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The Oxygen Isotope Geochemistry of Igneous Rocks*

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Abstract. Oxygen isotope analyses have been obtained for 443 igneous rock and mineral samples from various localities throughout the world. Detailed studies were made on the Medicine Lake, Newberry, Lassen, Clear Lake, S. E. Guatemala, Hawaii and Easter I. volcanic complexes and on the Bushveld, Muskox, Kiglapait, Guadalupe, Duluth, Nain, Egersund, Lac St. Jean, Laramie, Skaergaard, Mull, Skye, Ardnamurchan and Alta, Utah plutonic complexes, as well as upon several of the zoned ultramafic intrusions of S. E. Alaska.

Basalts, gabbros, syenites and andesites are very uniform in O^{18}/O^{16}, commonly with δ-values of 5.5 to 7.0 per mil. Many rhyolite obsidians, particularly those from oceanic areas and the Pacific Coast of the United States, also lie in this range; this indicates that such obsidians are differentiates of basaltic or andesitic magma at high temperatures (about 1,000° C). They cannot represent melted sialic crust. The only plutonic granites with such low δ-values are some of the hypersolvus variety, suggesting that these also might form by fractional crystallization. Obsidians from the continental interior, east of the quartz-diorite line, have higher δ-values. This is compatible with their having assimilated O^{18}-rich sialic crust.

A correlation generally exists between the O^{18}/O^{16} ratios of SiO_2-rich differentiates and the chemical trends in volcanic complexes. High O^{18}/O^{16} ratios accompany those trends having the lower Fe/Mg ratios, while ferrogabbro trends are associated with depletion in O^{18}. Variations in oxygen fugacity may be responsible for these effects, as abundant early precipitation of magnetite should lead to both O^{18}-enrichment and Fe-depletion in later differentiates. Plutonic granites have higher O^{18}/O^{16} ratios than their volcanic equivalents, because (a) their differentiation occurred at much lower temperatures, or (b) they are in large part derived from O^{18}-rich sialic crust by partial melting or assimilation. Also, the oxygen isotope fractionations among coexisting minerals are distinctly larger in plutonic rocks than in volcanic rocks. This is in keeping with their lower crystallization temperatures and their longer cooling history, which promotes post-crystallization oxygen isotope exchange.

Hydrated obsidians and perlites have δO^{18}-values that are much different from their primary, magmatic values. A correlation exists between D/H and O^{18}/O^{16} ratios in hydrated volcanic glass from the western U.S.A., proving that the isotopic compositions are a result of exchange with meteoric waters. The O^{18} contents of the glasses appear to be about 25 per mil higher than their associated waters; hence, these hydrated glasses have not simply absorbed H_2O, but they have exchanged with large quantities of it.

The igneous rocks from Mull, Skye, Ardnamurchan and the Skaergaard intrusion are all abnormally depleted in O^{18} relative to "normal" igneous rocks. This is a result of their having exchanged at high temperatures with meteoric water that was apparently abundant in the highly jointed plateau lavas into which these igneous rocks were intruded. In part, this exchange occurred with liquid magma and in part with the crystalline rock; in the latter case the feldspar was more easily exchanged and has become much more depleted in O^{18} than has coexisting quartz or pyroxene.

The later differentiates of the Muskox intrusion are markedly O^{18}-rich, but this is not a result of fractional crystallization. It is in large part a result of deuteric exchange between feldspars

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and an oxygen-bearing fluid (H_2O ?) that was either O^{18}-rich or had a relatively low temperature. This phenomenon was also observed in a number of granophyres from other localities, particularly those containing brick-red alkali feldspar. The exchanged feldspars in all these examples are turbid or cloudy, and may be filled with hematite dust. It is concluded that most such feldspar in nature is the result of deuteric exchange and is probably drastically out of oxygen isotopic equilibrium with its coexisting quartz.

Introduction

The purpose of the present study is to obtain a broad understanding of oxygen isotope variations in igneous rocks throughout the world, and thereby to delineate the O^{18}/O^{16} ratios of the magmas from which these igneous rocks were formed. Effort is concentrated upon the calc-alkaline magma-types (i.e., the basalt-andesite-dacite-rhyolite series and its plutonic equivalents) as these constitute the most abundant igneous rocks on Earth. We also include detailed studies of the oxygen isotope variations that occur during magmatic differentiation in several gabbro-granophyre complexes and several young volcanic provinces.

A beginning was made on these various problems by SILVERMAN (1951) and TAYLOR and EPSTEIN (1962a, 1962b, 1963), particularly with regard to the plutonic igneous rock-types. As a result, the O^{18}/O^{16} variations in the Southern California batholith and in the Skaergaard intrusion, east Greenland, are relatively well understood. Oxygen isotope relationships in igneous meteorites, notably the basaltic achondrites, were worked out by TAYLOR *et al.* (1965). Almost no data are available on volcanic rocks, however, except for a few analyses of coexisting phenocrysts in basalts and trachytes by GARLICK (1966).

Oxygen isotope analyses represent a hopeful new tool with which one can attack some of the classic problems of igneous petrology. Oxygen is by far the most abundant element in igneous rocks and in the liquid, solid, and gaseous phases that are important in magmatic phenomena. O^{18}/O^{16} measurements provide a practically unique way to characterize different kinds of quartz, for example, as this important mineral is generally so pure that distinction by other chemical techniques is difficult. In addition, the effects of interaction between an igneous rock and oxygen-bearing fluids or gases are commonly discernible by oxygen isotope measurements on the mineral assemblage alone.

Equilibrium oxygen isotope fractionations among several important igneous minerals are known at temperatures extending up into the magmatic range, through laboratory calibration experiments. In all known cases, the oxygen isotope fractionations between any two minerals decrease with increasing temperature of formation, in a simple, systematic manner (generally falling off linearly on a $1/T^2$ plot, where T is the absolute temperature in °K). These relations allow us to make quantitative inferences about existence of equilibrium and temperature of crystallization in a mineral assemblage (e.g., see O'NEIL and CLAYTON, 1964; and O'NEIL and TAYLOR, 1967). Such data also throw light upon sequence of crystallization, genetic relationships between rock types, subsequently imposed metamorphic events, and recrystallization in the presence of aqueous fluids.

The present study utilizes the broad background of theoretical and experimental knowledge now available on processes of oxygen isotope fractionation to fill in some of the gaps in our knowledge of O^{18}/O^{16} variations in igneous rocks and minerals. To be more specific, we discuss the implications of O^{18}/O^{16} data with regard to: (1) the importance of fractional crystallization as a process of magmatic differentiation; (2) whether assimilation of country rock plays an important role in magmatic evolution; (3) possible differences in mode of origin of volcanic and plutonic igneous rocks; (4) the presence or absence of equilibrium in an igneous mineral assemblage; (5) the effects of secondary hydration of volcanic glass and the origin of perlites; and (6) the effects of late-stage deuteric or hydrothermal recrystallization in igneous rocks, including the possible interaction between magmas and meteoric waters in shallow portions of the Earth's crust.

Analytical Results

The analytical data on O^{18}/O^{16} ratios of 170 samples of rocks and minerals from volcanic complexes are given in Table 1. Corresponding data for 273 samples from plutonic and hypabyssal igneous rocks are given in Table 2. In all cases, oxygen was extracted from the minerals and rocks by reacting the samples with fluorine at 500—600° C (see TAYLOR and EPSTEIN, 1962a); generally, 2 or more extractions were done on each sample. The oxygen gas samples were quantitatively converted to CO_2, and this gas was analyzed in a sensitive mass spectrometer.

The analytical data on D/H ratios in volcanic glass samples are much less extensive than the O^{18}/O^{16} data, but 18 samples were analyzed for both oxygen and hydrogen; the D/H values are presented in Table 3 along with the H_2O contents of the samples. The hydrogen was extracted by heating the samples in vacuum with an induction heater to 1200—1400° C, passing the evolved H_2O over hot uranium metal, and analyzing the released hydrogen in a mass spectrometer (see GODFREY, 1962). Water contents were calculated from the amount of hydrogen collected, as measured in a calibrated manometer.

Both the oxygen and the hydrogen isotopic data are reported as δ-values (EPSTEIN, 1959):

$$\delta = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right] 1000$$

where R_{sample} is either O^{18}/O^{16} or D/H in the sample material, and R_{standard} is the corresponding ratio in some standard: the standard used for both oxygen and hydrogen is Standard Mean Ocean Water or SMOW (CRAIG, 1961b; and CLAYTON and MAYEDA, 1963). The δ-values of oxygen in the present study vary from -8.4 to $+16.3$ per mil, or from values 0.84 per cent lower in O^{18} than SMOW to values 1.63 per cent higher than SMOW. The D/H values are all negative, varying from -86 to -161 per mil. The analytical error is ± 0.1—0.2 per mil for O^{18}/O^{16} and ± 2—3 per mil for D/H.

In this study, we are interested in variations in δO^{18} and δD in rocks and minerals, but we are also interested in the fractionations or differences in δO^{18} among coexisting minerals in the same rock. These fractionations are most easily reported as Δ, here defined as:

$$\Delta_{A-B} = 1{,}000 \ln \alpha_{A-B}$$

where α_{A-B} is the fractionation factor for the coexisting minerals A and B (i.e. R_A/R_B). Δ_{A-B} is to a very close approximation simply equal to $\delta_A - \delta_B$.

Table 1. *Oxygen isotope analyses of volcanic igneous rocks and minerals*

Description and location of samples			δO^{18} $(^0/_{00})$	
Medicine Lake Highland, Northern California. (See Fig. 11 and ANDERSON, *1941)*				
ML-24	Massive basalt, 6 mi. W of Medicine Lake	Whole rock	5.9 ± 0.1	(2)[a]
ML-16	Lake basalt, 2 mi. NE of Medicine Lake	Whole rock	6.1	(1)
ML-11	Lake basalt, just E of Medicine Lake	Whole rock	5.9	(1)
ML-56	Modoc basalt, 2.3 mi. NE of Glass Mountain	Whole rock	6.8 ± 0.1	(4)
ML-11-4	Andesite, N of Garnet Mountain, SW 1/4 of Sec. 25, T.44 N., R.1 E.	Whole rock	6.4	(1)
ML-27	Older platy olivine andesite, 5 mi. N of Medicine Lake	Whole rock	5.5	(1)
ML-26	Platy andesite, 2 mi. N of Medicine Lake	Whole rock	5.4 ± 0.2	(3)
ML-19	Later platy olivine andesite, 2 mi. E of Medicine Lake	Whole rock	5.8 ± 0.2	(2)
ML-21	Later platy olivine andesite, 1.7 mi E of Medicine Lake	Whole rock	5.6	(1)
ML-25	Dacite from Medicine flow, 1.5 mi. N of Medicine Lake, W side of flow	Whole rock	8.5 ± 0.1	(3)
ML-13	Dacite from Medicine flow, 1 mi. N of Medicine Lake, E edge of flow	Whole rock	8.5 ± 0.1	(4)
ML-20	Pumiceous dacite from Hoffmann flow, 2.5 mi. E of Medicine Lake, W edge of flow	Whole rock	7.8	(1)
ML-55	Obsidian from rhyolite-dacite composite flow, 3 mi. NE of Glass Mountain	Whole rock	7.4 ± 0.2	(3)
ML-59	Older rhyolite obsidian, 5 mi. NE of Glass Mountain	Whole rock	6.2 ± 0.1	(3)
ML-65	Older rhyolite obsidian, 3.5 mi. S of Little Glass Mountain	Whole rock	6.1 ± 0.1	(3)
ML-66	Older rhyolite obsidian, 7 mi. S of Little Glass Mountain	Whole rock	6.3 ± 0.1	(3)
ML-17	Obsidian from perlitic rhyolite, 1.5 mi. SW of Mt. Hoffmann	Whole rock	6.0 ± 0.2	(2)
ML-57	Rhyolite obsidian from Glass Mtn. flow, 2 mi. NE of Glass Mountain	Whole rock	7.3 ± 0.1	(2)
ML-57 a	Rhyolite obsidian from Glass Mtn. flow, 2 mi. NE of Glass Mountain	Black glass Grey glass	7.3 7.0	(1) (1)
ML-63	Rhyolite obsidian from Little Glass Mtn. flow, 1 mi. N of Little Glass Mtn.	Whole rock	7.7 ± 0.2	(4)
ML-23	Rhyolite obsidian from Little Glass Mtn. flow, 1 mi. NE of Little Glass Mtn.	Whole rock	7.6 ± 0.1	(3)
Doe-8	Rhyolite obsidian from Little Glass Mtn. flow (sample 8 of DOE, 1967)	Whole rock	6.8 ± 0.2	(2)
Clear Lake volcanic area, Lower Lake quadrangle, California. (See ANDERSON, *1936)*				
CL-18-3	Mt. Konocti rhyodacite, 2.5 mi. NE of Kelseyville, S side of Soda Bay road	Sanidine Groundmass	8.9 8.8	(1) (1)
CL-20-3	Older rhyolite obsidian, 2.7 mi. due S of Mt. Konocti, W side of Rte. 29	Whole rock	9.4	(1)

[a] Analytical error is average deviation from the mean. Numbers in parentheses indicate number of separate analyses.

Table 1 (Continued)

Description and location of samples			δO^{18} $({}^0/_{00})$	
CL-9-3	Older rhyolite obsidian, 3 mi. SE of Mt. Konocti, E side of Konocti Bay road	Whole rock	9.3	(1)
CL-10-3	Older rhyolite obsidian, W side of Konocti Bay road, 0.5 mi. N of Rte. 29	Black glass	9.3	(1)
		Grey glass	9.5	(1)
CL-19-3	Older rhyolite obsidian, E side of Konocti Bay road, 0.5 mi. N of Rte. 29	Plagioclase (An_{30})	8.9	(1)
		Black glass	9.2	(1)
Doe-5	Recent rhyolite obsidian from flow 1 mi. SE of Borax Lake (no. 5 of DOE, 1967)	Whole rock	10.2 ± 0.1	(2)
Lassen Volcanic National Park, Northern California. (See WILLIAMS, *1932)*				
LP-11	White Mountain dacite, white, vesicular, 1 mi. E of White Mountain	Glassy groundmass	7.3	(1)
		Quartz	8.2 ± 0.1	(2)
		Andesine	6.9	(1)
		Biotite	5.9 ± 0.0	(3)
		Hornblende	5.8 ± 0.1	(3)
		Magnetite	3.4 ± 0.0	(2)
T-553	1915 dacite, Lassen Peak, dense, black, porphyritic glass	Glassy groundmass	7.3	(1)
		Quartz	8.6	(1)
		Sodic andesine	7.2 ± 0.1	(2)
T-206	Pink dacite, roadcut in the center of Chaos Jumbles	Whole rock	7.2 ± 0.1	(2)
LNP-36	Raker Peak pyroxene andesite, N side of Hat Creek road, near Emigrant Pass	Whole rock	6.5	(1)
LNP-41	Kaolinized Brokeoff andesite, on trail west of Bumpas Hot Springs	Whole rock	7.1	(1)
LNP-33	1851 basalt, contains quartz xenocrysts, 1 mi. S of Butte Lake	Whole rock	6.7	(1)
		Quartz xenocryst	9.1	(1)
T-955	Lassen basalt, summit of Mt. Lassen, extruded in 1915 activity	Whole rock	6.7	(1)
Newberry Crater, Paulina Lakes, Central Oregon. (See WILLIAMS, *1935)*				
PL-1-3	Porphyritic black andesite, Paulina Falls, at W outlet of Paulina Lake	Whole rock	6.2	(1)
PL-8-3	Porphyritic black andesite, 1 mi. E of East Lake	Whole rock	6.5	(1)
PL-7-3	Basalt, SE edge of East Lake, roadcut on S side of road	Whole rock	5.9	(1)
PL-3-3	Rhyolite pumice, mantles S side of caldera, S edge of Paulina Lake	Whole rock	6.3	(1)
PL-11-3	Rhyolite, grey, crystalline, base of N-facing scarp, 1 mi. S of Paulina Lake	Whole rock	6.3	(1)
PL-5-3	Grey obsidian from rhyolite dome, due S East Lake, on N side of road	Whole rock	6.3	(1)
PL-6-3	Clear black obsidian, younger obsidian flow at SE corner of East Lake	Whole rock	6.1 ± 0.0	(4)
PL-4-3	Black obsidian from youngest obsidian flow in caldera, SE of Paulina Lake	Whole rock	5.9 ± 0.2	(2)

Table 1 (Continued)

Description and location of samples			δO^{18} ($^0/_{00}$)	
Three Sisters volcanic area, Cascade Range, Central Oregon. (See Williams, *1944)*				
3S-16	Glassy rhyodacite from Recent obsidian dome, 6 mi. S of South Sister Peak	Whole rock	6.7 ± 0.1	(2)
3S-11	Rhyodacite obsidian from Obsidian Cliffs, 3.5 mi. W of North Sister Peak	Whole rock	6.7 ± 0.1	(2)
Owyhee reservoir volcanic area, Melheur County, Southeastern Oregon. (See Corcoran, *1965)*				
T-148	Owyhee rhyolite, red-brown, aphanitic, rare phenocrysts, just E of Owyhee Dam	Whole rock	7.0	(1)
T-140	Owyhee rhyolite, yellow-brown, porphyritic-aphanitic, Brandon Ranch, Owyhee R.	K feldspar	5.6	(1)
T-143	Owyhee olivine basalt, overlies T-148, just S of Owyhee Dam in Owyhee River	Whole rock	6.5 ± 0.1	(2)
Mono craters volcanic area, Sierra Nevada, East-Central California. (See Putnam, *1938)*				
T-807	Clear, black obsidian, Panum Crater, just SW of Mono Lake	Whole rock	8.0	(1)
Mono-2	Porphyritic black obsidian, 7 mi. SE of Lee Vining, S of Rte. 120	Whole rock	7.9 ± 0.2	(2)
Mono-7	Grey, vesicular pumiceous rhyolite glass, top of flow, 2 mi. E of June Lake	Whole rock	8.2	(1)
BT-1a	Bishop tuff, pink, porphyritic ash-flow tuff, Power House road, Owens Gorge, Sec. 9, R. 31 E., T. 5 S., Casa Diablo Mtn. Quad.	Quartz	8.2 ± 0.2	(2)
Other volcanic rocks from California				
W-772	Black obsidian from Obsidian Butte, SE edge of Salton Sea, Imperial Co., Calif.	Whole rock	6.1 ± 0.2	(4)
T-326	Rhyolite ash-flow tuff, Miocene, Dante's View, E side of Death Valley	Whole rock	14.0 ± 0.1	(2)
		Quartz	9.8	(1)
		Sanidine	8.2	(1)
		Biotite	6.1 ± 0.1	(3)
T-341d	Black obsidian with lithophysae, Coso Hot Springs, Inyokern N. O. T. S.	Whole rock	8.2	(1)
Coso-2	Black obsidian from 1-inch thick flow, Coso Hot Springs, Inyokern N. O. T. S.	Whole rock	8.1	(1)
DV-2	Vitrophyre from ash-flow, rhyolite tuff, 3.5 mi. NE of Shoshone, Inyo County	Red-brown glass	12.7	(1)
		Black glass	13.3	(1)
Cf-2-3	Vitrophyre from ash-flow tuff, 4.2 mi. N of Said Valley reservoir Rte. 139	Black glass	5.9 ± 0.1	(4)
T-1033	Rhyolite, grey, aphanitic, Na-rich, Sonoma Co., Valley of the Moon quarry, 4 mi. E of Kenwood	Whole rock	8.3	(1)
T-1027	Rhyolite perlite, Sonoma Co., Rte. 12, 3 mi. N of Sonoma, Sonoma Valley Improvement Club House	Whole rock	10.6	(1)
T-129	Augite andesite, light-grey, aphanitic, finely vesicular, eastern Tehama Co.	Whole rock	7.5 ± 0.1	(2)

Table 1 (Continued)

Description and location of samples			δO^{18} $(^0/_{00})$	
Other volcanic rocks from the Northwestern United States				
Doe-15	Hydrated obsidian from Walcott tuff, lower Ferry Hollow, Idaho (see Doe, 1967)	Whole rock	6.4 ± 0.3	(2)
Doe-31	Hydrated obsidian, John Day area, 17 mi. NNW of Madras, Oregon (see Doe, 1967)	Whole rock	10.6	(1)
Doe-39	Hydrated obsidian, 0.3 mi. N of the forks of Bamber Creek, Wash. (Doe, 1967)	Whole rock	9.1	(1)
Silver Peak quadrangle volcanic area, Nevada				
617-307	Dacite vitrophyre, holohyaline, from welded tuff, 1.4 mi. S of Shiprock Hill	Whole rock	10.7	(1)
617-308	Devitrified dacite ash-flow tuff, 0.6 mi. NE of Shiprock Hill	Whole rock	8.6	(1)
617-264	Rhyolite vitrophyre flow, from Rhyolite Ridge, 0.6 mi. SW of Coyote Hole	Whole rock	9.2	(1)
617-295	Rhyolite perlite from flow, 0.6 mi. SSW of Valcalda Spring	Whole rock	9.9	(1)
Pilot Mountains volcanic area, Mineral County, Nevada. (See Nielsen, *1963)*				
506—730	Rhyodacite, light-grey, f. g. to aphanitic, from Mammoth rhyodacite dome	Whole rock	7.8	(1)
506-752	Vitrophyre (54% black glass), ash-flow tuff, 1 mi. N of Mammoth mine	Whole rock Quartz	9.8 9.7	(1) (1)
506-715	Dacite vitrophyre, ash-flow tuff, 2 mi. SE of Battles Well, NE Pilot Mtns.	Whole rock	7.9	(1)
506—707	Hornblende andesite, dark grey (35% glass), 2 mi. N of Battles Well	Whole rock	7.1	(1)
Black Mountain volcanic area, Nye County, Nevada. (See Noble, *1965)*				
D100126	Nonhydrated rhyolite glass separate, Gold Flat Member of the Thirsty Canyon Tuff	Whole rock	7.0	(1)
N121AF	Sanidine separate from Gold Flat Member of the Thirsty Canyon Tuff	Sanidine	7.1	(1)
Volcanic rock samples from Arizona				
T-111	Rhyolite glass, porphyritic perlite, S side of Salt River, W of Horse Mesa dam	Whole rock Quartz Oligoclase Biotite Magnetite	13.1 ± 0.3 9.8 8.7 5.8 ± 0.3 3.6 ± 0.0	(2) (1) (1) (2) (2)
Ariz-5	Perlite containing black obsidian marekanite nodules, Superior, Gila County	Black obsidian Grey perlite	7.9 ± 0.1 12.4	(3) (1)
T-944	Rhyolite glass, grey, N bank of Salt River, 0.2 mi. W of Mormon Flat dam	Whole rock	13.9	(1)
Ariz-1-6	Black vitrophyre from ash-flow rhyolite tuff, Rte. 78, Greenlee Co., just NE of Big Lue Mtn.	Whole rock	14.2	(1)

Table 1 (Continued)

	Description and location of samples		$\delta\,O^{18}$ ($^0/_{00}$)	
T-657	Olivine basalt from pre-875 A.D. flow, Sunset Crater, N of Flagstaff	Whole rock	6.2	(1)
Volcanic rock samples from New Mexico				
Doe-30	Hydrated obsidian from S slope of Castle Knob, 6 mi. NE of Silver City (Doe, 1967)	Whole rock	15.5 ± 0.1	(2)
		Sodic andesine	7.2	(1)
T-579	Andesite, light-grey, aphanitic, contains cristobalite, Cerro Lagre	Whole rock	6.8 ± 0.2	(2)
Doe-28	Obsidian nodule from old perlite, Arroyo Hondo perlite, Jemez Mountains	Whole rock	7.1 ± 0.2	(2)
Doe-29	Los Posos obsidian, Jemez Mountains, probably Pleistocene (No. 29, Doe, 1967)	Whole rock	6.9 ± 0.1	(2)
NM-4-4	Obsidian, Jemez Creek Canyon, 0.7 mi. S of Rio San Antonio, Sandoval County	Whole rock	6.9 ± 0.1	(3)
Volcanic rock samples from Colorado and Utah				
Col-4-4	Black vitrophyre at base of Treasure Mtn. rhyolite tuff, 3.3 mi. S of Wolf Creek Pass, Mineral County, Colorado	Whole rock	9.9 ± 0.1	(2)
		Andesine	7.0 ± 0.0	(2)
		Biotite	5.9 ± 0.1	(2)
Col-11-4	Quartz latite from Alboroto rhyolite, San Juan Mtns., 2.9 mi. N of Spring Creek Pass, Colorado	Whole rock	10.2 ± 0.2	(2)
Wards-obs	Obsidian, clear, black glass, near Black Rock, Millard County, Utah	Whole rock	8.0 ± 0.0	(2)
Doe-12	Vitrophyre, 2 mi. N of Kreutzer mine, Miners Creek, near Creede, Colorado	Whole rock	11.3	(1)
Volcanic rock samples from other parts of the United States				
Doe-40	Obsidian, Cougar Creek vent dome, Yellowstone National Park, Wyo. (Doe, 1967)	Whole rock	7.4 ± 0.1	(2)
YNP-3	Obsidian, Obsidian Cliffs, Yellowstone National Park, Wyoming	Whole rock	7.1	(1)
Mn-22-3	Black vitrophyre glass, Cretaceous, Rte. 91, 1 mile S of Wolf Creek, Montana (described by Barksdale, 1951)	Whole rock	10.8 ± 0.1	(2)
		Sodic andesine	7.9	
Wisc-6	Rhyolite porphyry, Keweenawan, Black River, Wisconsin	Quartz	8.4 ± 0.0	(2)
LTS-4	Red rhyolite porphyry with red K feldspar phenocrysts, Copper Peak, Keweenaw Peninsula, Michigan	Whole rock	12.3	(1)
		K feldspar	12.1	(1)
Volcanic rock samples from Hawaii (Oahu and Maui)				
9960	Nepheline-melilite basalt, Kalihi flow, Honolulu series, Oahu (Winchell, 1947)	Whole rock	6.4 ± 0.0	(3)
10400	Nepheline basalt, Training School flow, Honolulu series, Oahu (Winchell, 1947)	Whole rock	6.2 ± 0.2	(3)

Table 1 (Continued)

