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H- AND O-ISOTOPE GEOCHEMISTRY OF SERPENTINITE AND SERPENTINIZATION

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ABSTRACT

The common serpentine minerals produced by serpentinization of ultramafic rocks include lizardite, chrysotile and/or antigorite. Stable isotopic studies on serpentines show that the oceanic serpentines, the continental antigorite and continental lizardite-chrysotile have overlapping isotopic compositional fields. This suggests that the terms "continental antigorite" and "continental lizardite-chrysotile" should not give any genetic implications. Oxygen isotopic geothermometer demonstrates that antigorite forms at higher temperatures than lizardite and chrysotile. The serpentinization fluids for oceanic serpentines, continental lizardite-chrysotile and continental antigorite are mainly seawater, meteoric water and metamorphic water, respectively, based on their isotopic characteristics. All these interpretations, however, should only refer to the last geologic process the serpentinites have experienced.

The possible difference in isotopic behavior among serpentines caused by the differences in chemistries and structures are not known. Future experimental work will be needed to settle the problems.

INTRODUCTION

Most ultramafic rocks, collected either from continents or from oceans, are partially or completely serpentinized. This fact, combined with the geophysical evidence of the layered oceanic crust, led Hess (1955, 1965) to propose an oceanic crustal model consisting of a basal serpentinized peridotite layer (layer 3) 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 view of an uniformly serpentinized peridotite layer 3, however, has been questioned by many workers (for example, Cann, 1968; Christensen, 1970; Coleman, 1971). In addition, the origin of the fluid responsible for the serpentinization of this layer 3 is also a matter of controversy. Some authors agreed with the juvenile origin but others favored a seawater origin (Hess, 1965; Vdovykin and Dmitriyev, 1968; Thompson and Melson, 1970). To reconcile these problems it is important to understand the serpentinization process of ultramafic rocks; then we can specify the temperature condition, evaluate the possible sources of serpentinization fluid, and define whether serpentinization occurs in the mantle or crust or both. Hydrogen and oxygen stable isotopes are good indicators of formation temperature and the origin and nature of the fluid involved, and have been applied in this way since the 1970s.

Several factors are vital for the H- and O-isotope studies of serpentinization. They are (1) chemistry and structure of serpentine minerals, (2) fractionation relations of serpentine minerals, (3) serpentinization temperatures, (4) fluid/rock ratio during serpentinization, and (5) the preservation of isotope compositions of serpentine minerals. In the light of our recent studies on serpentinite in Taiwan, we will present a critical review on these subjects of serpentinization and discuss some intrinsic and induced problems here.

Table 1.
Polytypic classification of serpentine polymorphs (Wicks and Whittaker, 1975).

Lizardite*	Chrysotile*	Parachrysotile*
1T (lizardite)	$2M_{cl}$ (clinochrysotile)	
2H (2-layer lizardite)	$2Or_{cl}$ (orthochrysotile)	
3T (3-layer lizardite)	$1M_{cl}$ (1-layer clinochrysotile)	
6H (6-layer lizardite)		

* Lizardite – flat-layer structure
Chrysotile – cylindrical structure with x parallel to the cylinder axis
Parachrysotile – cylindrical structure with y parallel to the cylinder axis.

SERPENTINE MINERALOGY

The serpentine minerals ($Mg_3Si_2O_5(OH)_4$) have been divided into three structural groups, i.e. flat layers (lizardite), cylindrical layers (chrysotile), and corrugated layers (antigorite) (Whittaker and Zussman, 1956). This structural classification has since been revised on the basis of theoretical polytypic stacking sequences for trioctahedral 1:1 layer silicates by Wicks and Whittaker (1975) and the results are shown in Table 1. In this new classification scheme, antigorite is not considered in terms of polytypes because the layer stacking of antigorite is exerted by direct bonding between the layers instead of by hydrogen bonding, which is the basis of the theoretical polytypic stackings (Wicks and Whittaker, 1975). In addition, detailed mineral chemical studies showed that antigorite has a higher SiO_2 content and lower MgO and H_2O contents than other serpentine minerals (Whittaker and Wicks, 1970; Dungan, 1974). This small but distinct difference in chemical compositions is expected from the structural point of view, and that led Dungan (1974) to accept Kunze's (1958) structural formula, $Mg_{2.813}Si_2O_5(OH)_{3.673}$, for antigorite. It is therefore proposed that antigorite is not a polymorph of other serpentines, whereas lizardite, chrysotile and parachrysotile are polymorphs (Dungan, 1974; Whittaker and Wick, 1979). For convenience, the term "serpentines" is used in this paper as a general name to represent lizardite, chrysotile and/or antigorite when it is not specified.

