

OXYGEN AND HYDROGEN ISOTOPE STUDIES OF THE SERPENTINIZATION OF ULTRAMAFIC ROCKS IN OCEANIC ENVIRONMENTS AND CONTINENTAL OPHIOLITE COMPLEXES†

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ABSTRACT. Oxygen and hydrogen isotopic analyses have been obtained on 19 oceanic chrysotiles and lizardites and 1 oceanic antigorite from dredge-hauls at three locations along the Mid-Atlantic Ridge (43°N, 1°N, and 22°S), the Puerto Rican Trench, and the Blanco Fracture Zone in the Pacific Ocean. Lizardite-chrysotile serpentines were also analyzed from continental ophiolite bodies at Vourinos, Greece (10 samples); San Luis Obispo, Calif. (16); Del Puerto, Calif. (4); Wilbur Springs, Calif. (1); Stonyford, Calif. (3); Canyon Mtn., Oreg. (3); and New Caledonia (3); in addition to 3 antigorites from Del Puerto. There is typically a wide variation in δO^{18} in a single ophiolite complex; the lowest δO^{18} values tend to occur in the interior, partially serpentinized portions of the ultramafic body. The isotopic compositions of the oceanic and continental lizardite-chrysotile fall in different ranges (Oceanic: $\delta\text{D} = -35$ to -68 , $\delta\text{O}^{18} = +0.8$ to $+6.7$; Vourinos: $\delta\text{D} = -88$ to -114 , $\delta\text{O}^{18} = +2.1$ to $+12.7$; San Luis Obispo: $\delta\text{D} = -82$ to -91 , $\delta\text{O}^{18} = +3.8$ to $+9.3$; other ophiolites: $\delta\text{D} = -80$ to -149 , $\delta\text{O}^{18} = +6.3$ to $+9.2$). Therefore, different types of waters must be involved in the serpentinization of ophiolitic and oceanic ultramafic rocks. Heated ocean water, perhaps mixed with some magmatic water, is apparently responsible for submarine serpentinization. Most of the lizardite-chrysotile in continental ophiolites probably formed from hot, exchanged meteoric ground waters, mixed meteoric-magmatic waters, and/or mixed meteoric-connate waters; the small quantities of antigorite in these bodies apparently form in the presence of non-meteoric metamorphic waters. The isotopic evidence strongly suggests that most of the serpentine in ophiolite complexes was not originally formed from ocean water. Some of the O^{18} -depleted serpentines in the Vourinos and San Luis Obispo complexes can conceivably be interpreted as having formed in this manner, but if so, *all* these serpentines must have later undergone essentially total D/H exchange with other types of waters. Thus, if ophiolite complexes truly represent exposures of oceanic crust and mantle, they probably were largely unserpentinized prior to their emplacement on land.

INTRODUCTION

The purpose of this study is to investigate the D/H and $\text{O}^{18}/\text{O}^{16}$ values of serpentine samples dredged from various oceanic environments and to compare these results with those obtained on serpentines from well-documented ophiolite complexes. This can provide a unique method of examining the origin of the waters involved in the serpentinization of such ultramafic rocks. Except for one sample from St. Paul's Rocks ($\delta\text{D} = -39$, $\delta\text{O}^{18} = +6.3$, Sheppard and Epstein, 1970, serpentine type not reported) and a serpentinite dredged from the Mid-Atlantic Ridge ($\delta\text{D} = -60$, $\delta\text{O}^{18} = +4.6$, Epstein, 1966, quoted in Taylor, 1967a) no previous δO^{18} or δD analyses have been made on oceanic serpentines.

In an earlier paper (Wenner and Taylor, 1971) on the temperatures of serpentinization of ultramafic rocks based on $\text{O}^{18}/\text{O}^{16}$ fractionation between coexisting serpentine and magnetite, we tentatively concluded that lizardite-chrysotile serpentinization of alpine ultramafic rocks com-

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monly occurs at about 100°C. However, somewhat higher temperatures were indicated for oceanic samples (125°C for one lizardite, 180°C for one chrysotile sample), and antigorite serpentinization apparently occurs at markedly higher temperatures (220° to 460°C).

The presence of large amounts of serpentinized ultramafic rocks in oceanic trenches and ridges, together with the geophysical evidence suggesting that the main oceanic crust consists essentially of three distinct layers, led Hess (1955, 1965) to propose an oceanic crustal model consisting of a basal layer (layer 3) composed of serpentinized peridotite, overlain by about 1 km of basalt (layer 2) and a thin layer of sediment (layer 1). In this model, ultramafic mantle material above the 500°C isotherm is thought to be serpentinized by interaction with water rising from the deeper mantle. This layer of serpentinized peridotite is envisioned as spreading out laterally away from ridges due to mantle convection.

Although serpentinized peridotites are commonly found at mid-ocean ridge sites along with basalts, amphibolites, gabbros, and their metamorphosed equivalents (Aumento, 1970; Bowin, Nalwalk, and Hershey, 1966; Miyashiro, Shido, and Ewing, 1969), other workers (for example, Cann, 1968; Christensen, 1970; Coleman, 1971b) have questioned Hess' notion of the layer 3 composition being a uniformly serpentinized peridotite. Also, the origin of the H₂O responsible for submarine serpentinization is still a matter of controversy. Thompson and Melson (1970), measuring the boron contents of oceanic serpentines, suggested that juvenile waters had to be involved in serpentinization if metamorphism occurred at moderately high temperatures (300°–500°C). For sea water to have been involved in serpentinization, they suggest that such a process must have taken place at relatively low temperatures (< 200°C). Hess (1964), in commenting on the measured Sr⁸⁷/Sr⁸⁶ values from serpentines from the Puerto Rican Trench and St. Paul's Rocks, suggests that the serpentine samples may have been contaminated by Sr from sea water. Vdovykin and Dmitriyev (1968) examined the organic matter in unaltered to completely serpentinized peridotites dredged from the Mid-Indian Ridge and argue that the lizardite–chrysotile serpentines formed only from juvenile waters, whereas a secondary serpentine (described as antigorite, but unsupported by X-ray diffraction analyses) formed from sea water.

Ophiolite complexes consist of a sequence of ultramafic rocks successively overlain by gabbros and basalts, which are in turn overlain by radiolarian cherts or other marine sediments. Although their origin is still controversial, ophiolites are presumed by many investigators to represent on-land exposures of oceanic crust and mantle (Coleman, 1971a; Bailey, Blake, and Jones, 1970). Under such an interpretation, the gabbro-peridotite contact would represent an exhumed oceanic Moho. Therefore, it is clearly important to compare the ophiolite serpentines with oceanic serpentines.

Recently Bailey, Blake, and Jones (1970) and Page (1972) have reinterpreted as ophiolites some ultramafic rocks in California that

separate the Great Valley Sequence from the Franciscan Formation. According to Bailey, Blake, and Jones (1970), serpentine had to be in existence *prior* to the deposition of the overlying Great Valley Sequence clastic sediments and prior to the thrust faulting that was responsible for causing the ophiolite sequence to be exposed on land: some of this serpentine is found within the Great Valley Sequence (one sample from the Wilbur Springs locality in California was examined in this study).

EXPERIMENTAL TECHNIQUES

The proportions of the various serpentine minerals were semi-quantitatively determined by X-ray diffraction studies on most of the samples analyzed in this research (see table 1). The reflection peaks used for discriminating among the serpentine minerals antigorite, chrysotile, and lizardite are those given by Whittaker and Zussman (1956) and Aumento (1970). All samples were examined for minor amounts of other minerals, particularly brucite.

All serpentine mineral separates were reacted with fluorine in the temperature range of 575° to 600°C for 24 hours. Extraction of the resulting oxygen was carried out in the manner described by Taylor and Epstein (1962).

The experimental technique used in the extraction of hydrogen from serpentine is similar to that described by Friedman (1953) and Godfrey (1962). To test if all the adsorbed water in chrysotile can be removed by preliminary outgassing, a sample was placed in contact with deuterium-enriched water for 4 days. After outgassing (200°C for 2 hours) of adsorbed water, isotopic analysis of the remaining water (assumed to be structural OH) revealed negligible contamination (< 1 percent), similar to what is observed in kaolin minerals (Roy and Roy, 1957).

In addition, a series of serpentine samples of distinct mineralogy from various localities were treated using different extraction techniques and varying conditions of preliminary outgassing (Wenner, ms). None of the δD values of the samples examined varied by more than 5 per mil, while most were within the generally accepted experimental range (2–3 per mil). Therefore it is concluded that the extraction technique utilized in this study is valid.

All isotopic data are reported as δ -values in per mil relative to SMOW. Fractionations, reported in this paper as Δ , are defined as

$$\Delta \text{ serp-water} = 1000 \ln \alpha \text{ serp-water} \approx \delta \text{ serp} - \delta \text{ water}$$

The analytical error in δO^{18} is about 0.1-0.2 per mil.

SAMPLE LOCALITIES AND DESCRIPTIONS

Oceanic Serpentes

Puerto Rican Trench.—Samples of serpentine and serpentinized peridotite, together with talc, sedimentary rocks, and minor basalts were dredged from the north wall of the Puerto Rican Trench by Bowin,

TABLE 1
Summary of isotopic, mineralogic, and petrographic studies
of the oceanic serpentines studied in this work

Sample	Mineralogy*	δD^{**}	$\delta O^{18:3**}$	Petrographic description†
<i>Puerto Rican Trench</i>				
Ch 19-2-2	C	-51 ± 1	0.8 ± 0.1	S; fg iso grains (see Bowin, Nalwalk, and Hersey, 1966, p. 262)
Ch 19-10-2	C	-58	3.6 ± 0.2	S; imt > b > xf
<i>Mid-Atlantic Ridge (43°N)</i>				
All 32-8-22	C groundmass	-60	1.9 ± 0.1	S; imt > b > xf (<2mm wide)
"	C vein	-68	1.9	
All 32-8-54	A	-31 ± 2 (3)	2.0 ± 0.1	S; "picrolite" veins (<10mm wide)
All 32-8-70	C	-59	3.2 ± 0.1	S; highly fractured, imt >> xf
All 32-8-74	C	-60	2.1 ± 0.0	S; massive; amt > b > xf
All 32-8-80	C cross fiber vein	-59	6.1	S.P.; amt > b; all cross cut by xf and carb veins
"	C matrix S	-61	2.8 ± 0.2	
<i>Mid-Atlantic Ridge (1°N)</i>				
All 20-48-1	L bastite	-53	6.7	S; mt > b (<1mm)
"	L mesh texture	-55 ± 0	4.4 ± 0.0	
All 20-26-118	L	-44	4.6 ± 0.0	Mylonitized S.P.; alternating layers of S and S.P.
<i>Mid-Atlantic Ridge (22°S)</i>				
All 60-9-3	L + C bastite	-35	3.3	S; mt > b (?); b has irregular shape;
"	L + C mesh texture	-46	3.5	t xf and carb veins
All 60-9-5	L + C	-48	3.3	S; imt > b (deformed); repl of mt by fg platy S
All 60-9-7	talc > A rim	-37	3.0	highly sheared S with talc patches
"	L + C core	-55	2.6	S; mt > b > xf
All 60-9-70	C outer rim	-50	2.8 ± 0.1	S; white outer rind, highly sheared, massive
"	C inner rim	-46 ± 1	3.3	S; highly sheared xf veins
<i>Blanco Fracture Zone</i>				
1a	L	-57 ± 0	4.6	S
1b	L + C	-49 ± 2	2.4 ± 0.1 (3)	S

* Serpentine mineralogic notation: C-chrysotile, L-lizardite, A-antigorite. All major serpentine mineralogy determined by X-ray diffraction analyses.

