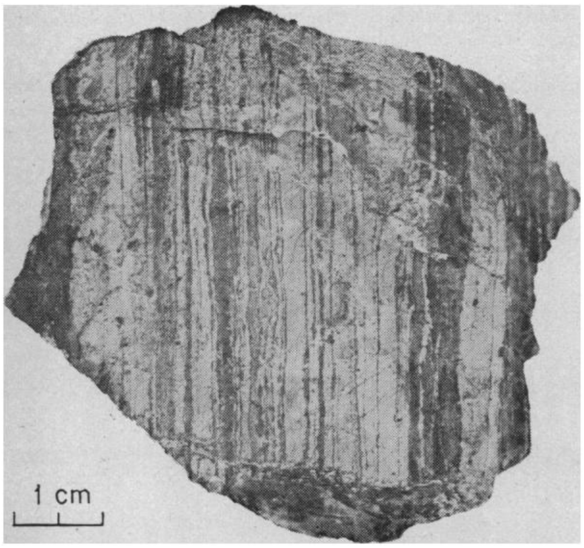
The brown hornblende mylonites are characterized by abundant large augen (up to 1 cm across) of brown hornblende. Less abundant and smaller augen of plagioclase, titan-biotite, clinopyroxene, olivine, scapolite, zircon, and allanite (*14*) occur. Although CaO (10 to 12 percent) and Fe (7.0 to 10.4 percent) are in the range of many hornblendes, the brown hornblende augen are uncommonly high in TiO_2 (1.3 to 2.0 percent), Al_2O_3 (15 to 17 percent), Na_2O (2.5 to 3.1 percent), and K_2O (1.0 to 1.8 percent) and low in SiO_2 (37 to 40 percent). Compositionally similar hornblendes have been reported from a garnet-hornblende nodule postulated to be of upper mantle origin (*15*) and in alkalic igneous rocks which crystallized in continental crust (*16*). Optically similar brown hornblende has been reported in the "pseudogabbro" bands of the Tinaquillo peridotite (*12*). Such hornblendes evidently are stable over a wide range of pressure-temperature conditions.

In the St. Paul's intrusion recrystallized assemblages suggestive of high temperatures occur in the matrix of some mylonites and in veinlets. In the spinel peridotite mylonites, such assemblages commonly contain olivine, pargasite, phlogopite, carbonate, and sulfide (mainly pyrite). In the brown hornblende mylonites, a much more complex suite, including some rare minerals, characterizes the recrystallized assemblages: scapolite (*17*), magnetite-ilmenite, analcite, titan-biotite, chloro-apatite, chloro-hornblende (*18*) (like dashkesanite), carbonates, and sulfides (including chalcopyrite) have so far been recognized. The stability of olivine in association with hydrous minerals suggests that these assemblages recrystallized in excess of 430°C (*19*); this temperature is reached in the crust at about 15 km, based on the commonly postulated average crustal geothermal gradient (30°C/km). This depth is below the M-discontinuity in even the areas of thick oceanic crust beneath the mid-Atlantic Ridge (*20*).

Hess (*21*) has drawn attention to the compositional similarity of the spinel peridotite mylonites to the olivine nodules common in alkali olivine basalts. Because of their low content of basaltic constituents, Tilley (*7*) and Hess (*21*) rejected previously analyzed spinel pe-

Table 2. Mineralogy and locality of analyzed samples (*35*).

Sample	Mineralogy
7-327	*"Pyroxene type" spinel peridotite mylonite.* Primary assemblage: olivine, enstatite, diopside, chromian spinel. Recrystallized assemblage: olivine, pargasite. Dredge 7, R.V. *Chain* Cruise 35.
7-479	*"Amphibole type" spinel peridotite mylonite.* Primary assemblage: olivine, enstatite, pargasite, chromian spinel, blue spinel ($Sp_{80}He_{20}$), and phlogopite. Recrystallized assemblage: olivine, pargasite, phlogopite, calcite, and pyrite. Dredge 7, R.V. *Chain* Cruise 35.
18-900	*"Amphibole type" spinel peridotite mylonite,* enriched in pargasite. Primary assemblage: olivine, enstatite, pargasite, chromian spinel. Recrystallized assemblage: olivine and pargasite. Considerable secondary serpentine. Dredge 18, R.V. *Chain* Cruise 35.
SE-13	*Brown hornblende mylonite.* Primary assemblage: brown hornblende, plagioclase, magnetite-ilmenite, scapolite, apatite, allanite. Recrystallized assemblage: scapolite, chloro-hornblende, apatite, titan-biotite, analcite, sphene, natrolite. Near north side of Southeast Islet; from band 3 m thick. *Atlantis II*, Cruise 20.