Description and location of samples			$\delta\ O^{18}$ ($^0/_{00}$)	
10403	Melabasalt, 100 ft. S of Makapuu Head triang. sta., Oahu (WENTWORTH et al., 1947)	Whole rock	7.0 ± 0.1	(3)
9986	Melabasalt porphyry, Haiku stream, Koolau series, Oahu (WENTWORTH et al., 1947)	Whole rock	6.9 ± 0.1	(2)
P1102	Andesite, Kula series, Kalahaku Cliff, Maui	Whole rock	6.0 ± 0.1	(4)
P1104	Oligoclase andesite, Kula series, W rim of Halea Kala Crater, Maui	Whole rock	5.9 ± 0.0	(4)
Volcanic rock samples from Mexico and Central America. (See MC BIRNEY *and* WEILL, 1966)				
Baja-3	Rhyolitic ash-flow tuff, E coast of Baja California, 31°10′ N, 114°40′ W	Whole rock	8.0 ± 0.0	(2)
T-921	Rhyolite porphyry from ash-flow tuff, El Tigre, Mexico	Whole rock	9.5 ± 0.1	(2)
G-664	Rhyolite obsidian, E edge Ixtepeque flow, Obrajuelo Complex, SE Guatemala	Whole rock	7.0 ± 0.1	(3)
G-649	Rhyolite flow, aphanitic, SW wall of Obrajuelo crater, SE Guatemala	Whole rock	7.9 ± 0.1	(4)
G-656	Rhyolite glass, Tempisque flow, 2 km E of Agua Blanca, SE Guatemala	Whole rock	8.2 ± 0.2	(3)
G-644	Pumiceous rhyolite, H_2O-rich, center of Obrajuelo crater at lake edge, Guatemala	Whole rock	11.5 ± 0.3	(2)
G-648	Rhyolite pumice, H_2O-rich, outer slope of Obrajuelo crater, SE Guatemala	Whole rock	10.6	(1)
G-651	Basalt, contains quartz xenocrysts, Cerro Composante, flow at N edge, Guatemala	Whole rock	6.2 ± 0.1	(2)
G-706A	Granodiorite xenolith, ejecta from Obrajuelo crater, SE Guatemala	Whole rock	8.8 ± 0.3	(2)
G-645	Olivine norite bomb, near base of W rim of Obrajuelo cone, SE Guatemala	Whole rock	7.4 ± 0.1	(2)
N-258	Hydrated obsidian lens in ignimbrite, Vuelta la Barranca, NW Nicaragua	Whole rock Plagioclase	12.0 ± 0.3 7.1 ± 0.2	(2) (2)
H-2	Rhyolite ignimbrite, basal layer, U.S. Embassy residence, Tegucigalpa, Honduras	Whole rock Quartz	10.2 ± 0.3 9.2	(3) (1)
H-3	Rhyolite ignimbrite, quartz-rich, 3 km N of Tegucigalpa, central Honduras	Whole rock	7.7	(1)
H-65	Rhyolite ignimbrite, 4 km S of La Entrada, central Honduras	Whole rock	10.6 ± 0.3	(2)
H-75	Rhyolite ignimbrite, 4 km N of San Lucas on road to Guinope, central Honduras	Whole rock Quartz	10.2 8.8	(1) (1)
H-85	Rhyolite ignimbrite, near Paraiso, south-central Honduras	Quartz Sanidine	9.3 8.4	(1) (1)
G-706	Diorite xenolith, ejecta from Obrajuelo crater, 3 mi. S of Agua Blanca, Guatemala	Whole rock	7.5	(1)

Table 1 (Continued)

Description and location of samples			δO^{18} (‰)	
Easter Island volcanic complex, East Pacific Rise				
PV 650	Rhyolite obsidian, Cerro Ourito flow, Mount Ourito (A. E. J. ENGEL)	Whole rock	6.0 ± 0.2	(4)
Pat-El	Rhyolite obsidian, Cerro Ourito flow (specimen of PATTERSON and DUFFIELD, 1963)	Whole rock	5.9 ± 0.1	(4)
PV 652	Alkali basalt, Easter Island (4.66 wt. % K_2O, A. E. J. ENGEL)	Whole rock	6.2 ± 0.1	(4)
PV 653	Alkali basalt, Easter Island (1.00 wt. % K_2O, A. E. J. ENGEL)	Whole rock	5.9 ± 0.1	(5)
PV 651	Alkali basalt with tholeiitic affinities (0.58 wt. % K_2O, A. E. J. ENGEL)	Whole rock	5.6 ± 0.2	(2)
Tholeiitic basalts dredged from the East Pacific Rise. (See ENGEL *and* ENGEL, *1964a)*				
PD 1P	Porphyritic basalt ($H_2O^+ = 0.38$, $H_2O^- = 0.01$), 7°47′ S, 108°10′ W, 1700 meters	Groundmass Bytownite	5.9 ± 0.1 6.1 ± 0.1	(3) (4)
PD 3D	Basalt ($H_2O^+ = 0.54$, $H_2O^- = 0.06$), 12°52′ S, 110°57′ W, 2300 meters depth	Whole rock	5.9 ± 0.2	(4)
PD 3B	Basalt, same location as PD 3D	Whole rock	5.5 ± 0.1	(6)
PD 4G	Basalt ($H_2O^+ = 0.30$, $H_2O^- = 0.01$), 18°25′ S, 113°20′ W, 3200 meters depth	Whole rock	5.8 ± 0.0	(3)
Tholeiitic basalts dredged from the Mid-Atlantic Ridge. (See ENGEL *and* ENGEL, *1964b)*				
AD 2-1	Basalt ($H_2O^+ = 0.70$, $H_2O^- = 0.95$), 22°40′ S, 13°16′ W, 2910 meters depth	Whole rock	7.3 ± 0.2	(4)
AD 3—3	Basalt ($H_2O^+ = 0.62$, $H_2O^- = 0.61$), 5°47′ S, 11°25′ W, 2380 meters depth	Whole rock	6.7 ± 0.2	(6)
AD 5-5	Basalt ($H_2O^+ = 0.64$, $H_2O^- = 0.57$), 9°39′ N, 40°27′ W, 2982 meters depth	Whole rock	7.2 ± 0.1	(4)
AD 5-18	Basalt ($H_2O^+ = 0.50$, $H_2O^- = 0.44$), same location as AD 5-5	Whole rock	7.0 ± 0.2	(3)
Sta. 7	Basalt ($H_2O^+ = 0.83$, $H_2O^- = 0.13$), unpublished analysis by A. POLDERVAART	Whole rock	5.9 ± 0.1	(2)
Volcanic rock samples from other parts of the world				
T 104	Alkali basalt, Tenerife, Canary Islands, E Atlantic Ocean	Whole rock	6.2	(1)
T 778	Dacite, light gray, aphanitic, summit of Mt. Pelée, Martinique, West Indies	Whole rock	6.8 ± 0.1	(4)
T 949	Vitrophyre porphyry, Kastelruth near Ponte Gardena, N of Bolzano, Italy	Black glass Sanidine	16.3 9.6	(1) (1)
Lip-1	Rhyolite pumice glass, Lipari Island, N of Sicily, Mediterranean Ocean	Whole rock	8.0	(1)
Vesuv 4	Leucite phonolite porphyry, Mt. Vesuvius, Naples, Italy	Leucite Groundmass	8.3 8.4	(1) (1)
Arran 5	Pitchstone, Corrygills type, Arran, Scotland (see TYRRELL, 1928)	Whole rock	14.5	(1)

Table 2. *Oxygen isotope analyses of plutonic and hypabyssal igneous rocks and minerals*

Description and location of samples			$\delta\ O^{18}(^0/_{00})$	
Union Bay ultramafic complex, Cleveland Peninsula, Southeastern Alaska. (See Ruckmick *and* Noble, *1959)*				
UB 10	Massive magnetite from olivine clinopyroxenite, 1.1 mi. W of Mt. Burnett	Magnetite	3.8 ± 0.0	(2)[a]
UB 19	Magnetite pyroxenite, 1.8 mi. N of abandoned Nakat cannery	Magnetite	3.3 ± 0.0	(2)
UB 11	Massive magnetite, on coast, E side of Union Bay, 1 mi. N of Nakat cannery	Magnetite	3.9 ± 0.0	(2)
UB 32	Magnetite pyroxenite, 1.3 mi. N of abandoned Nakat cannery	Diopsidic augite	5.9	(1)
UB 95	Hornblende pyroxenite, on coast, E side of Union Bay, 0.3 mi. N of cannery	Hornblende	7.6	(1)
UB 157	Massive magnetite in hornblende pyroxenite, 0.2 mi. W of peak 2544, Mt. Burnett	Magnetite	4.1 ± 0.0	(2)
UB 183	Diopside vein in dunite, 0.6 mi. NE of peak 2535 in Dunite core of complex	Diopside	5.4 ± 0.0	(2)
UB 224	Olivine clinopyroxenite, 0.8 mi. S of peak 2535, just S of dunite core	Whole rock	5.7	(1)
UB 226	Olivine clinopyroxenite, just W of UB 224	Whole rock	5.4 ± 0.2	(2)
UB t-3	Chromite segregation in dunite, 0.2 mi. W of peak 2535, dunite core	Chromite	4.5	(1)
Klukwan magnetite pyroxenite body, NW of Haines, Southeastern Alaska. (See Wells *and* Thorne, *1953)*				
Kluk 51	Magnetite-rich hornblende clinopyroxenite, SW portion of Klukwan body	Magnetite	3.3	(1)
Kluk 2	Magnetite pyroxenite, SW edge of Klukwan body	Diopsidic augite Magnetite	5.4 ± 0.0 3.0 ± 0.0	(2) (2)
Kluk 1	Hornblende pyroxenite, W edge of Klukwan body	Biotite	6.2	(1)
Duke Island ultramafic complex, Southeastern Alaska. (See Irvine, *1959; 1967)*				
1-31-3	Hornblende pyroxenite (Irvine, 1959, p. 66)	Diopsidic augite Hornblende Magnetite	5.7 5.2 0.8 ± 0.2	(1) (1) (2)
R-38-2	Olivine clinopyroxenite (Irvine, 1959, p. 66)	Diopsidic augite	5.4	(1)
N-39-6	Hornblende gabbro (Irvine, 1959, p. 41)	Hornblende Plagioclase (An$_{57}$)	5.3 7.3	(1) (1)
1-27-1	Hornblende-anorthite gabbroic pegmatite (Irvine, 1959, p. 46)	Hornblende	5.8	(1)
N-40-1	Hornblende-anorthite gabbroic pegmatite (Irvine, 1959, p. 46)	Anorthite (An$_{98}$)	7.1	(1)

[a] Analytical error is average deviation from the mean. Numbers in parentheses indicate number of separate analyses.

Table 2 (Continued)

Description and location of samples			$\delta O^{18}(^0/_{00})$	
N-36-8	Pyroxene gabbro (Irvine, 1959, p. 32), also see Taylor and Epstein (1962a)	Labradorite (An_{61})	7.3	(1)
		Hornblende	5.5	(1)
		Magnetite	2.9	(1)
Other samples from ultramafic complexes in Southeastern Alaska. (See Taylor, *1967c)*				
Ann-25	Hornblende pyroxenite, W border of Annette Island dunite body	Whole rock	5.6 ± 0.1	(2)
Ann-16	Serpentinized dunite, center of Annette Island dunite body	Whole rock	2.6 ± 0.1	(2)
Snet-58	Massive magnetite from magnetite-hornblende pyroxenite body, Port Snettisham	Magnetite	4.4 ± 0.0	(2)
Sukoi-1	Pegmatite pyroxenite, Sukoi Islands ultramafic body	Diopsidic augite	5.5	(1)
Bushveld igneous complex, South Africa. (See Hall, *1932)*				
BV 3	Norite, m. g., quarry at Bon Accord, N of Pretoria, S border of complex	Labradorite	7.1	(1)
R 8	Noritic anorthosite, Rustenberg, Transvaal, platinum mine	Labradorite	7.1	(1)
		Hypersthene	5.9	(1)
BV 11	Syenite, very coarse grained, Leeuwfontein, 15 mi. NE of Pretoria	Alkali feldspar	6.9 ± 0.1	(2)
		Hornblende	5.2	(1)
BV 7	Granophyre, dike in red granite, Salt Pan, N rim, N of Pretoria, Transvaal	Whole rock	7.6	(1)
		Quartz	8.3	(1)
		Hornblende	5.4	(1)
BV 6	Granophyre, near Pyramid Station, road from Pretoria to Salt Pan, Transvaal	Whole rock	8.0	(1)
DG 3692	Bobbejaankop granite, Zaaiplats Tin Mine, contains brick-red alkali feldspar	Quartz	8.2 ± 0.0	(2)
		Alkali feldspar	9.4 ± 0.0	(3)
DG 2665	Granite, very coarse grained, Pokwani, eastern Transvaal	K feldspar	6.9	(1)
Muskox intrusion, Coppermine River area, District of MacKensie, Canada. (See Smith, *1962)*				
59-1050D	Norite, chilled marginal zone of feeder dike, 0.6 mi. N of Coppermine River	Whole rock	6.8 ± 0.0	(2)
60-416	Olivine clinopyroxenite, layer 11, unit 15 of Smith (1962), east limb of body	Clinopyroxene	6.2	(1)
60-530B	Olivine clinopyroxenite, layer 16, unit 16 of Smith (1962), east limb	Whole rock	6.3 ± 0.1	(2)
60-18618	Drill core, 585′ depth, orthopyroxenite, layer 31, unit 18 of Smith (1962)	Plagioclase	7.6 ± 0.0	(2)
		Orthopyroxene	6.6	(1)
60-18618	Drill core, 323′ depth, websterite, part of layer 31	Plagioclase	7.9	(1)
		Whole rock	6.9 ± 0.2	(2)
60-18618	Drill core, 200′ depth, gabbro, layer 32, unit 22 of Smith (1962), east limb	Plagioclase	7.7 ± 0.2	(2)
		Orthopyroxene	6.9	(1)
		Whole rock	7.3 ± 0.1	(3)
60-302	Gabbro, layer 36, unit 22 of Smith (1962), 1.5 mi. SW of Transition Lake	Plagioclase	8.0 ± 0.1	(3)
		Orthopyroxene	6.5 ± 0.0	(2)
		Clinopyroxene	6.4 ± 0.0	(2)

Table 2 (Continued)

Description and location of samples			$\delta\, O^{18}(^0/_{00})$	
60-1119A	Gabbro, layer 38, unit 21 of Smith (1962), 2.3 mi. W of Transition Lake	Plagioclase	9.6	(1)
60-767	Granophyric gabbro, layer 39, unit 24 of Smith (1962), west limb of body	Plagioclase Clinopyroxene	9.9 ± 0.2 6.7 ± 0.2	(3) (2)
60-408	Granophyric gabbro, layer 40, unit 25 of Smith (1962), west limb of body	Quartz K feldspar Hornblende	9.2 ± 0.0 11.3 ± 0.1 6.3	(3) (2) (1)
60-550A	Mafic granophyre, layer 41, unit 26 of Smith (1962), west limb of body	Quartz Whole rock	9.4 ± 0.1 10.7 ± 0.0	(3) (2)
60-632	Mafic granophyre, layer 42, unit 26 of Smith (1962), east limb of body	Whole rock Hornblende	11.5 7.0	(1) (1)
60-550E	Granophyre, grey, layer 42, unit 27 of Smith (1962), west limb of body	Quartz Whole rock	12.1 ± 0.1 12.3 ± 0.2	(2) (3)
LTS 1a	Granophyre, grey, layer 42, unit 27 of Smith (1962), east limb of body	Quartz Whole rock	11.8 11.7	(1) (1)
LTS 2-1	Granophyre, grey, layer 42, unit 27 of Smith (1962), east limb of body	Quartz Biotite Whole rock	11.7 6.6 ± 0.1 11.5	(1) (3) (1)
60-631	Quartzite, roof rock, overlies east limb of body, Hornby Bay Group	Whole rock	11.2	(1)
Kiglapait layered intrusion, Cape Kiglapait, Labrador. (See Morse, *1966)*				
Kig 23	Troctolite from basal Lower Zone, 0.7 km SW of Hare Pt. (ca. 10% crystallized)	Whole rock	6.4	(1)
Kig 49	Olivine gabbro from lower Upper Zone, 0.8 km SW of Spar Brook mouth (88%)	Plagioclase (An_{50})	7.0	(1)
Kig 54	Magnetite-rich gabbro, just N of mouth of Patsy Brook (94.5% crystallized)	Plagioclase (An_{40}) Clinopyroxene Ilmenite Magnetite	7.1 5.7 3.1 2.8	(1) (1) (1) (1)
Kig 61	Ferrosyenite, about 1 mi. upstream from mouth of Patsy Brook (99.2%)	Whole rock	6.2	(1)
Kig 64	Upper ferrosyenite, 0.7 km upstream from Kig 61 (99.9% crystallized)	Mesoperthite Whole rock	6.6 5.9	(1) (1)
Kig 65	Uppermost ferrosyenite, just NE of Kig 64 (> 99.9% crystallized)	Whole rock	5.9	(1)
Kig 68	Upper Border Zone gabbro, fine-grained, 0.2 km NE of Kig 65	Whole rock	5.9	(1)
Guadalupe complex, Western Sierra Nevada, California. (See Best, *1963)*				
Cf-23-3	Gabbro, lower zone of complex, N side of Rte. 140, 0.3 mi. E of roadjunction	Whole rock	5.9	(1)
Cf-22-3	Gabbro, N side of Rte. 140, 0.3 mi. W of junction with road to Hornitos	Whole rock	7.4	(1)
Cf-24-3	Mafic granodiorite from agmatite, E side of Rte. 140, 0.9 mi. W of Mt. Bullion Rd.	Whole rock	7.6	(1)

Table 2 (Continued)

Description and location of samples			$\delta\ O^{18} (^0/_{00})$	
Cf-25-3	Granophyre, grey, N side of Rte. 140, 0.5 mi. E of Mt. Bullion Road	Whole rock	9.6 ± 0.1	(3)
		Quartz	11.2 ± 0.1	(3)
Sudbury lopolith, Ontario, Canada				
Sudbury 10	Pegmatitic granophyre, roadcut 2 mi. E of Windy Lake, W of Onaping Falls	Alkali feldspar	8.4	(1)
		Hornblende	5.6	(1)
Sudbury 21	Norite, railroad cut at Hardy mine collar, 0.1 mi. from NW footwall contact	Labradorite	7.3	(1)
SDY-16	Micropegmatite, grey, railroad cut just NW of Onaping Falls	Whole rock	7.8	(1)
Duluth gabbro complex, Northeastern Minnesota				
Dul-1	Anorthosite mass in Duluth gabbro, 20 mi. NE of Duluth on shore Lake Superior	Labradorite	5.9	(1)
LTS-1	Red-rock granophyre, medium-grained, Enger Tower in city of Duluth	Quartz	8.0 ± 0.2	(2)
		Magnetite	1.0 ± 0.0	(3)
		Alkali feldspar	14.2	(1)
		Whole rock	10.6 ± 0.2	(2)
LTS.2	Red-rock granophyre, medium-grained, from Endion Sill (see ERNST, 1961)	Whole rock	10.8 ± 0.2	(3)
LTS-3	Mafic granodiorite, Duluth	Whole rock	6.9	(1)
Nain anorthosite complex, Labrador. (See WHEELER, *1960)*				
N 35	Anorthosite, 1.8 mi. S of Tammarvialuk Brook-Khingughutik Brook junction	Calcic andesine	7.4	(1)
N 37	Anorthosite, peak overlooking Khingughutik Brook, 0.3 mi. NE of N 35	Calcic andesine	7.6 ± 0.0	(2)
N 71	Anorthosite, S shore, Tessiarsuyungoakh Lake, 62°32′ W, 56°35′ N, W of Nain	Calcic andesine	7.6	(1)
N 1	Anorthosite, shore of Paul Island, just E of Nain	Calcic andesine	7.2	(1)
N 24	Anorthosite, E side of Port Manvers Run, 0.9 km SW of Hare Pt.	Calcic andesine	6.5	(1)
N 30	Anorthosite, white, granulated, on shoreline, 0.5 mi. S of Nain	Clacic andesine	7.0	(1)
N 12	Magnetite-hypersthene anorthosite pegmatite, 0.7 mi. SW of Nain	Calcic andesine	7.0	(1)
		Hypersthene	5.9	(1)
		Magnetite	3.4 ± 0.1	(2)
N 39	Quartz monzonite, 0.1 km SW of contact with paragneiss, 62°46′ W, 56°53′ N	Whole rock	8.9 ± 0.2	(2)
N 41	Manvers granite, f.g., dike in Kiglapait gabbro, 0.9 km SW of Kig 49	Whole rock	9.1	(1)
Egersund anorthosite complex, Southern Norway. (See MICHOT, *1961)*				
Eg 1	Anorthosite, Egersund-Ogna massif, just E of Egersund	Andesine	6.9	(1)
Eg 6a	Anorthosite, Regeland, about 18 km SE of Egersund, 75′ W of mangerite contact	Andesine	6.2	(1)

Table 2 (Continued)

Description and location of samples			$\delta\ O^{18}(^0/_{00})$	
Eg 5a	Anorthosite, Haland massif, on Highway 40, near Mong, 11 km SE of Egersund	Andesine	7.1	(1)
Eg 8b	Anorthosite, Tellnes massif, open pit at Tellnes Fe-Ti ore body	Andesine	5.8	(1)
Eg 38	Anorthosite, Helleren massif, collected just W of Barstad	Megacryst Matrix	6.3 6.7	(1) (1)
Eg 7	Norite pegmatite, on road W of Tellnes mine, about 27 km SE of Egersund	Plagioclase Hypersthene	6.5 5.7	(1) (1)
Eg 6b	Mangerite (syenite), Regeland, 50′ E of anorthosite contact, 125′ E of Eg 6a	Whole rock	6.0	(1)
Lac St. Jean anorthosite complex, Quebec				
LSJ-1	Anorthosite, 0.2 mi. S of junction of Rtes. 16 and 55 on E side of Rte 55	Plagioclase	6.9	(1)
LSJ-5	Anorthosite, 3 mi. N of Jonquiere, just S of dam on Saguenay River	Plagioclase	6.7	(1)
LSJ-6	Anorthosite, San Bruno quarry, E side of Lac St. Jean	Plagioclase	6.5 ± 0.0	(2)
LSJ-7	Anorthosite, Chutes des Passes quarry, 150 mi. N of Lac St. Jean	Plagioclase	6.7	(1)
P-15-G	Anorthosite, St. Gedeon quarry, E side of Lac St. Jean	Plagioclase	6.8	(1)
LSJ-9	Syenite, Lac des Comissaires, 20 mi. S of Lac St. Jean	K feldspar	7.4	(1)
Laramie anorthosite complex, Wyoming				
L-36	Anorthosite, 20 mi. NNE of Laramie, Wyoming	Calcic andesine	7.5	(1)
L-13	Anorthosite, 30 mi. N of Laramie, N part of massif, on Rte. 34, 2.5 mi. E of syenite body	Calcic andesine	7.5	(1)
L-407	Anorthosite, 17 mi. NE of Laramie, southern part of massif	Calcic andesine	7.0	(1)
L-4	Hypersthene syenite, N part of massif, on Rte. 34, 1.5 mi. W of anorthosite	K feldspar	7.6	(1)
L-23	Ilmenite-magnetite ore segregation, 18 mi. NE of Laramie, E part of massif	Ilmenite	4.4	(1)
L-3	Quartz monzonite, roadcut on Rte. 34, 1 mi. SW of L-4, 1 mi. E of older gneiss	K feldspar	9.1	(1)
San Gabriel Mountains anorthosite complex, Southern California				
SG 13	Anorthosite, west-central Acton 15′ Quad., 2 mi. W of Messenger Flats, N of Road	Andesine	6.8	(1)
SG 10	Syenite, west-central Acton 15′ Quad., 3.5 mi. W of Messenger Flats, N of road	K feldspar	7.2	(1)
SG 3	Apatite-ilmenite-magnetite ore segregation, 1.3 mi. E of Dagger Flat, Pacoima Canyon	Magnetite	3.7	(1)

Table 2 (Continued)

Description and location of samples			$\delta O^{18} (^0/_{00})$	
Skaergaard intrusion, East Greenland. (See WAGER *and* DEER, *1939, and* TAYLOR *and* EPSTEIN, *1963)*				
EG 4442	Gabbro, coarse-grained, tranquil zone of marginal border group, 30 m from outer contact on Ivnarmiut	Labradorite Clinopyroxene	5.9 ± 0.2 5.0 ± 0.2	(2) (2)
EG 4312 +	Ferrodiorite, 1860 m. level in layered series, lower UZb, NE of house area	Andesine Apatite Magnetite Augite	6.5 ± 0.2 4.7 2.6 ± 0.0 5.3	(2) (1) (2) (1)
EG 1721	Apophysis (10 in. thick) of intrusion, on coast, 10 m from S margin	Whole rock	2.3	(1)
EG 4508	Chilled marginal gabbro, 0.3 m. in from contact at S margin, E side Skaergaard Bay	Whole rock	0.4 ± 0.1	(2)
EG 5271	Olivine gabbro, c.g., Upper Border Group (α), 900 m from S margin, at foot of W ridge of Tinden	Plagioclase Clinopyroxene	3.9 ± 0.1 4.0	(2) (1)
EG 1835	Hybrid zone of granophyre and fused gneiss inclusion, W Border Group, Mellemo	Plagioclase Augite Granophyre	4.4 4.1 7.6	(1) (1) (1)
Mull igneous complex, Inner Hebrides, Scotland. (See BAILEY *et al., 1924)*				
Mull 13	Mugearite of ring-dike complex, head of Loch Scridain, 1.7 mi. W of Derrynaculen	Whole rock	−0.1 ± 0.3	(2)
Mull 16	Granophyre, S of Benmore Lodge, NW side of Loch Ba, IV, p. 20 of BAILEY et al.	Quartz Alkali feldspar	+3.3 ± 0.1 −0.8	(2) (1)
Mull 19	Granophyre, grey, quarry just S of Salen, fresh, unweathered	Quartz Whole rock	+2.6 ± 0.3 +3.4	(2) (1)
Mull 20	Spotted granophyre, cone sheet, 50 yds. NNW of Manse, Craignure Bay (II, p. 20, BAILEY *et al.*, 1924)	Whole rock	−0.7	(1)
Ardnamurchan igneous complex, Western Scotland. (See RICHEY *and* THOMAS, *1930)*				
Ard 8	Gabbro, c. gr., from Great Eucrite ring dike, 1 mi. NW of Achnaha on Allt Sanna	Labradorite Augite	+4.7 ± 0.1 +4.6	(3) (1)
Ard 9	Tonalite, near center of Centre 3, $^1/_2$ mi. E of Achnaha (II, p. 89, RICHEY and THOMAS)	Plagioclase	+3.3 ± 0.1	(2)
Ard 12	Granophyre, middle of composite cone sheet, 1840 ft. NW of Mingary Pier	Whole rock	+2.6 ± 0.0	(2)
Ard 13	Quartz dolerite, footwall margin, composite cone sheet, 1760′ NW of Mingary Pier	Whole rock	+1.9 ± 0.2	(2)
Ard 18	Big feldspar basalt, porphyritic margin of dike, along shore about 4 mi. E of Ben Hiant	Labradorite Groundmass	+6.3 ± 0.0 +6.7 ± 0.1	(3) (2)
Ard 20	Grigadale granophyre, 1.7 mi. E of Lighthouse (III, p. 84, RICHEY and THOMAS)	Quartz Magnetite Whole rock	−6.0 −8.4 −6.3	(1) (1) (1)