** No \pm indicates one analysis; \pm indicates average deviation (for two separate analyses if no number in parenthesis); number in parenthesis indicates number of analyses.

† Abbreviations used in petrographic and hand specimen descriptions: S-serpentine, S.P.-serpentinized peridotite, S.D.-serpentinized dunite, carb-carbonate, opq-opaque, b-bastite, fg-fine grained, imt-isotropic mesh texture, amt-anisotropic mesh texture, mt-mesh texture, repl-replace, t-trace, xf-cross fiber, iso-isotropic.

Nalwalk, and Hersey (1966). Three types of ultramafic rocks were distinguished: one type, normal chrysotile-lizardite (Ch 19-10-2), is from the contact between serpentinized peridotite and overlying Upper Cretaceous sedimentary rocks. A second chrysotile type (Ch 19-2-2), dredged from a deeper level, has an uncommon texture consisting of small anhedral isolated grains. A third type, antigorite plus talc (not studied in this research), was dredged from the bottom of the main scarp.

Mid-Atlantic Ridge (43°N).—Serpentine samples dredged from the Mid-Atlantic Ridge near 43°N lat are described by Phillips and others (1969). Five samples were analyzed from a 200 kg dredge haul made up only of serpentinized peridotite.

Mid-Atlantic Ridge (1°N).—Serpentine samples were dredged at 0°56'N, 29°22'W, depth 2380 to 1660 m, near St. Paul's Rocks; the latter are largely spinel-peridotite mylonite and hornblende mylonite (Melson and others, 1967). One of the analyzed samples is a completely serpentinized peridotite with normal, relatively undeformed texture (All 20-48-1). The other (All 20-26-118) is a banded serpentinite-peridotite mylonite.

Mid-Atlantic Ridge (22°S).—Samples from this locality were dredged from a fracture zone along the Mid-Atlantic Ridge at 21°56'S, 11° 48'W at a depth between 2770 to 3400 m. Two of the samples (All 60-9-3 and All 60-9-5) represent "normal" mesh texture-bastite serpentinite, whereas another (All 60-9-7) contains an outer rind of talc.

Blanco Fracture Zone.—Two small serpentinite pebbles from a depth of 3600 m were collected from the Blanco Fracture Zone, an east-trending lineament located in the Pacific Ocean 300 km off the coast of Oregon.

Ophiolite Complexes

Vourinos, Greece.—The Vourinos Complex in northern Greece (Moore, 1969) is a type-example of the classic "ophiolite suite". It lies along the boundary between the Pelagonian Massif (largely marble) and the younger Meso-Hellenic sediments; some 40 km to the southwest is the Pindos ophiolite complex.

According to Moore (1969), the Vourinos Complex was originally emplaced into Lower Jurassic (?) sediments and then covered unconformably by Cretaceous limestone; later the area was involved in a Tertiary (?) regional metamorphism and orogeny. The complex consists dominantly of layered and complexly folded ultramafic rocks, along with smaller amounts of gabbro, diorite, quartz diorite, and pillow lavas (see fig. 1).

Serpentine has the following modes of occurrence in the Vourinos Complex.

1. It occurs throughout the complex as a partial alteration of the primary minerals of the ultramafic zone (samples 43a, 70c, 683a, 685a) and of the ultramafic-gabbro transition zone (sample 590a).

2. A massive to schistose basal serpentinite unit, containing inclusions of marble, peridotite, and rodingite, is shown on figure 1 as a separate mappable unit 100 m to 1 km wide. One serpentinite sample (3c) from this unit was examined, as well as one of the partially serpentinitized peridotite inclusions (522b).

3. Serpentinite (represented by sample 225a) occurs in relatively narrow east-trending bodies in the ultramafic zone; some of these grade into the basal serpentinite.

4. Massive serpentinite (represented by sample 188a) occurs near the upper parts of the ultramafic zone and is shown as a mappable unit in figure 1.

5. Serpentinite (11a) also occurs as a breccia in which about 50 percent of the clasts are derived from the local ultramafic rock.

Moore's (1969) suggests that serpentine may have formed in two distinct episodes. The basal serpentinite is presumed to have formed during Jurassic emplacement of the hot, nearly solid ultramafic body in a submarine environment. At a later period, perhaps during Tertiary (?) metamorphism, the serpentine breccias and perhaps the east-trending

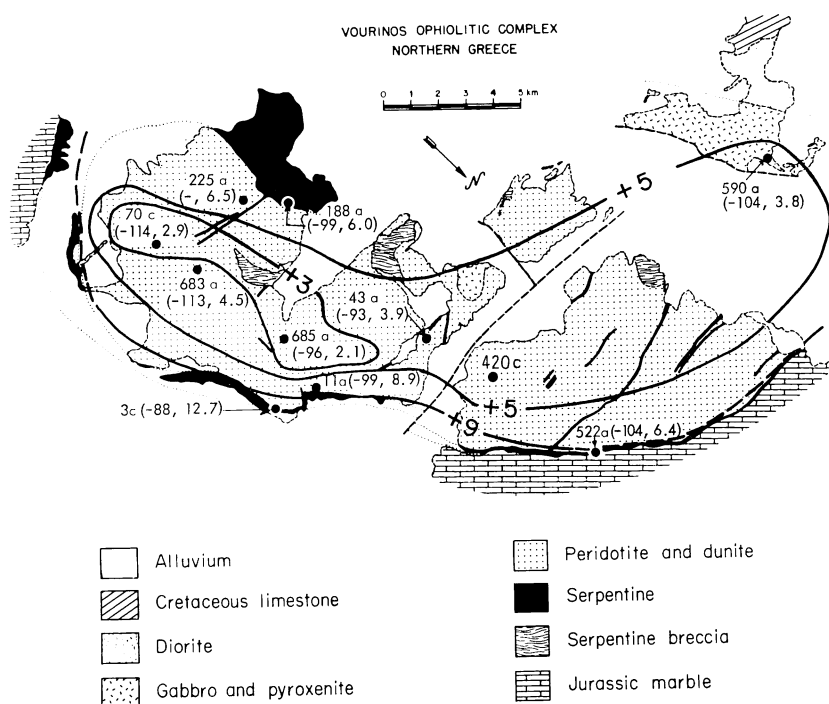


Fig. 1. Geologic map of the Vourinos Complex, Greece (modified after Moore's, 1969) showing sample localities and isotope data for serpentinite (all lizardite-chrysotile). Notation: sample no., (δD , δO^{18}). Generalized δO^{18} contours have been drawn on the map to illustrate the lower δO^{18} values of the partially serpentinitized samples from the interior of the intrusion as well as the O^{18} -enrichment of the basal serpentinite.

serpentine and part of the basal serpentinite may have formed as a result of gas explosions involving aqueous fluids, perhaps derived from underlying sediments.

San Luis Obispo, Calif.—Five serpentine samples were collected from the ophiolite complex described by Page (1972). The locations of the samples are shown in figure 2. Two of these (SL-27-3, SL-27-4) are from the dark zones which border the prominent 1.5 m thick diabase dike shown in figure 4 of Page (1972). These dikes are interpreted by Page (1972) as “feeders” to the overlying volcanic unit of the ophiolite complex, and the field relations suggest that the contact serpentinization may have occurred during cooling of the dikes.

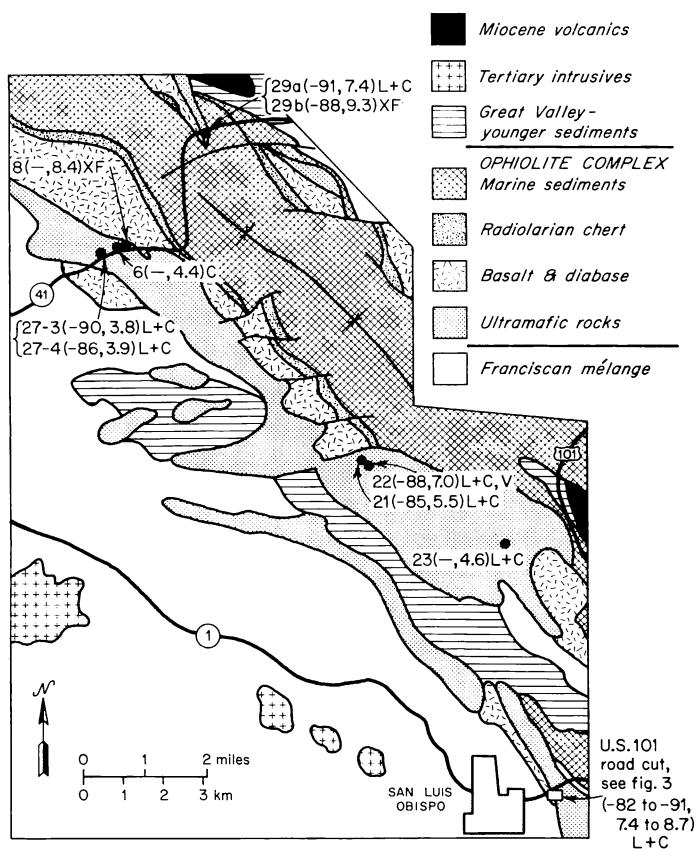


Fig. 2. Geological map of the San Luis Obispo ophiolite complex (modified after Page, 1972, and Jennings, 1958) showing SL sample localities and isotope data for serpentine. Notation: sample no., (δD , δO^{18}); mineralogy: L = lizardite, C = chrysotile, XF = cross fiber vein, V = vein. The Highway 101 roadcut and locality 29 are both completely serpentinized; the other samples are from partially serpentinized peridotite. SL-27-3 is 15 cm and SL-27-4 is 30 cm from the contact of a 1.5 m thick diabase dike.

Six serpentinite samples were also collected for isotopic analysis from a small roadcut exposure that transects the contact of an elongate, 14 km long body of serpentinite, just north of San Luis Obispo (fig. 3). This body is apparently a continuation along strike of the ophiolite complex delineated by Page (1972); it is similar to the numerous highly sheared, completely serpentinized masses that occur in the Franciscan melange (Hsu, 1968).

Del Puerto, Calif.—The ultramafic rocks of the Del Puerto (Mt. Boardman) area are considered by Bailey, Blake, and Jones (1970) to be part of an ophiolite succession; a major thrust fault is thought to separate the ophiolite-Great Valley Sequence rocks from the coeval eugeosynclinal rocks of the Franciscan Formation. This represents a major reinterpretation of the geologic setting as discussed by Maddock (1964) and as illustrated in figure 4. Serpentinization is extensive along the margins, whereas the main part of the ultramafic body shows only partial alteration; this serpentinization may have occurred after final emplacement of the ultramafic rocks, but prior to folding (Saad, 1969).

Wilbur Springs, Calif.—Although some of the serpentinized ultramafic rocks of the Wilbur Springs area form part of an ophiolite succession (Bailey, Blake, and Jones, 1970), the one sample examined in this study was selected from a sedimentary serpentinite unit within the Great Valley Sequence (part of ds_2 unit shown in fig. 1, p. 172, by Moiseyev, 1968).