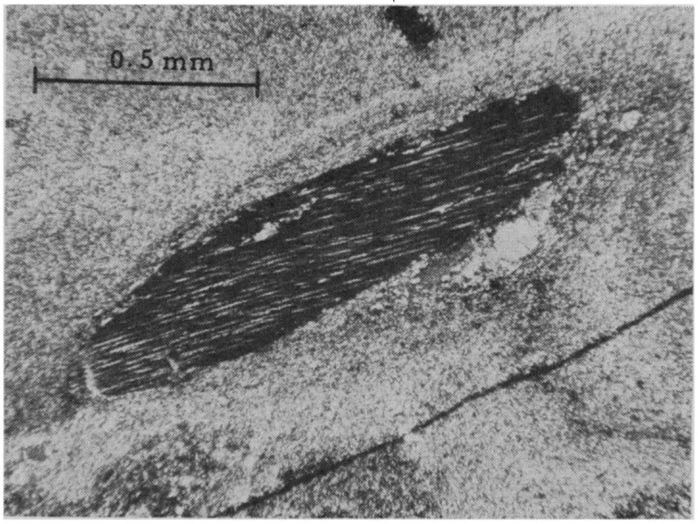


Fig. 1 (left). Interbanded spinel peridotite and brown hornblende mylonites, Southeast Islet, St. Paul's Rocks. Fig. 2 (right). Enstatite augen with diopside exsolution lamellae (viewed with crossed nicols, enstatite at extinction). Spinel peridotite mylonite, Northwest Islet, St. Paul's Rocks. Clinoenstatite, although searched for in several samples, was not found.

ridotite mylonites from St. Paul's Rocks as representative of rocks likely to yield basaltic magma on partial fusion. Tilley (*7*) in fact suggested that they are perhaps residua of partial fusion. Our two new analyses of low-pargasite mylonites (7-327 "pyroxene type," and 7-479 "amphibole type," Table 1) are in accord with these views, and, like the analyses of Tilley (*7*), show that the "amphibole" and "pyroxene" types may have essentially identical compositions.

Table 1 includes a pargasite-rich spinel peridotite mylonite (18-900) which is markedly high in basaltic constituents, such as Na, which tend to be concentrated in pargasite. This analysis is similar to the "1 : 3 pyrolite" of Green and Ringwood (*22*), a postulated mantle composition composed of 1 part basalt and 3 parts dunite, and thought likely to yield basalt on partial fusion. This pargasite-rich mylonite most closely approaches the postulated average composition of St. Paul's Rocks (Table 1), although we estimate that such pargasite-rich mylonites compose only about 5 percent of the islets as a whole.

The brown hornblende mylonites (SE 13, Table 1), although ultrabasic, are remarkably high in Al_2O_3, TiO_2, CaO, the alkalies, P_2O_5, and Cl (*23*). They contain abundant normative diopside, anorthite, and nepheline, and are thus compositionally similar to the alkali olivine basalts of many oceanic islands, which are on the average high in TiO_2 (*24*) and differ markedly from "oceanic tholeiites," probably the most abundant deep-sea basalts (*25*).

Although not yet determined, it is likely that the U, Th, and rare earth contents of the brown hornblende mylonites are unusually high compared to, for example, "oceanic tholeiites." This is suggested by the presence of accessory allanite (*14*) and zircon, as well as by the fact that igneous rocks compositionally similar to the brown hornblende mylonites are commonly enriched in these elements.

On the continents, igneous rocks compositionally similar to the brown hornblende mylonites (Table 1) occur (i) among the ultrabasic members of alkalic igneous rock provinces (*26*), (ii) in association with carbonatites (*27*), and (iii) as alkalic ultrabasic porphyritic dike rocks (lamprophyres). The high contents of volatiles, (Mg + Fe), (K + Na), and Sr especially suggest kinship to the lamprophyres (*28*). Continental igneous rocks compositionally like the St. Paul's brown hornblende mylonites may contain a few of the following minerals (*29*): brown hornblende, titan-augite, plagioclase, nepheline, melilite, apatite, hauyne, and sodalite. Scapolite, an abundant mineral of these mylonites, characteristically occurs in metamorphic rocks and, except for some pegmatites, does not occur as a primary mineral in igneous rocks (*30*).