It is well known that the oxygen isotope fractionation of minerals is mainly influenced by their chemical compositions but the hydrogen isotope fractionation is affected by chemical compositions, crystal structures, and hydrogen bonding (Taylor and Epstein, 1962; Suzuoki and Epstein, 1976; Graham *et al.*, 1980). The small difference in chemical compositions between lizardite/chrysotile and antigorite discussed previously may thus impose little difference on both H- and O-isotope behavior among serpentine minerals. However, the presence or absence of hydrogen bonding or even the difference in polytypic stacking sequences might have significantly different H-isotope effect among serpentine minerals and/or polytypes. These possible chemical and structural effects on isotope fractionations should be borne in mind in the following discussions.

ISOTOPE FRACTIONATIONS

Oxygen

So far no experimentally determined oxygen isotope fractionation curves involving the serpentine minerals have been reported. An empirical serpentine-water oxygen isotope fractionation relation obtained by Wenner and Taylor (1971) is based on (1) extrapolation of the empirical O-isotope fractionation relations among quartz, chlorite and ilmenite, and (2) assumption that the O-isotope fractionation between serpentine and chlorite is equal to zero. However, in the calculations Wenner and Taylor used the then unpublished quartz-water fractionation relations provided by Clayton *et al.* ($1000 \ell n\alpha$quartz-water $= 3.57(10^6/T^2) - 2.71$) that was later revised by Matsuhisa *et al.* (1979) ($1000 \ell n\alpha$quartz-water $= 3.34(10^6/T^2) - 3.31$, for 250 to 500°C). This revision would change the serpentine-water fractionation relation from $1.56(10^6/T^2) - 4.70$ (Wenner and Taylor, 1971) to $1.72(10^6/T^2) - 4.29$. That would in turn result in a ~0.8‰ difference in Δ values or a ~70°C difference in temperatures for these two serpentine-water equations in the temperature range of 300 to 400°C. In any comparative studies this internal inconsistency among O^{18} geothermometers should therefore be noted.

Hydrogen

Hydrogen isotope fractionation between serpentine and water has been empirically derived by Wenner and Taylor (1973) and experimentally determined by Sakai and Tsutsumi (1978). The results of these two studies differ significantly (Figure 1). Sakai and Tsutsumi (1978) believed isotopic equilibrium for their experiment and attributed the discrepancy between these two studies to the probable isotopic kinetic effect during serpentinization in nature. This view was later supported by Satake and Matsuo (1984) who demonstrated that hydrogen isotope fractionation for brucite-water (Figure 1) is similar to that for serpentine-water derived from natural samples (Wenner and Taylor, 1973) but is different from that presented by