Stonyford, Calif.—The serpentinized ultramafic rocks of the Stonyford area (Brown, 1964) are also considered by Bailey, Blake, and Jones (1970) to be part of an ophiolite complex. Two of the samples (47, 50) (~ 5 km north and ~ 6 km west of Stonyford, respectively) are from within a few meters of the Stony Creek Fault zone. One sample was collected within the interior part of the ultramafic mass about 2 km

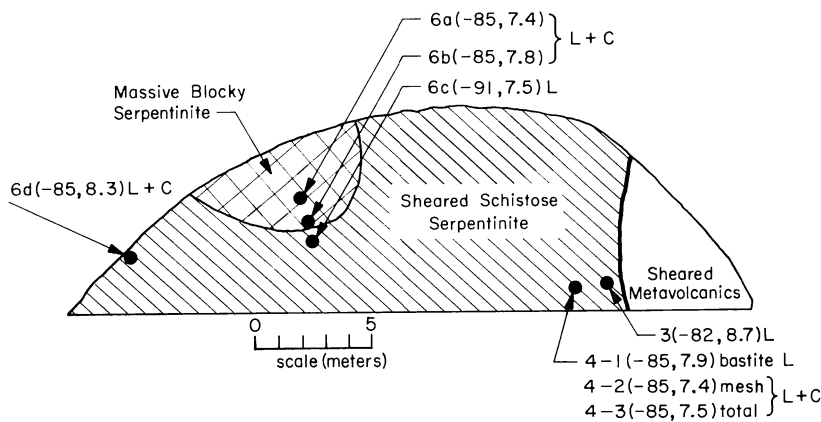


Fig. 3. Field sketch (vertical) of a large road cut in serpentinite on the southeast side of U.S. Highway 101 just north of the city limits of San Luis Obispo, Calif. (see fig. 2 for exact location). Notation: sample no., (δD , δO^{18}); mineralogy: L = lizardite, C = chrysotile.

from Stony Creek Fault (along Goat Mtn., see Brown, 1964). All were collected from highly sheared serpentinite bodies.

Canyon Mountain, Oreg.—This ultramafic body has many features in common with other ophiolite complexes (Coleman, 1971a); the rock types range from alpine peridotites and gabbroic rocks to albite granites (Thayer and Himmelberg, 1968). Three samples were selected from highly sheared and serpentinized portions of the ultramafic units of the complex along U.S. 395 south of Byron Gulch.

New Caledonia.—The New Caledonia ophiolite mass is thought to have been emplaced by thrusting of oceanic crust onto the land mass of New Caledonia during Oligocene time (Coleman, 1971a). Three analyzed serpentinite samples are from different localities within the ultramafic part of this ophiolite mass; sample 81-NC-62 is from a serpentinite mass in peridotite just below Yate's dam in the southeastern part of the island (22°S lat). Sample 66-NC-62c is part of a sheared serpentinite body occurring in low grade metamorphic rocks in the central region of the island near Devaud Station (21°15'S lat). Serpentinite sample 60-NC-62 is associated with chromite within the Tiebaghi Chrome mine in the northwestern part of the island (20°30'S lat).

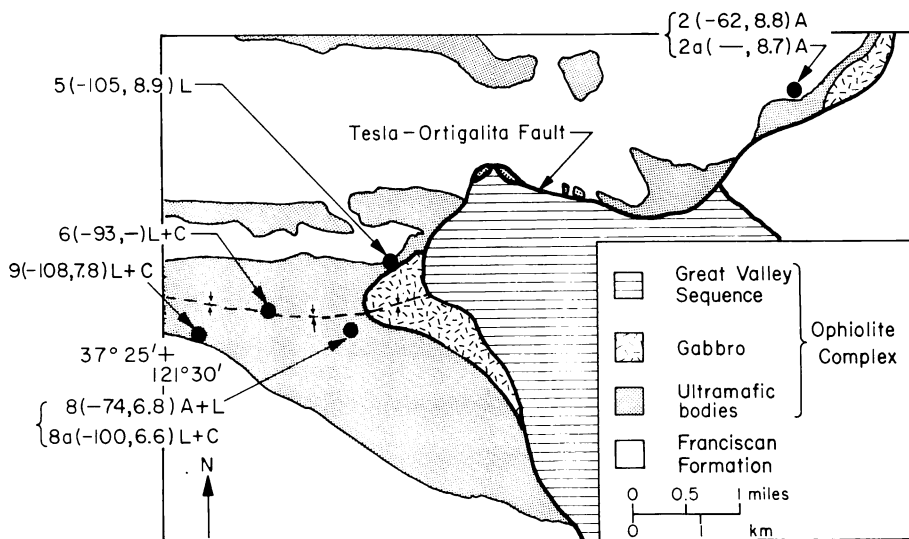


Fig. 4. Geologic map of the Del Puerto (Mt. Boardman) ultramafic body and vicinity, California (after Maddock, 1964), showing sample localities and isotope data. According to the interpretation of Bailey, Blake, and Jones (1970), ultramafic rocks, gabbro, and lower sections of the Great Valley sequence form an ophiolite suite. According to this view, the main ultramafic mass is separated from the Franciscan Formation by a major fault zone, referred to as the Coast Range Thrust, and the Tesla-Ortigalita fault would be a less important feature. Notation: sample no., (δD , δO^{18}); serpentinite mineralogy: A = antigorite, L = lizardite, C = chrysotile. Note that samples 6, 9, and 8a are partially serpentinized dunites; the other samples are all serpentinites, with sample 8 representing a serpentine breccia in a dolomite matrix.

TABLE 2

Summary of isotopic, mineralogic, and petrographic studies of the serpentinite samples from the ophiolite complexes studied in this work**

Sample	Mineralogy	δD	δO^{18}	Petrographic description
<i>New Caledonia</i>				
81-NC-62	L + C*	-84 ± 1	9.0 ± 0.0	S.P.; amt; slight repl orthopyroxene
66-NC-62c	L + C	- 88	7.3	S; amt > b > xf
60-NC-62	L + C*	—	8.5 ± 0.0	S; (layered)
<i>Wilbur Springs</i>				
1	C	- 98	9.2	S; highly deformed b in matrix of fg platy S; possible S breccia
<i>Stonyford</i>				
47	L + C*	-80 ± 1	7.4 ± 0.2	S; amt > b; xf
50	L + C*	-104	7.4 ± 0.1	S; amt > b
52	L + C*	- 99	9.0	S; amt > b; xf
<i>Canyon Mountain</i>				
18	L + C*	-147	8.2	S; amt
24	L + C*	-149	—	S; amt > xf associated with opq veins
27	L + C*	-130	6.3	S; amt > b; xf

* Serpentine mineralogy determined by petrographic examination only.

** See figures 1, 2, 3, and 4 for the data on the Del Puerto, San Luis Obispo, and Vourinos bodies and table 1 footnotes for description of notation.

ANALYTICAL RESULTS

The isotopic, mineralogic, and petrographic data for the oceanic serpentines are summarized in table 1, and those of the ophiolite complexes in table 2 and figures 1, 2, 3, and 4. The isotopic data are plotted on δD - δO^{18} diagrams in figures 5 and 6.

A simplifying feature of the present study is the fact that the δO^{18} values of primary pyroxenes and olivines from unserpentinized ultramafic bodies are so uniform, irrespective of petrologic type (Taylor and Epstein, 1962; Reuter, Epstein, and Taylor, 1965; and Taylor, 1968). However, no previous δO^{18} analyses of primary ultramafic minerals from oceanic peridotites or ophiolite complexes are reported in the literature. Therefore, we analyzed a few pyroxenes (table 3) from the Vourinos

TABLE 3

Oxygen isotope analyses of pyroxenes from ultramafic rocks

Sample	δO^{18} (‰)
Orthopyroxene, All 42-2-14, Mid-Atlantic Ridge, 3°50' S	+6.3
Orthopyroxene, Vourinos VC 420c*	+6.3
Clinopyroxene, Vourinos VC 590a	+5.8
Average of 3 samples (Taylor and Epstein, 1962)	+6.1
Average of 8 samples (Taylor, 1968)	+5.8

* This sample contains late-stage dolomite veins with $\delta O^{18} = +26.0$, probably indicating deposition by the same types of aqueous solutions that were responsible for the high- O^{18} basal serpentinites.

complex and from a submarine dredge-haul obtained at 3°50'S at a depth of 3570 m on the Mid-Atlantic Ridge (Thompson, Melson, and Bowen, 1969). Note that these ophiolitic and oceanic pyroxenes are isotopically indistinguishable from the pyroxenes of other ultramafic bodies. Therefore, it seems safe to assume that, prior to serpentinization, the ultramafic rocks studied in the present research all had essentially "normal" δO^{18} values of about +5 to +6.

Isotopic Temperatures of Serpentinization

In order to calculate the isotopic composition of the waters that may have been in equilibrium with the various serpentines studied in this research, it is necessary first to estimate the temperatures of serpentinization. Such estimates have been made on a few of the same samples analyzed in this work, based on measured O^{18}/O^{16} fractionations between coexisting serpentine and magnetite (Wenner and Taylor, 1971). These temperature estimates are: 235°C for antigorite sample All 32-8-54 (Mid-Atlantic Ridge, 43°N, #54), 180°C for chrysotile sample All 32-8-70 (Mid-Atlantic Ridge, 43°N, #70), 125°C for lizardite sample All 20-26-118 (Mid-Atlantic Ridge, 1°N, #118), 85°C for lizardite sample 6c from the San Luis Obispo body, and 225°C for antigorite sample 2a from the Del Puerto body.

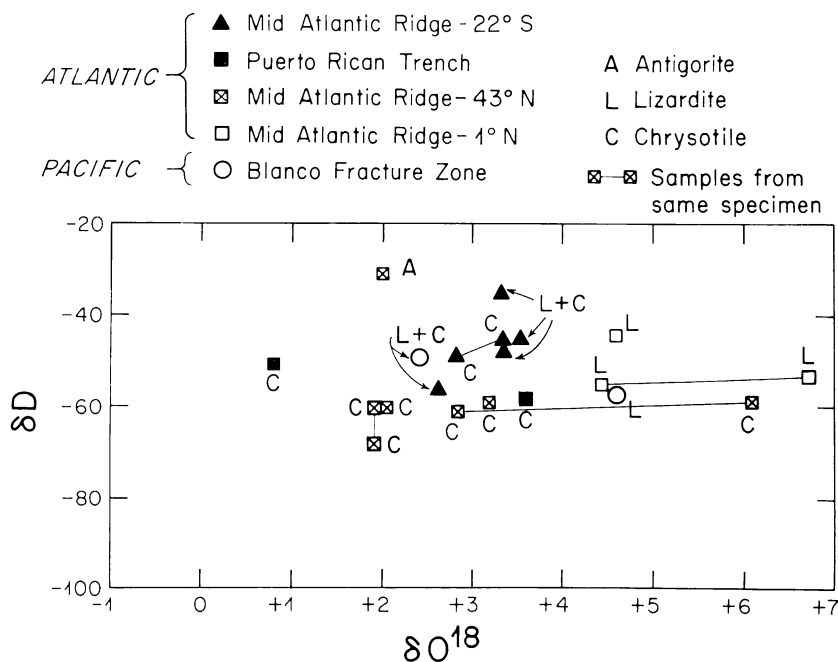


Fig. 5. Isotopic compositions of all oceanic serpentine samples examined in this study. Tie lines connect separately analyzed textural components from the same specimen.