We have recognized few clues which suggest that the brown hornblende and spinel peridotites are genetically related by a single process acting on an originally homogeneous body, such as gravity differentiation prior to mylonitization, a suggested origin for the spinel peridotite mylonites (*31*), or metamorphic differentiation during mylonitization. On the contrary, the pervasive mylonitization, the juxtaposition of assemblages which may have equilibrated to markedly different pressure-temperature environments, and the diversity of rock types are more consistent with movement of a relatively hot (but solid) plastic rock mass through the suboceanic mantle, and incorporation and shearing out of a variety of unrelated rock types during ascent. The amount of hydrous and chlorine-rich phases in the recrystallization assemblages suggests that each of these rock types contained, during the intrusion, an abundant interstitial fluid phase.

We have noted above similarities between the mylonites of St. Paul's and such continental high-temperature, peridotite-rich intrusions as those of the Lizard complex (England) and of Tinaquillo, Venezuela. Like the St. Paul's intrusion, these latter also contain diverse mineral assemblages; in their cases, however, some of this diversity is attributed to inclusion of crustal contact rocks (*11, 12*). The thinness of the suboceanic crust makes such inclusion a less likely explanation for the heterogeneity of St. Paul's. A more attractive hypothesis is that the diverse rock types found here were derived in fact from the suboceanic upper mantle, and thus bear directly on its heterogeneity, mineralogy, and composition.

Previous geochemical studies of

samples from St. Paul's Rocks, such as those on rare earth elements (*32*), and strontium isotopes (*33*), evidently were done on the spinel peridotite mylonites. Taken alone, neither the spinel peridotite mylonites nor the brown hornblende mylonites have compositions thought to be appropriate for the average composition of the mantle. The former, as a whole, are much too low and the latter much too high in alkalies and probably in U and Th to be appropriate for parental basalt materials, or to be consistent with oceanic heat flow. The pargasite-enriched mylonite (18-900, Table 1) and the estimated average of the mylonites are both more in accord with suggested average mantle compositions.

Clearly, additional analytical studies are needed to evaluate the idea that, as a whole, St. Paul's Rocks material is acceptable as compositionally representative of the mantle. We are continuing our study of this interesting intrusion, both on the suites of samples from the islets and on the extensive suites of samples obtained by dredging about the intrusion.

WILLIAM G. MELSON
EUGENE JAROSEWICH
U.S. National Museum,
Washington, D.C. 20560
VAUGHAN T. BOWEN
GEOFFREY THOMPSON
Woods Hole Oceanographic Institution,
Woods Hole, Massachusetts 02543