Table 2 (Continued)

Description and location of samples			$\delta\ O^{18}(^0/_{00})$	
Skye igneous complex, Inner Hebrides, Western Scotland. (See Harker, *1904 and* Wager *et al., 1965)*				
Skye 1	Granite, quarry SE of lodge, N end of Creag Strollamus, S of Scaplay Sound	Quartz	+1.0±0.2	(2)
		Oligoclase	−3.1	(1)
Skye 7	Epigranite, Maol na Gainmhich, NW shore Loch Ainort (Wager *et al.*, 1965,2)	Quartz	+3.5	(1)
		Alkali feldspar	−5.2±0.2	(2)
Skye 5	Basalt dike, 4′ thick, headland $2^1/_2$ mi. E of Sconser Lodge, N of Maol na Gainmhich	Basalt margin	−2.1±0.3	(2)
		Labradorite	+1.0±0.1	(2)
Skye 14	Granite, marscoite, N side of body (Traverse k-1, Wager *et al.*, 1965)	Quartz	+4.9	(1)
		Plagioclase	+0.1	(1)
Skye 13	Granophyre (felsite), Coastal traverse, Moll (k-1, Wager *et al.*, 1965)	Whole rock	−3.5	(1)
Skye 22	Beinn an Dubhaich granite (see Tuttle and Bowen, 1958, p. 140—142)	Quartz	+7.3±0.0	(2)
		Alkali feldspar	+4.9	(1)
		Magnetite	−0.1	(1)
Skye 24	Gabbro with cloudy plagioclase, N side of Loch Scavaig, Cuillins	Labradorite	−3.8±0.1	(2)
		Augite	+1.6±0.1	(2)
Skye 26	Granite from Red Hills, N of Torrin, E of Strath Mor	Quartz	+4.5±0.2	(2)
		Alkali feldspar	−0.7	(1)
Slieve Gullion igneous complex, NE Ireland. (See Reynolds, *1950)*				
SIGI-8	Porphyritic granophyre, inside ring structure, quarry at Lislea	Quartz	+7.1	(1)
SIGI-10	Granodiorite, block in granophyric dolerite, $^1/_8$ mi. SE of Adaroyle Station	Quartz	+8.0±0.1	(2)
Alta granodiorite stock, Central Wasatch Mountains, Utah. (See Wilson, *1961)*				
A 95	Nonporphyritic granodiorite, NW shore of Twin Lake reservoir, 500 ft. from contact	Quartz	9.7±0.3	(3)
		K feldspar	8.0±0.1	(3)
		Andesine	7.3±0.1	(3)
		Hornblende	5.5±0.2	(2)
		Biotite	4.3±0.0	(2)
A 69	Porphyritic granodiorite core of stock, E shore of Lake Mary, small quarry	Groundmass	7.0	(1)
A 58	Subporphyritic granodiorite outlier, 400′ W of lower end Mt. Millicent ski lift	Quartz	8.9±0.1	(3)
		Whole rock	8.0	(1)
A 198AP1	Aplite margin of 3 in. dike 500 ft. S of top of Mt. Tuscarora	Quartz	9.7	(1)
		Whole rock	8.4	(1)
A 198AP2	Pegmatite core of above dike, which cuts nonporphyritic granodiorite	Quartz	9.6	(1)
		K feldspar	7.5	(1)
New England granitic igneous rocks of Paleozoic Age				
M-DI-1	Rapakivi granite, E Penobscot Bay, Oak Pt., Deer Isle, Maine (Stewart, 1956)	K feldspar	8.1	(1)
M-9	Granite, med. gr., Mt. Desert Island, Maine, E side of Somes Sound, 2 mi. NNW of Northeast Harbor	K feldspar	7.8±0.1	(3)

Table 2 (Continued)

Description and location of samples			$\delta O^{18}(^0/_{00})$	
H-1	Binary granite, N side Rte. 26, bottom of grade E of Dixville Notch, New Hamp.	Quartz	10.6	(1)
		Muscovite	7.6 ± 0.1	(2)
		Oligoclase	8.1	(1)
		Biotite	4.6	(1)
H-3	Gneissic granite, 1.6 mi. N of Glen Ellis scenic area turnoff, W side Rte. 16, near Jackson, New Hampshire	Quartz	15.3	(1)
		Oligoclase	12.9	(1)
		Muscovite	12.6 ± 0.0	(2)
		Biotite	9.9	(1)
H-11	Binary granite, Rte. 103 near Lake Sunapee, 7.8 mi. NW of Bradford, New Hamp.	Quartz	12.3	(1)
		K feldspar	10.7	(1)
		Muscovite	9.6 ± 0.0	(2)
		Biotite	6.6	(1)
		Garnet	7.9	(1)
H 6b	Conway granite, miarolitic, coarse gr., S side Rte. 302, 3.2 mi. E of Bartlett, New Hampshire	Quartz	9.0 ± 0.1	(3)
		Alkali feldspar	7.5 ± 0.1	(3)
Asc 11	Biotite granite, roadcut 1.3 mi. ESE of summit of Mt. Ascutney, Vt., elev. 1600 ft.	Alkali feldspar	6.8 ± 0.0	(3)
NE 36	Barre "light" biotite granite, Rock of Ages quarry, Barre, Vermont	Whole rock	9.1	(1)
Ne 10	Quincy riebeckite granite, No. 1 Quarry, Quincy, Mass. (see TUTTLE and BOWEN, 1958)	Quartz	6.6 ± 0.1	(3)
		Alkali feldspar	5.9 ± 0.1	(3)

Sierra Nevada and Southern California batholiths, California. (Also see TAYLOR *and* EPSTEIN, *1962a)*

T-209	Cathedral Peak biotite granite, 1 mi. NE of Tenaya Lake, Yosemite National Park	K feldspar	8.3	(1)
Sierra 1	Arch Rock granite (granodiorite), Yosemite National Park, Sierra Nevada	Whole rock	8.9 ± 0.2	(2)
T 587	Jawbone Canyon granite porphyry, Jawbone Canyon, SE sierra Nevada	Quartz	9.6 ± 0.2	(2)
SCB 4	Rubidoux Mtn. leucogranite, just W of Riverside, Calif. (TAYLOR and EPSTEIN, 1962a)	Hornblende	6.2 ± 0.2	(2)
SCB 6	San Jose tonalite, Sierra San Pedro Martir, Baja Calif. (TAYLOR and EPSTEIN, 1962a)	Magnetite	2.0	(1)

Other granitic igneous rock samples from North America

On-4-2	Centre Lake granite alaskite, N side Rte. 109, 10.0 mi. S60W from Bancroft, Ont.	Whole rock	9.5	(1)
Que-7-2	Alaskite granite, 3.1 mi. N of Baie des Roches, 13.2 mi. S of Tadoussac, Quebec	Whole rock	9.3	(1)
Dome-1	Granite, Dome stock, Red Lake, Ontario (Dome "east" of SHIMA et al., 1963)	Whole rock	11.2	(1)
T-1074	Bokan granite (Na-rich, with uranothorite), Prince of Wales I., S. E. Alaska	Quartz	8.5 ± 0.0	(2)
		Whole rock	8.0	(1)
T-723	Pike's Peak granite, coarse gr., Florrisant, Colorado	K feldspar	8.3	(1)

Table 2 (Continued)

Description and location of samples			$\delta\, O^{18}(^0/_{00})$	
NE 75	Alaskitic granite, Missouri Red Granite Quarry, St. Francois Mtns., SE Missouri	K feldspar	8.6 ± 0.1	(2)
Wa-1-3	Tatoosh granodiorite, medium gr., 1.5 mi. E of Louise Lake, Stevens Canyon Road, Mt. Rainier National Park, Washington	Whole rock	6.3	(1)
ZL-9	Towne Mtn. biotite granite, Llano, Texas (ZARTMAN, 1964)	Quartz	9.3	(1)
G-616	Biotite granite, basement complex, Rio El Tambor, near Rosario, Guatemala	Whole rock	8.9 ± 0.3	(2)
Granitic igneous rock samples from Eurasia and Africa				
Oslo-19	Granite, ekerite, Oslo igneous complex, 2 mi. NW of Osterud, Norway	Quartz	8.5	(1)
		Alkali feldspar	7.4	(1)
T-682b	Orbicular granite, Kangasniemi, Finland (similar to Fig. 5b, p. 463, ESKOLA, 1938)	Orbicule core	9.0 ± 0.1	(2)
		Zone 2, Fig. 5b	9.0 ± 0.0	(2)
		Zone 3, Fig. 5b	9.7	(1)
		Matrix granite	9.4 ± 0.2	(2)
		Miarolitic quartz	10.3	(1)
RK-1	Rapakivi granite, Jokue, Iitti, SE Finland	Oligoclase rim	8.6	(1)
		K feldspar core	8.8	(1)
SR 5	Biotite granite, New Siberia quarry, 10 km SE of Sverdlovsk, U.S.S.R.	Whole rock	9.4	(1)
SR 12	Hornblende granodiorite, Bovak quarry, 20 km SE of Novosibirsk, U.S.S.R.	Whole rock	9.4	(1)
T-1036	Biotite quartz monzonite, Precambrian, Duwadami, Saudi Arabia, 70 km. W of Riyadh	Whole rock	9.5	(1)
Egypt 4	Biotite granite, from Obelisk quarries, Aswan, Egypt	Quartz	10.1	(1)
		Oligoclase	9.3	(1)
DG 1689	Biotite granite, oldest Precambrian, Halfway House, Transvaal, South Africa	K feldspar	6.8	(1)
Granitic igneous rocks from Oceanic Islands				
N. Z. 40	Biotite granite, Honeys Garden, Chalky Inlet, SW tip South Island, New Zealand	Quartz	10.5	(1)
		K feldspar	9.3	(1)
Bounty-1	Biotite granodiorite, Bounty Island, southwest Pacific Ocean (WASSERBURG *et al.*, 1964)	K feldspar	7.5	(1)
Mahe-1	Mesoperthite granite (alaskitic), Island of Mahé, Seychelles Archipelago (WASSERBURG *et al.*, 1964)	Quartz	4.1	(1)
		Alkali feldspar	2.6 ± 0.0	(2)
Miscellaneous plutonic and hypabyssal igneous rock samples				
T-826	Palisades diabase, 25 ft. above the base of sill, Weehawken, New Jersey	Whole rock	7.3 ± 0.2	(2)
SI-7-3	Anorthosite, Boulder Creek, Stillwater complex, Montana, highest anorthosite in the intrusion	Labradorite	6.8	(1)
BC-1-3 a	Norite, Purcell diabase sill, S side of road, 0.75 mi. W of Kitchener, B. C.	Whole rock	6.3 ± 0.3	(2)

Table 2 (Continued)

Description and location of samples			δ O^{18}(‰)	
BC-1-3b	Granophyre, gray, fine gr., same location as above, veins and dikes in norite	Whole rock	8.9 ± 0.2	(2)
PGP 6	Red-rock granophyre, Pigeon Pt., NE Minnesota	Quartz Alkali feldspar Whole rock	9.6 ± 0.1 12.8 11.5	(2) (1) (1)
HM 9	Diorite porphyry, Henry Mountains, Horseshoe Ridge laccolith (ENGEL, 1959)	Andesine Hornblende Groundmass	9.7 ± 0.2 7.1 ± 0.1 9.3 ± 0.0	(4) (3) (2)
HM 13	Syenite porphyry, Henry Mountains, Utah	K feldspar	8.8	(1)
K 103 A	Syenite, Kungnat Fjeld alkaline complex, south Greenland (UPTON, 1960)	K feldspar	6.5	(1)
T-100	Syenite, just W of Cuttingsville, Vermont	K feldspar	6.9	(1)
PC 2	Hornblende syenite, Port Coldwell complex, N of Lake Superior, Ontario, Canada	Alkali feldspar Hornblende	7.2 5.4 ± 0.2	(1) (2)
PC 4	Nepheline syenite, Port Coldwell complex, N of Lake Superior, Ontario, Canada	Nepheline Hornblende	6.7 4.6	(1) (1)
Mn-12-3	Syenite pegmatite from central portion of Shonkin Sag laccolith, Montana	K feldspar Biotite	8.1 5.5	(1) (1)
Mn-6-3	Leucite-augite syenite dike, Highwood Mountains, Montana	Leucite Augite	10.5 5.9	(1) (1)
Mn-11-3	Shonkinite from base of Shonkin Sag laccolith, Montana	Augite Groundmass	6.9 8.1	(1) (1)

Analytical error is average deviation from the mean. Numbers in parentheses indicate number of separate analyses.

Isotopic Relationships between Igneous Minerals and Rocks

O^{18}/O^{16} Ratios of Coexisting Minerals

The oxygen isotope fractionations among coexisting minerals in volcanic and plutonic igneous rocks are compared in Figs. 1, 2 and 3, utilizing data from the present work, TAYLOR and EPSTEIN (1962a, 1963), and GARLICK (1966). Note that the O^{18}/O^{16} fractionations, here reported as Δ or 1,000 ln α, are clearly smaller in rhyolites, dacites and basalts than in granites, tonalites and gabbros. Also observe that Δ-values are in general larger in metamorphic rocks than in plutonic igneous rocks. These effects must be principally a result of differing temperatures of formation in the various rock types, as it is well known both from theory and experiment that the equilibrium Δ-values for a given mineral pair decrease with increasing temperature. Rhyolitic melts that crystallize at the low values of P_{H_2O} characteristic of the volcanic environment may be 200—300°C hotter than equivalent H_2O-rich plutonic melts (TUTTLE and BOWEN, 1958).

The general sequence of O^{18}-enrichment among coexisting minerals is identical in volcanic and plutonic igneous rocks and in metamorphic rocks. That is, the order of decreasing O^{18} content in any rock is: quartz-feldspar-muscovite-biotite-magnetite and feldspar-pyroxene-hornblende-ilmenite-magnetite. Such consistencies in widely disparate rock types strongly indicate an approach to oxygen

Table 3. *Deuterium-hydrogen ratios and H_2O contents of volcanic glass samples*

Sample No.	Sample description	δ D(‰)		H_2O content (wt. per cent)
T-1027	Rhyolite perlite, Sonoma Co., California	-110 ± 6	(3)	2.83
Doe-15	Hydrated obsidian, Walcott tuff, Idaho	-161 ± 4	(2)	2.74
Doe-31	John Day hydrated obsidian, Oregon	-133 ± 2	(3)	5.65
Doe-39	Bamber Creek hydrated obsidian, Washington	-138	(1)	4.95
506-715	Dacite vitrophyre, Pilot Mtns., Nevada	-137 ± 4	(2)	2.40
506-752	Vitrophyre, ash-flow tuff, Pilot Mtns., Nevada	-139	(1)	2.32
T-111	Horse Mesa dam perlite, Arizona	-101 ± 1	(3)	2.79
Ariz-5	Superior perlite, Gila Co., Arizona	-114 ± 3	(2)	3.66
Ariz-1-6	Vitrophyre, ash-flow tuff, Greenlee Co., Arizona	-120 ± 1	(2)	2.84
Doe-30	Hydrated obsidian, Silver City, New Mexico	-119 ± 2	(2)	4.15
NM-4-4	Obsidian (non-hydrated), Jemez Creek, New Mexico	-89	(1)	0.29
Col-4-4	Vitrophyre, Treasure Mtn. tuff, Colorado	-146 ± 2	(5)	3.02
Doe-12	Vitrophyre, Miners Creek, near Creede, Colorado	-130 ± 6	(2)	3.98
Mn-22-3	Cretaceous vitrophyre, Wolf Creek, Montana	-91 ± 5	(5)	8.05
G-644	Pumiceous rhyolite, Obrajuelo Crater, Guatemala	-86	(1)	3.95
G-648	Rhyolite pumice, Obrajuelo Crater, Guatemala	-90	(1)	3.94
N-258	Hydrated obsidian in ignimbrite, NW Nicaragua	-102	(1)	2.78
T-249	Vitrophyre porphyry, Ponte Gardena, N of Bolzano, Italy	-133	(1)	4.58

Analytical error given is average deviation from the mean. Numbers in parentheses indicate number of separate analyes.

isotopic equilibrium in the assemblages (see Taylor and Epstein, 1962b), as also do the relationships illustrated in Figs. 1, 2 and 3. However, complete isotopic equilibrium was obviously not attained in all the rocks shown in the figures, because had it been we should expect that all points in each diagram would plot on a smooth curve (presumably straight lines through the origin, such as the ones shown in the figures).

In view of the lack of evidence for complete equilibrium, it is questionable whether the smaller Δ-values of volcanic rocks are due solely to their higher temperatures of crystallization. Other possibilities that must be considered are:

(1) The minerals in H_2O-rich plutonic igneous rocks may continue to undergo post-crystallization, deuteric, oxygen-isotope exchange, whereas the rapid quenching and loss of volatiles from extrusive igneous bodies effectively prevents such exchange among phenocrysts. Such exchange in plutonic environments has been demonstrated by Anderson (1968) in studies of plagioclase-magnetite fractionations in anorthosites and also in the present work in studies of pyroxene-magnetite fractionations in ultramafic rocks from S. E. Alaska. The latter is discussed more fully below.

(2) The phenocrysts in a volcanic rock presumably coexisted simultaneously with the same melt phase, whereas in plutonic rocks the minerals are commonly zoned and crystallized at different stages. If the isotopic composition of the melt changes during crystallization, the measured Δ-values for a mineral pair may be larger than the equilibrium Δ-value (Taylor and Epstein, 1962b). Such non-equilibrium

effects are large only in late-crystallizing phases and thus would be unimportant among coexisting phenocrysts in a volcanic rock.

(3) The chemical compositions of volcanic and plutonic minerals are not necessarily similar, and this can also affect the equilibrium Δ-values for any given mineral pair. For example, biotites and hornblendes from volcanic rocks are commonly much more deficient in H_2O (OH) than those from plutonic rocks (Friedman *et al.*, 1964). It has been postulated that OH-deficient mica or hornblende would be richer in O^{18}, relative to another coexisting equilibrium phase, than would normal mica or hornblende (Taylor and Epstein, 1962b; Taylor *et al.*, 1967). Therefore, smaller values of $\Delta_{\text{Quartz-Biotite}}$ or $\Delta_{\text{Feldspar-Biotite}}$ could in part be attributed to this effect.

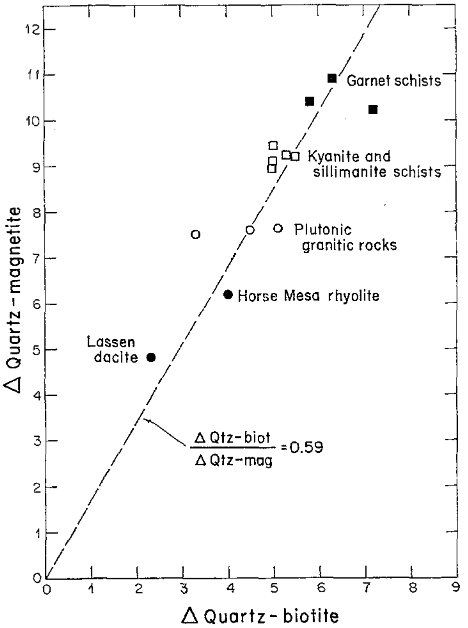

Fig. 1

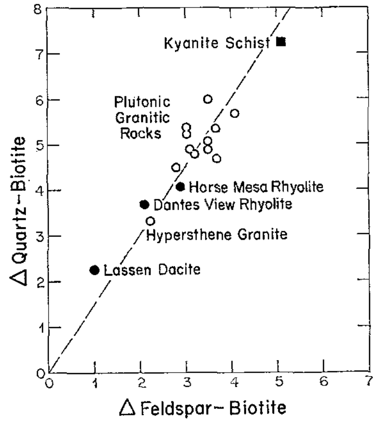

Fig. 2

Fig. 1. Relationship between Δ-values of quartz-magnetite and quartz-biotite for quartz-biotite-magnetite assemblages from igneous and metamorphic rocks. Data are from the present study, Taylor and Epstein (1962a) and Garlick and Epstein (1967)

Fig. 2. Relationship between Δ-values of quartz-biotite and feldspar-biotite for quartz-feldspar-biotite assemblages in igneous rocks and a kyanite-zone schist studied by Taylor *et al.* (1963)

(4) A special problem exists with respect to magnetite. If clear-cut magnetite phenocrysts can be separated from a volcanic rock, all of the above arguments apply equally well to this mineral as to the other phenocrysts. However, generally speaking, magnetite is separated by magnetic means; this means that magnetite from the groundmass and from reaction between phenocrysts (e.g. augite) and melt is incorporated in the phenocryst fraction. Pyroxene, hornblende, and biotite phenocrysts commonly react to form magnetite during the extrusion and vesiculation of a volcanic rock, and there is no assurance that such magnetite forms in equilibrium with other phenocrysts, particularly as it is so rapidly formed. The magnetite from the Horse Mesa rhyolite perlite (Fig. 1) was carefully separated and is thought to represent only original phenocryst material, but the

magnetite from the Lassen dacite is probably made up of both types. It may be significant that the plagioclase-magnetite fractionation is 5.1 per mil in the former and only 3.5 per mil in the latter.

Regardless of the complicating factors mentioned above, a good case can be made that many of the Δ-values shown in Figs. 1, 2 and 3 may reflect temperatures of final equilibration or "freezing in" of oxygen isotopes in the respective assemblages. However, these can be utilized as geothermometers only if the laboratory calibration curve for each particular mineral pair has been worked out. Quartz-water and magnetite-water curves have been obtained by O'Neil and Clayton (1964) and feldspar-water curves have been worked out by O'Neil and Taylor (1967). Slight revisions are presently being made in the quartz and magnetite curves, so only rough temperature estimates can be made for pairs which include these minerals. These are given in Table 4; it must be remembered that these are based on the assumption that the minerals crystallized in isotopic equilibrium with one another. The "temperatures" were derived, following Taylor (1968), by arbitrarily assuming that the plagioclase-magnetite fractionation at equilibrium is:

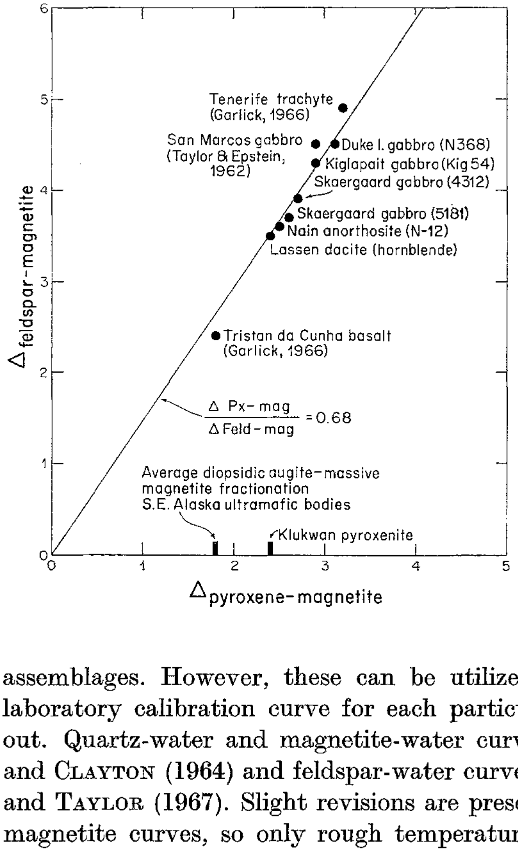

Fig. 3. Relationship between Δ-values of feldspar-magnetite and pyroxene-magnetite for feldspar-pyroxene-magnetite assemblages in igneous rocks. Data are from the present study, Taylor and Epstein (1962a, 1963) and Garlick (1966)

$$\Delta_{\text{Plagioclase (An}_{45}\text{)-Magnetite}} = 1.0 + 4.0\ (10^6 \cdot T^{-2})\ .$$

The justification for doing this is that such an equation gives "reasonable" temperatures of formation for a variety of feldspar-magnetite pairs in igneous and metamorphic rocks; it is useful only because it allows us to treat the isotopic data in a systematic fashion. The actual temperature-values listed in Table 4 are therefore not particular meaningful, but the relative temperatures have significance for those pairs that were formed in isotopic equilibrium. The above

Table 4. *Oxygen isotope "temperatures" of feldspar-magnetite, quartz-magnetite, pyroxene-magnetite and quartz-biotite pairs from various igneous rocks analyzed by* Taylor *and* Epstein *(1962a),* Garlick *(1966),* Anderson *(1968) and the present work*

Sample	Feldspar-magnetite	Quartz-magnetite	Pyroxene-magnetite	Quartz-biotite
1. Basalt, Tristan da Cunha	1,310°[a]	—	1,290°	—
2. Trachyte, Tenerife	810°	—	765°	—
3. Skaergaard gabbro 5181	940°	—	920°	—
4. Skaergaard gabbro 4312+	915°	—	890°	—
5. Kiglapait gabbro 54	850°	—	835°	—
6. Duke I. gabbro N-36-8	770°	—	790°	—
7. Nain anorthosite 12	965°	—	950°	—
8. San Marcos gabbro	770°	—	835°	—
9. Lac St. Jean anorthosite	1,050°[b]	—	—	—
10. S.E. Alaska magnetite pyroxenite	—	—	1,295°[c]	—
11. Klukwan magnetite pyroxenite	—	—	990°	—
12. Duke I. hornblende pyroxenite	—	—	530°	—
13. San Jose tonalite	650°	665°	—	670°
14. Bonsall tonalite	—	—	—	615°
15. Woodson Mt. granodiorite	610°	670°	—	595°
16. Rubidoux leucogranite	615°	665°	—	895°
17. Lassen dacite, LP-11	990°	1,040°	—	1,305°
18. Horse Mesa rhyolite, T-111	750°	805°	—	745°
19. Dante's View rhyolite, T-326	—	—	—	880°

[a] Temperatures are given in degrees Centigrade.