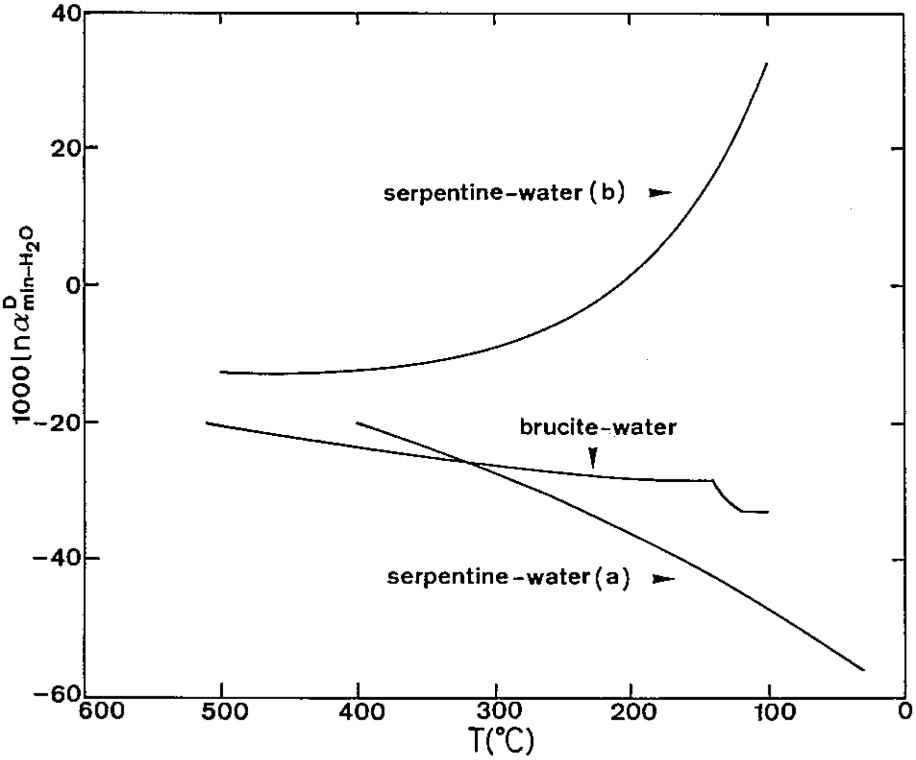

Figure 1. Hydrogen isotope fractionation curves for serpentine-water (a) (Wenner and Taylor, 1973), serpentine-water (b) (Sakai and Tsutsumi, 1978) and brucite-water (Satake and Matsuo, 1984).

Sakai and Tsutsumi (1978). They suggested that the difference in the hydrogen isotope fractionation between the experimentally determined brucite-water system and the serpentine-water system cannot be accounted for by the hydrogen bonding but might be attributed to the structural difference between brucite and serpentine. They further argued that the similarity of hydrogen isotope fractionation between the brucite-water system obtained experimentally and the serpentine-water system obtained empirically (Wenner and Taylor, 1973) is due to the preferential hydrogen isotope exchange under natural conditions between the brucite layer and the tetrahedral layer in serpentine structure. However, using the same arguments, Graham *et al.* (1980) commented that the Northrop-Clayton interpolation method, which is used for hydrogen isotope fractionation experiments, may not be applicable to minerals in which hydrogen is present in more than one structural site, such as in serpentine. In other words, the experimentally determined hydrogen isotope fractionation relation between serpentine and water (Sakai and Tustsumi, 1978) may be questioned. Another important thing one should note is that clinochrysotile is the serpentine mineral used in the experimental work of Sakai and Tsutsumi (1978) while data of laboratory calibrated chrysotile, and natural antigorite, lizardite and deweylite (a serpentine-like mineraloid of probable low-temperature weathering origin) were used in deriving the empirical relation (Wenner and Taylor, 1973). Since hydrogen bonding and mineral structure affect D/H fractionation (Suzuoki and Epstein, 1976; Graham *et al.*, 1980; Satake and Matsuo, 1984), the different serpentine minerals (or even diffenent polytypes) used may be partly responsible for the apparent discrepancy between experimental and empirical serpentine-water fractionation relations. Obviously, further studies are needed in this regard. At the present time, however, the empirically derived serpentine-water fractionation relation by Wenner and Taylor (1973) is preferred by most workers because of the possible isotopic kinetic and structural effects that have yet to be taken into accounts in the experiments (Ikin and Harmon, 1983; Yui, 1984).

STABLE ISOTOPE COMPOSITIONS OF SERPENTINES

The stable isotopic studies of serpentines were first taken by Wenner and Taylor (1971, 1973, 1974). They suggested that the serpentines generally have preserved their isotopic compositions since their formation (more rigorous discussion will be followed in later section). Wenner and Taylor (1973, 1974) also showed that the oceanic serpentines (including lizardite, chrysotile, and antigorite), the continental antigorite, and the continental lizardite-chrysotile (including those of ophiolite [the term "ophiolite" used here includes both ophiolite complexes and alpine serpentine bodies of Wenner and Taylor (1973, 1974)], kimberlite, stratiform and zoned complexes, and Precambrian sill/dike) each have characteristic H- and O-isotopic compositional fields (Figure 2). They concluded that these characteristic isotope compositions may indicate that the original ultramafic rocks were serpentinized in different environments, i.e. in oceanic, continental metamorphic, and continental near surface environments respectively. The terms (oceanic serpentines, continental antigorite, and continental lizardite-chrysotile), although derived from field occurrences, therefore have genetic implications. Subsequent stable isotopic studies on serpentinization by Magaritz and Taylor (1974), Heaton and Sheppard (1977), Hoernes *et al.* (1978), Barnes *et al.* (1978) and Ikin and Harmon (1983) depicted similar results, but more recent researches by Bonatti *et al.* (1984) and Yui (1984) yielded different results (see Figure 2). Bonatti *et al.* (1984) showed that the serpentines of serpentinized peridotite collected from the Vema and Romanche fracture zones in the Atlantic Ocean have O-isotopic compositions ranging from +3.0 to