References and Notes

1. Located at 0°56′N, 29°22′W: consists of five larger islets and four sizeable rocks separated by narrow channels; combined subaerial surface little more than 0.01 km^2. Published reports of St. Paul's Rocks were summarized by W. L. Tressler, S. Bershad, and W. H. Berninghausen in *U.S. Navy Hydrographic Office Technical Report HO 31, 1-63* (1956). We have followed their nomenclature for the individual islets.
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3. C. E. Tilley, *Am. J. Sci.* **246**, 483 (1947).
4. H. H. Hess, *Bull. Geol. Soc. Am.* **71**, 235 (1960).
5. We landed on and sampled each major islet [Northwest, Northeast, Southeast, Southwest (Main), and South Islets, and the larger of the Southwest Rocks].
6. We have recently summarized some other aspects of the St. Paul's survey [*Oceanus* **12**(4), 2 (1966) and, in an abstract, *Geol. Soc. America, Program 1966 Meetings*, p. 138]. A complete cruise report and several articles are in preparation.
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14. The allanite is not metamict but rather well crystallized, shows strong yellow to reddish-brown pleochroism, and is strongly zoned. Some allanites contain considerable amounts of P or Mg, but this contains only 0.1 percent P and about 0.7 percent Mg. From this mineral in SE-13 (Table 2), the microprobe obtained high count rates for $L\alpha_1$ radiation of Ce and La; about 10 percent rare earth oxides, mainly Ce_2O_3 and La_2O_3, as well as between 0.5 and 2 percent ThO_2, are commonly found in allanites.
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16. ———, *Trans. Roy. Soc. New Zealand* **85**, 251 (1958).
17. The scapolite (intermediate compositions, around Ma_{60}) contains between 1.9 and 2.3 percent Cl; S less than 0.05 percent, suggests high CO_2.
18. $K\alpha_1$ radiation from Cl excitation was about 40 times as intense from the blue as from the brown hornblende; adequate standards are being sought for quantitative Cl determinations. The chloro-hornblende, pale blue to yellow pleochroic prisms, rims typical brown hornblende augen, especially commonly at contacts of brown hornblende with post-mylonitization scapolite-chloro-apatite veinlets.
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23. We have avoided samples contaminated at the surface by salt spray or by phosphates from guano. The analyzed brown hornblende mylonite is extremely fresh in the hand specimen. Furthermore, the chlorine and phosphorus, elements likely to represent contamination, occur in the recrystallized assemblage scapolite + chloro-apatite + chloro-hornblende, an assemblage suggestive of metamorphic temperatures.
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33. P. M. Hurley, H. W. Fairbairn, W. H. Pinson, *Natl. Acad. Sci.–Natl. Res. Council Publ.* **1188**, 149 (1964).
34. Dr. Stan Hart of the Carnegie Institution determined Sr, Sr 87/86, Rb, and K in samples collected during this study.
35. The samples described here are being entered into the collections of the U.S. National Museum under the following numbers: 110685 (7-327), 110686 (7-479), 110687 (18-900), and 110393-13 (SE-13).
36. The Brazilian government gave permission for the landings. For their help, we thank the officers, men and scientists of cruises 35 (1963) of R.V. *Chain* and 20 (1966) of R.V. *Atlantis II*. Harold Banks gave technical assistance and R. F. Fudali critically reviewed the manuscript. Eugene Jarosewich was the analyst for Table 1. At the Smithsonian Institution this study was assisted by Smithsonian research grants and by NASA; at the Woods Hole Oceanographic Institution, support came from the AEC, the ONR, and the NSF. All this support is gratefully acknowledged. This is contribution No. 1896 from the Woods Hole Oceanographic Institution.

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Diffusion of Water in Zeolites

Abstract. *The self-diffusion coefficient* D *of water occluded in samples of near-faujasite has been determined by pulsed field-gradient spin-echo nuclear magnetic resonance. The value of* D *in square centimeters per second* $\times$ 10^5 *at 30°C is 1.34, 1.65, and 1.88 in the following zeolites, respectively:* Na X, Ca X, *and* Ca Y (X *and* Y *being an indication of ratio of silicon to aluminum in the zeolites). By comparison, the value of* D *in pure water at 30°C is* 2.5×10^{-5} *cm*^{2}*/sec. Arrhenius activation energies for* D *are 6.9, 6.8, and 5.6 kilocalories per mole, respectively, for the three faujasites and 5.0 kcal/mole for pure water. Thus, there appears to be little difference in diffusion behavior between free water and water occluded in faujasite.*

How the properties of a liquid are modified in the vicinity of a solid is a subject that has often been discussed. An interesting class of solids lending itself to an investigation of this question is that of the porous crystalline aluminosilicates known as zeolites or molecular sieves. An interesting property of a liquid, related to its structure, is diffusion. Since water normally fills the cages of a zeolite in equilibrium with the atmosphere, it seems natural to find that several studies have been devoted to self-diffusion of water in zeolites (*1*, *2*).

Generally, it was found that the self-diffusion coefficient *D* of water occluded in these crystals was substantially smaller than that of pure water. Thus, Barrer and Fender (*2*) report a value of *D* equal to 1.26×10^{-7} cm^2/sec for water in chabazite at 45°C. This is more than 100 times less than the corresponding value for pure water.

These low figures are easily explained by the hindrance to motion of water molecules as they diffuse through the very small channels of the zeolites under study. However, one structure exists that presents wider channels and larger cavities than are found in the crystals studied thus far (*3*). This is faujasite (or near-faujasite in the synthetic form), a structure resulting from the stacking of SiO_4 and AlO_4 tetrahedra in a cubo-octahedron arrangement. Thus, cavities about 12 Å in diameter are formed that contain about 30 water molecules when the zeolite is