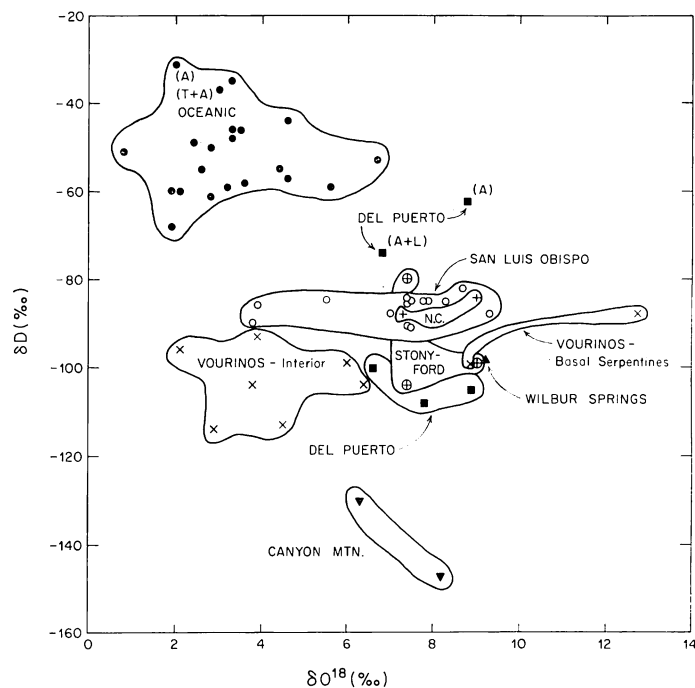


Fig. 6. δD - δO^{18} diagram showing the isotopic compositions of all oceanic and ophiolite serpentine samples examined in this study. The oceanic samples are all lizardites and/or chrysotiles, except for two samples labelled A (antigorite) and T + A (talc + antigorite). All the ophiolite serpentines consist of lizardite-chrysotile except two samples from Del Puerto (A and A + L), which are, respectively, antigorite and antigorite + lizardite. Note that the isotopic compositions of the ophiolite serpentines are clearly distinct from those of the oceanic samples. N.C. = New Caledonia.

We shall, for purposes of discussion only, assume that the oceanic samples for which no O^{18}/O^{16} temperatures were obtained also formed at temperatures similar to the 3 analyzed samples of Wenner and Taylor (1971), (that is, antigorite $\sim 235^\circ\text{C}$, chrysotile $\sim 180^\circ\text{C}$, lizardite $\sim 125^\circ\text{C}$, mixture of lizardite and chrysotile $\sim 155^\circ\text{C}$). All lizardite-chrysotile serpentines from the ophiolite complexes are arbitrarily assumed to have formed at either 100° or 200°C , similar to the range of isotopic temperatures measured for lizardite-chrysotile serpentines by Wenner and Taylor (1971). As will be pointed out below, within the limits of about 50° to 300°C , most of the arguments presented in this paper are qualitatively valid irrespective of the exact temperatures at which serpentinization occurs.

Tentative Equilibrium-Fractionation Curves for Serpentine-Water

Although no direct laboratory calibrations of the system serpentine-water have yet been made, it is possible to estimate the temperature dependency of the O^{18}/O^{16} fractionation, using the relationship ΔO^{18} serpentine-water $\approx 1.56 (10^6/T^2) - 4.70$, (Wenner and Taylor, 1971, p.

177). With this, we can then estimate roughly the oxygen isotopic composition of waters that are assumed to have been in equilibrium with the serpentines discussed in this paper. For example, from the above relationship, we obtain $\Delta O^{18} = 6.5$ at 100°C , 5.1 at 125°C , 3.8 at 155°C , 2.9 at 180°C , 2.3 at 200°C , and 1.3 at 235°C .

The tentative D/H fractionation curve for serpentine-water given in figure 7 is estimated from the following:

1. The serpentine-water fractionation at very low temperature is based on the δD values of deweylite, a serpentine-like mineral structurally similar to antigorite (Lapham, 1961). This Pennsylvania deweylite, found as a surficial coating on open fractures in serpentinite, appears to be of secondary supergene origin. It is assumed to have equilibrated with present-day, local meteoric waters, giving a ΔD value of approximately -56 at 20° to 30°C (Wenner, ms).

2. Assuming that the antigorite sample All 32-8-54 formed in equilibrium with pure ocean water and that its δD value was "frozen in" at nearly the same temperature as its δO^{18} value, we obtain a ΔD serpentine-water of about -31 at 235°C .

3. It is assumed that lizardite sample All 20-26-118 also formed by reaction with ocean water, giving an approximate ΔD serpentine-water of -45 at 125°C .

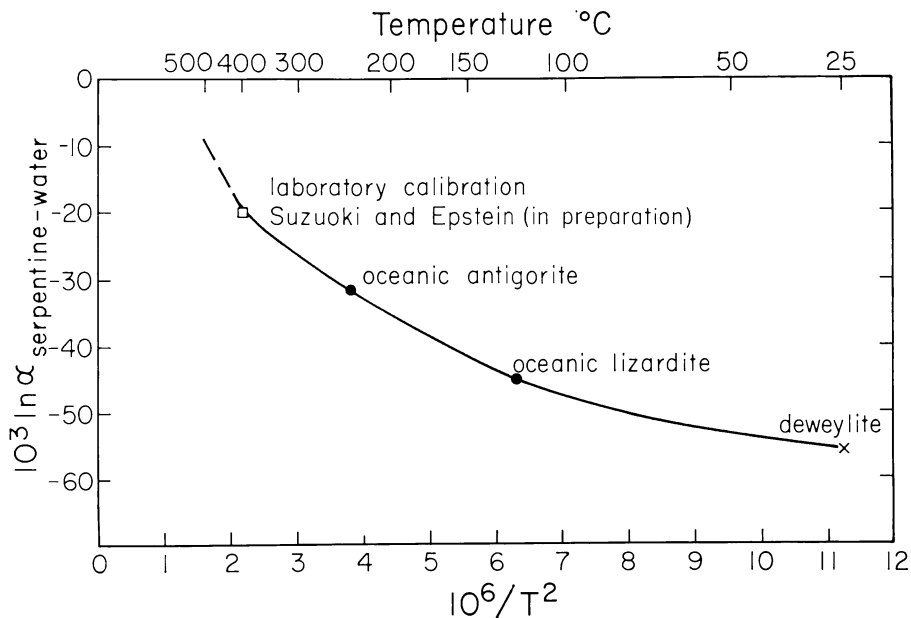


Fig. 7. Estimated D/H serpentine-water geothermometer based on a tentative laboratory measurement at 400°C by Suzuoki and Epstein (in preparation) and the δD analyses of 3 natural samples (see text).

4. From exchange experiments, Suzuoki and Epstein (in preparation) estimated a ΔD serpentine-water of -20 at 400°C .

Although these 4 different serpentine-water fractionations are certainly tentative, they produce a systematic fractionation curve that shows an increase of ΔD with decreasing temperatures (fig. 7); this is theoretically the most likely trend, thus giving general support to the validity of the assumptions. Based on these relationships, ΔD values of -48 , -41 , -38 , and -36 per mil are obtained for serpentine-water at 100° , 155° , 180° , and 200°C , respectively.

Considerations of Variable Water/Rock Ratios

In determining the origin of the waters involved in serpentinization, we are more interested in the isotopic composition of the H_2O prior to its entry into the ultramafic body than after it has undergone exchange. The two values will be the same only if the serpentine has equilibrated with an *infinite* reservoir of water. The quantity of water that can circulate through an ultramafic body undergoing serpentinization is restricted, particularly because the serpentinization reaction probably involves volume expansion; completely serpentinized ultramafic bodies may be relatively impermeable to circulating waters. We must therefore consider the problem of varying the water/rock ratio during serpentinization.

The relative proportions of exchanging water to exchanging silicate can be estimated using a closed-system model of the type employed by Sheppard, Nielsen, and Taylor (1969). This model considers a system initially composed of r atom percent of exchangeable silicate oxygen and w atom percent of water oxygen. Thus, to a close approximation, ignoring any water used up during the reaction, we have:

$$\text{Initially: } r \delta_{\text{si}} + w \delta_{\text{wi}} = Z$$

$$\text{Finally: } r \delta_{\text{sf}} + w \delta_{\text{wf}} = Z$$

where δ_{si} = initial isotopic composition of silicates

δ_{sf} = final

δ_{wi} = initial isotopic composition of water

δ_{wf} = final

Z = constant for the system

$$\text{Then: } \frac{\delta_{\text{si}} - \delta_{\text{sf}}}{\delta_{\text{wf}} - \delta_{\text{wi}}} = \frac{w}{r}$$

Such a model can be used to set a minimum limit on the relative proportions of fluid to exchanged silicate.

In this model, we assume attainment of isotopic equilibrium and that δ_{si} is olivine with a $\delta\text{O}^{18} = +5.0$ per mil. Then, δ_{sf} is the measured δO^{18} value of the serpentine, and δ_{wf} is the δO^{18} value of the water in equilibrium. In this treatment, various values of w/r are assumed, and δ_{wi} is calculated. The lower limit of w/r is obviously controlled by the stoichiometric content of H_2O in serpentine, because at least this much water had to enter the system. For the ideal serpentine composition $w/r = 2/7 = 0.285$.

Serpentinization of Ultramafic Rocks in a Submarine Environment

The isotope data for the various oceanic serpentine samples given in figure 5 indicate the following:

1. The δD and δO^{18} values of the oceanic serpentinites form a distinct grouping different from all other types of serpentines analyzed to date (see figs. 6 and 8). The δD values, in particular, are very heavy and fairly restricted ($\delta D = -31$ to -68), and the δO^{18} values are generally lighter than most continental serpentinites.

2. The various textural and mineralogic types tend to have distinctly different δO^{18} and δD values. For example, in sample All 20-48-1, the bastites (lizardite) are 2.3 per mil heavier in δO^{18} than in the mesh-texture type (lizardite, minor chrysotile), although both have similar δD values. In sample All 32-8-22, the mesh-texture material and a cross-cutting vein (both chrysotile) have identical δO^{18} values but differ in

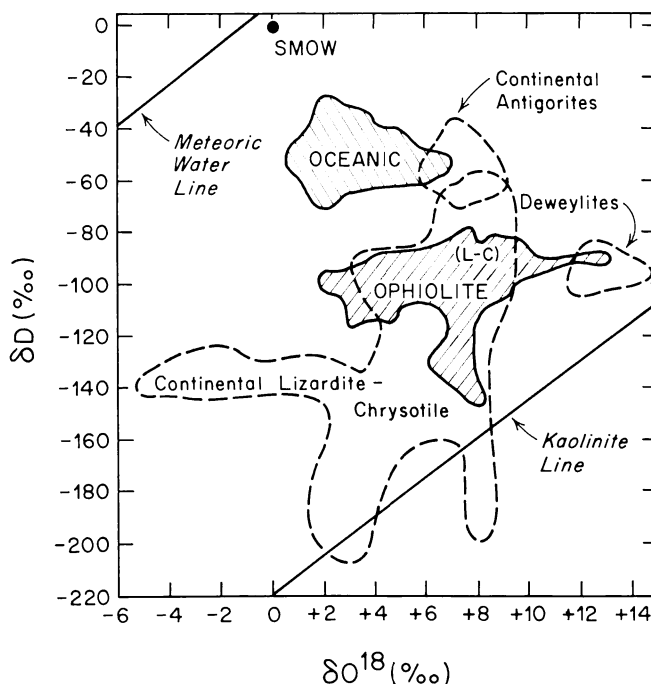


Fig. 8. δD - δO^{18} diagram comparing the oceanic and ophiolite serpentinites from figure 6 with all other serpentinites examined to date (Wenner and Taylor, 1969; Wenner, ms). The positions of the latter serpentinites are encircled and include many samples of alpine serpentinites from North America and the Caribbean area, as well as serpentinized ultramafic igneous bodies from Southeast Alaska, the Ural Mountains, and Quebec. The analyses of the low-temperature serpentine-like mineral deweylite are also delineated. The position of the meteoric water line, standard mean ocean water, and the kaolinite line of Savin and Epstein (1970) are shown for reference. L-C = lizardite-chrysotile. Note that the oceanic serpentinites are clearly distinct from all other serpentinites, particularly the continental lizardite-chrysotile samples.