[b] Based on average O^{18}/O^{16} fractionation between anorthosite plagioclase and massive magnetite ore bodies (Anderson, 1968).

[c] Based on average O^{18}/O^{16} fractionation between pyroxenite diopsidic augite and massive magnetite ore bodies.

Samples 1 and 2 from Garlick (1966); Samples 3, 8, 13, 14, 15 and 16 from Taylor and Epstein (1962a); Sample 9 from Anderson (1968).

equation was also utilized by Taylor (1968), and it is closely compatible with other isotopic geothermometers discussed by Garlick and Epstein (1967), O'Neil and Clayton (1964), and Taylor (1967a). By combining the above equation with data of O'Neil and Taylor (1967, equation on p. 1425), together with the empirical observation that $\Delta_{\text{pyroxene-magnetite}} = 0.68\,\Delta_{\text{plagioclase-magnetite}}$ (Fig. 3) and that $\Delta_{\text{quartz-biotite}} = 0.59\ \Delta_{\text{quartz-magnetite}}$ (Fig. 1), we obtain tentative geothermometers that give the other temperatures listed in Table 4. It should be clearly understood that while the temperature-values listed in Table 4 are arbitrary, they are at least all compatible with one another and they provide a useful way of comparing oxygen isotope data on various mineral pairs.

The highest temperatures indicated in Table 4 are given by the Tristan da Cunha basalt (about 1300°C), and Anderson and Clayton (1966) also report a 2.5 per mil plagioclase-magnetite fractionation in a basalt that would be equivalent to a temperature of about 1280°C. All plutonic gabbros give lower temperatures 770—965°), with the lowest temperatures being given by two hornblende gabbros, the San Marcos and N-36-8. In terms of other geological estimates of temperatures of crystallization of basaltic magmas the above values are not totally unreasonable. However, the basalt "temperatures" seem a little high and the gabbro "temperatures" a little low, suggesting either non-equilibrium or that the gabbros have undergone post-crystallization oxygen isotope exchange. The latter is suggested by the fact that BUDDINGTON and LINDSLEY (1964) have shown that the Fe-Ti oxides of the Skaergaard gabbros have undergone recrystallization down to a temperature of about 870° C, in fair agreement with the estimates of 890—940° C in Table 4. Also, the values of 835—850° C for the Kiglapait gabbro no. 54 are similar to the 810—840° C obtained by MORSE (1966) on similar specimens, utilizing BUDDINGTON and LINDSLEY'S curves.

The highest plutonic "temperatures" are given by mineral pairs that do not actually coexist, namely the pairs plagioclase-magnetite from the Lac St. Jean anorthosite (ANDERSON, 1968) and diopsidic augite-magnetite from the southeastern Alaska ultramafic bodies. These represent fractionations obtained from average values of these minerals in essentially monomineralic bodies of anorthosite and pyroxenite, together with typical values of the associated massive magnetite ore bodies. As pointed out by ANDERSON (1968), if these can be considered to have originally equilibrated under magmatic conditions, then by dealing with essentially monomineralic rock masses we can eliminate practically all problems of isotopic re-equilibration during cooling. Note that the value of 1295° C for the primary crystallization of the Alaskan magnetite pyroxenites is similar to estimates made by PRESNALL (1966) from phase equilibria studies. TAYLOR and NOBLE (1968) have shown that there are textural and chemical reasons for believing that the magnetite in the Alaskan intrusions was deuterically recrystallized, and the very low "temperature" obtained for a hornblende-rich pyroxenite from Duke I. is consistent with such an interpretation. The Klukwan magnetite pyroxenite has preserved a relatively high temperature of 990° C, perhaps because it is magnetite-rich and because the lack of hornblende suggests it may have been relatively "dry" relative to the Duke I. sample.

The rhyolite and dacite samples give "temperatures" that are 100—300° C higher than their plutonic equivalents. This is probably due to post-crystallization exchange in the tonalites and granites, as the 600—670° C values shown by these rocks are somewhat low compared with other petrological estimates. The quartz-biotite "temperatures" are abnormally high in the Lassen dacite and the Rubidoux leucogranite, either because of lack of equilibrium or perhaps because the biotite is chemically abnormal (low H_2O content ?).

Relation between Whole-Rock and Mineral O^{18}/O^{16} Ratios

It is important in a study of O^{18}/O^{16} relationships of igneous rocks to determine the isotopic compositions of the silicate-melt phases from which these various rocks crystallized. The only way in which this can be done directly is to analyze the rapidly quenched, supercooled liquid (i.e. the silicate glass) itself. Many analyses of rhyolite glass samples have been obtained in the present study, but it will be shown below that of these, only the obsidians with low H_2O contents (i.e., non-hydrated samples) give O^{18}/O^{16} ratios characteristic of the magma from which they formed.

Knowledge of the δ-values of minerals from a plutonic igneous rock places certain limits on the O^{18}/O^{16} ratio of the magma from which the rock crystallized. If a rock body crystallized in place from a melt of its own chemical composition, then except for some loss of volatiles, the O^{18}/O^{16} ratio of the whole rock should be representative of the original magma. Even in magma chambers in which crystal settling has occurred, it may be possible to infer something about the O^{18}/O^{16} ratio of the melt phase (Taylor and Epstein, 1962b; 1963). Previous studies have shown that the O^{18}/O^{16} ratio of the feldspar in an igneous rock can provide a reasonably good estimate of the O^{18}/O^{16} ratio of the melt from which it crystallized. In gabbroic melts the plagioclase is thought to be about 0.3 to 0.5 per mil richer in O^{18} than the melt, and in granitic melts the feldspars appear to have been 0.2—0.4 per mil lower in O^{18} than the melt. In intermediate rocks such as tonalites, the plagioclase and melt presumably have similar O^{18}/O^{16} ratios. At equilibrium, quartz is always richer in O^{18} than coexisting silicate melt; the degree of O^{18}-enrichment depends upon the chemical composition of the melt (Taylor and Epstein, 1963).

In many volcanic rocks the relationships inferred above can be demonstrated by direct analysis. Some pertinent data are given in Figs. 4 and 8, where it is shown that plagioclase phenocrysts are lower in O^{18} than coexisting glassy matrix in obsidians, but higher in O^{18} than the groundmass of basalts. Other minerals could be used to estimate the O^{18}/O^{16} ratio of a given igneous melt, but feldspars are the most ubiquitous and closest to the O^{18}/O^{16} ratio of the melt itself. Of course, loss of volatiles will presumably cause a slight change in the O^{18}/O^{16} ratio of the groundmass of a volcanic rock. However, unless very large isotopic fractionations occur during boiling and vesiculation this change should be no more than 0.1—0.2 per mil.

Rhyolitic glasses with H_2O contents higher than 0.5—1.0 weight per cent (e.g. perlites and pitchstones) do not in general have O^{18}/O^{16} ratios similar to those of their coexisting feldspar phenocrysts. In some instances the glasses are 5 to 6 per mil richer in O^{18} than their quartz and feldspar, and it is obvious that these glasses have been drastically altered. The H_2O-rich rhyolitic glasses have whole-rock O^{18}/O^{16} ratios ranging from $\delta = +5.9$ to $+16.3$, whereas the "normal" rhyolites and obsidians range only from $\delta = +5.9$ to $+10.2$ (see Fig. 4). Hydrogen isotope studies by Friedman and Smith (1958) demonstrated that most of the H_2O in perlites was of meteoric origin, and it is reasonable to suppose that their peculiar O^{18}/O^{16} ratios are also a result of interaction with meteoric waters. Mineral-rock isotopic relationships in various "normal" types of volcanic rocks are illustrated in Fig. 4, and the O^{18}/O^{16} ratios of whole-rock samples of hydrated obsidian, perlite, vitrophyre and ash-flow tuff are compared with δ-values of their constituent minerals in Fig. 4 and 5.

The data of Figs. 4 and 5 indicate that the crystalline groundmass in many rhyolitic rocks (principally ash-flow-tuffs) need not be representative of the original silicate melt. This difference in O^{18} content probably arises during hydration of glass shards in the matrix and/or during the alterations that accompany devitrification of the matrix. It is apparent that the observed changes in O^{18} content that have taken place in perlites and welded tuffs cannot be a result of simple addition of meteoric water, however. If this were true the perlites would all be lower in O^{18} than the original melt, because meteoric waters are low in O^{18} (commonly about -3 to -7 per mil), but in fact most of the hydrated glass samples have abnormally high O^{18}/O^{16} ratios, commonly $+10$ to $+15$ per

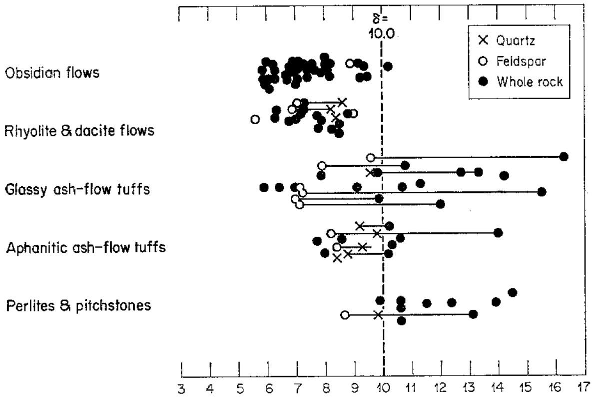

Fig. 4. Graph showing δ-values of quartz, feldspar and groundmass (glassy or aphanitic) in rhyolitic and dacitic volcanic rocks of various types

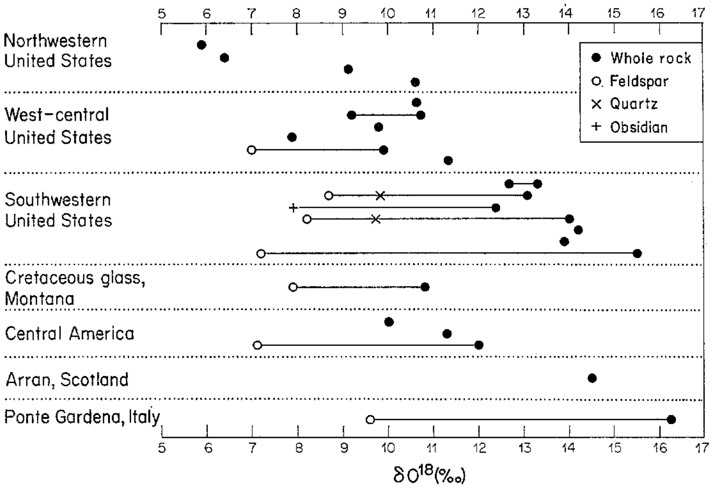

Fig. 5. Plot of δ-values of minerals and whole-rock samples from hydrated obsidians and perlites as a function of geographic position of the specimen-localities

mil. A simple material-balance calculation, for example, shows that the addition of 5 weight per cent H_2O (with $\delta = -7$) to a rhyolitic glass should lower the δ-value of the glass from 9 to about 7.5. This implies that the perlites and welded tuffs exchange with large amounts of water and take on δ-values that are at least 15—20 per mil higher than the water itself.

An interesting geographic relationship is exhibited by the perlite samples from the continental United States. As a group the samples from the northwestern U.S.A. are lower in O^{18} than those from the west-central states (Colorado, southern Nevada, central California); the samples from southern California, Arizona and New Mexico are all higher in O^{18} than any of the above (see Fig. 5). This distribution parallels the presentday distribution of O^{18}/O^{16} in meteoric water samples in the three regions, and the correlation suggests that one of the principal factors controlling the O^{18}/O^{16} ratios of hydrated volcanic glasses must be the local ground water or rainfall.

From the point of view of the present study, the above discussion indicates that unless a "normal" relationship is observed between phenocrysts and groundmass, one must discard the whole-rock O^{18}/O^{16} analysis from any survey of the oxygen isotopic composition of truly igneous rocks. Also, if a glassy rock contains more than 0.5 to 1.0 weight per cent H_2O, its O^{18}/O^{16} ratio is very likely not representative of the melt from which it formed. The original O^{18}/O^{16} ratios of the rock or glass must be inferred in some other manner; in subsequent discussions this is done by either (a) estimating the δ-value from the measured O^{18}/O^{16} ratios of quartz or feldspar phenocrysts, or (b) by analyzing unhydrated glass such as residual obsidian nodules embedded in a perlite matrix. An example of the latter is given by the Superior, Arizona perlite which contains obsidian nodules with $\delta = 7.9$, surrounded by perlitic matrix with $\delta = 12.4$. This rock has been enriched in O^{18} by 4.5 per mil during hydration and interaction with meteoric waters, but the unhydrated obsidian nodules have been unaffected.

The question arises as to what effect the exchange with meteoric waters has on the phenocrysts themselves. This cannot yet be answered with certainty, but the data of Figs. 4 and 5 indicate that the effects, if present, must be very minor. The phenocysts in rocks whose groundmass has been drastically altered do not seem to have abnormal δ-values, when compared with phenocrysts from unaltered rocks. This is exceptionally well-demonstrated by the Horse Mesa glassy rhyolite, in which coexisting magnetite, biotite, plagioclase and quartz all have perfectly "normal" δ-values even though the glass in which they are imbedded has been enriched in O^{18} by at least 4 to 5 per mil during hydration. The only rhyolite sample whose phenocrysts are "abnormal" in O^{18}/O^{16} ratio is the Copper Peak rhyolite porphyry. This rock is brick-red in color and contains K feldspar phenocrysts that are also brick-red; the unusually high O^{18}/O^{16} ratios of the whole rock and the K feldspar ($\delta = 12.3$ and 12.1, respectively) are probably a result of the same type of processes that produce peculiar O^{18}/O^{16} ratios in red-rock granophyres (see below, and TAYLOR, 1967b).

Relationship between D/H and O^{18}/O^{16} in Volcanic Glass

The D/H ratios of 12 samples of hydrated volcanic glass of Tertiary or Pleistocene age from the western United States are plotted as a function of their whole-rock O^{18}/O^{16} ratios in Fig. 6. Note that there is a rough correlation with geographic position, the more northerly samples being generally lower in D/H; this is similar to the effect pointed out above for O^{18}/O^{16}. A line can be drawn through the plotted points in Fig. 6 that is roughly parallel to the line of present-day meteoric waters; the equation for the latter is:

$$\delta D = 8\,\delta\,O^{18} + 10 \quad \text{(CRAIG, 1961a)}$$

The variation observed in Fig. 6 can only be explained if the H_2O in these hydrated obsidians is a result of interaction with ground or surface waters. Their H_2O contents vary from 2.32 to 5.65 weight per cent, all much higher than in true obsidians.

The relationship in Fig. 6 thus confirms the conclusion of FRIEDMAN and SMITH (1958) that meteoric water is involved in the formation of high-water-content perlitic glass. Their conclusion was based on D/H analyses alone. These authors noted that 9 obsidians from the western United States with H_2O contents of 0.09 to 0.29 weight per cent had very uniform D/H ratios, with $\delta D = -92$ to -127; This contrasts with the values of associated perlites, which have δD from -91 to -194, and show a pronounced geographic variation. The lightest sample, with $\delta D = -194$, is from Yellowstone Park, Wyoming, and is 33 per mil lower than the Idaho sample analyzed in the present study. FRIEDMAN and SMITH (1958) also were able to estimate that the fractionation between glass and coexisting meteoric water is about 35 per mil, with the water concentrating the heavy isotope.

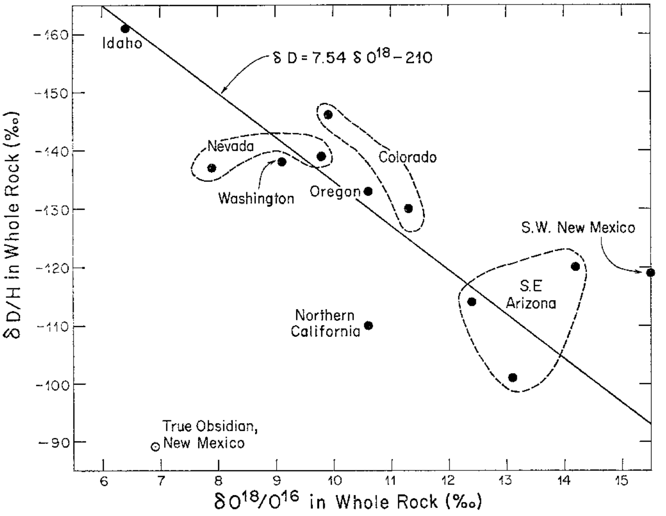

Fig. 6. Plot of D/H ratios vs. O^{18}/O^{16} ratios for perlites and hydrated obsidians from the western United States. Included are data on a true obsidian from the Jemez Mtns., New Mexico

Let us assume that the D/H fractionation factor for volcanic glass-water exchange is 0.965. Then a line can be drawn through the points plotted in Fig. 6 assuming that the O^{18}/O^{16} fractionation factor is constant also, and if this is done a good fit to the datapoints is obtained with an oxygen isotopic fractionation factor of 1.0245. The line in Fig. 6 is the result of the application of these constant fractionation factors to the meteoric water line; its equation is:

$$\delta D = 7.54\ \delta O^{18} - 210$$

The relationship of this hypothetical "hydrated volcanic glass" line to the meteoric water line is shown in Fig. 7.

There is no *a priori* reason why the fractionation factors should be constant during hydration of volcanic glass, but if hydration occurred over a relatively narrow temperature range (for example, normal atmospheric temperature) and if the hydration represents an approach to some kind of metastable isotopic equilibrium, then we might expect the fractionations to be roughly constant. However, the water contents are variable and in some cases phenocrysts constitute part of whole-rock samples analyzed for O^{18}; hence, we are not strictly comparing isotopic relationships on similar materials. Nonetheless, a fractionation factor of 1.0245 is not unreasonable for equilibrium between an aluminosilicate and water at low temperatures. If we extrapolate the alkali feldspar-water curve of O'Neil and Taylor (1967) down to low temperatures such a fractionation factor would correspond to a temperature of about 50° C. Also, it is interesting

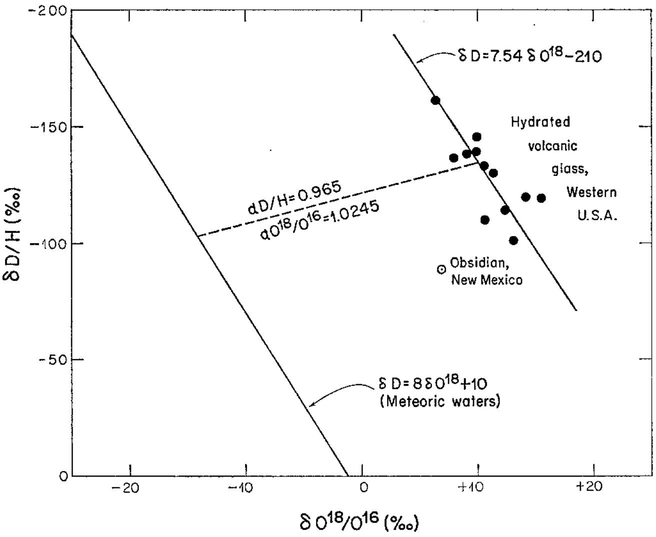

Fig. 7. Relationship between the data of Fig. 6 and the meteoric-water line of Craig (1961a). The line through the volcanic glass data-points was derived from the meteoric water line, assuming constant fractionation factors for volcanic glass-water exchange (0.965 for D/H and 1.0245 for O^{18}/O^{16})

to note that Savin and Epstein (1968) have obtained the following line for kaolinites that have exchanged oxygen and hydrogen with meteoric waters at atmospheric temperatures:

$$\delta D = 7.6\ \delta O^{18} - 220$$

The similarity of the "kaolinite" and "hydrated volcanic glass" equations is obvious.

Some of the volcanic glass samples analyzed in the present study lie well off the line in Fig. 6. One of these is a true obsidian from New Mexico (H_2O content = 0.29%), and this is to be expected. The others, however, are three samples from Central America, one from Italy, and a specimen of Cretaceous glass from Montana. The latter is particularly interesting (see Barksdale, 1951) because it is one of the oldest glasses that is known to have escaped devitrification; it also has by far the highest H_2O content of any of the samples analyzed. This Cretaceous glass has a much higher D/H ratio than the nearby Tertiary samples, which is perhaps to be expected in view of the probably different climatic conditions in the Cretaceous. The δD of -91 is compatible with a warmer, less continental climate in Montana during the Cretaceous. The δD-values of -86 to -102 for the Guatemala and Nicaragua samples are reasonable in terms of present-day meteoric waters in these regions, but the δO^{18}-values are 3 to 4 per mil lower than would be predicted on the basis of Fig. 6. The Nicaraguan sample actually plots within the spread of data-points of Fig. 6, and the Guatemalan samples are neither perlites nor H_2O-rich obsidians, but are pumiceous rhyolites. If hydration occurred at slightly higher temperatures than in the other samples, this might decrease the glass-H_2O O^{18}/O^{16} fractionation factor sufficiently to explain their O^{18}/O^{16} ratios.

In summary, it has been demonstrated beyond all doubt that volcanic glasses with high H_2O contents (>2 weight per cent) are generally a result of secondary hydration by interaction with ground waters or surface waters at low temperatures. The process of hydration involves exchange of oxygen in the silicate glass with large amounts of the water; the glass takes on an O^{18}/O^{16} ratio controlled by the composition of the local meteoric water, and roughly 25 per mil higher in O^{18} than the water. Water clearly must be able to move in and out of the glass with ease, presumably along the myriad cracks and imperfections present in perlitic glass. The mechanism may be analogous to that postulated for oxygen exchange between feldspars and aqueous solutions at higher temperatures (O'NEIL and TAYLOR, 1967).

Oxygen Isotope Variations in Igneous Rock-Types

Causes of O^{18}/O^{16} Variation in Igneous Rocks

Oxygen isotope variations in igneous rocks can be brought about by a variety of different mechanisms and it is useful to briefly discuss each of these before we turn to a detailed consideration of the data in Tables 1 and 2. One mechanism has already been discussed above, namely the interaction and absorption of meteoric H_2O by volcanic glass. Weathering processes can produce similar effects if significant amounts of clay minerals, for example, are present in the igneous rocks. We are going to ignore both of the above mechanisms in subsequent discussions because: (1) the original O^{18}/O^{16} ratio of the unhydrated glass or unaltered rock can generally be closely estimated from analyses of constituent phenocrysts of quartz and feldspar; and (2) all rocks analyzed are fresh and free from weathering products except as otherwise indicated, and even in cases of strong weathering the quartz is commonly completely unaffected, thus retaining its original δ-value.

Oxygen isotope variations can accompany magmatic differentiation. Changes in O^{18}/O^{16} ratio can come about through crystal settling or crystal armoring, if the crystals removed from interaction with the residual silicate melt are different in O^{18} content from the melt. Early crystallization of magnetite (a low-O^{18} mineral) should enrich the melt in O^{18}, whereas early crystallization of quartz will deplete the melt in O^{18}. The types of minerals crystallizing, their sequence of crystallization, their temperatures of formation, the degree to which they are effectively removed from interaction with the melt by armoring and/or settling, and so forth, all will affect the oxygen isotope changes that occur in the melt phase. The above factors vary with magma composition, P_{H_2O}, oxygen fugacity, silicate melt viscosity, etc., so the exact nature of the oxygen isotope changes that should occur during magmatic differentiation would be very difficult to predict even if we had full knowledge of the equilibrium fractionation factors for oxygen isotope exchange for all the important igneous minerals at magmatic temperatures. Therefore, we cannot *a priori* predict in any given case whether the melt phase should increase, decrease, or remain constant in O^{18} content during crystallization. However, we know enough at the present time to state that: (1) the O^{18} changes will be small, except in the late stages of crystallization; (2) other factors equal, the O^{18} changes will be significantly smaller during differentiation of melts under volcanic conditions or under low P_{H_2O} because the various mineral-melt fractionation factors are smaller at the higher temperatures of crystallization of such melts; (3) early formation of magnetite is commonly favored by relatively high oxygen fugacities, and this should tend to enrich the melt in O^{18}; (4) even if crystal settling or crystal armoring does not occur, the melt will in general change its O^{18} content during crystallization, because the isotopic fractionations between minerals and melt depend upon the chemical composition of the melt phase (which changes progressively during differentiation). For a greater discussion of these subjects, see the papers of TAYLOR and EPSTEIN (1962b, 1963) and GARLICK (1966).

The more SiO_2-rich the melt, the greater will be its O^{18} content at exchange equilibrium with a given mineral such as quartz. This is evidenced by the fact that plagioclase concentrates O^{18} relative to basaltic melts, but is depleted in O^{18} relative to granitic melts. In fact it is possible that granitic melts might roughly follow some such relationship as is given below, relative to coexisting H_2O:

$$\Delta_{\text{melt-H}_2\text{O}} \approx (2.6\,\gamma + 0.9)\,(10^6 T^{-2}) + 2.8\,\gamma - 5.5$$

where

$$\gamma = \text{Si}/(\text{Si} + \text{Al})$$

The above equation was derived for crystalline aluminosilicates (O'NEIL and TAYLOR, 1967), and although there is as yet no real justification for applying it to aluminosilicate melts, there are indications that the isotopic fractionation between liquid silicates and solids of the same chemical composition are very small at magmatic temperatures (e.g. see GARLICK, 1966). Therefore, if equilibrium is continuously maintained during crystallization, there ought to be a progressive increase in O^{18} content of the melt phase as the SiO_2 content of the melt increases.

The assimilation of country rocks into a magma chamber can affect the O^{18}/O^{16} ratio of the magma, because many sedimentary and metasedimentary rocks have higher δ-values than the common igneous rocks. At one extreme, limestones and cherts may be 20 to 25 per mil richer in O^{18} than the igneous rocks, but the common sandstones, shales and arkoses are only enriched by about 5 to 10 per mil over basalts and gabbros. To a first approximation, the oxygen isotope effects of assimilation are determined simply by the amount of material added to the magma and its average O^{18}/O^{16} ratio. Thus, if a magma with $\delta = 7.0$ assimilates 10 per cent shale with $\delta = 14.0$, its O^{18}/O^{16} ratio is increased to $\delta = 7.7$. Most metasedimentary rocks and essentially all meta-igneous rocks, however, have δ-values even lower than 14.0. Hence, to produce an increase of 2 to 3 per mil in any magma probably requires assimilation of an amount of country rock equal to about 1/2 that of the original magma, which seems prohibitively high.