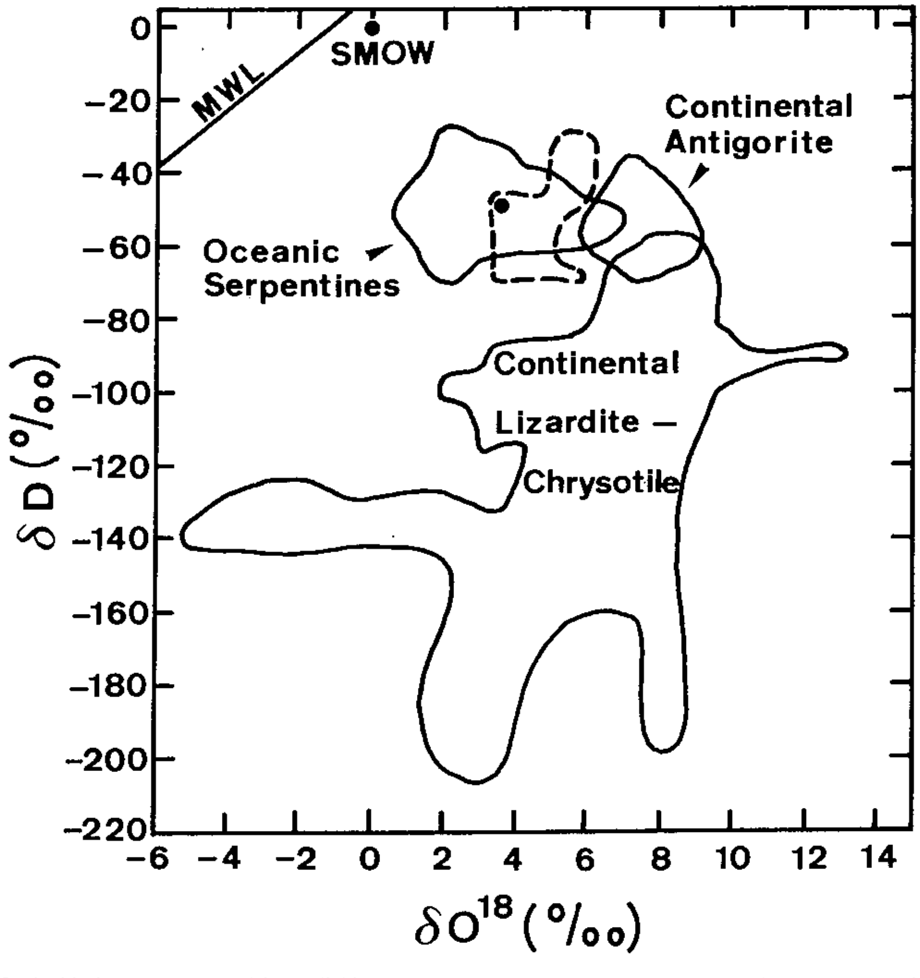

Figure 2. Stable isotopic compositional fields for serpentines from various geologic environments postulated by Wenner and Taylor (1973, 1974). Dashed line circles the compositional field of antigorite and closed circle marks the isotopic composition of lizardite from ophiolites in Taiwan (Yui, 1984).

+12.4‰. Although they did not present exact H-isotopic compositions, from their estimated serpentinization temperatures (30 to 177°C), these serpentines should have H-isotopic compositions of −40 to −55‰. In the stable isotopic studies on serpentinization of ophiolites in Taiwan, Yui (1984) found that the antigorites in these ophiolites have O-isotopic compositions as low as +3.5‰ (+3.5 to +6.2‰) with H-isotopic compositions of −32 to −69‰. In addition, Yui (1984) also showed that some rare lizardites in these ophiolites have isotopic compositions of ($\delta D = -49$, $\delta^{18}O = +3.6$). In contrast to data of Wenner and Taylor (1973, 1974) (Figure 2), these new data, clearly depict that the oceanic serpentines, the continental antigorite, and the continental lizardite-chrysotile do not have distinct stable isotopic compositional fields but rather show completely or partially overlapped fields. This may imply that some continental ultramafic rocks which now contain antigorite and/or lizardite-chrysotile might have originally been serpentinized in an oceanic environment. It then leads to the suggestion that the terms "continental antigorite" and "continental lizardite-chrysotile" should be purely occurrence-descriptive and should not give any genetic implications, though the term "oceanic serpentines", with some doubt, might still indicate an oceanic serpentinization environment (Yui, 1984).