δD by 8 per mil. Conceivably, these effects could be due to non-equilibrium, but more likely they simply represent various stages of serpentinization in which the temperatures and/or isotopic compositions of the waters were different.

3. There is no marked correlation between the isotopic compositions and geographic locations. However, 6 different chrysotile samples from a single dredge haul from the Mid-Atlantic Ridge ($43^{\circ}N$) have uniform δD values of -59 to -68 that are lower than at any other oceanic site. The Mid-Atlantic $22^{\circ}S$ samples also fall within a relatively narrow isotopic range ($\delta O^{18} = +2.6$ to $+3.5$; $\delta D = -35$ to -55), as do 3 lizardite samples from the Mid-Atlantic $1^{\circ}N$ locality ($\delta O^{18} = +4.4$ to $+6.7$; $\delta D = -44$ to -55).

4. A sample of pure antigorite (All 32-8-54) is distinct in its hydrogen and oxygen isotopic composition ($\delta D = -32$; $\delta O^{18} = +2.0$) from all the other oceanic serpentine samples as well as all continental samples.

5. The serpentine δO^{18} values range from $+0.8$ to $+6.8$ per mil, and the most O^{18} -depleted sample has a very unusual texture that is distinct from all other known oceanic serpentines (see Bowin, Nalwalk, and Hersey, 1966). Except for a single cross-fiber vein, the chrysotile-rich samples are all O^{18} -depleted relative to the lizardite-rich samples. If all these serpentines formed from the same kind of water, the chrysotiles *must* have formed at significantly higher temperatures than the lizardites.

Utilizing the serpentine-water isotopic fractionation curves discussed previously, we can estimate the isotopic compositions of waters that initially entered the oceanic ultramafic-rock systems; these calculated waters are given for water/rock (w/r) ratios of unity and infinity in figure 9.

For one of the samples (antigorite sample #54) additional water/rock ratios of 0.6, 2, 5, and 10 are shown to facilitate comparison. Note the δO^{18} values of a calculated water for a w/r value of 2 lies roughly intermediate between the δO^{18} values for unity and infinity; this is approximately true for all other samples illustrated in figure 9 as well. Furthermore, for w/r values higher than 2, the calculated water rapidly approaches that for infinite w/r ratios; with water/rock ratios greater than about 5, the effects are virtually indistinguishable from w/r = ∞ .

The importance of ocean water in submarine serpentinization is clearly shown in figure 9. Excluding 2 samples with $\delta O^{18} = +1.6$ and $+3.2$, the total range in δO^{18} for 18 calculated (w/r = ∞) waters is remarkably uniform (-2.1 to $+0.7$, mean = -0.5). The calculated δD values of the waters also cluster near the ocean water δD value but tend to be somewhat lower in deuterium than ocean water. Ocean waters and coastal and island meteoric waters are the only common waters known to have isotopic compositions in the range given in figure 9, and meteoric waters would not have access to ultramafic rocks in a submarine environment. The water/rock ratio for most of the oceanic ser-

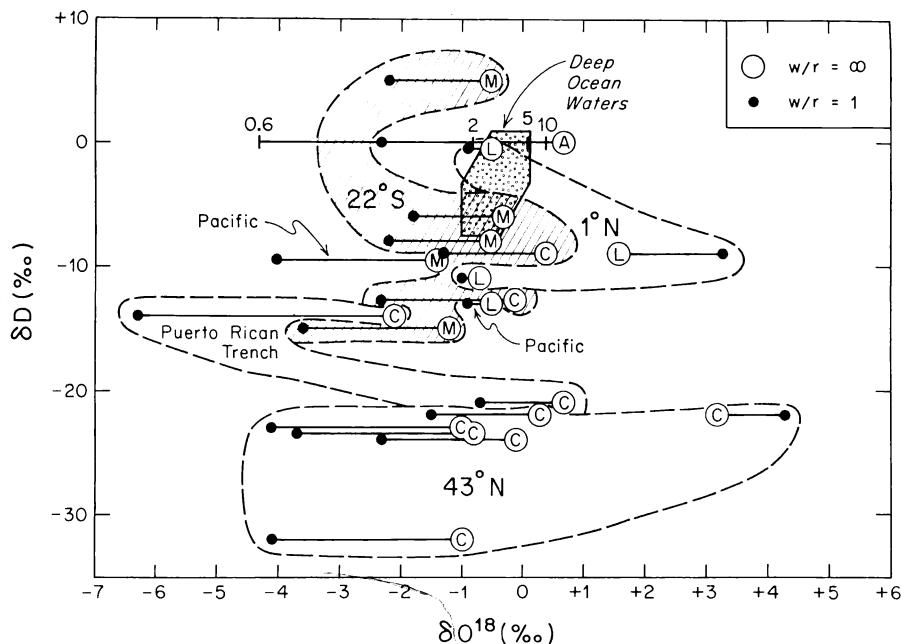


Fig. 9. δD - δO^{18} diagram of the calculated waters assumed to have equilibrated with the various oceanic serpentines shown in figure 5. A = antigorite, C = chrysotile, L = lizardite, M = mixture of lizardite and chrysotile. The assumed temperatures are discussed in the text. The calculated waters are given for both low ($w/r = 1$) and high ($w/r = \infty$) water/rock ratios; the different values are connected by tie lines for each sample. For antigorite sample no. 54 ($43^\circ N$), the isotopic compositions of waters are calculated for several different water/rock ratios. Note in particular that for w/r values > 5 , the calculated waters become nearly identical to the "infinitely" high ($w/r = \infty$) values. The field of deep ocean waters is delineated, based on the present-day data of Craig and Gordon (1965) and Redfield and Friedman (1969), but also extending the field to δD values as low as -7 and δO^{18} values as low as -1 to take into account changes in the isotopic composition of the ocean if the Antarctic and Greenland ice sheets were reduced in size or absent. Inasmuch as most of the calculated waters for $w/r = \infty$ have δO^{18} values near that of deep ocean water, this figure suggests that ocean water was a dominant constituent of the aqueous fluid, and that relatively high water/rock ratios are involved in serpentinization of ultramafic rocks in the oceanic environment.

pentines must be greater than unity (probably ~ 2) because most of the calculated ($w/r = 1$) waters are clearly much too O^{18} -depleted to be considered as reasonable in an oceanic environment.

The small variation that does exist among the estimated δO^{18} values may be due to the actual temperatures being slightly different from those assumed. For example, the bastite fraction of sample All 20-48-1 from the Mid-Atlantic Ridge ($1^\circ N$) has a $\delta O^{18} = +6.7\text{‰}$. The δO^{18} value of the water in equilibrium with the serpentine would be 1.6‰ lower and exactly coincide with that of ocean water if serpentinization occurred at about $100^\circ C$ rather than $125^\circ C$. If the late-stage chrysotile vein of sample All 32-8-80 formed at about $105^\circ C$ instead of $180^\circ C$, it could have

formed from a water identical in δO^{18} to that calculated for the matrix chrysotile (that is, $\delta\text{O}^{18} = -0.1$).

If the $\text{O}^{18}/\text{O}^{16}$ and D/H ratios of an oceanic serpentine are both “frozen in” at the same temperature and neither are subsequently altered, one might expect *all* serpentine samples to lie along a single curve such as the one illustrated in the δD - δO^{18} plot in figure 10; this defines the approximate δD - and δO^{18} -values of serpentine in equilibrium with sea water at 500° to 100°C. However, only three samples lie very close to this curve, and two of these were selected in originally ascertaining the D/H fractionation factors utilized in this report. All other serpentines lie below this curve to varying degrees.

It is therefore conceivable that many of the samples have only preserved their δO^{18} -values and have continued to reequilibrate their D/H values during retrograde cooling in the presence of circulating waters. The δD values of the serpentines would in such cases become lighter, thus moving vertically downward from the “equilibrium curve” in figure 10 to their present positions. The antigorite sample may have

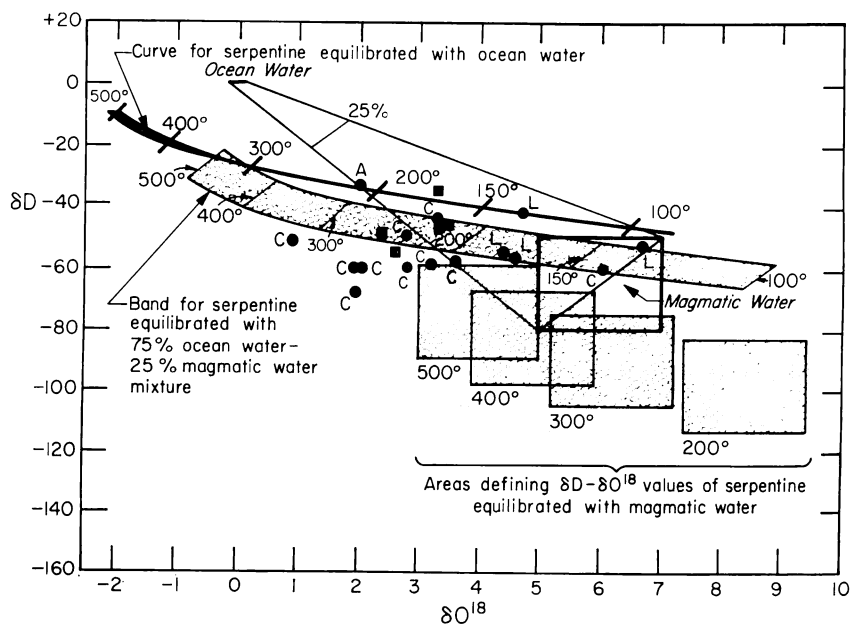


Fig. 10. δD - δO^{18} diagram showing the hypothetical isotopic compositions of serpentines equilibrated with various waters that conceivably could be involved in sub-oceanic serpentinization. All such calculated serpentines are shown with either a solid or shaded pattern. The possible waters under consideration are only magmatic waters and ocean water. The analyzed serpentines are shown as solid circles: C = chrysotile, L = lizardite, A = antigorite. The squares indicate L + C. Most analyzed oceanic serpentines lie relatively close to the fields of those calculated serpentines that either equilibrated with pure ocean water or with a 75 percent ocean water-25 percent magmatic water mixture. It appears that none of the analyzed oceanic serpentines could have formed from pure magmatic waters.

essentially "frozen in" its D/H ratio at high temperatures (about 235°C) in equilibrium with sea water, whereas many of the chrysotile samples may not have done so. Until we obtain more laboratory data on the kinetics of isotopic exchange between the various serpentine polymorphs and water, we cannot definitely rule out these possibilities. However, based on experiments by Kikuchi (1970) and for reasons that are discussed in detail elsewhere (see Wenner, *ms*) appreciable D/H retrogradation apparently does not occur at such low temperatures; therefore, we must consider other mechanisms that might explain the distribution of points in figure 10.

Mixing of magmatic waters with ocean water would lower the D/H ratio of water. The estimated isotopic compositions of serpentines formed in equilibrium both with pure magmatic water and with a mixture of 25 percent magmatic water and 75 percent ocean water are also given in figure 10.