Assimilation effects also involve complications. Even though blocks of country rock may be only partially assimilated into a magma, oxygen exchange could occur (perhaps through an aqueous phase) between the incorporated block and the melt. This would increase the O^{18}/O^{16} ratio by larger amounts than would be predicted on the basis of the amount of actual assimilation alone. Also, dehydration and/or decarbonation generally will accompany assimilation and these will cause isotopic changes in the magma. The aqueous phase ought to be isotopically almost identical to the silicate melt because of the small fractionation and because isotopic exchange is rapid at magmatic temperatures (see O'NEIL and TAYLOR, 1967); however, diffusion or distillation processes favor the light isotope, and loss of H_2O from the magma might therefore result in a slight enrichment of the melt in O^{18}. Decarbonation very likely produces the opposite effect, as at equilibrium CO_2 is at least 5 per mil higher in O^{18} than coexisting H_2O at magmatic temperatures (UREY, 1947). On the one hand, assimilation of O^{18}-rich limestone can produce a marked increase in O^{18} content of a magma, but on the other hand loss of CO_2 tends to produce a decrease. There is no *a priori* way to predict which effect will prevail in a given case, but there is some empirical evidence that contact metamorphism and partial assimilation of carbonate rocks produces a net lowering of O^{18}/O^{16} ratio (TAYLOR, 1968; SHIEH and TAYLOR, 1968).

Separation of an aqueous vapor phase either through degassing of assimilated country rock or because of "second boiling" can produce appreciable isotopic effects through exchange with the melt or with previously crystallized material in another part of the magma chamber. This is particularly true if the exchange occurs at temperatures significantly lower than the temperature at which the aqueous phase was originally formed; the result will be a higher O^{18}/O^{16} ratio in the exchanged melt or rock, because the feldspar-H_2O and melt-H_2O fractionations are increasingly positive at successively lower temperatures below about 550°C (O'NEIL and TAYLOR, 1967). Exchange appears to occur readily with feldspars in such circumstances (and probably with silicate melts, as well), whereas quartz and certain other minerals are much more resistant to alteration or recrystallization (TAYLOR, 1967b; GARLICK and EPSTEIN, 1967).

A final mechanism of importance is the interaction between the magma and H_2O from an extraneous source. For example, in shallow intrusions that are emplaced into rocks charged with ground water, we can expect that there will be exchange or even large-scale influx of H_2O into the magma. This can involve a large reduction in the δ-value of the magma, particularly at its margins, because meteoric waters are much lower in O^{18} than the common igneous rocks. TAYLOR and EPSTEIN (1963) demonstrated that the marginal gabbro of the Skaergaard intrusion had exchanged with extraneous water and that the plagioclase in the exchanged rock was affected to a greater extent than the coexisting pyroxene. If meteoric water is involved, one can expect very large isotopic changes, and these will be larger in magmas emplaced at high latitudes or high altitudes. Other waters (e.g. metamorphic waters) could also produce effects at the margins of magma chambers, and these would probably result in an increase in O^{18}/O^{16} ratio.

In summary, O^{18}-enrichment in magmas can be brought about by equilibrium magmatic differentiation, by assimilation of sedimentary or metasedimentary rocks, by exchange with adjacent metamorphic waters, or by late-stage, low-temperature exchange with deuteric aqueous fluids. Depletion in O^{18} can be brought about by assimilation and massive decarbonation of limestones, by exchange and interaction with meteoric waters at high temperatures, or possibly by loss of H_2O during low-pressure vesiculation in a volcanic environment, because at temperatures above 800° C the H_2O will in general be richer in O^{18} than coexisting feldspar or melt. Any primary CO_2 lost by the magma also should produce a depletion in O^{18} in the residual melt. If non-equilibrium crystallization occurs as a result of armoring or crystal settling, the melt can become either depleted or enriched in O^{18}, but the effects will be small except for the very late differentiates.

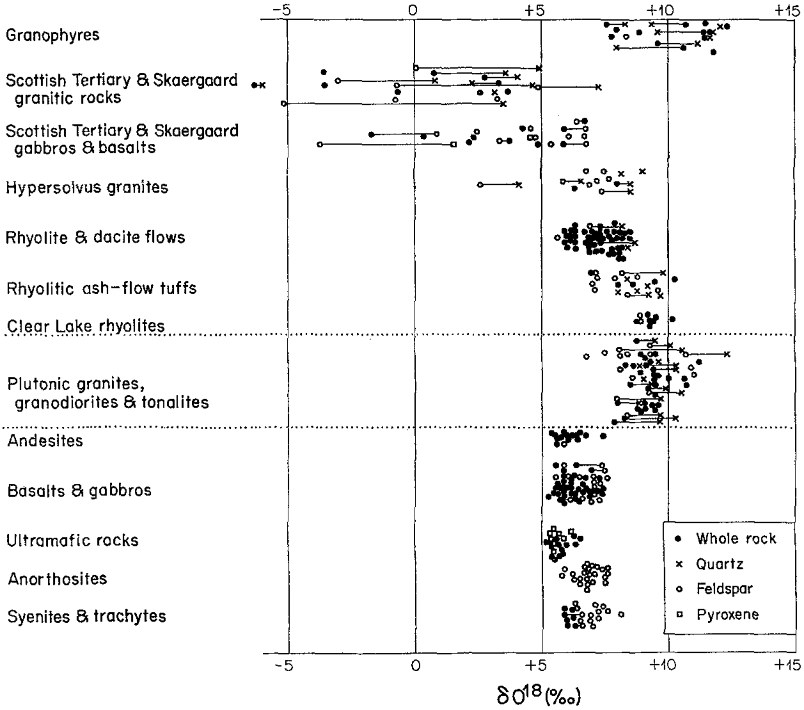

Fig. 8. Plot of δO^{18}-values for quartz, feldspar, pyroxene and whole-rock for a variety of igneous rocks throughout the world. Data are from the present study, Taylor and Epstein (1962a, 1963), Reuter *et al.* (1965) and Garlick (1966)

Ultramafic Rocks

Ultramafic igneous rocks have been analyzed for O^{18} content by Taylor and Epstein (1962a), Reuter *et al.* (1965) and in the present work (see Fig. 8). The ultramafic rocks exhibit a very narrow range in O^{18}/O^{16}, from $\delta = 5.4$ to 6.6 per mil for olivine-pyroxene rock types; one hornblendite sample has $\delta = 7.0$. Of

16 peridotites, pyroxenites and dunites analyzed, 13 lie in the range $\delta = 5.4$ to 5.8; the other 3 have $\delta = 6.0$, 6.4 and 6.6. One strongly serpentinized dunite has $\delta = 2.6$, suggesting a lowering of O^{18} during serpentinization by about 3 per mil; this probably implies that serpentinization in this instance resulted from alteration of the dunite by meteoric waters.

Pyroxene δ-values in ultramafic rocks range from 5.4 to 6.4 per mil (8 samples). These may be compared with values of 5.4 to 6.3 per mil for 9 pyroxenes from chondritic meteorites; the latter show whole-rock δ-values of 4.8 to 6.0 (29 samples), whereas pallasite olivines vary from 3.4 to 4.0 per mil (3 samples) and 3 hypersthene achondrites vary from 3.7 to 4.3 (TAYLOR *et al.*, 1965; REUTER *et al.*, 1965). Thus terrestrial peridotites are practically identical to chondrites in O^{18}/O^{16}, but they are 1 to 2 per mil higher than the achondrite and pallasite ultramafic meteorites.

Basalts and Gabbros

The O^{18}/O^{16} ratios of all analyzed whole-rock basalts (32 samples) and diabases and gabbros (15 samples) lie in the range $\delta = 5.5$ to 7.4, except for the marginal gabbros and fayalite ferrogabbros of the Skaergaard intrusion, the upper gabbroic differentiates of the Muskox intrusion, and some diabases and gabbros from the Scottish Tertiary igneous province (Ardnamurchan and Skye). These exceptions are discussed individually in a subsequent section. Basalt plagioclase (7 samples), gabbro plagioclase (17 samples) and anorthosite plagioclase (23 samples) all lie in the range $\delta = 5.6$ to 7.6, again excepting those localities mentioned above. To a first approximation, therefore, essentially all mafic igneous rocks lie in a very narrow range of O^{18} content, and basalts, gabbros and anorthosites are isotopically almost indistinguishable from one another (Fig. 8).

However, the mean δ-value of basaltic plagioclase is $+6.2$, that of gabbro plagioclase is $+7.1$ and of anorthosite plagioclase is $+6.8$. These differences may be significant and they probably are in part a result of the larger fractionations in plutonic gabbros as compared with basalts. Also, post-crystallization exchange very likely occurs between the plagioclase and its coexisting minerals during cooling of a gabbro, but is negligible between phenocrysts and groundmass in a basalt. If we eliminate 4 unusually O^{18}-rich basalts dredged from the Mid-Atlantic Ridge, the mean δ-value of 28 whole-rock basalts is $+6.1$, whereas the mean for the whole-rock gabbros is $+6.7$. It thus appears that the gabbros are on the average about 0.5 per mil higher in O^{18} than the basalts, but this is probably a result of biased geographic sampling. None of the gabbros are from oceanic areas, but 18 of the basalts are from oceanic islands or have been dredged from the ocean floor. In addition, the continental basalts are on the average 0.3 per mil higher in O^{18} than the oceanic basalts (if we exclude the 4 Mid-Atlantic Ridge samples). Thus there is a suggestion that mafic igneous rocks from continental regions are 0.3 to 0.5 per mil richer in O^{18} than equivalent samples from oceanic areas. Such differences might arise through contamination of the continental basalts with the O^{18}-rich granitic or metasedimentary portions of the continental crust.

No differences in O^{18} content are noticeable between alkali-olivine basalts and tholeiitic basalts. In fact, the oceanic tholeiites, which are chemically rather uniform (ENGEL and ENGEL, 1964a; 1964b) span the entire range of δ-values from 5.5 to 7.3, but this large range is a result of the high O^{18} contents of 4 aforementioned basalts dredged from the Mid-Atlantic Ridge. These 4 samples are probably abnormally high in O^{18} because of partial alteration and exchange with sea water; note in Table 1 that their H_2O contents (especially H_2O-) are much larger than the low-O^{18} tholeiites from the Pacific Ocean. All 4 Pacific Ocean tholeiites and 2 Atlantic tholeiites have δ-values in the range 5.5 to 5.9, and 7 alkali-olivine basalts from Canary Is., Gough I., Flores I. and Easter I. lie between 5.6 and 6.2 per mil (see Table 1 and GARLICK, 1966). The mean of these 13 analyses, +5.9, is probably the best available estimate of the average δO^{18} of primary, uncontaminated basaltic magma. This value is only slightly higher than that of the average ultramafic rock, and is thus perfectly compatible with the hypothesis that ultramafic rocks and basaltic magmas are derived from a common source (the upper mantle?) where they were in approximate isotopic equilibrium with each other at very high temperatures (> 1200° C).

ENGEL and ENGEL (1964b) have pointed out some chemical similarities between basaltic achondrite meteorites and oceanic tholeiites. Both rock types have very low K contents, for example. However, this similarity does not hold true for their oxygen isotopic compositions, as basaltic achondrites have very uniform δ-values in the range +4.2 to +4.5 per mil (TAYLOR *et al.*, 1965). These achondritic meteorites are thus considerably lower in O^{18} than the terrestrial basalts.

Andesites, Trachytes and Syenites

Oxygen isotope analyses of feldspars and whole-rock samples of andesites, trachytes and syenites are plotted in Fig. 8. These rock types are essentially indistinguishable from basalts, as 15 continental and oceanic andesites show a range from $\delta = 5.4$ to 7.5, with a mean of 6.2. However, 13 of these lie between 5.4 and 6.8; two samples from California and Nevada have $\delta = 7.5$ and 7.1, respectively, and 4 oceanic samples from Gough, Flores and the Hawaiian Is. range from 5.6 to 6.1. Three oceanic trachytes have $\delta = 6.0$, 6.3 and 6.3, and alkali feldspars from 2 others have $\delta = 6.3$ and 6.4 (GARLICK, 1966).

Four whole-rock syenites have $\delta = 5.9$ to 6.2, and K feldspar from 10 others ranges from 6.5 to 7.6. If we make the reasonable assumption that the feldspar-whole rock fractionation in syenites is about 0.6 per mil, the average whole rock δ-value of 14 syenites becomes +6.3. It should be noted that these tabulations do not include nepheline syenites, and also they ignore a calcite syenite from Colorado (TAYLOR *et al.*, 1967) and the syenite pegmatite from the central part of the Shonkin Sag laccolith, both of which have K feldspar with $\delta = 8.1$.

The strong coincidence that basalts, andesites, trachytes and syenites each show a narrow range of O^{18}/O^{16} with average δ-values of about 5.9 to 6.3 per mil indicates that these rock types are all related in some manner. It is very reasonable to assume that the andesites, trachytes and syenites are derived from parent basaltic magma by some process of magmatic differentiation, as proposed by BOWEN (1928). Except for those isolated samples with unusually high O^{18}/O^{16} ratios, it is unlikely that any significant assimilation of sedimentary country rocks could have been involved in the differentiation process.

Granitic and Rhyolitic Igneous Rocks

All granitic and rhyolitic igneous rock types are treated together in this section. These include tonalites (quartz diorites), granodiorites, quartz monzonites, calc-alkaline granites, alkali granites and granitic pegmatites among the plutonic varieties, and dacites, rhyodacites, quartz latites, rhyolites, obsidians, welded tuffs (ash-flow tuffs), vitrophyres and perlites among the volcanic types. Granophyres and micropegmatites from layered gabbroic intrusions are also included. The general range of SiO_2 contents represented by these rocks is 62 to 75 weight per cent, and all the rock types contain appreciable amounts of normative and/or modal quartz. In succeeding paragraphs the term "granitic" is used in its broad sense, and makes reference to any or all of the above-listed rock types.

In direct contrast to the narrow range of O^{18} exhibited by ultramafic rocks, basalts, gabbros, andesites and syenites is the very large variation shown by the granitic igneous rock types. Examples are known whose whole-rock δ-values range from -6.3 to $+17.0$. Nonetheless, there are distinctive groupings of rock types within the above limits, and the simplest way to discern these relationships is to subdivide the whole-rock δ-values into separate groupings, as follows:

Highest O^{18} (HH Group)	$\delta \geqq 10.3$
High O^{18} (H Group)	$\delta = 7.8$ to 10.2
Intermediate O^{18} (I Group)	$\delta = 7.0$ to 7.7
Low O^{18} (L Group)	$\delta = 5.5$ to 6.9
Lowest O^{18} (LL Group)	$\delta \leqq 5.4$

The O^{18}/O^{16} boundaries of the above groups are somewhat arbitrary, but were chosen using these criteria: (1) Almost all plutonic granites, particularly the large batholithic masses, have δ-values in the H-Group; (2) Almost all basalts and gabbros have δ-values in the L-Group range, and in view of the uniformity of O^{18} in mafic igneous rocks it is plausible that other igneous rock types (such as the andesites and syenites discussed previously) which commonly have δ-values in the L-Group range may be genetically related to basaltic magmas; (3) Granitic igneous rocks with δ-values higher than 10.2 or lower than 5.5 are rare and generally include only late-stage granophyric differentiates, granitic pegmatites, or gneissic (metamorphic ?) granites from Precambrian basement complexes.

In Fig. 9 histograms are presented showing the relative abundances of the various granitic rock types in each oxygen isotope grouping. Note that granophyres cover a wide range of O^{18} and are not particularly concentrated in any single group. The lowest δ-values shown by granitic rocks are given by the granophyres from the Skaergaard intrusion and from the Scottish Tertiary igneous province, and the highest value is obtained on a pegmatite from Winchester, California ($+17.0$). The rhyolitic ash-flow tuffs tend to be concentrated in the H-Group, along with most plutonic granites. Obsidian flows, however, are strongly concentrated in the L- and I-Groups.

Table 5 is a chart which lists the "granitic" rocks analyzed in this study according to their positions within the O^{18}-groupings. Also included are a few granitic pegmatites analyzed by Taylor and Epstein (1968).

What are some of the significant features shown by Figs. 8 and 9 and Table 5 ? First, note that plutonic granites are almost completely absent from the L-Group, their only 4 representatives being the Tatoosh granodiorite from Washington, the Quincy granite from Massachusetts, the Ascutney granite from Vermont and the Beinn an Dubhaich granite from the Isle of Skye. The Tatoosh granodiorite has clear-cut volcanic affinities in that it is an unroofed pluton related to extrusive rocks of the Mt. Rainier volcanic field (FISKE *et al.*, 1963), and the other 3 rocks are all granites of the hypersolvus type (TUTTLE and BOWEN, 1958). All 4 of these L-Group granites are from relatively small-sized intrusions, and it is interesting that most of the I-Group plutonic granites shown in Table 5 also are hypersolvus granites or are from minor intrusive bodies.

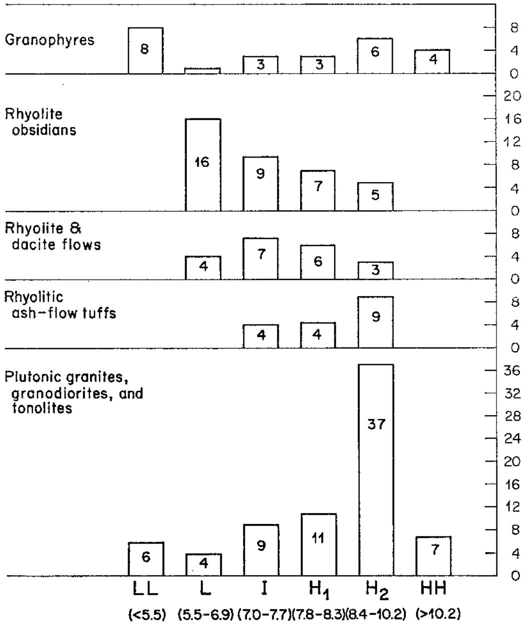

Fig. 9. Histograms showing the relative abundances of various granitic igneous rock types in the LL, L, I, H_1, H_2 and HH oxygen isotope groups, as defined in the text and in Table 5

On the other hand, by far the most abundant rock types in the H-Group are samples from the great plutonic bodies that make up batholiths in Precambrian basement complexes or Paleozoic and Mesozoic orogenic belts. These rock types generally contain two feldspars (a plagioclase and an alkali feldspar) and crystallized at relatively high P_{H_2O} under deep-seated conditions. The batholithic granites are particularly concentrated in the high-O^{18} portion of the H-Group (the H_2 part). Many ash-flow tuffs also fall in the H_2-Subgroup, but obsidians and rhyolite flows with such δ-values are very rare, the only examples being rhyolites from the Clear Lake area, California and dacites from Medicine Lake Highland. It is very clear from these data that rhyolite obsidians are *not* simply "normal" plutonic granitic magmas that have somehow reached the surface; most calc-alkaline granitic rocks must therefore have formed in a different manner from rhyolite obsidians.

For plutonic rock types the simple picture of generally increasing O^{18}/O^{16} ratio in the sequence ultramafic rock-gabbro-tonalite-granodiorite, granite, demonstrated by TAYLOR and EPSTEIN (1962a, Fig. 2), probably still should be considered valid even though we now know of numerous exceptions to the rule. The conclusions of TAYLOR and EPSTEIN (1962a, p. 469—470) as to the bearing of oxygen isotope studies on the origin of plutonic granodiorites, quartz monzonites and granites therefore still apply. We must, however, eliminate hypersolvus granites and granophyres from this grouping, and we should emphasize two further points: (1) If the plutonic granites form by differentiation from gabbroic parent magmas, this must occur at significantly lower temperatures (i.e. higher P_{H_2O}) than those at which hypersolvus granites and obsidians are formed; if the temperatures were 200—300° C lower we might expect that oxygen isotopic fractionation factors between crystals and melt would be sufficiently large to produce the higher O^{18}/O^{16} ratios of the plutonic granites. (2) The possibility of hybridization or mixing of magmas must be considered; the isotope data could be explained if granitic magmas that were formed by deep-seated fractional melting of O^{18}-rich metasediments could undergo varying degrees of mixing or exchange with gabbroic and andesitic rocks or magmas. Thus, while the origin of the plutonic granites must remain ambiguous at the present state of our knowledge of oxygen isotope geochemistry, it is essentially impossible for the L-Group hypersolvus granites to have formed by melting of metasedimentary rocks.

A few plutonic granites fall in the LL-Group, but all are granophyres or shallow granites from the Scottish Hebrides, the Skaergaard intrusion and the Seychelles Islands. These are so markedly different in O^{18} content from all other granitic igneous rocks that they demand a unique explanation. The only obvious manner in which such low δ-values could arise is by mixing or exchange between the magmas and low-O^{18} meteoric ground waters. This demands emplacement and crystallization under relatively shallow conditions, because the intrusion must penetrate into the ground water zone; this requirement is satisfied by the above occurrences. Many of these rock types also exhibit peculiar quartz-feldspar O^{18}/O^{16} fractionations that indicate non-equilibrium; commonly the feldspars appear to have exchanged with oxygen-bearing fluids (aqueous ?) to a greater degree or down to lower temperatures than has the coexisting quartz. These phenomena are described in more detail below when we discuss the O^{18}/O^{16} variations in all the igneous rocks of the Skaergaard intrusion and the Tertiary igneous province of Scotland. Practically the only other conceivable mechanisms that could produce such marked depletion of O^{18} are (1) boiling off of CO_2 from the magmas, either by assimilation of carbonate rocks or because of an abnormally high primary content of CO_2; or (2) these granitic rocks might represent a very late stage of fractional crystallization in a magma body in which the crystals settling out have an average O^{18}/O^{16} ratio higher than the coexisting liquid, as originally proposed by TAYLOR and EPSTEIN (1963) for the late-stage granophyres of the Skaergaard intrusion. There is no evidence that mechanism (1) has occurred, and in fact one granite from the Scottish Hebrides that has been completely emplaced into carbonate country rock, the Beinn an Dubhaich granite, is one of the few in that region which is not strongly depleted in O^{18}. Also, mechanism (2) is not plausible, because at least in the case of the Scottish Hebrides several less highly differentiated rocks than the granites and granophyres also show marked O^{18}-depletion, including basalts, gabbros, oligoclase andesites and tonalites.

Table 5. *Chart showing the distribution of various granitic igneous rock types, by sample locality, in* and EPSTEIN *(1962a; 1963), except as indicated in the table. The data for the Adirondack granites*

LL Group *$\delta \leqq 5.4$*	L Group *$5.5 \leqq \delta \leqq 6.9$*	I Group *$7.0 \leqq \delta \leqq 7.7$*
Granophyres		
Skaergaard (3) Mull (3) Ardnamurchan (2)	Slieve Gullion, Ireland	Guadalupe complex (mafic) Enger Tower, Duluth, Minn. Bushveld complex
Rhyolite obsidians		
—	Medicine Lake, older (5) Newberry Crater, Oregon (3) Three Sisters, Oregon (2) Salton Sea, Calif. Jemez Mtns., New Mexico (2) Easter Island (2) Iceland [c]	Medicine Lake, younger (5) Jemez. Mtns., New Mexico Yellowstone Park, Wyoming (2) Ixtepeque, Guatemala
Rhyolite and dacite flows		
—	Newberry Crater (2) Mt. Pelee, Martinique Owyhee dam, Oregon	Lassen Park dacites (3) Black River, Wisconsin Deccan, India (2) [c] Owyhee dam, Oregon
Rhyolitic ash flow tuffs		
—	—	Silver City, New Mexico Treasure Mtn. tuff, Colorado N.W. Nicaragua Thirsty Canyon tuff, Nevada

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[a] GARLICK and EPSTEIN, 1967; [b] SILVERMAN, 1951; [c] GARLICK, 1966; [d] CLAYTON and EP-

The only granitic rocks that lie in the HH-Group are some late-state granophyres from the Muskox intrusion and a number of deep-seated plutonic granites, most of which are Precambrian, but two of which are muscovite granites from New Hampshire. Of course, many pegmatites also have isotopic compositions in this range, and some other granophyres have whole-rock δ-values above 10.3, but the feldspars in these rocks have all undergone isotopic exchange, and the O^{18}/O^{16} ratios of the granophyric melts are estimated from the δ-values of their quartz. No volcanic rocks have yet been found with primary, igneous δ-values in the HH-Group; all the high-O^{18} extrusive rocks yet found have undergone secondary hydration and/or alteration, as previously discussed.

It should be observed that the O^{18}/O^{16} ratios of granitic gneisses and other metamorphosed granitic rocks may be a result of metamorphism, as it is known that gross changes in O^{18}/O^{16} can occur in rock units during regional metamorphism (TAYLOR, 1964; GARLICK and EPSTEIN, 1967). In general, metamorphism results

the LL, L, I, H_1, H_2, and HH oxygen isotope groups. Data are from the present work or from TAYLOR
are from TAYLOR *(1968), and the granitic pegmatites are from* TAYLOR and EPSTEIN *(1968)*

H_1 Group $7.8 \leqq \delta \leqq 8.3$	H_2 Group $8.4 \leqq \delta \leqq 10.2$	HH Group $\delta \geqq 10.3$
Sudbury, Ontario (2) Bushveld complex	Muskox intrusion, Canada (mafic) Guadalupe complex, Calif. Purcell diabase, B. C. Pigeon Pt., Minnesota Bayfield Co., Wisconsin[b]	Muskox intrusion, Canada (4)
Mono Craters, Calif. (3) Coso Hot Springs, Calif. (2) Superior, Arizona Millard Co., Utah	Clear Lake, Calif. (5)	
Medicine Lake dacite Sonoma Co., Calif. (Na-rich) Pilot Mtns. rhyodacite, Nevada S. E. Guatemala (2) Lipari Is., Italy	Medicine Lake dacites (2) Clear Lake rhyodacite, Calif.	
Wolf Creek, Montana Eastern Baja California San Lucas, Central Honduras Bishop tuff, Calif.	Alboroto quartz latite, Colorado Silver Peak Quadrangle, Nevada Death Valley, California Central Honduras (2) Horse Mesa dam, Arizona Pilot Mtns., Nevada Ponte Gardena, northern Italy El Tigre, Mexico	

STEIN, 1958; [e] TAYLOR and EPSTEIN, 1964; [f] SCHWARCZ, 1966.

in a raising of the δ-values of igneous rocks as a result of exchange and oxygen communication with surrounding metasediments, so such a process can be expected to produce HH-types. This could explain why several gneissic granites from the Adirondack Mtns. fall in the HH-Group (Table 5, and TAYLOR, 1968). However, HH-Group rocks could also arise through melting of O^{18}-rich metasediments (origin of some muscovite granites?) or by alkali metasomatism of such rocks. They might also form simply by large-scale assimilation of O^{18}-rich country rock into a "normal" granitic magma. As a possible example of the latter, SHIEH and TAYLOR (1968) have shown that the margins of several granitic stocks in Nevada and California are HH-Group, while the central portions are normal H-Group. These phenomena could also have resulted from partial exchange between the intrusions and the country rock through the medium of an aqueous vapor phase. Any or all of the above explanations also might apply to granitic pegmatites that lie in the HH-Group.