SERPENTINIZATION TEMPERATURES

Serpentinites mainly consist of serpentines (lizardite, chrysotile, and/or antigorite) with minor amounts of chlorite, talc, brucite, magnetite, carbonates, and some relict olivine, pyroxenes and chrome spinel. Due to the absence of proper mineral pairs for chemical geothermometry and to the sluggishness of transformation experiments among serpentines, the conditions in which the various serpentines form are not well constrained. However, field evidence and experimental data do suggest that antigorite forms at temperatures higher than 300 to 350°C and lizardite and chrysotile are produced at lower temperatures (Nitsch, 1971; Evans *et al.*, 1976).

Wenner and Taylor (1971) studied the O-isotopic compositions for coexisting serpentine and magnetite. They found that normal lizardite-chrysotile and coexisting magnetite have Δ values (difference between $\delta^{18}O$ of serpentine and magnetite) ranging from 10.0 to 15.1. The Δ values for coexisting antigorite-magnetite are significantly smaller, between 4.8 and 8.6. Assuming isotopic equilibrium, the difference between these two sets of Δ values was presumably due to the difference in serpentinization temperatures. On the basis of the oxygen isotopic fractionation relation for serpentine-water system, Wenner and Taylor (1971) further derived an oxygen isotope geothermometer for serpentine-magnetite. This geothermometer then gives the following temperatures: continental lizardite-chrysotile, 85 to 115°C; oceanic lizardite and chrysotile, 130 and 185°C respectively; oceanic antigorite, 235°C; and continental antigorite, 220 to 460°C. These results confirm the general idea derived from petrogenetic and experimental data, i.e. antigorite forms at higher temperatures than lizardite and chrysotile. It is also in accord with the conclusion made by Barnes *et al.* (1967) and Barnes and O'Neil (1969) who suggested that some serpentinization of continental ultramafic rocks may be occurring today in a near-surface environment. These calculated isotopic temperatures (especially for most antigorites), however, appear to be abnormally low compared with geological evidence. Wenner and Taylor (1971) suggested that these anomalously low isotopic temperatures may be due to retrograde effect, isotopic disequilibrium, or incorrectness of the postulated serpentine-magnetite oxygen isotope geothermometer. Yui (1984) also pointed out that during prograde metamorphism antigorite may replace pre-existing lizardite-chrysotile. This antigorite and those magnetites that once coexisted in equilibrium with pre-existing lizardite-chrysotile may not attain isotopic equilibrium since magnetite is one of the minerals most resistant to O^{18} exchange. Bottinga and Javoy (1973) commented that with the large number of assumptions used to derive the oxygen isotope serpentine-magnetite geothermometer, the temperatures thus estimated may be too low by as much as 100°C, though Evans *et al.* (1976) claimed that the isotopic temperatures obtained by Wenner and Taylor (1971) are in excellent agreement with the PT-net for serpentines derived by them from field evidence and experimental data. These different opinions may thus suggest that the oxygen isotope serpentine-magnetite geothermometer may be reliably applicable only to serpentinites with simple geologic history or to late-stage serpentinization.

SERPENTINIZATION FLUID AND FLUID/ROCK RATIO

Fluid (mainly water) is a necessary phase in the serpentinization of ultramafic rocks. To understand the source of this fluid helps the knowledge of serpentinization environment. Since different fluids involved in geologic processes show different stable isotope characters (Taylor, 1974), a serpentinization environment can therefore be inferred from the isotopic compositions of serpentines and the estimated serpentinization temperatures.