If pure magmatic water were involved in serpentinization at 200° to 500°C, then the serpentines would all lie within the various rectangles shown in figure 10. Only two of the oceanic serpentines lie close to any of the rectangles involved with 100 percent magmatic water (the 500°C area), clearly showing that magmatic water cannot be the sole constituent of the aqueous solutions involved in sub-oceanic serpentinization.

If serpentine were originally formed from pure primary magmatic water and later exchanged with sea water, one would expect these serpentines primarily to display heavier δD -values, since hydroxyl exchange would probably predominate. In effect, such serpentines would be expected to move nearly vertically upward from the rectangles indicated in figure 10. Inasmuch as only 2 or 3 samples in figure 10 lie along such upward paths, this is not likely as a general mechanism.

Many of the oceanic serpentines lie within a calculated serpentine band in figure 10, based on equilibration with a mixture of 25 percent magmatic water and 75 percent ocean water. In particular all the lizardites and the antigorite, as well as some of the chrysotiles, either lie on the pure ocean water curve or within or very near the calculated (25–75 percent) serpentine band. Some of the chrysotiles fall significantly below this band, but it is particularly interesting that chrysotile sample All 32-8-70 ($\delta D = -59$, $\delta O^{18} = +3.2$), with a serpentine-magnetite temperature of 180°C (Wenner and Taylor, 1971), lies in near proximity to the 200°C contour on the band shown in figure 10. In fact, all the lizardite and chrysotile samples that lie close to the band also fall within the low-temperature end of the band ($<250^\circ\text{C}$), namely in the range of temperatures that seem to be most realistic for such types of serpentine.

The possible role of metamorphic waters also has to be examined. If primary magmatic waters equilibrated with submarine basalts at fairly low temperatures before being involved in serpentinization (such a water, in effect, would be classified as a metamorphic-type water), the δO^{18} values might be different from those hitherto considered. For ex-

ample, a juvenile or primary magmatic water of $+6.5$ equilibrating with basalt at about 200°C would attain a $\delta\text{O}^{18} = -1.4\text{‰}$, assuming that δO^{18} basalt $= +5.9$ (Taylor, 1968) and ΔO^{18} basalt-water $\approx \Delta\text{O}^{18}$ plagioclase-water $= +7.3$ (extrapolation to 200°C of data of O'Neil and Taylor, 1967). Such a water would, however, retain its original primary δD value (-50 to -80 per mil) because basalts contain very little H_2O . Such a water would also *have* to exchange with basalts at temperatures very close to 200°C in order to attain a δO^{18} value similar to that of sea water; this is because mineral-water fractionations are very temperature sensitive in this general range. It is likely, therefore, that exchanged magmatic waters would show a wide range in δO^{18} ; this makes them unlikely candidates for most sub-oceanic serpentinization, because the latter is apparently produced by H_2O with a relatively uniform δO^{18} in the range -2 to $+1$ (assuming $w/r > 2$, see fig. 9).

Serpentinization of Ultramafic Rocks in the Vourinos Ophiolite Complex

All the analyzed Vourinos serpentine samples are composed solely of lizardite and chrysotile. As shown in figure 1, the δD values vary only from -114 to -88 per mil. Serpentes from the interior portions of the ultramafic zone have slightly lighter δD values than samples that occur near the outer margins of the complex. All the completely serpentinized rocks fall within the δD range -88 to -99 .

In contrast, the δO^{18} values exhibit a very wide variation from $+2.1$ to $+12.7$ per mil. This δO^{18} variation is greater than that observed in serpentine from *any other* ultramafic body examined to date (Wenner, ms). The most O^{18} -depleted samples come from the interior portions of the complex and the serpentines from the *partially* serpentinized ultramafic zone all have relatively low δO^{18} values ($+3.4\text{‰}$, average of 4 samples).

The serpentines from four *completely* serpentinized ultramafic rocks all have relatively heavy δO^{18} values. Samples from the massive serpentinite zones in the upper part of the complex have an average $\delta\text{O}^{18} = +6.2$. The highest δO^{18} values ($+12.7$ and $+8.9$), however, are found in the sheared basal serpentinite zone (3c) and a nearby breccia zone (11a) located close to the sedimentary carbonate section that underlies the complex.

If one assumes $w/r = \infty$ and that all the lizardite-chrysotile type serpentinization at Vourinos occurred between 100° and 200°C , then at 100°C the calculated waters range in δD from -44 to -69 and in δO^{18} from -4.4 to $+6.2$; at 200°C , the values are $\delta\text{D} = -55$ to -81 and $\delta\text{O}^{18} = -0.2$ to $+10.4$ (see fig. 11). Such isotopic compositions are reasonable for heated meteoric ground waters, if we assume that the waters with high δO^{18} values were produced by exchange with the adjacent O^{18} -rich limestones. Inasmuch as the serpentinite and underlying carbonates are intimately interlayered at the basal contact, the fluids involved in serpentinization probably would have readily exchanged with the carbonates, even at fairly low temperatures. For example, Clayton

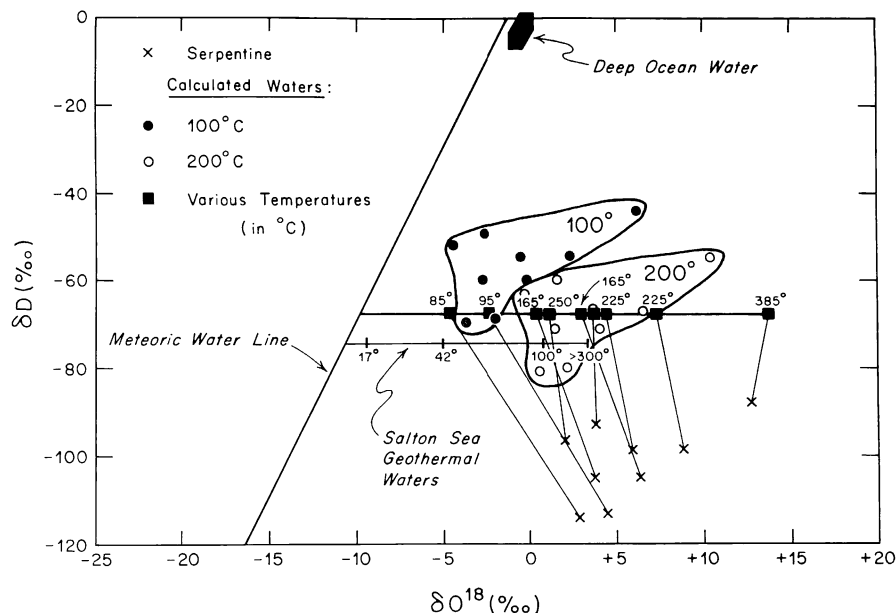


Fig. 11. δD - δO^{18} diagram of calculated ($w/r = \infty$) waters in equilibrium with the Vourinos serpentines at arbitrary assumed temperatures of 100° and 200°C. Also shown are the isotopic compositions of the Vourinos serpentines (crosses) and, joined by tie-lines, the coexisting waters in equilibrium with these serpentines at various temperatures, assuming a single geothermal water system with $\delta D = -68$. Note that although there is an overall similarity between this hypothetical single δD hydrothermal system and the Salton Sea geothermal water system (Craig, 1966), this model demands that the basal serpentinite form at very high temperatures ($\sim 385^\circ\text{C}$), while the serpentine in the central part of the complex must form at relatively low temperatures (85° - 100°C).

and others (1966) suggest that carbonates readily exchange and reach isotopic equilibrium with water at temperatures as low as 100°C . Extensive isotopic communication with the basement carbonates, however, appears restricted to the basal serpentinite unit and perhaps to the nearby serpentine breccia zones.

The δO^{18} values of serpentinized peridotites from the nearby Pindos Complex (Javoy, 1972) are generally depleted in O^{18} compared to un-serpentinized peridotites and dunites reported by Taylor and Epstein (1962), Reuter, Epstein, and Taylor (1965), and Taylor (1967a). The relatively light whole-rock δO^{18} values of the Pindos peridotites ($\delta O^{18} = +3.6$ to $+4.8$) suggest that the serpentines in these samples may have light δO^{18} values, perhaps comparable to those observed in the partially serpentinized peridotites from Vourinos. Thus, heated meteoric ground waters may also have been involved in serpentinization of the Pindos Complex. Note that several recent studies have conclusively demonstrated the importance of meteoric ground water interaction with epizonal igneous intrusions, even to depths as great as 5 km or more (Taylor, 1971; Taylor and Forester, 1971).

Because of the large variation in δO^{18} and δD of the calculated Vourinos waters, there is a possibility that several different types of waters (that is, meteoric-conate, meteoric-metamorphic, or exchanged meteoric) may be involved in the Vourinos serpentinization. Nevertheless, it is useful to examine whether a single meteoric water system (exhibiting a wide range in O^{18} but with a single δD value) can alone be responsible for all serpentinization. If we arbitrarily assume that the lowest temperature of serpentinization at Vourinos is about 85°C , which is the lowest serpentine-magnetite temperature obtained by Wenner and Taylor (1971), and if we also assume that the water/rock ratios were large, then we obtain a δD for the H_2O in equilibrium with sample 70c to be -68 . We can, by suitable adjustment of the temperature, force the waters in equilibrium with all the Vourinos serpentines to coincide with this δD value. These data are summarized in figure 11. Such a model requires that there be a very wide range of temperatures of serpentinization (approx. 80° to 400°C), and that the basal serpentinite must form at very high temperatures, while the interior serpentines form at relatively low temperatures.

The pattern shown in figure 11 for the Vourinos Complex single δD system is similar to that displayed by typical geothermal water systems, such as the one in the Salton Sea area, Calif. (Craig, 1966), where geothermal waters exhibit a progressive O^{18} -enrichment with increasing temperatures. There is, however, no *a priori* reason to believe that the basal- and breccia-zone serpentinites should have formed at such markedly higher temperatures than the other serpentines shown in figure 11. Even considering the exothermic nature of the serpentine reaction, it is just as plausible that the border-zone serpentinites formed at *lower* temperatures than the interior serpentines, particularly in view of the fact that greater amounts of water probably circulated through the margins of the intrusion than through the partially serpentinized central zone.

A perhaps more reasonable model than the single δD geothermal water system is one in which the temperatures of serpentinization increase as one moves into the interior of the body. This could come about, for example, if serpentinization occurred during cooling of the complex, compatible with the suggestion of Moores (1969) that the Vourinos Complex was emplaced as a hot, perhaps largely solidified mass, and that protoclastic deformation preceded serpentinization. Assuming high w/r values, all the δO^{18} values of the Vourinos serpentines could have been produced from a water with a variable δD value but with a uniform original δO^{18} of about zero, if the partial serpentinization of the interior parts of the ultramafic zone occurred at about 200°C , the intermediate portions at 135° to 155°C , and the upper serpentinites at about 100°C . However, this model would require abnormally *low* temperatures of about 25°C for the basal serpentinites. Thus, it is very unlikely that serpentinization at Vourinos was caused by a single geothermal water

system, either one with a uniform δD value, or one with a uniform initial δO^{18} value.

One might assume, however, that it is not realistic to choose such high water/rock ratios as were assumed in the above discussion. Therefore, in figure 12, smaller w/r values equal to 1 and 0.5 are also calculated. For w/r values = 1, the waters involved in partial serpentinization of dunite and peridotite in the central ultramafic zone are all uniformly very low in δO^{18} (~ -10 to -5); these values are characteristic of meteoric waters in which very little O^{18} -exchange has occurred, particularly with rocks such as the sedimentary carbonates at Vourinos. The calculated waters for w/r = 0.5 straddle the meteoric water line and are even more O^{18} -depleted than the w/r = 1 calculated waters. These are unrealistically low δO^{18} values for natural waters that might be involved in serpentinization, as such hydrothermal waters should certainly have undergone some " O^{18} shift" away from the meteoric water line.