Table 5 (Continued)

LL Group $\delta \leqq 5.4$	L Group $5.5 \leqq \delta \leqq 6.9$	I Group $7.0 \leqq \delta \leqq 7.7$
Plutonic granites, granodiorites and tonalites		
Skye granites (4)	Quincy granite, Mass.	Conway granite, New Hampshire
Seychelles I. granite	Ascutney granite, Vermont	Oslo granite (Na-rich), Norway
Ardnamurchan tonalite	Beinn an Dubhaich granite, Skye	Bounty I. granodiorite
	Tatoosh granodiorite, Wash.	Deer River granite, Maine
		Bushveld complex (2)
		"Old" granite, Transvaal
		Slieve Gullion granodiorite
		Westerly, R.I. granite[c]
Granitic pegmatites		
	Huntsville, Ontario	Wausau, Wisconsin
	Petaca pegmatite, New Mex.	Pala, California (2)
	Cribbensville, New Mexico	

It is conceivable that some of the very O^{18}-rich granitic rocks represent a late stage in the fractional crystallization of magmas in which the settled crystals are lower in average O^{18} content than the coexisting melt. This is particularly appealing as an explanation of the granitic pegmatites, as many of these are probably very late, residual, differentiates that have formed at relatively low temperatures where isotopic fractionation factors are largest. The high O^{18} contents of the late-stage granophyres of the Muskox intrusion, however, are definitely *not* a result of pure fractional crystallization (see below), nor does this seem to be a likely explanation for the plutonic granites or granite gneisses that fall in the HH-Group.

Rhyolitic ash-flow tuffs cannot be distinguished from "normal" plutonic granites, and it seems plausible that these rock types have common origins. Representatives

H_1 Group $7.8\leqq\delta\leqq8.3$	H_2 Group $8.4\leqq\delta\leqq10.2$	HH Group $\delta\geqq10.3$
Alta granodiorite, Utah (3) Mt. Desert I. granite, Maine Deer Isle rapakivi, Maine Bokan granite, S.E. Alaska Hanover granodiorite[a] Bonsall tonalite, Calif. San Jose tonalite, Baja Calif. Towne Mtn. granite, Texas Migmatite granite, S. Dakota[b]	Labrador granites (2) Canadian Shield granites (2) Adirondack granites (6) Laramie quartz monzonite, Wyoming Dixville Notch granite, New. Hamp. Barre granite, Vermont Sierra Nevada granodiorites (3) Sierra Nevada granite porphyry Woodson Mt. granodiorite, Calif. Rubidoux leucogranite, Calif. Pike's Peak granite, Colorado St. Francois Mtns. granite, Missouri Guatamala granodiorites (2) Orbicular granite, Finland Rapakivi granite, Finland Novosibirsk granodiorite, U.S.S.R. Sverdlovsk granite, U.S.S.R. Duwadami quartz monzonite, Arabia Aswan monumental granite, Egypt Chalky Inlet granite, New Zealand Ries Kessel granites (2)[e] Alta stock aplite granite, Utah Elberton granite, Georgia Chester Dome sodic granodiorite, Vt.[a] Pike's Peak granites[f]	New Hampshire muscovite granites (2) Red Lake, Ontario Adirondack granites (4)
Pala, California Alta stock, Utah	Fitchburg, Mass. Harding, New Mexico Pacoima, Calif. Ramona, Calif. Randville, Michigan	Rock Creek, Sierra Nevada, Cal. Varutrask, Sweden Lincoln, S. Dakota Keystone, S. Dakota Santa Rosa Mtns., Nevada Winchester, Calif.

of each can be found throughout the I, H_1 and H_2 classes, but both are clearly predominant in the H-Group. Some ash-flow tuffs overlap obsidians in O^{18}/O^{16} ratio, but as a group the obsidians are distinctly different. The prevalence of obsidians and hypersolvus granites in the L and I Groups is readily explained if they are high-temperature differentiates of basaltic magma; it is reasonable to expect that the O^{18}/O^{16} ratio of the melt phase would remain about constant under such conditions (as is the case for the andesites, trachytes and syenites), or would increase very slightly because of the tendency of SiO_2-rich materials to concentrate O^{18}.

Obsidians exhibit an interesting geographic distribution with respect to their O^{18}/O^{16} ratios, as can be seen in Fig. 10. All L-Group obsidians (and rhyolite flows, as well) are either from oceanic areas or from the West Coast of the United

States, except for two samples from the Jemez caldera, New Mexico. All H-Group obsidians are from the continental interior of the United States, east of the quartz-diorite line of Moore (1959), except for the very peculiar samples from Clear Lake, California. This is strongly suggestive that contamination with O^{18}-rich crustal material has played a role in the evolution of these rhyolite obsidians, as is also indicated by the work of Doe (1967) on Pb isotopes in obsidians and granites. However, the obsidian sample with the most peculiar Pb isotopic composition, the Cougar Creek obsidian from Yellowstone Park, is not particularly unusual in O^{18}/O^{16} ratio, and the obsidian with the most unusual O^{18}/O^{16} ratio, from Clear Lake, is not at all abnormal in Pb isotopic composition (see Doe, 1967). There does not appear to be any correlation between the lead and oxygen isotopic compositions of any of the granitic rock types.

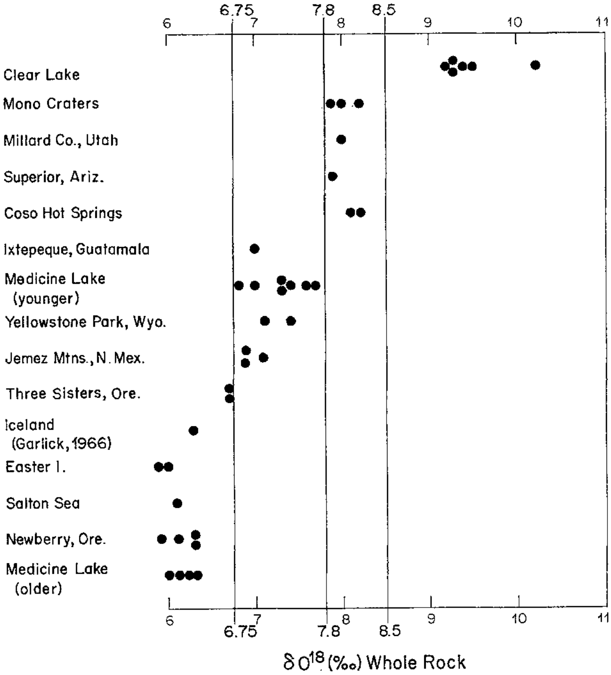

Fig. 10. Plot of O^{18}/O^{16} ratios of whole-rock samples of obsidians (all with low H_2O contents) from various localities. The vertical lines at $\delta = 6.75$, 7.8 and 8.5 are arbitrarily chosen to illustrate the geographic groupings

O^{18}/O^{16} Variations in Individual Igneous Complexes

Medicine Lake Highland, California

A generalized geologic map of the Medicine Lake Highland (after Anderson, 1941) is given in Fig. 11, showing sample locations and the sequence of igneous extrusion. Oxygen isotope data are plotted as a function of this sequence in Fig. 12. Practically continuous chemical gradations exist from basalts through andesites, dacites and rhyolites, but these late Pliocene to Recent eruptions did not take place in a simple order, and the O^{18}/O^{16} ratios of the rocks do not correlate at all with the SiO_2 contents of the rocks. The general order of increasing O^{18}/O^{16} ratio is: andesites-basalts-rhyolites-dacites. However, when the δ-values of the rocks are plotted against age (Fig. 12), a pattern emerges; there appears to be a general increase in the O^{18} content of each rock type with decreasing age. The most clear-cut variation, however, is that all of the pre-Modoc flows are very low in O^{18}, the total variation being from $\delta = 5.5$ to 6.3. Thus, the older basalts, andesites and rhyolite obsidians lie in the L-Group or "normal" basaltic range.

The Recent flows are all O^{18}-rich, even including the Modoc basalt, with $\delta = 6.8$. All of the Recent rhyolite obsidian samples from Glass Mountain and Little Glass Mountain are distinctly richer in O^{18} than *any* of the older rhyolite obsidians, even though there are no major differences in chemical composition among the rhyolites (ANDERSON, 1941, Table 5, p. 399). The dacites, which average at least 6 weight per cent less SiO_2 than the rhyolites, are richer in O^{18} by about 1 per mil. These complex variations in O^{18} cannot be explained by any straightforward or simple process of magmatic differentiation; they suggest that at least two different mechanisms were involved in the evolution of these magmas.

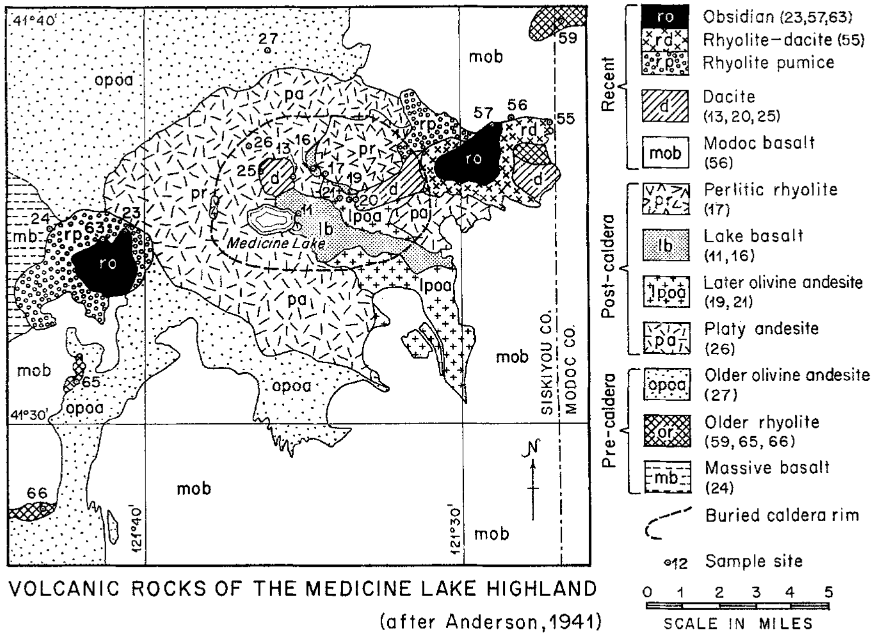

Fig. 11. Geologic map of the Medicine Lake Highland (after ANDERSON, 1941) showing sample localities of specimens analyzed for O^{18}/O^{16}

In Fig. 13, we plot the chemical variations observed by ANDERSON (1941) on ternary diagrams such as those used by NOCKOLDS and ALLEN (1953). In contrast to many other volcanic complexes (see Fig. 14), the plotted points in Fig. 13 do not define a single smooth curve. The dacites and Modoc basalts are markedly depleted in Fe and higher in K/Na relative to a smooth curve drawn through the Lake basalts, the andesites and the rhyolites. Although it may not be strictly legitimate to treat these data as two separate differentiation sequences, for purposes of the following discussion we shall refer to the andesite curves as

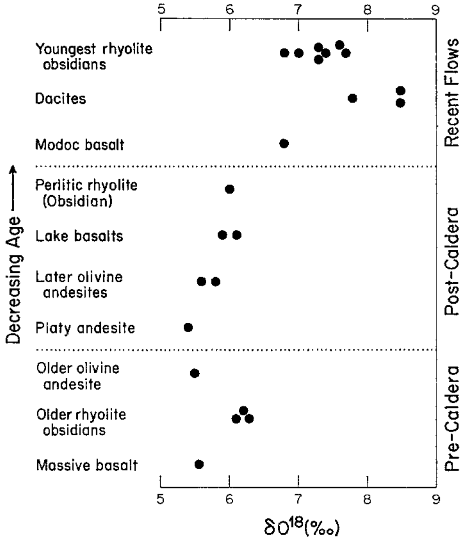

Fig. 12. Plot of O^{18}/O^{16} ratios of whole-rock samples from the Medicine Lake Highland as a function of the sequence of extrusion

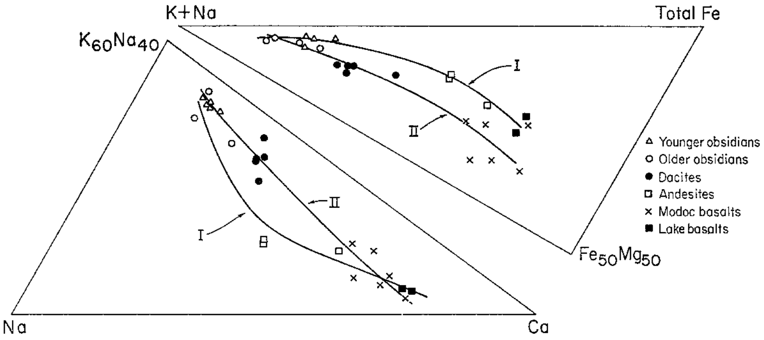

Fig. 13. Plot of chemical analyses of rocks from the Medicine Lake Highland (Anderson, 1941) on ternary diagrams such as those used by Nockolds and Allen (1953). The two ternary diagrams (total alkalies-total Fe-Mg and K-Na-Ca) are broken to conserve space, but are otherwise identical to those of Fig. 14

Medicine Lake I and the dacite curves as Medicine Lake II. These curves are compared with similar curves for the Clear Lake, Lassen, Southern California batholith, Newberry, S. E. Guatemala, Lesser Antilles, Easter Island and Skaergaard igneous complexes in Fig. 14; O^{18}/O^{16} data have been obtained for all these localities.

Although the major chemical variations at Medicine Lake do not correlate at all with the oxygen isotope data, the more subtle variations shown in Fig. 13 do. The rocks that plot on curve II are definitely richer in O^{18} than those that define curve I. The oxygen isotope data therefore suggest that the Lake basalts, andesites and older rhyolite obsidians represent a differentiation trend (higher in Fe/Mg and lower in K/Na) in which essentially no change in O^{18}/O^{16} ratio occurs, whereas the Modoc basalts and dacites (and possibly the younger obsidians) define a different trend in which O^{18}/O^{16} increases sharply with increase in SiO_2 content.

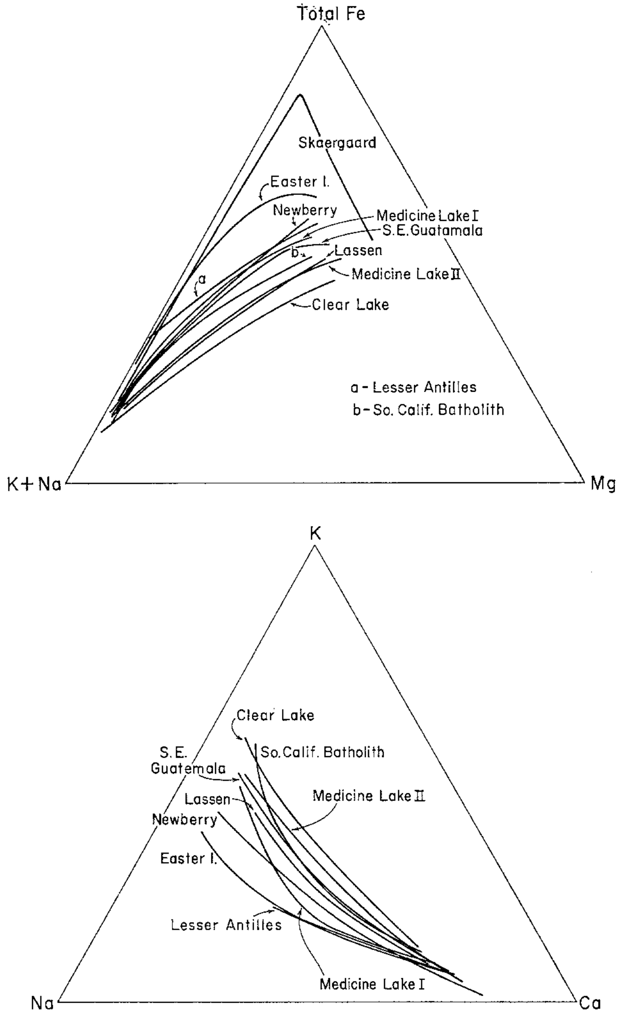

Fig. 14. Ternary diagrams showing the chemical variations in various igneous complexes on which O^{18}/O^{16} data have been obtained. The upper diagram indicates variations in atomic abundances of Fe, K + Na, and Mg; the lower diagram indicates variations in K, Na and Ca. The diagrams are patterned after Nockolds and Allen (1953). Data are from Wager and Deer (1939), Williams (1932, 1935); Anderson (1936, 1941), Larsen (1948), and A. R. McBirney (personal communication)

Perhaps the younger obsidians have δ-values intermediate between the older obsidians and the dacites because of an intermingling or hybridization of magmas from the two trends. In this connection, it is worth noting that a rhyolite-dacite composite flow was erupted from Glass Mountain, made up of separate dacite and rhyolite magmas erupted simultaneouly (Anderson, 1941, p. 376).

The dacites are similar in O^{18} content to plutonic tonalites and granodiorites from the Sierra Nevada and Southern California batholiths, but the obsidians are much lower in O^{18} than the quartz monzonites and granites of these batholiths. The obsidians clearly were not formed by the type of process which formed the granites, nor can they be re-fused material from a hypothetical batholith underlying the Medicine Lake Highland. The dacites, of course, conceivably could arise by such a mechanism. The andesites and older obsidians definitely cannot have been contaminated with crustal rocks to any significant degree.

Clear Lake Area, California

The Pleistocene to Recent volcanic activity in the Clear Lake area has been described by ANDERSON (1936). Only silicic volcanics have been analyzed for O^{18}/O^{16}: 4 Pleistocene rhyolite obsidians and a rhyodacite, and one Recent rhyolite obsidian. There is a progression in O^{18} content from the rhyodacite ($\delta = 8.8$) through the older obsidians ($\delta = 9.2$ to 9.5) to the young obsidian ($\delta = 10.2$). The rhyolitic rocks from this area are unique in that they are higher in O^{18} than any other obsidians yet analyzed (Fig. 10). If these are the result of differentiation from basaltic magma, there has been an enrichment of 3 to 4 per mil during the differentiation process.

The Clear Lake volcanics show a very unusual chemical trend as well as an unusual O^{18}/O^{16} trend relative to other volcanic complexes (Fig. 14). The Clear Lake rocks fall at one end of the spectrum of curves in Fig. 14, being on the whole lowest in Fe/Mg and highest in K/Na. Whatever the process that is responsible for the unique chemical trend, it is probably also the explanation of the high O^{18}/O^{16} ratios, particularly since it is completely analogous to the situation in the Medicine Lake volcanics. The Medicine Lake II curve lies between the Medicine Lake I and Clear Lake curves, and the δ-values of the Medicine Lake dacites lie between the Medicine Lake obsidians and the Clear Lake rhyolites.

Newberry Crater, Oregon

The Newberry volcanic area (WILLIAMS, 1935) is almost identical in geologic setting to the Medicine Lake Highland, both areas lying 30 to 35 miles east of the High Cascades. The volcanic rocks are very similar as well, except that at Newberry the underlying shield volcano that pre-dated caldera formation was basaltic instead of andesitic; also, andesites are much less common at Newberry and dacites are absent. The O^{18}/O^{16} ratios of the Newberry volcanics are indistinguishable from the pre-Modoc volcanics at Medicine Lake (Figs. 12 and 15), which also include only basalts, andesites and rhyolites. Essentially no variation in O^{18}/O^{16} occurs throughout the differentiation sequence from basalt ($\delta = 5.9$) through andesite (6.2 to 6.5) to rhyolite ($\delta = 5.9$ to 6.3).

The chemical trend of the Newberry volcanics is very similar to the Medicine Lake I curve (Fig. 14), and is thus perfectly compatible with the oxygen isotopic similarities. The Newberry obsidians are slightly lower in O^{18}/O^{16} than the Medicine Lake obsidians, but they are also somewhat lower in K/Na ratio. The andesite samples are somewhat higher in O^{18} at Newberry, and they are also strongly porphyritic compared with the samples from Medicine Lake. It can be definitely inferred that crustal contamination with sediments, metasediments and/or plutonic granitic rocks is not important in the formation of the Newberry rhyolites.

Lassen National Park, California

The Lassen volcanic area, studied by WILLIAMS (1932), is typical of the Pleistocene to Recent volcanoes of the High Cascades. It differs from Medicine Lake and Newberry in the absence of obsidian flows and the paucity of rhyolites in general.

The most abundant rocks are andesites and dacites, and far greater volumes of these were extruded than at Newberry or Medicine Lake; also, these rocks commonly contain hornblende and biotite, both of which are rare or absent in the latter areas.

Two basalts and one andesite from the Lassen area have slightly higher O^{18} contents ($\delta = 6.5$ to 6.7) than analogous rocks from Medicine Lake or Newberry, except for the Modoc basalt. This is perhaps not unexpected as one of these Lassen basalts contains quartz xenocrysts, suggesting contamination by a more silicic rock. The dacites are all similar to one another in O^{18}/O^{16} ($\delta = 7.2$ to 7.3 for the glassy groundmass or whole-rock), and contain quartz with a lower δ-value than found for the quartz xenocrysts mentioned above. There is a clear-cut increase of O^{18} in going from the basalts and andesites to the dacites (Fig. 15), but the latter are lower in O^{18} than the Medicine Lake dacites; this is all compatible with the curves on the diagrams of Fig. 14 in that the Lassen curves are similar to those of Medicine Lake II but exhibit a somewhat lower K/Na ratio.

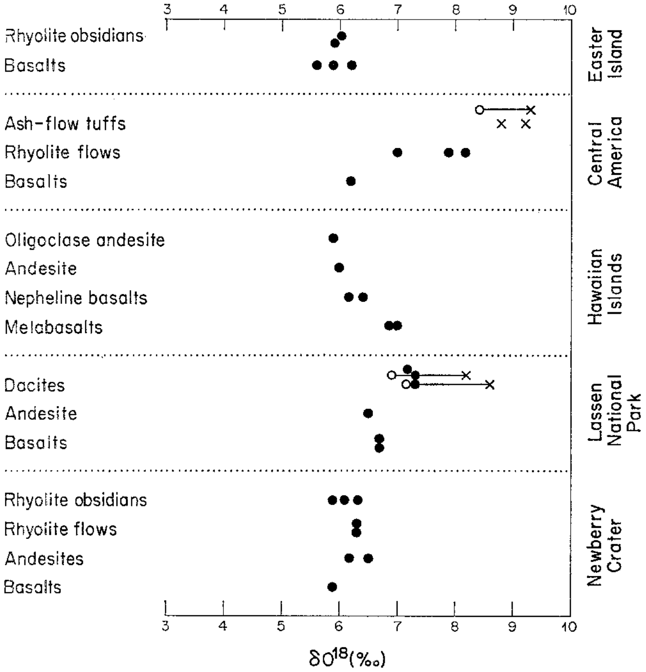

Fig. 15. Graph showing variations of O^{18}/O^{16} in quartz (crosses), feldspar (open cicles) and whole-rock (black circles) in several volcanic complexes

It is plausible to conclude that differentiation of the Lassen magmas occurred in much more H_2O-rich environments (deeper ?) than at Medicine Lake or Newberry where biotite is essentially absent and hornblende is rare and largely confined to the dacites. It is therefore conceivable that higher P_{H_2O} is part of the explanation for the high O^{18}/O^{16} ratios in the Lassen and Medicine Lake dacites. Obviously, contamination with O^{18}-rich country rock cannot be ruled out at Lassen, however.

The Lassen hornblendes and biotites are all strongly resorbed and replaced by magnetite; thus, crystallization of the magnetite occurred in a near-surface environment at very low P_{H_2O}, so the 1,000° C temperature estimated for LP-11 dacite (Table 4) is not unreasonable. The kaolinized andesite, LNP-41, has undergone a low-temperature hydrothermal alteration, and its low O^{18}/O^{16} ratio strongly implies that meteoric water must have been an important component of the hydrothermal solutions. Otherwise, a much larger δ-value would have been observed. CRAIG (1963) has shown that present-day geothermal waters at Lassen are in fact of meteoric origin, so the above result is not unexpected.

Southeastern Guatemala and Central Honduras

Two contrasting types of volcanic complexes have been studied from Central America, and these are described by WILLIAMS *et al.* (1964) and McBIRNEY and WEILL (1966). In southeastern Guatemala about 5 cubic kilometers of Recent rhyolite obsidian in various domes and flows has been erupted along with about an equal volume of basalt, forming the Obrajuelo Complex; the chemical variations in these rocks are shown graphically in Fig. 14. In Central Honduras several thousand cubic kilometers of rhyolite ash-flow tuff was erupted in late Miocene time, forming a vast plateau (McBIRNEY and WEILL, 1966). Oxygen isotope analyses of some of these rocks are given in Fig. 15.

Referring back to Table 1, note that several isotopic analyses are not plotted in Fig. 15: G-644 and G-648 are the H_2O-rich pumiceous rhyolite samples that are abnormally high in O^{18}/O^{16} as a result of having apparently absorbed about 4 per cent meteoric water; these were erupted into Laguna de Obrajuelo when the lake may have been filled with water (A. R. McBIRNEY, personal communication), perhaps explaining why hydration of these glasses seems to have occurred at higher temperatures than are generally involved in the formation of perlites. The whole-rock isotopic analyses of the ash-flow tuffs H-2 and H-75 clearly cannot represent the original O^{18}/O^{16} ratios of the ignimbrite magmas because they are 1.0 to 1.4 per mil higher than their quartz phenocrysts; hence, the whole-rock values of the other ignimbrites H-3 and H-65 are also considered untrustworthy and only quartz and feldspar δ-values are plotted in Fig. 15.