The fluid involved in the formation of oceanic serpentines must be either seawater or magmatic (juvenile) water. Hess (1955, 1965) proposed that serpentinization of oceanic crust layer 3 is caused by the interaction of ultramafic rock with water rising from the deep mantle. This view was supported by Thompson and Melson (1970). They demonstrated that oceanic serpentinites contain approximataly 70 to 100 ppm boron. This B concentration is about 10 to 30 times that of unserpentinized peridotite. Although seawater contains 4 to 5 ppm B, Thompson and Melson (1970) suggested juvenile water as the possible source of serpentinization fluid based on the fact that during seawater-basalt interaction B is significantly leached from the rock and on the assumptions that B would behave similarly during seawater-peridotite interaction and that oceanic serpentinization takes place at temperatures higher than 200°C. However they also suggested that if seawater has been involved, serpentinization must have taken place at relatively low temperatures (<200°C). On the other hand, on the basis of the isotopic compositions of oceanic serpentines ($\delta D = -35$ to -68‰ and $\delta^{18}O = +0.8$ to $+6.7$‰, see Figure 2) and inferred serpentinization temperatures (150 to 250°C), Wenner and Taylor (1973) estimated the isotopic compositions of serpentinization fluid to be $\delta D = +5$ to -30‰ and $\delta^{18}O = -2$ to $+3$‰. This result therefore implies that the fluid involved in oceanic serpentinization is most likely seawater. The small shift in isotopic compositions from seawater (0, 0) may be due to the presence of minor amount of magmatic water or may result from seawater-rock interactions. These two controversial opinions were later unraveled by the works of Seyfried and Dibble (1980) and Bonatti *et al.* (1984). During the experimental study of seawater-peridotite interaction, Seyfried and Dibble (1980) found that the B content of seawater changes little during high-temperature (300°C) water-rock interaction but decreases significantly during the cooling stage (300 to 25°C). They thus concluded that the enrichment of B in oceanic serpentinite (Thompson and Melson, 1970) may reflect retrograde reaction with seawater after serpentinization. Bonatti *et al.* (1984) also depicted an inverse relationship between boron content in serpentinites and isotopic temperatures of serpentinization for samples collected from the fracture zones of Atlantic Ocean. This result is in agreement with Wenner and Taylor (1973) and Seyfried and Dibble (1980) that the uptake of B for oceanic serpentinite from seawater occurs at relatively low temperatures and the fluid responsible for oceanic serpentinization is mainly of seawater origin.

The isotopic compositions of continental lizardite-chrysotile are in the range of -49 to -205‰ for hydrogen and -5.0 to $+14.1$‰ for oxygen (Wenner and Taylor, 1973, 1974; Magaritz and Taylor, 1974; Ikin and Harmon, 1983). The δD values for most continental lizardite-chrysotile (except those of Precambrian sill/dike) show a very good systematic correlation with geographic location and latitude (Wenner and Taylor, 1973), similar to the δD distribution of present day meteoric waters. It strongly suggests that meteoric waters were predominantly involved in lizardite-chrysotile type serpentinization. Since both formation waters and hydrothermal fluids contain a significant meteoric component (Craig *et al.*, 1956; Clayton *et al.*, 1966), they are also possible candidates. This suggestion is in accord with the relatively lower lizardite-chrysotile serpentinization temperatures deduced from the isotope geothermometer. The oxygen isotope compositions of continental lizardite-chrysotile, however, do not directly correlate with the δD values as the meteoric waters. This was interpreted to be the results of isotopic exchange with country rocks (Wenner and Taylor, 1974) or due to waters with abnormal O-isotope compositions (Magaritz and Taylor, 1974). Wenner and Taylor (1974) also suggested that the δD-latitude correlation relation for these continental lizardite-chrysotiles discussed above would suggest that this lizardite-chrysotile type serpentinization should occur recently or at most during Tertiary. Since most ophiolites contain lizardite-chrysotile serpentinites, the ultramafic rocks in the ophiolites were probably largely unserpentinized prior to their emplacement onto the continent if ophiolite complexes truly represent exposures of ancient oceanic crust and mantle (Wenner and Taylor, 1974). It should be pointed out here that this conclusion is based on a presumption that lizardite-chrysotiles have not changed their isotopic compositions since their formation.