The possible role of sea water in the Vourinos serpentinization must be examined, since many authors have proposed that ophiolite

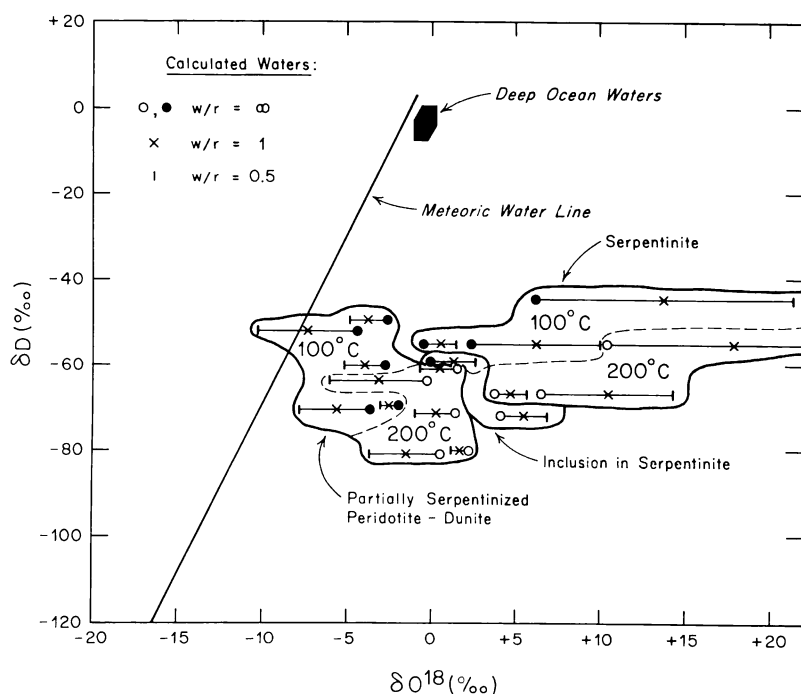


Fig. 12. δD - δO^{18} diagram of calculated waters in equilibrium with the Vourinos serpentines at 100° and 200°C for different values of w/r (0.5, 1.0, and ∞). The waters that exchanged with the partially serpentinized ultramafic rocks are clearly isotopically distinct from those that formed the serpentinites. Note that for the partially serpentinized samples, the w/r = 0.5 values are lower in O^{18} than the w/r = ∞ values, while the opposite is true for the serpentinites; the 200°C w/r = 0.5 value for the O^{18} -rich serpentinite would plot well off to the right of the figure.

serpentines originally form in a submarine environment. The relatively light δD values, considerably different from those of true oceanic serpentines, are incompatible with an origin from ocean waters. It is *conceivable*, nevertheless, that some of the serpentines may have formed originally in the presence of sea water over a wide range of temperatures, and that later the δD values of these serpentines were lowered as a result of massive D/H exchange in the presence of meteoric-hydrothermal fluids. This latter possibility is made feasible by the fact that the δO^{18} values of many of the Vourinos serpentines in the partially altered peridotites and dunites are similar to those of the oceanic serpentines (see fig. 6).

The textural relations of the peridotite inclusions in the basal serpentinite suggest that the pervasive partial serpentinization of the ultramafic zone may have predated the formation of the massive serpentinite zones. Thus, the partial serpentinization of the ultramafic zone by low- O^{18} waters may have occurred during a time when the ultramafic body was not in its present position in near proximity to the basal carbonates. This fits the early-stage oceanic serpentinization hypothesis, at least in terms of timing. It requires, however, that the δD values of *all* the serpentine samples in the ultramafic zone had to be lowered subsequently by about 50 per mil, presumably by the fluids responsible for the basal serpentinization. This would have had to occur without appreciable O^{18} exchange of the ultramafic-zone serpentines. Also, why should the ultramafic-zone serpentines attain lower δD values than the basal serpentines in such a process? On the other hand, it is possible to avoid all these difficulties if one assumes that the basal serpentinization and the partial serpentinization were both produced by meteoric-hydrothermal waters in a continental environment, but at different stages of the Mesozoic emplacement history of the complex and/or in the Tertiary (?) orogenic episode described by Moores (1969).

Summing up, we agree with Moores (1969) that at least two different serpentinization events (probably separated in time) very likely occurred at Vourinos. One event presumably involved low- O^{18} meteoric waters and resulted in a pervasive partial serpentinization of the ultramafic zone of the complex. The other involved relatively O^{18} -rich waters (probably exchanged meteoric, but conceivably metamorphic and/or magmatic) that must have been in isotopic communication with the carbonates that are presently juxtaposed against the base of the Vourinos Complex. If ocean waters were at all involved in any of this serpentinization, all hydrogen isotopic evidence of such an event has been totally obliterated.

Serpentinization of Ultramafic Rocks in the San Luis Obispo Ophiolite Complex

Lizardite-chrysotile samples from the San Luis Obispo area (fig. 2) show a wide range in δO^{18} (+3.8 to +9.3), but a very uniform δD (−82 to −91). The serpentinization is very complex, particularly in the highly

sheared border zones of the ultramafic body. Nevertheless, except for the late-stage chrysotile veins, at a given outcrop locality the δO^{18} values appear to be very uniform; this is well shown by the data obtained at a large roadcut on U.S. highway 101 (fig. 3). At this locality, 7 serpentine samples of differing mineralogy and texture (bastite, mesh-texture, et cetera) exhibit an overall δO^{18} variation of only +7.4 to +8.7. Note that sample 6d, a buff-colored serpentinite from the soil horizon, is only slightly O^{18} -enriched. This indicates that no appreciable isotopic exchange takes place in serpentine during this type of weathering.

The O^{18} -variations in the San Luis Obispo Complex, though less extreme, are similar to those observed at Vourinos. In both complexes, the highest δO^{18} values are found near the margins in the completely serpentinized portions of the body. Thus, most of the comments made previously about Vourinos may also apply to the San Luis Obispo body, except that the D/H variation is much smaller and only a single meteoric-hydrothermal event seems to be required. The lack of limestone in the surrounding country rocks at San Luis Obispo is probably the reason why the δO^{18} values do not extend to such high values as at Vourinos.

The overall δO^{18} variations at San Luis Obispo can perhaps best be explained by assuming a systematically declining temperature of serpentinization outward from the interior parts of the ultramafic body. This situation might arise if serpentinization occurred during cooling of the body, perhaps after injection of the dike complex. Sample 6c from the highway 101 roadcut apparently formed at about 85°C from a water with $\delta\text{O}^{18} \approx 0$, based on its serpentine-magnetite $\text{O}^{18}/\text{O}^{16}$ fractionation (Wenner and Taylor, 1971); if this "temperature" is approximately correct, then we can estimate temperatures of serpentinization of the other analyzed samples, assuming large water/rock ratios in the ultramafic bodies and a uniform $\text{O}^{18}/\text{O}^{16}$ ratio in the initial water. These approximate temperatures are: $\sim 60^\circ\text{C}$ for the SL-29 cross-fiber chrysotile vein, $\sim 120^\circ\text{C}$ for SL-21, collected within 0.1 km of the contact, $\sim 140^\circ\text{C}$ for samples SL-6 and SL-23 well inside the ultramafic body, and $\sim 150^\circ\text{C}$ for SL-27-3 and SL-27-4, collected next to a diabase dike.

The cross-fiber chrysotile veins in the San Luis Obispo complex are commonly O^{18} -enriched relative to the host serpentinite (see fig. 2). This feature is consistent with the above interpretation that serpentinization continued to occur throughout a period of declining temperatures, because if the late-stage veins formed at lower temperatures from the same kind of water, they would all attain higher δO^{18} values.

Samples SL-27-3 and SL-27-4 were collected from a serpentinite developed along the contact of a diabase dike. This serpentinite is zoned parallel to the contact, indicating a clear genetic relationship to the dike; thus, the serpentine may have formed from circulating waters during cooling of the dike. Assuming that the isotopic compositions of these serpentines have been preserved since their origin, this interpretation

would imply that these dikes cannot have been intruded in a submarine environment; thus they could not represent feeder dikes for the overlying ophiolite volcanic sequence as suggested by Page (1972). The isotope data would therefore seem to favor the hypothesis, tentatively rejected by Page, that these dikes are genetically related to the abundant Miocene mafic volcanic rocks present in the San Luis Obispo area (see fig. 2). It is important to determine the ages of these dikes shown in figure 4 of Page (1972), either by radiometric dating or by further geologic investigations. If it could be demonstrated definitely that they were in fact the same age as the ophiolite complex which is probably about 155 m.y. old based on dating of the Del Puerto and Elder Creek ophiolite complexes by Lanphere (1971), this would indicate strongly that these serpentines have *not* retained their primary δD values.

Serpentinization of Ultramafic Rocks in the Other Ophiolite Bodies

The lizardite-chrysotile samples from the ophiolite bodies in New Caledonia, at Del Puerto, Wilbur Springs, and Stonyford, Calif., and at Canyon Mountain, Oreg. have a relatively restricted range in δO^{18} (+6.3 to +9.2), but a large δD variation (−80 to −149). Considering the complex serpentinization histories of all these bodies, as evidenced by their complicated textures, it is remarkable that the δO^{18} values should be so similar in 5 widely separated bodies.

The bulk of the serpentine from the Del Puerto ultramafic body is lizardite and chrysotile with a uniform δD of −108 to −93‰. However, the small outlying serpentinite body (sample 2, fig. 4) is almost entirely antigorite with $\delta D = -62$. Sample 8, a mixture of antigorite and lizardite, has a δD value (−74) intermediate between that of the pure antigorite and the lizardite-chrysotile. Thus we may simply be dealing with two isotopic end-members, an antigorite with $\delta D \approx -60$ and a chrysotile with $\delta D \approx -100$. The Del Puerto antigorite is similar in δD and δO^{18} to many other antigorites throughout North America, consistent with the notion that antigorite typically forms in the presence of deep-seated, metamorphic-type waters (Wenner and Taylor, 1969). The lowest- O^{18} samples at Del Puerto occur in the interior portions of the main ultramafic body (note the similarity to Vourinos and San Luis Obispo); the serpentines from the outer margins of the main body and from the small outlying mass are 1.0 to 3.3 per mil heavier.

Estimates of the isotopic compositions of waters involved in serpentinization of the various ophiolite bodies are illustrated in figure 13. The δD values of these calculated waters (except for the antigorites from the Del Puerto body) display a very good correlation with the geographic distribution observed in present-day meteoric waters from these same general localities (see Friedman and others, 1964; Dansgaard, 1964; White, Barnes, and O'Neil, 1973). For example, the δD values of present-day fresh waters in the California Coast Ranges vary from about −30 to −70 as one moves from south to north or inland away from the coast, whereas in central Oregon they average about −90 to −100.

Note in figure 13 that the calculated waters at San Luis Obispo are heaviest in δD ; this is consistent with the fact that the San Luis Obispo body is the southernmost Pacific Coast ophiolite studied, and with the fact that it lies nearer the coast and at a lower elevation than the other bodies; it lies southwest of the San Andreas fault, so that during the Cretaceous and Tertiary it was located even further south than at present. In figure 13, the calculated waters for the Canyon Mountain, Oreg. ophiolite are lowest in δD , consistent with its being the most northerly area examined in this research.