With the above exceptions, we may observe that the Obrajuelo rhyolite flows are intermediate in O^{18}/O^{16} ratio between the basalts and the Honduras ash-flow tuffs. This is identical to the general relationships for all obsidians and ash-flow tuffs (Fig. 8). The Obrajuelo flows ($\delta = 7.0$, 7.9, 8.2) are similar in O^{18} content to the rhyolite flows of the continental United States (Jemez Mtns., Mono Craters, Yellowstone Park, etc.) and it should be noted that the Obrajuelo magmas also came up through a thick sialic basement complex composed of Paleozoic and Mesozoic metamorphic and plutonic rocks (WILLIAMS *et al.*, 1964). Several samples of the basement complex were analyzed for O^{18}/O^{16}, a granodiorite collected from outcrop ($\delta = 8.9$) and 3 xenoliths in ejecta of the Obrajuelo crater, a granodiorite ($\delta = 8.8$), a diorite ($\delta = 7.5$) and a norite ($\delta = 7.4$). It is obvious that the rhyolite flows are not simply fused basement granodiorite, even though

McBirney and Weill (1966) report that the rhyolites are chemically similar to a partially fused fraction of typical basement rock. However, their slight O^{18}-enrichment relative to basalts might be the result of contamination of a parent basaltic magma by the sialic basement.

On the other hand, the estimated δ-value of the Honduras ignimbrite magma is about 8.5 to 8.7, based upon the quartz and feldspar analyses. This is almost identical to the basement granodiorite, and therefore these ash-flow tuffs conceivably could represent melted sialic crust. Such an origin is also compatible with Sr^{87}/Sr^{86} ratios on many of these same samples, obtained by Pushkar (quoted in McBirney and Weill, 1966, Fig. 7), because the Obrajuelo obsidian has a Sr^{87}/Sr^{86} ratio identical to basalts and andesites from Central America, whereas the ignimbrites and basement rocks show a wide range. However, inasmuch as the whole-rock samples of the ignimbrites do not have primary magmatic O^{18}/O^{16} ratios, some of the spread in Sr^{87}/Sr^{86} might also be due to the secondary alteration processes.

Oceanic Islands

The O^{18}/O^{16} ratios of volcanic rocks from oceanic islands all show similar features, so they are considered only briefly here. In all cases, the more SiO_2-rich and alkali-rich "later differentiates" are either very slightly lower in O^{18} or very slightly higher in O^{18} than the basaltic "parent magmas".

Hawaiian Islands. Isotopic data on samples from Maui and Oahu are given in Fig. 15. The andesite and oligoclase andesite (both from Maui) are distinctly lower in O^{18} than the Koolau series melabasalts from Oahu, but only slightly lower than the Honolulu series nepheline basalts from Oahu. Inasmuch as the andesites and nepheline basalts are almost identical in O^{18}/O^{16} to the value accepted for primary, uncontaminated basaltic magma ($\delta = 5.9$), it is reasonable to assume that the melabasalts may be abnormally O^{18}-rich for some unspecified reason (slight low-temperature alteration ?).

Easter Island. Oxygen isotope analyses of 3 alkali basalts and 2 rhyolite obsidians from Easter Island on the East Pacific rise are given in Fig. 15. The δ-values of the obsidians (5.9, 6.0) lie within the range shown by the basalts, so no change in O^{18}/O^{16} is discernible in the differentiation sequence. Note that these obsidians are slightly lower in O^{18} than the average Newberry obsidian; this is another example compatible with our previous correlations between O^{18} contents and the chemical trends shown in Fig. 14, as the Easter Island curves follow a higher Fe/Mg and a lower K/Na path than any of the volcanic complexes previously discussed, including Newberry.

Lesser Antilles. Only one sample from the Lesser Antilles has been studied in this work, the dacite from the 1902 eruption of Mont Pelée in Martinique. However, the δ-value of 6.8 for this rock lies in the "basaltic" range, suggesting that little or no change in O^{18} content has occurred during differentiation. This is compatible with the chemical trends indicated in Fig. 14.

Azores Islands. Garlick (1966) analyzed 3 samples from Flores Island in the Azores Group, a basalt, a trachyandesite and a trachyte. All had essentially identical δ-values of 5.9, 6.1 and 6.0, respectively.

Gough Island. GARLICK (1966) analyzed 2 basalts, a trachyandesite and 2 trachytes from Gough Island in the South Atlantic Ocean. All had very similar δ-values in the range 5.6 to 6.3.

Canary Islands. A basalt from Tenerife in the Canary Islands ($\delta = 6.2$) was analyzed in the present study. GARLICK (1966) analyzed feldspar and augite in a trachyte from Tenerife, obtaining δ-values of 6.4 and 4.7, respectively. This suggests essentially no change in O^{18}/O^{16} occurred during differentiation.

Iceland. One sample of rhyolite obsidian from Iceland has a δ-value of 6.3 (GARLICK, 1966).

Seychelles Islands. The Seychelles Islands in the Indian Ocean are completely atypical oceanic islands in that they are constituted of late-Precambrian granite (BAKER, 1963). A sample of granite from Mahé, the largest island, has been studied in the present work, the same specimen analyzed by WASSERBURG *et al.* (1964). Oxygen isotope analyzes were made of coexisting microperthite ($\delta = 2.6$) and quartz ($\delta = 4.1$) in this sample, which is a typical hypersolvus granite. These O^{18}/O^{16} ratios are abnormally low relative to typical igneous rocks, and although other explanations are possible, it is plausible that the Mahé granite was emplaced at a relatively shallow level in the crust, and could therefore have interacted with meteoric water when it was intruded.

Muskox Layered Intrusion, Canada

The Muskox intrusion outcrops over a length of about 75 miles in the Coppermine River area, Northwest Territories, Canada (SMITH, 1962; IRVINE and SMITH, (1967). A nearly vertical feeder dike forms the southernmost 37 miles of outcrop, and the northern portion opens up into a gently dipping (4°) layered series of ultramafic rocks, gabbros and granophyres. The layered series is funnel-shaped in cross-section and is 6,000 to 6,500 feet thick. Although there are several cyclic repetitions, there is a general gradation upward from layers of dunite and olivine clinopyroxenite through peridotite, websterite and orthopyroxenite, and up into gabbro. The gabbro becomes gradually richer in interstitial granophyre upward, and a thin sheet of granophyre forms the roof of the intrusion (SMITH, 1962).

Oxygen isotope ratios of several rocks and minerals from the Muskox intrusion are shown in Fig. 16. The layer numbers are those supplied to the writer by T. N. IRVINE; the corresponding map-units of SMITH (1962) are given in Table 2. Note that most of the oxygen isotopic analyses are from the upper differentiates that compose less than 10 per cent of the intrusion. The isotopic composition of the original Muskox magma is probably best estimated from the δ-value of the chilled margin of the feeder dike ($\delta = 6.8$). This presumably represents the O^{18}/O^{16} ratio of the original basaltic liquid, but inasmuch as the liquid was carrying large amounts of olivine in suspension the O^{18}/O^{16} ratio of the entire magma was probably somewhat lower than this. It is impossible with these few data to make a valid material-balance calculation comparing the whole layered series with the feeder dike, but it appears that the layered series is overall a little richer in O^{18} than the parent magma.

The most impressive feature of the oxygen isotope data is the progressive upward enrichment of the layered series in O^{18}, from $\delta = 6.2$ to $\delta = 12.3$. This is in striking contrast to the volcanic complexes discussed above, and the late-stage granophyres are even more O^{18}-rich than most plutonic granites (Fig. 8). It is apparent that this O^{18}-enrichment cannot be ascribed wholly to a simple process of fractional crystallization, because very peculiar oxygen isotope relationships are observed among the coexisting minerals in many of these rocks. These are: (1) Below layer 36, relatively "normal" O^{18}/O^{16} ratios are observed in plagioclase and pyroxene, and the fractionations between these minerals ($\Delta = 0.8$, 1.0) are similar to those observed in gabbros from other localities. (2) Above layer 36 the feldspars are all abnormally O^{18}-rich, and the discrepancies increase upward in the layered series. (3) Plagioclase-pyroxene Δ-values of 1.5 to 3.2 in layers 36 to 39 are much larger than is expected for equilibrium at magmatic temperatures (see Fig. 3), but the pyroxenes themselves have essentially "normal" δ-values. (4) Above layer 40, the quartz-feldspar fractionations are in most cases completely reversed from their equilibrium values; in granophyric gabbro 60—408 the alkali feldspar is 2.1 per mil higher in O^{18} than coexisting quartz, and in 60—550 A quartz is 1.3 per mil lower than the whole rock, suggesting that the quartz-feldspar fractionation is about — 2 per mil.

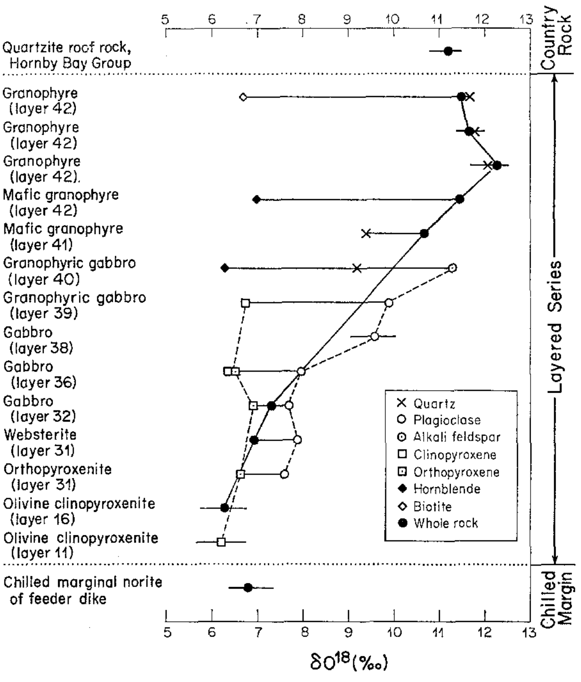

Fig. 16. Graph of the O^{18}/O^{16} ratios of samples from the Muskox intrusion, Canada as a function of position in the intrusion. Samples in the layered series are from layer 11 (lowest) upward to layer 42 (highest). The order of the samples in layer 42 itself, however, is arbitrary and has no relation to height in the intrusion

The mafic minerals, pyroxene, hornblende and biotite, all show similar δ-values throughout the layered series, from $\delta = 6.2$ to 7.0. Feldspar, however, varies from 7.6 to at least 11.3, and quartz varies from 9.2 to 12.1. These variations cannot be reconciled with simple crystal-melt equilibria, and it is certain that some process of O^{18}-enrichment has taken place in which feldspar is affected to a much greater extent than coexisting pyroxene or quartz. The only plausible mechanism by which this could occur is through post-crystallization exchange between the rocks and a transient, oxygen-bearing, fluid-phase. In this connection, we should point out that the granophyric gabbros and granophyres which show the marked non-equilibrium effects contain either turbid, cloudy, gray plagioclase or turbid, brick-red alkali feldspar.

The association of "abnormal" O^{18}/O^{16} ratios with brick-red alkali feldspar has also been observed in a number of other red-rock granophyres (TAYLOR, 1967b), including the Pigeon Point and Enger Tower granophyres from Minnesota (Table 2). It is very likely that in each case these effects are brought about by late-stage (deuteric ?) exchange between an aqueous gas phase and the granophyres. O'NEIL and TAYLOR (1967) have shown that feldspars readily exchange oxygen with alkali chloride solutions at high temperatures; this is much faster for feldspars than for quartz, and the feldspars so exchanged are turbid and filled with fluid inclusions. To produce the effects shown in Fig. 16, this exchange would have to occur either with O^{18}-rich water at magmatic temperatures, or with "normal" magmatic water ($\delta = 7$ to 9) at lower temperatures. It is difficult to conceive of a mechanism whereby very O^{18}-rich waters might be introduced into the intrusion. The only feasible possibility would seem to be inward diffusion of waters that had exchanged with surrounding O^{18}-rich country rock at high temperatures. If we are restricted to water that was an intrinsic part of the Muskox magma, we may illustrate possible effects with the following example. Water in exchange equilibrium with An_{50} plagioclase ($\delta = 7.4$) would be 1.6 per mil higher in O^{18} than the plagioclase at 1000° C and thus would have $\delta = 9.0$ (O'NEIL and TAYLOR, 1967). If this H_2O migrated upward from the gabbro portion of the layered series and came into contact with granophyre at 500° C, the alkali feldspar in that rock would attain a $\delta = 10.5$, assuming the amount of H_2O is large relative to the amount of feldspar. By sufficient juggling of the above temperatures it should be possible to explain the isotopic effects actually observed in the Muskox intrusion.

The quartz in granophyric rock types from layers 40 and 41 has $\delta = 9.2$ to 9.4; these are typical values for plutonic granitic rocks, and it is tempting to speculate that O^{18}-enrichment of this amount might be due to simple fractional crystallization alone. If so, this would ease the burden on the two types of exchange processes envisioned above, and it would imply that such quartz was completely inert during the deuteric alteration. The granophyres from layer 42, however, contain quartz with $\delta = 11.7$ to 12.1 and would definitely seem to have been affected by the exchange process. A way out of this dilemma is to assume that layer 42 granophyres exchanged with the aqueous solutions while they were still at least partially molten silicate liquids. Any quartz that crystallized later would then be O^{18}-rich. Evidence in favor of this concept is that (1) the quartz-feldspar Δ-values are clearly much more "normal" in the layer 42 granophyres than in the lower ones; (2) the 3 layer 42 granophyre samples do not contain brick-red alkali feldspar; (3) much of the feldspar in these granophyres is clear and free of turbidity; and (4) the quartz-biotite Δ-value of 5.1 per mil in one of them is typical of "normal" plutonic granitic rocks (TAYLOR and EPSTEIN, 1962a).

The layer 42 granophyres also conceivably could have become enriched in O^{18} through assimilation of overlying roof rock. However, the single analyzed sample of quartzite is lower in O^{18} than the granophyres. In summary, the later differentiates of the Muskox intrusion may in part have become O^{18}-rich through assimilation and/or through simple fractional crystallization; in any case, superimposed upon such a primary isotopic trend are much more important effects that have resulted from exchange with aqueous solutions of unknown origin. The latter process seems to have occurred before the uppermost granophyres were completely crystalline. It is probable that the intrusion was an open system during crystallization, in that the hypothetical solutions were largely derived from a deeper magma or from the adjacent country rock; this would explain why the layered series appears to have an average O^{18}/O^{16} ratio higher than that of the parent Muskox magma.

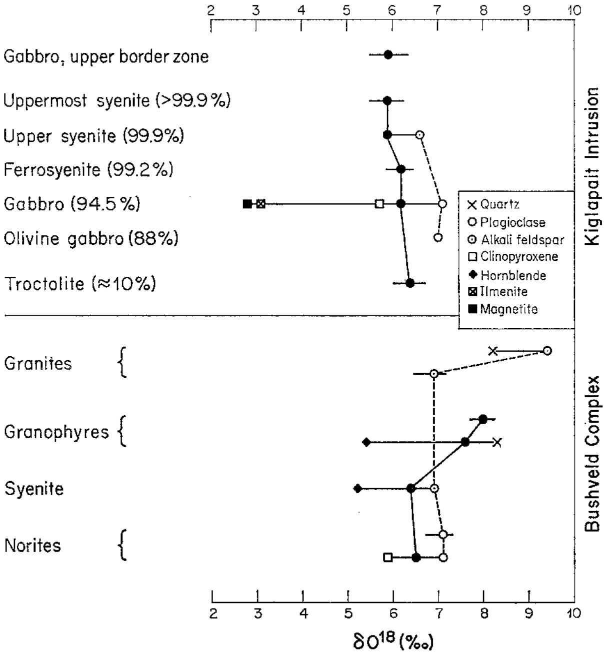

Fig. 17. Graph of O^{18}/O^{16} ratios of samples from the Kiglapait intrusion, Labrador and the Bushveld complex, South Africa. The per cent values given for the Kiglapait rocks indicate the per cent of the layered series that had crystallized at the time the particular rock formed (MORSE, 1966)

Kiglapait Layered Intrusion, Labrador

The Kiglapait intrusion, studied by MORSE (1966), is a bowl-shaped body measuring 27 by 32 km in plan. The lower 85 per cent of the layered series is a troctolite, and this grades upward into olivine gabbro, ferrodiorite and finally ferrosyenite at the very top; the entire series is some 20,000 feet thick. Oxygen isotope analyses of a few layered-series rocks and an upper border zone gabbro are given in Fig. 17. A very slight depletion in O^{18} has occurred during differentiation, from $\delta = 6.4$ in a lower troctolite to $\delta = 5.9$ in the uppermost ferrosyenites. This is obviously not a sequence in which equilibrium was continuously maintained between the silicate liquid and the cumulate crystals, because at equilibrium K feldspar should be higher in O^{18} than coexisting andesine or labradorite.

Although a complete series of chemical analyses is not available, the petrographic data of MORSE (1966) indicate that the Kiglapait intrusion has undergone a ferrogabbro-type of differentiation analogous to that observed in the Skaergaard intrusion, but with somewhat less Fe-enrichment. The Kiglapait chemical trend probably lies between the Easter Island and Skaergaard curves of Fig. 14. Therefore, the O^{18}/O^{16} results are compatible with our previous discussions of volcanic complexes, in that the very high Fe/Mg curves of Fig. 14 are associated with slight O^{18}-depletion in the later differentiates.

Bushveld Complex, South Africa

The enormous Bushveld complex (HALL, 1932) obviously cannot be characterized by the few oxygen isotope analyses obtained in the present work (Fig. 17), but we may note the following: (1) the syenite and norite are isotopically identical; (2) the granophyres are 1 to 1.5 per mil higher in O^{18} than the norites; (3) the Bobbejaankop granite contains quartz and feldspar that are violently out of isotopic equilibrium, but the δ-value of its quartz is perfectly compatible with that of K feldspar in the Pokwani granite.

The Bobbejaankop granite is composed of brick-red alkali feldspar that is turbid and full of identifiable hematite; thus, except for its very coarse grain size this granite is completely analogous to the Muskox granophyres described previously. It must be assumed that aqueous solutions have permeated this rock subsequent to its crystallization and exchanged oxygen with the feldspar while leaving the quartz virtually unaffected. Prior to this alteration, the granite was very likely a "normal" hypersolvus granite similar to the Pokwani specimen. This alteration probably occurred during a late stage in the crystallization of the Bushveld complex, and it very likely was associated with the abundant fluorite and tin mineralization in the Bobbejaankop granite and adjoining rocks (SÖHNGE, 1944).

Ignoring the complicating features in the Bobbejaankop granite, there is a slight O^{18}-enrichment in the Bushveld series in the sequence: norites and syenites — granites — granophyres. The O^{18}/O^{16} ratios are about what would be expected for equilibrium differentiation at high temperatures.

Other Gabbro-Granophyre Associations

Guadalupe Complex. The Guadalupe complex (Jurassic ?) in the foothills of the Sierra Nevada (BEST, 1963) shows a progressive increase in O^{18} content in the sequence gabbro — mafic granodiorite — granophyre, from $\delta = 5.9$ to 9.6. However, the quartz in the grey granophyre is unusually O^{18}-rich relative to the whole-rock δ-value, and this sequence may not be a result of simple fractional crystallization.

Sudbury Lopolith. The grey granophyre from the upper part of the Sudbury intrusion in Ontario is about 1 to 1.5 per mil higher in O^{18} than the norite.

Duluth Complex. The Enger Tower and Endion Sill granophyres are both red-rocks and are abnormally O^{18}-rich; however, quartz from the former has $\delta = 8.0$, suggesting that prior to the red-rock alteration the granophyres were only 1 to 1.5 per mil higher in O^{18} than the Duluth gabbro. There thus appears to be a slight O^{18}-enrichment in the sequence gabbro — mafic granodiorite — granophyre.

Purcell Diabase, British Columbia. Gray granophyre from the Purcell sill is 2.6 per mil higher in O^{18} than the adjacent diabase; its δ-value (8.9) is typical of plutonic granitic rocks.

Anorthosite-Syenite (Mangerite) Complexes

O^{18}/O^{16} analyses of several samples from the vast Precambrian anorthosite complexes at Nain, Labrador; Egersund, Norway; Lac St. Jean, Quebec; Laramie, Wyoming; and the San Gabriel Mountains, California are given in Table 2. In each of these cases the syenites and mangerites are isotopically very similar to the anorthosites. It is practically impossible that assimilation of sialic crust could be involved in the differentiation of these complexes. Their O^{18}/O^{16} ratios are perfectly compatible with differentiation from primary basaltic or andesitic magma.

The quartz monzonites and granites associated with two of the above complexes (Nain and Laramie) have δ-values similar to "normal" plutonic granites. These are not necessarily genetically related to the anorthosites, however, and they could have originated by any of the mechanisms proposed for H-Group granitic rocks. A few Precambrian anorthosite bodies, notably the ones in the Adirondack Mountains, are much richer in O^{18} than those listed above; TAYLOR (1968) has shown that the O^{18}-enrichment is a result of regional metamorphism subsequent to the emplacement of these bodies.

Tertiary Igneous Complexes, Inner Hebrides, Scotland

The Tertiary igneous complexes of Mull, Skye and Ardnamurchan are among the classical localities of igneous petrology, and the report of an O^{18}-depleted granite from Skye by GARLICK (personal communication, 1967) suggested that these areas might be complicated in the same manner previously found for the Skaergaard intrusion and the Seychelles Islands. Accordingly, oxygen isotope analyses were obtained on a variety of igneous rocks from the Inner Hebrides, and the results are given in Fig. 18.

The data in Fig. 18 are somewhat surprising in that essentially every analyzed sample is abnormally low in O^{18} content relative to analogous rocks in other parts of the world. The only rocks which even approach "normal" isotopic compositions are the Beinn an Dubhaich granite from Skye and the Great Eucrite and Big-Feldspar basalt dike from Ardnamurchan (see HARKER, 1904, and RICHEY and THOMAS, 1930, for description of these rock types). In addition to being depleted in O^{18}, most of the rock types are highly variable in O^{18} content. For example, granitic quartz varies varies from -6.0 to $+7.3$, gabbro plagioclase from -3.8 to $+4.7$, and plagioclase phenocrysts in basalt from $+1.0$ to $+6.3$. Such variations are enormous in comparison to those observed in most igneous rocks.

Another feature of Fig. 18 is that in practically every case where coexisting minerals were analyzed the measured Δ-values are highly abnormal. Most of these rocks clearly represent "disturbed" systems in the same way as do the red-rock granophyres previously referred to. However, instead of the feldspar being richer in O^{18} than the quartz, we commonly find that the feldspars are much lower in O^{18} than is consistent with equilibrium at any reasonable magmatic temperature. Quartz-feldspar Δ-values of 2.4, 4.1, 4.8, 5.2 and 8.7 are observed instead of the normal 1.0 to 1.5 found in most granites. Similar effects are observed in the gabbros, in that plagioclase-pyroxene Δ-values vary from -5.4 to $+0.1$ instead of the normal $+0.9$ to $+1.3$ in most gabbros.

The conclusion is practically inescapable, therefore, that these magmas have interacted and exchanged with an external oxygen-bearing phase that had a low O^{18}/O^{16} ratio. The only suitable candidate is meteoric water. which we must assume was present in fractures and joints in the country rocks when the igneous rocks of the Inner Hebrides were emplaced. Let us accept this as a "working hypothesis" and test it by examining the data of Fig. 18 in more detail.

First, if meteoric water was present in the country rocks we would expect it to interact with all the igneous rocks, independent of rock type; this seems to be true, because basalts, gabbros, granites, granophyres, a tonalite and an oligoclase andesite all show O^{18}-depletion. Second, we should expect the effects to be highly variable because they would be dependent upon porosity and permeability of the country rock, size of the particular intrusion, its rate of crystallization, its temperature and many other factors that would affect the rate of influx of H_2O into the magma; the great variability of the δ-values has already been noted. Third, we should expect feldspar to be more highly exchanged than coexisting quartz or pyroxene, if exchange continued to take place after crystallization of these minerals, and this also seems to have occurred. We should note that the low-O^{18} feldspars in these rocks are generally turbid or cloudy, particularly those most strongly depleted in O^{18}.

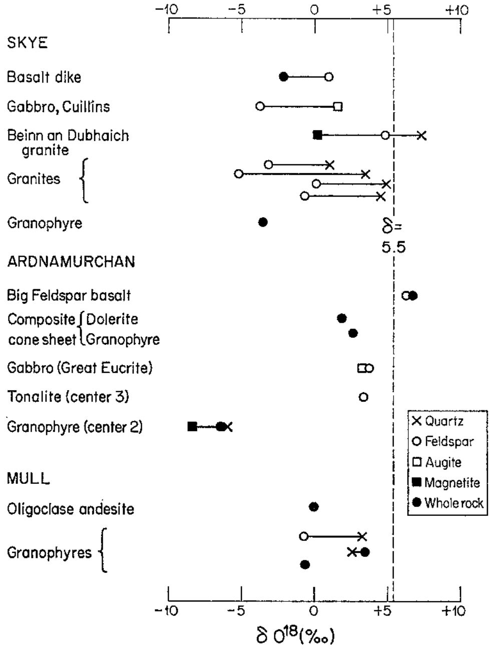

Fig. 18. Graph of O^{18}/O^{16} ratios of samples from the Tertiary volcanic province of Scotland, including the Isle of Skye, the Isle of Mull and the peninsula of Ardnamurchan. The vertical line at $\delta = 5.5$ separates the Scottish rocks on the left from the field of "normal" igneous rocks on the right

It would *a priori* be expected that meteoric water could only have an important effect on igneous rocks if the latter were intruded at shallow depths into highly porous and permeable country rock. This requirement is very well satisfied in the Hebrides because the intrusions are generally ring dikes or cone sheets forming the shallow roots of volcanoes or calderas, and the principal country rock is a thick series of well-jointed plateau basalt flows. It is well known that some of the most important aquifers for ground water storage and movement are plateau basalts such as are found in the Pacific Northwest of the United States. All of the samples listed in Fig. 18 are part of ring-dike complexes intruded into the plateau lavas, except for the Beinn an Dubhaich granite of Skye which is emplaced into Cambrian limestone and dolomite, and the Big-Feldspar basalt of Ardnamurchan which is a dike intruded into Moine Schists. It can hardly be a coincidence that these two rocks are the only ones in Fig. 18 that project over into the range of "normal" igneous δ-values (above $\delta = 5.5$). The quartz in the Beinn an Dubhaich granite is typical for a hypersolvus granite, but its feldspar is about 1 per mil too low in O^{18}/O^{16}. The large plagioclase phenocrysts in the Big-Feldspar basalt are essentially "normal" but the coexisting groundmass is then too high by about 0.5 per mil. Thus, even in these most favorable cases, there exist isotopic complexities that may be the result of minor interaction with meteoric waters.

Other things being equal, the larger the intrusion the more likely that it will by sheer volume swamp out the effects of adjacent meteoric water. The Great Eucrite is the largest single ring dike at Ardnamurchan; it also is part of Center 3, which was largely emplaced into pre-existing ring dikes of Center 2. Its relatively small O^{18}-depletion seems explicable on the basis of both its size and the type of country rock involved. The tonalite is from a much smaller body in Center 3, and the highly depleted Grigadale granophyre is from a still smaller body from Center 2. It is also worth noting that the marginal dolerite from the composite cone sheet is lower in O^{18} than the granophyre from the middle of the sheet.

The plateau lavas in the Inner Hebrides were poured out over a land-surface and were piled up, flow upon flow, to form a plateau of great height; at Mull a thickness of at least 6,000 ft. of these rocks remains, despite prolonged erosion (Richey, 1961). It is conjectured that the Hebrides were only part of a vast volcanic land that embraced the Faeröes, Iceland, Greenland and Jan Mayen. This region is very northerly; in fact it spans the Arctic Circle. In combination with the hypothetical high elevation of the plateau this practically insures that a heavy rainfall (and snowfall?) of low-O^{18} H_2O would be present, even during the early Tertiary. The joints and fracture-openings in the plateau lavas would almost certainly have been filled with ground water, and this would have been constantly replenished during the long time interval involved in the intrusion and crystallization of the ring-dike complexes.

To sum up, we conclude that meteoric water was definitely a factor in the formation of the Tertiary igneous rocks of western Scotland, although it is not known to what extent this has affected the chemical compositions of the various rocks. The coexisting minerals in many rocks are violently out of isotopic equilibrium, and in most cases the feldspars have undergone oxygen isotopic (and cation?) exchange after they crystallized. In many of the samples it is almost certain that exchange occurred between meteoric water and the silicate melts themselves; most of the low-O^{18} quartz and pyroxene probably crystallized from O^{18}-depleted magmas. A final line of evidence indicating the abundance of ground water in the country rocks of these complexes is the large number of intrusive dikes and sills of pitchstone; the high H_2O contents of these rocks are due to influx of meteoric water (see the previous section on D/H ratios). One pitchstone sample from Arran has $\delta O^{18} = +14.5$, indicating that it exchanged at very low temperatures. Using the 1.0245 fractionation factor suggested previously for perlite formation, this suggests that the meteoric water may have had a δ-value of about -10. For comparison, the groundwater in Iceland at present has $\delta = -10$ to -13 (FRIEDMAN and SMITH, 1958; CRAIG, 1961a).

Skaergaard Intrusion

An oxygen isotope study of the Skaergaard intrusion of east Greenland was carried out by TAYLOR and EPSTEIN (1963), but a few new analyses have been made and are given in Table 2 and Fig. 19. These data reinforce the conclusions of TAYLOR and EPSTEIN that meteoric water penetrated the marginal gabbros of the Skaergaard intrusion and caused marked O^{18}-depletion and isotopic disequilibrium in the marginal rocks. Most notable of the new samples is the fine-grained chilled marginal gabbro (EG 4508) which has the lowest O^{18}/O^{16} ratio of any of the Skaergaard rocks. Marginal border rocks have thus been found which extend to lower δ-values than are observed in the late-stage differentiates at the top of the Skaergaard layered series. In addition, low-O^{18} samples have now been found in the Upper Border Group (EG 5271).

These new isotopic data suggest that a re-interpretation of some of the conclusions of TAYLOR and EPSTEIN (1963) may be in order. It was concluded that the marked O^{18}-depletion of the late differentiates of the Skaergaard intrusion was due to fractional crystallization, in which the average δ-value of the settled crystals was about 1 per mil higher in O^{18} than the coexisting silicate melt. Even though there was evidence for O^{18}-depletion in the marginal rocks of the intrusion because of exchange with meteoric water, this was a much smaller effect than was observed in the hedenbergite andesinite and hedenbergite granophyres of the late differentiates. Also, the Skaergaard intrusion was considered to be relatively "dry" because of the lack of hornblende and biotite, there was no mineralogic evidence that meteoric water had entered well into the interior of the intrusion, and no significant oxidation of Fe^{+2} had occurred in the late differentiates.

However, now we have observed abundant evidence for the presence of meteoric water in the Scottish intrusions, and δ-values in some of those are considerably lower than in any of the Skaergaard samples. Also, the low O^{18} contents of the Upper Border Zone rocks can probably only be explained by influx of meteoric water, particularly since a "reversed" plagioclase-pyroxene fractionation is observed in sample EG 5271. The geologic setting of the Skaergaard intrusion is similar to that of the Scottish intrusions, in that the body is a funnel-shaped intrusion that transects a flat-lying unconformity between basement gneiss and a 5 km-thick section of plateau basalts. The latter are a part of the extensive volcanic plateau referred to in the previous section. Abundant meteoric water appears to have percolated down through at least 15,000 ft. of jointed lavas. The border samples in Fig. 19 that are most depleted in O^{18} are those in which the adjacent country rocks are the plateau basalts. The gabbro picrite and the tranquil zone gabbro are both from the N.W. border of the intrusion where the country rock is basement gneiss.

Because of the new aspects of the problem outlined above, we can no longer be so dogmatic concerning the origin of O^{18}-depletion in the late differentiates. This by no means implies that this isotopic depletion *must* be a result of exchange with meteoric water, although a glance at Fig. 19 would suggest that whatever is the origin of the outward depletion of O^{18} in the border series, the same mechanism must apply to the late differentiates of the layered series. There are difficulties with such a hypothesis, because the marked O^{18}-depletion in the border zone is only observed within a few feet of the contact, whereas the late granophyres of the layered series are well inside the intrusion and are overlain by at least a 1 km-thick section of Upper Border Group rocks (Wager and Deer, 1939). Therefore, we must explain why these late differentiates are much lower in O^{18} than rocks through which the meteoric waters obviously had to pass. This can only be explained if there were a steady influx of meteoric water into the intrusion where it could continue to exchange with the liquid magma in the upper part of the layered series. As the amount of magma steadily decreased because of crystallization, we would expect it to become progressively depleted in O^{18} by exchange with new quantities of meteoric water (which, of course, at this stage would be superheated steam).

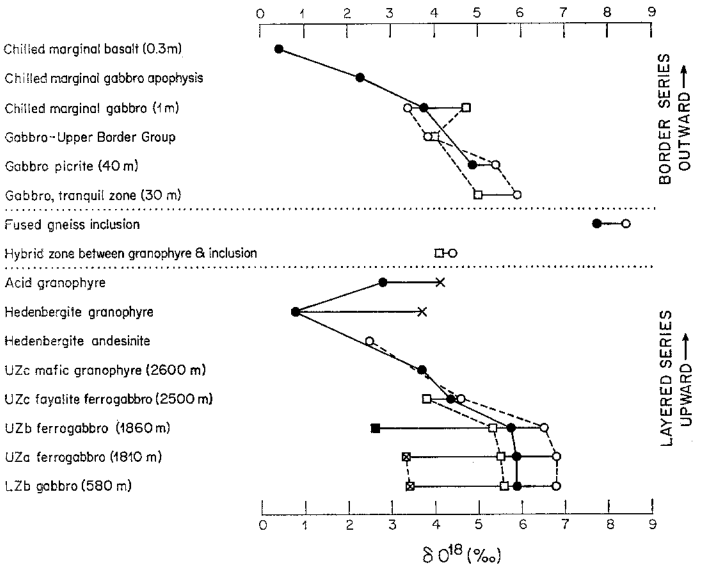

Fig. 19. Graph of the O^{18}/O^{16} ratios of samples from the Skaergaard intrusion, east Greenland as a function of position in the intrusion. Data are from the present study and from Taylor and Epstein (1963). The symbols have the same meaning as in Figs. 16 and 17

The ferrogabbro trend of magmatic differentiation is a peculiar one, and by analogy with the differentiation trends we have discussed previously (see Fig. 14), we might expect that such a trend would produce at least a slight O^{18}-depletion in the later differentiates. This has happened at the Kiglapait intrusion and the Skaergaard intrusion represents even stronger Fe-enrichment. Also, the Skaergaard differentiation progressed to much more SiO_2-rich rocks than did the Kiglapait.

Therefore, it would be premature at this time to rule out the possibility that marked O^{18}-depletion can occur during fractional crystallization of the ferrogabbro type, as proposed by TAYLOR and EPSTEIN (1963). Further isotopic studies, particularly those involving D/H studies, should provide a final answer to this question.

Granites with Unusual Textures

One orbicular granite has been examined in the present study, a specimen from Kangasniemi, Finland (see ESKOLA, 1938, Fig. 5b, p. 463). Analyses were made outward from the center of one orbicule to the matrix granite. Very little change in O^{18} was observed in this traverse, other than a correlation of high O^{18} contents with the more leucocratic layers. This is a typical H-Group plutonic granite in everything but its orbicular texture, and even though crystallization may have been intermittent and perhaps involved periodic fluctuations in P_{H_2O}, the total change from orbicule core to matrix is only from $\delta = 9.0$ to 9.4.

Two rapakivi granites were studied, one from Iitti in Finland, and one from Deer Isle, Maine (STEWART, 1956). Both these granites are normal H-Group, although they are a little lower in O^{18} than the average plutonic granite. A K feldspar core and oligoclase mantle from a single crystal in the Finnish specimen both have almost identical δ-values; the K feldspar is only 0.2 per mil higher in O^{18} than the oligoclase, compatible with isotopic equilibration of the two phases at magmatic temperatures. Neither the rapakivi granites nor the orbicular granite seem to have originated in any way different from "normal" plutonic granites, at least in so far as their O^{18}/O^{16} ratios are concerned.

Conclusions

Fractional Crystallization

The present study has demonstrated that volcanic and plutonic igneous rocks in general have distinctly different O^{18}/O^{16} ratios. These differences are very minor for basalts and gabbros, but for rhyolites and granites they are appreciable. In Fig. 20 we plot the whole-rock O^{18}/O^{16} ratios of a large number of igneous rocks against a "differentiation index" of the type used by LARSEN (1948). As far as the oxygen isotope data are concerned, almost all of the rocks plotted on Fig. 20 conceivably could have arisen by fractional crystallization of basaltic magma; but if so, the crystallization conditions had to be drastically different for the volcanic and plutonic magmas.

The isotopic differences between rhyolite obsidian and plutonic granite magmas may arise simply through their different temperature and P_{H_2O}. Rhyolite obsidians have low H_2O contents; they therefore must have erupted at very high temperatures, at least 950°C or higher based on the data of TUTTLE and BOWEN (1958). It is logical to assume that they also were at least this hot in their magma chambers prior to eruption because (a) they generally show little vesiculation, indicating that no appreciable H_2O was lost during extrusion, and (b) they are commonly 95 to 99 per cent glass, and therefore cannot have been internally heated by evolution of any significant amount of latent heat of crystallization. This is in direct contrast to plutonic granite magmas which in general must have crystallized at relatively high P_{H_2O} in order to stabilize biotite and hornblende; such magmas probably exist at temperatures as low as 700° C or below.

A temperature change from 1,000° C to 700° C can have a large effect on oxygen isotopic fractionation factors. For example, the plagioclase-magnetite fractionation would increase by about 1.7 per mil over that interval. In addition, the phases crystallizing may be markedly different in the two situations; biotite and hornblende crystallize more abundantly in the water-rich plutonic magmas. These minerals tend to be lower in O^{18} than any of the common igneous minerals except magnetite. Anything which promotes their crystallization should have a tendency to drive the later differentiates towards more O^{18}-enrichment. Added to the larger fractionation factors, this effect could account for much of the O^{18}-enrichment shown by the plutonic granitic rocks in Fig. 20; it also could explain the high O^{18}/O^{16} ratios of certain volcanic rocks such as the Lassen and Medicine Lake dacites and most of the ash-flow tuffs. The latter rocks commonly contain biotite and hornblende, indicating that they existed at depth in an environment high in P_{H_2O}. They also are explosively erupted, indicating a high volatile content, and they are largely crystalline, thus providing the internal heating necessary to bring the remaining rhyolite liquid up to the high temperature required by the low P_{H_2O} at the Earth's surface.

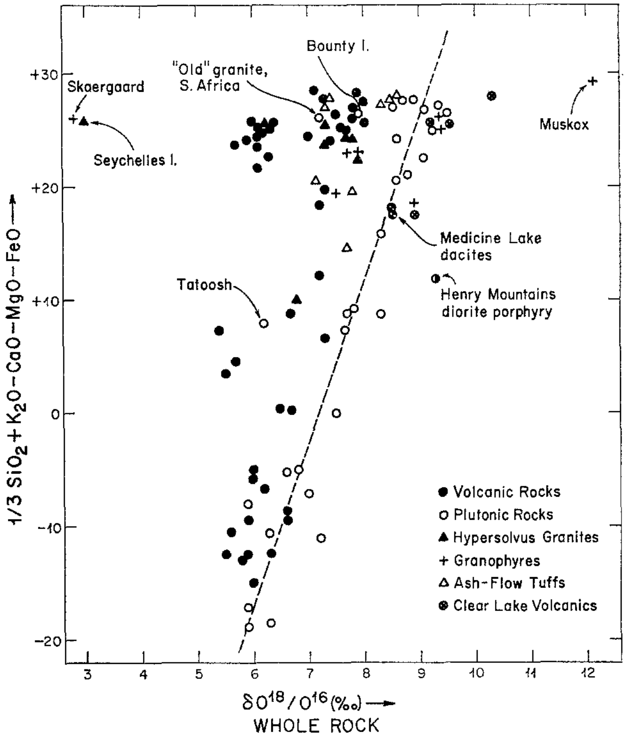

Fig. 20. Plot of O^{18}/O^{16} ratios of various igneous rocks vs. their Larsen "differentiation index" — $1/3\,SiO_2 + K_2O - FeO - CaO - MgO$ (weight per cent). In many cases the chemical analyses are on the same specimens analyzed for O^{18} content, but in other cases chemical analyses of similar samples were used. The chemical data are from a variety of literature sources. The diagonal dashed line is drawn through the data-points for plutonic rocks (open circles), and is similar in position to the line for the Southern California batholith drawn by Taylor and Epstein (1962b). Volcanic rocks in general show a much smaller δ-value at a given Larsen index than do plutonic rocks, but the differences are negligible for Larsen values lower than —5 (i.e., for basalts and gabbros)

It may be that the so-called "differentiation trends" such as those in Fig. 14 are not the result of fractional crystallization. However, in certain situations this seems to be the only feasible mechanism that could produce marked enrichment in SiO_2 and alkalies without any changes in O^{18}/O^{16} ratio (e.g., Newberry, Easter Island, older Medicine Lake, etc.); therefore, the existence of a good correlation between the trends in Fig. 14 and O^{18}/O^{16} ratios suggests that such a mechanism has to be strongly considered for all.

The correlation of low O^{18}/O^{16} ratios with trends following high Fe/Mg curves is consistent with the concept that oxygen fugacity may strongly influence the path of magmatic differentiation. The position of magnetite in a given sequence of crystallization is considered to be an important control on whether a ferrogabbro or a calc-alkaline type of differentiation occurs (OSBORN, 1962). Because magnetite has by far the lowest O^{18} content of the common igneous minerals, changes in its crystallization behavior can also affect the oxygen isotopic changes that occur during differentiation. Although only qualitative statements can be made at present, it is clear that abundant precipitation of early magnetite (favored by high f_{O_2}) should produce both O^{18}-enrichment and Fe-depletion in later differentiates, which is exactly the correlation observed in the igneous-rock series of Fig. 14. It is still an open question, however, as to whether a strong ferrogabbro trend actually can lead to a marked O^{18}-depletion in the later differentiates. Such an effect is observed in the Skaergaard intrusion, but as we have pointed out above, the O^{18}-depletion there may be a result of interaction with meteoric waters.

Fractional Melting

Even though the oxygen isotopic differences between various "granitic" igneous rocks probably are explicable in terms of differing paths of fractional crystallization, it is at least equally probable that they reflect a much more fundamental difference in mode of origin. The H-Group granitic rocks may have high O^{18}/O^{16} ratios because they ultimately originate from O^{18}-rich sedimentary rocks. The oxygen isotope data readily permit plutonic granites and ash-flow tuffs to be derived by partial melting of eugeosynclinal sediments or metasediments. However, they do place certain restrictions on such hypotheses, because the great abundance of granitic rocks in the H-Group could not have been brought about by simple melting of the above rock types. Closed-system melting of metasedimentary rocks ought to produce a wide spectrum of isotopic compositions from about $\delta = 9$ to 15, whereas in fact there is a marked concentration at $\delta = 8$ to 10. Thus, melting must occur in conjunction with exchange and homogenization of oxygen isotopes among great masses of rock at depth in an orogenic belt. Homogenization can occur through large-scale mixing of the sub-crust or upper mantle through the medium of an aqueous gas phase. The H-Group O^{18}/O^{16} ratios would then be defined by (a) mixing of the high-O^{18} geosynclinal pile with low-O^{18} basaltic material, or (b) by a rough tendency towards isotopic equilibration of the granitic magmas with basaltic material. All of the above presumably must take place at temperatures of roughly 600° to 750°C.

It is generally not seriously proposed that granitic magmas originate by partial melting in the upper mantle, but if they did, temperatures of about 1,000°C might be involved. Any eugeosynclinal sediments downbuckled into the upper mantle and able to exchange oxygen at these high temperatures with the surrounding reservoir of mafic or ultramafic rock would undoubtedly take on O^{18}/O^{16}

ratios similar to, or only slightly higher than, basalts. In other words, the oxygen isotope data permit just such an origin for the L- and I-Group obsidians and hypersolvus granites. This is unlikely on other grounds, particularly as there are no conceptual difficulties involved in accepting the derivation of relatively tiny bodies of obsidian and hypersolvus granite by fractional crystallization. It should be pointed out, however, that andesites might very well form by just such a mechanism.

The HH-Group granitic rocks are the ones most likely to have formed by simple melting of O^{18}-rich metasediments, as none of the complications outlined above need necessarily apply. For example, the muscovite granites of New Hampshire and many granitic pegmatites have very high O^{18}/O^{16} ratios compatible with such an origin. Their high muscovite contents are also suggestive of derivation from aluminous sediments. The Dome east stock from Red Lake, Ontario, also falls in this category as it is one of the granites analyzed by Shima *et al.* (1963) that shows great enrichment in S^{34}/S^{32}, indicative of an origin from sedimentary rocks.

Another item of interest is that the only subsolvus granites that have O^{18}/O^{16} ratios lower than the H-Group also have unusual geologic settings. These are the "Old" granite from South Africa and the Bounty Island granodiorite (Fig. 20). The "Old" granite is at present one of the oldest rocks known on Earth (about 3.2 b.y., Allsopp, 1961) and the Bounty Island rock is isolated from continental sialic crust at least 250 miles. It is tempting to speculate that the low O^{18}/O^{16} ratios may have resulted from the fact that these rocks originated and were emplaced in areas where there was little or no O^{18}-rich sialic crust available to raise their δ-values.

Assimilation

Assimilation of sialic crust is suggested as the reason why obsidians from the continental interior of the United States have higher O^{18}/O^{16} ratios than Pacific Coast or oceanic obsidians. This also may be the explanation why continental gabbroic rocks have slightly higher average O^{18}/O^{16} ratios than oceanic basalts. There is no way of discounting the possible existence of such assimilation in the derivation of any I-, H- or HH-Group rocks. In Particular, I-Group andesites would be very suspect in this regard. Assimilation obviously cannot have been important in L-Group rocks, however.

Any rocks that seem to have abnormally high δ-values on Fig. 20 are plausible candidates for magmatic assimilation. The Clear Lake volcanics are O^{18}-rich, and xenocrysts of sanidine are abundant in the Mt. Konocti rhyodacite (Anderson, 1936). Also, the Henry Mtns. diorite porphyry is definitely out of place on Fig. 20, and this rock is known to be contaminated with crustal material because of the abundant population of xenocrystic zircons (L. T. Silver, personal communication).

Deuteric Phenomena

Oxygen isotope analyses are one of the most convenient ways (in some cases, perhaps the only way) of establishing whether a set of coexisting minerals was formed in equilibrium. In several igneous rocks studied in the present work it is clear that coexisting quartz and feldspar and/or coexisting feldspar and pyroxene are drastically out of oxygen isotopic equilibrium. Such relationships are readily explained only if post-crystallization oxygen exchange occurred between the mineral assemblage and some transient fluid phase (presumably an H_2O-rich gas in most circumstances), with the feldspar undergoing exchange more easily than the coexisting quartz or pyroxene. This phenomenon is perfectly compatible with known laboratory exchange rates of quartz or feldspar with aqueous, alkali-bearing solutions; it must be inferred from the natural data that pyroxene is more resistant to such exchange than is feldspar.

In every rock in which isotopic disequilibrium is observed, the feldspars have an unusual appearance. They are invariably turbid or cloudy, and they may be filled with fluid inclusions. Some workers have referred to this turbidity as kaolinization, but it is not a weathering phenomenon, and in most examples it is apparent that the cloudiness is only in part caused by kaolinite or sericite. Among other constituents, the feldspars may be filled with very fine hematite dust, as in the case of the red-rock granophyres or the Bobbejaankop granite, or with fine magnetite dust, as in the the Grigadale granophyre. It is logical to assume that this turbidity is a result of the isotopic exchange process, and O'NEIL and TAYLOR (1967) have shown in laboratory studies that reactions between feldspars and alkali chloride solutions produce similar effects.

The feldspars are commonly enriched in O^{18} by this exchange process in nature, typically producing HH-Group whole-rock δ-values; the feldspar in such samples commonly has a higher δ-value than the coexisting quartz. Because of these effects, the whole-rock O^{18}/O^{16} ratios of red-rock granophyres tell us nothing about the oxygen isotope changes that occur as a result of fractional crystallization in gabbro-granophyre complexes. Any granophyre that contains turbid feldspar is automatically suspect as having undergone such exchange, and inasmuch as alkali-bearing solutions are probably involved, it is also doubtful whether the Na_2O and K_2O contents of such rocks are determined by simple crystal-melt equilibria. It is not known to what extent the bulk chemical compositions of these rocks are affected by the process that has so "disturbed" the oxygen isotopic compositions, but other workers should be wary of interpreting the chemical compositions of granophyres solely in terms of either fractional crystallization or assimilation of country rock. Perhaps other criteria may be found by which this "metasomatic" process can be more fully investigated.

Interaction with Meteoric Waters

In certain geographically well-defined samples, the phenomena just described occur with a lowering of O^{18} in the feldspar rather than an increase. This is interpreted as being due to a much lower O^{18}/O^{16} ratio in the aqueous fluid, and the only feasible source for such low-O^{18} water is rainfall or ground water. The localities in which these effects are observed, namely at the Skaergaard intrusion and in the Tertiary igneous province of western Scotland, also are abundantly represented by LL-Group igneous rocks of all types. These rocks commonly contain low-O^{18} quartz and pyroxene as well as feldspar.

We therefore conclude that many of the rocks in these localities have been contaminated or exchanged with meteoric water while they were still magmas. The geologic settings of the intrusions are compatible with this concept because they all represent shallow, sub-volcanic, emplacement into a highly jointed series of plateau lavas that almost certainly were charged with ground water at the time of intrusion. The only LL-Group igneous rock known outside the two areas mentioned above is a hypersolvus granite from the Seychelles Islands; it is conceivable that this rock also interacted with meteoric water.

CRAIG (1963) demonstrated that present-day geothermal waters throughout the world are almost wholly composed of meteoric water that has undergone an "oxygen isotopic shift" towards higher δO^{18}-values. The new data in the present paper suggest that this shift may be brought about by actual exchange between ground waters and a crystallizing magma at depth in a volcanic terrane. In situations where the ground water is abundant, it would seem that an "oxygen isotope shift" occurs in the igneous rocks as well as in the waters, but in the reverse direction.

These high-temperature interactions between igneous rocks and meteoric waters must be clearly distinguished from low-temperature hydration of volcanic glass. Perlites and hydrated obsidians have been shown to undergo pronounced changes in O^{18} content during exchange and hydration at atmospheric temperatures. The perlites appear to take on an O^{18}/O^{16} ratio approximately 25 per mil higher than their associated meteoric water, indicating that they have exchanged with a large reservoir of such water. Their hydration is *not* simply due to absorption of water, but must involve exchange between the water and the oxygen of the silicate glass.

Correlation with Lead and Strontium Isotope Studies

The oxygen isotope data on obsidians are in agreement with Sr and Pb isotope studies (HEDGE, 1966; DOE, 1967) in that they are compatible with the obsidians having been derived by fractional crystallization of basaltic magma, with some contamination by Precambrian sialic crust in those samples from the continental interior of the United States. Pacific Coast obsidians have Pb and Sr isotopic compositions very similar to oceanic basalts, as is also true of their oxygen isotopic compositions with the single exception of the Clear Lake occurrence.

HAMILTON (1966) has obtained Pb isotope data on the Skaergaard intrusion and some Scottish Hebridean granites. A number of samples from these Tertiary intrusions are anomalous in that they give model lead ages of 1,000 to 1,400 million years. HAMILTON interpreted this as indicating that the Skye granites were *complete* melts of deep crustal material. However, these anomalous samples are also the ones that have very peculiar O^{18}/O^{16} ratios, and it is likely that the influx and exchange between the magmas and superheated meteoric water may be the explanation of the unusual Pb isotope ratios. Lead is a trace element largely confined to the feldspars; inasmuch as oxygen in feldspars of the Skye granites has commonly been exchanged, it is not unreasonable that the Pb would also be exchanged even though the concentration of Pb in these waters was probably very low.

It can hardly be a coincidence that a contact-metamorphic galena from the Beinn an Dubhaich granite is one of the few samples analyzed by HAMILTON (1966) that has a "normal" Tertiary Pb isotopic composition, as this granite is the only

Skye granite in the present study that has a "normal" O^{18}/O^{16} ratio. Also, several pitchstones from Skye have almost "normal" Pb values, and the data of DOE (1967) indicate that low-temperature hydration of volcanic glass apparently does not drastically alter the Pb isotopic composition of the glass. Therefore, it is plausible that the Pb isotopic compositions of the pitchstones and the galena may be more representative of the original magmatic Pb in the Scottish Tertiary igneous rocks than is the Pb in the isotopically exchanged epigranites. We should also note that the fayalite ferrogabbro of the Skaergaard intrusion contains Pb that is not at all typical of Tertiary basalt magma, and this also may have resulted by contamination with meteoric water. We must be very cautious in concluding that *any* chemical analyses on these intrusions represent primary, magmatic values.

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