This correlation of δD values suggests that much of the serpentinization of these ophiolite complexes occurred after their emplacement, perhaps during the Tertiary (or even the Quaternary?). In any case,

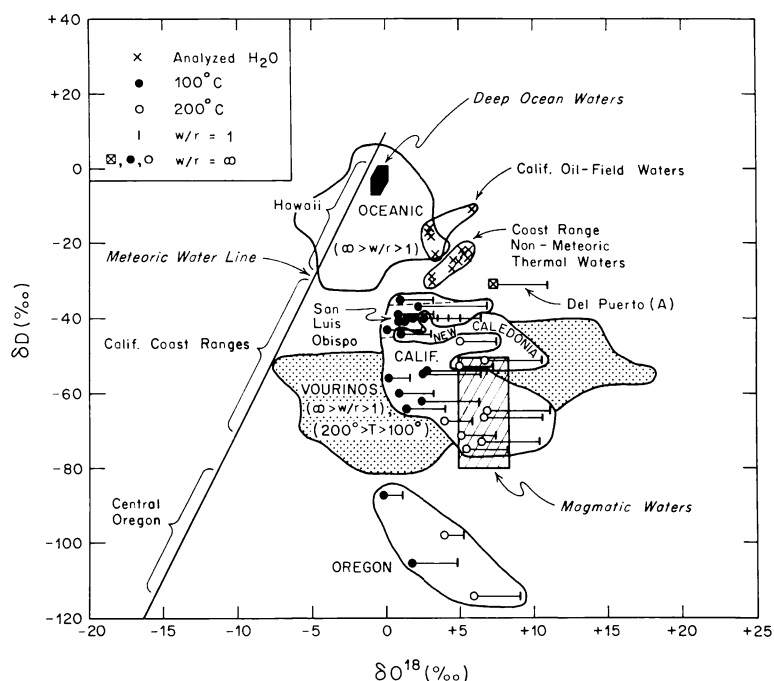


Fig. 13. δD - δO^{18} diagram of calculated waters in equilibrium at 100° and 200°C with the serpentines from ophiolite bodies in California, Oregon, and New Caledonia for different values of w/r between 1 and ∞ (connected by tie lines). Calculated waters from the San Luis Obispo body are for 100°C only and just include those from the U.S. 101 roadcut (fig. 3), as at this locality we have a direct serpentine-magnetite isotopic temperature determination. For comparison, the range of calculated waters for the Vourinos Complex (from fig. 11) and oceanic samples (from fig. 8) are also shown. In addition, the isotopic compositions of meteoric, magmatic, and ocean waters are indicated, as well as the range of meteoric water values in a typical oceanic island (Hawaii), the California Coast Ranges, and central Oregon (data from Taylor, 1967b; Sheppard, Nielsen, and Taylor, 1969; Craig, 1966; Friedman and others, 1964; Dansgaard, 1964). Also shown are data of White, Barnes, and O'Neil (1973), on some California oil field waters and some thermal spring waters of non-meteoric origin from the California Coast Ranges (including Wilbur Springs).

inasmuch as the calculated δO^{18} values of the waters in figure 13 lie well to the right of the meteoric water line, the meteoric waters at each locality must either have been heated and exchanged similar to the Salton Sea trend shown in figure 11, or they must have been heated and mixed with other types of waters, such as connate waters or possibly magmatic waters. Note that even at the present time there are many hot springs of clear-cut meteoric origin in the California Coast Ranges (for example, The Geysers, $\delta\text{D} \approx -50$; Bartlett Spring, $\delta\text{D} \approx -65$, see White, Barnes, and O'Neil, 1973). The cold, high-pH waters thought by Barnes and O'Neil (1969) to be responsible for some present-day serpentinization in the Coast Ranges are unexchanged meteoric waters that plot near the meteoric water line. They are thus not likely candidates to have produced the type of serpentinization discussed here.

The calculated waters for the lizardite-chrysotile serpentines of the continental ophiolite bodies could *conceivably* be interpreted as resulting from a mixture of meteoric and magmatic waters. For example, the lizardite-chrysotile serpentines from Del Puerto could have formed from about a 1:1 to 1:3 mixture of unexchanged meteoric and primary magmatic waters. However, no single mixing mechanism involving magmatic water can possibly explain the variation in all the calculated waters shown on figure 13, much less the isotopic data obtained on the other alpine serpentines from North America (Wenner and Taylor, 1969, 1971). Hence most lizardite-chrysotile serpentinization of the continental ophiolites also probably does not involve appreciable contribution of magmatic water.

White, Barnes, and O'Neil (1973) have reported some isotopically anomalous hot-spring (50° to 185°C) waters of probable metamorphic origin at Sulphur Bank and at Wilbur Springs in the Coast Ranges of California (see fig. 13). Their isotopic compositions are very similar to the calculated antigorite water from Del Puerto and the calculated (100°C) water of the anomalous Stonyford sample. It is obvious that by using a suitable mixture of exchanged meteoric waters with the anomalous non-metamorphic thermal waters, one can explain all the calculated waters involved in serpentinization of the California ophiolites. The occurrence of the anomalous hot spring waters at the Earth's surface, however, does mean that we can no longer *necessarily* assume from the isotopic evidence that samples such as the Del Puerto antigorite had to form under *deep-seated* metamorphic conditions.

CONCLUSIONS

The D/H and $\text{O}^{18}/\text{O}^{16}$ ratios of 20 serpentine samples from 5 different oceanic localities are distinctly different from the isotopic compositions of serpentines in 7 ophiolite complexes from Greece, New Caledonia, California, and Oregon. This strongly suggests that different types of waters were involved in the serpentinization of ultramafic rocks in these two diverse environments.

Estimates of the isotopic compositions of the hydrothermal waters that produced the oceanic serpentines range in δD from about +5 to -30 per mil and in δO^{18} from -2 to +3 per mil. Therefore, the dominant type of water involved in the serpentinization of submarine ultramafic rocks is most likely ocean water.

The data are compatible, however, with the presence of some magmatic H_2O (~25 percent) in the solutions responsible for submarine serpentinization. This "mixing" could conceivably come about simply by O^{18}/O^{16} and D/H exchange with hot, solidified igneous intrusions during convective circulation of ocean water along joints and fractures in such an igneous body beneath a mid-ocean ridge.

It should be pointed out that the measured δO^{18} values of the oceanic serpentines require that serpentinization must have taken place at elevated temperatures. If temperatures were as low as those suggested by Barnes and O'Neil (1969) for serpentinization in the California Coast Ranges, it would require waters with δO^{18} values as low as -5 to -10; such waters are not known to exist in submarine environments.

Estimates of the isotopic compositions of waters that produced the lizardite-chrysolite serpentines of continental ophiolite bodies range in δD from about -35 to -115 and in δO^{18} from -7 to +18 for Vourinos and from 0 to +11 for all other bodies. Such a wide variation strongly suggests that exchanged meteoric ground waters and/or mixed connate-meteoric waters had to be important in the serpentinization of these bodies. Some contribution of magmatic or metamorphic waters cannot be discounted, but we *can* rule out the possibility that ocean waters or connate waters were primarily responsible for the observed isotopic compositions of lizardite-chrysotile serpentines from ophiolites. Furthermore, the small amounts of antigorite associated with such bodies probably form only in the presence of some type of metamorphic water, definitely not ocean water. Because calculated water δD values for the lizardite-chrysotile serpentines show a systematic geographic relationship similar to the δD distribution of present-day, surface meteoric waters, much of the serpentinization of such ophiolite bodies probably occurred during the Cenozoic, perhaps largely after emplacement in their present locations.

Three ophiolite complexes were examined in some detail, namely Vourinos, San Luis Obispo, and Del Puerto. Considerable O^{18} variation was observed in the lizardite-chrysolite serpentine from each body but comparatively little D/H variation. The lowest δO^{18} values consistently occur in the interior, partially serpentinized portions of each complex. The outermost, completely serpentinized parts of these bodies tend to be high in O^{18} , particularly the basal serpentinite at Vourinos which is juxtaposed against high- O^{18} carbonate country rocks. Except for the latter situation, which is a special case, the internal O^{18} variations in the ophiolite complexes are all consistent with higher temperatures of serpentinization in the interior, possibly indicating that serpentinization

occurred during the cooling. Another factor that would help explain the O^{18} variations would be higher water/rock ratios in the exterior portions of the complex. It seems reasonable that greater volumes of H_2O probably circulated through the margins.

Late-stage, cross-cutting serpentine veins (particularly cross-fiber chrysotile) generally tend to be higher in O^{18} than their adjacent matrix serpentine. This is also consistent with either declining temperatures during the long interval of time over which serpentinization takes place or with higher water/rock ratios in the veins.

At the present time, we cannot definitely rule out the possibility that some of the low- O^{18} serpentines in the Vourinos and the San Luis Obispo ophiolites may have formed originally in the presence of heated ocean waters, and that later, after emplacement of these bodies into the continental crust, there was appreciable hydrogen isotope exchange between the existing serpentine and circulating meteoric-hydrothermal fluids. We know that D/H exchange between hydroxyl-bearing minerals and H_2O is in general easier than O^{18}/O^{16} exchange. However, if any of the other ophiolite serpentines were originally oceanic serpentines, they must *all* have been totally recrystallized and have lost essentially every vestige of their original δO^{18} and δD values; they are at present isotopically indistinguishable from the typical low-grade, alpine, lizardite-chrysotile serpentinites elsewhere in the world (see fig. 8).

It would thus appear that either (1) ophiolites are *not* remnants of oceanic crust and mantle, or more likely (2) most oceanic crust that may be emplaced on land by a possible obduction or subduction event is initially largely unserpentinized. The latter in turn implies that volume expansion concomitant with serpentinization may not be the mechanism by which the ultramafic bodies have risen to the levels in the Earth's crust at which they are presently found, because the isotopic data on lizardite-chrysotile serpentines in the ophiolite complexes are best interpreted as having resulted from relatively shallow-level serpentinization *after* emplacement into the crust. This interpretation is in disagreement with that of Bailey, Blake, and Jones (1970), who infer that the California Coast Range ophiolites were serpentinized in an oceanic environment prior to emplacement on-land. However, without doing violence to their basic model, we would raise the question whether serpentinization might have occurred principally during or after formation of the extensive Coast Range thrust fault, because according to figure 6 of Bailey, Blake, and Jones (1970), the areas under discussion were on-land at that time.

There are a variety of seismic velocity measurements (for example, see Ewing, 1969; Shor and Raitt, 1969) that, together with the experimental data of Christensen (1966) on the compressional velocities of serpentinized peridotites, support the idea that the oceanic upper mantle just below the Mohorovičić discontinuity must be largely unserpentinized. Therefore, this geophysical evidence is consistent with the arguments presented in this paper that the peridotite portions of ophiolite

complexes may only become heavily serpentinized after their emplacement within the continental crust.

ACKNOWLEDGMENTS

We wish to thank C. Bowin and G. Thompson of Woods Hole Oceanographic Institution for generously providing the oceanic samples; these were recovered on cruises supported by the AEC and NSF. We also wish to thank E. M. Moores who supplied the Vourinos samples, R. G. Coleman for the samples from New Caledonia, and T. Thayer for descriptions of sample localities at Canyon Mtn., Oregon. We are particularly grateful for valuable advice and laboratory assistance from S. Epstein and P. Yanagasawa, as well as for discussions with A. L. Albee, L. T. Silver, and T. Suzuoki. We wish to thank Ivan Barnes for a useful and critical review of the manuscript. Financial support was provided by grants from the NSF, Grant No. GA-12945, and the GSA Penrose Fund, Grant No. 1213-68.

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