In contrast to continental lizardite-chrysotile, continental antigorite is relatively restricted in both δD (–32 to –69‰) and $\delta^{18}O$ (+3.5 to +8.7‰) values (Wenner and Taylor, 1974; Magaritz and Taylor, 1974; Ikin and Harmon, 1983; Yui, 1984). This variation is generally coincident with the overall range of isotopic compositions of chlorite in metamorphic rocks (Wenner and Taylor, 1974). The estimated isotopic compositional field for waters involved in this type of serpentinization is also similar to that of metamorphic waters (Wenner and Taylor, 1974; Ikin and Harmon, 1983; Yui, 1984). Considering the field occurrences, the experimental phase diagrams (Evans *et al.*, 1976) and the inferred isotopic information for antigorite-type serpentinization, it is concluded that continental antigorite has formed during regional metamorphism in the presence of metamorphic water (Wenner and Taylor, 1974; Ikin and Harmon, 1983; Yui, 1984).

Fluid/rock ratio is a necessary factor in calculating the isotopic compositions of serpentinization fluid discussed above (Taylor, 1977). Wenner and Taylor (1973, 1974) made a lot of these calculations and, with some arguments and assumptions, they favored a large fluid/rock ratio (in terms of oxygen) for all types of serpentinization. This might be true for most oceanic serpentines since some oceanic ultramafic rocks are known to occur at oceanic fracture zones and hence are in direct contact with seawater (Bonatti and Hamlyn, 1981). Their conclusion, however, may not be so easily envisioned for all continental serpentines. Wenner and Taylor (1973, 1974) also admitted that some of their results for continental lizardite-chrysotile and continental antigorite can also be reasonably explained by low fluid/rock ratios. An example of low fluid/rock ratio (< 1.0) (in terms of oxygen) for antigorite type serpentinization in Fengtien ophiolite was also suggested by Yui (1984), whose conclusion was supported by similar O-isotopic compositions and successively decreasing H-isotopic compositions of serpentines formed during consecutive serpentinization stages, which are delineated by isotopic, mineralogic and textural data. His work therefore demonstrates that detailed isotopic, mineralogic and textural studies are necessary in order to deduce a more reliable fluid/rock ratio for any particular serpentinized ultramafic body.

PRESERVATION OF ISOTOPIC COMPOSITIONS OF SERPENTINES

All of the above discussions assume that the serpentines have preserved the isotopic compositions since their formation. This is a fundamental and important assumption, especially for ophiolitic serpentines, since they might have formed in oceanic environments in the first place. This problem has been elaborately discussed by Wenner and Taylor (1974). They suggested that the consistently smaller oxygen isotope Δ-values for antigorite-magnetite, relative to the normal lizardite/chrysotile-magnetite in all environments, are in accord with field inference and strongly indicate that the serpentines have preserved their oxygen isotopic compositions. They also showed that the relatively heavy and narrow range of δD values for all continental antigorites, irrespective of their latitude, evidently enunciates that antigorite undergoes negligible hydrogen isotopic exchange with low-δD meteoric waters that might have been in contact with continental antigorite for millions of years. In addition, numerous samples of antigorite in contact with late-stage, low-δD chrysotile veins show no evidence of isotopic exchange. Though continental lizardite-chrysotiles have correlated δD values vs latitude, which might be the results of later H-isotopic exchange with local meteoric waters, Wenner and Taylor (1974) pointed out that some continental lizardite-chrysotile, of Precambrian sill/dike have isotopic compositions inherited from ancient meteoric waters and that some matrix chrysotiles retain higher δD values than cross-fiber chrysotile veins. These two observations strongly support that lizardite-chrysotile, similar to antigorite, also undergoes no significant H-isotopic exchange. Wenner and Taylor (1974) therefore concluded, based on these arguments, that "... most serpentines ... probably have largely preserved the isotopic compositions they acquired at the time of their formation" (p. 1255). One should note that all the above reasonings can only signify that the serpentines have preserved the isotopic compositions they acquired during *the last geologic event* they experience but *not* at the time of their formation, unless one assumes that these serpentines formed during the last geologic event. This assumption, however, may be questioned by the following field and experimental data.

Firstly, direct sampling of the oceanic crust at fracture zones reveals the presence of substantial amounts of serpentinite (e.g., a wall of 4 km thickness composed entirely of serpentinized peridotite at Romanche fracture zone) (Bonatti and Honnorez, 1976; Bonatti and Hamlyn, 1981). It is therefore unjustifiable to assume that those ophiolites with lizardite-chrysotile serpentinite were all serpentinized after their on-land emplacement and under a near surface environment affected by meteoric waters. Secondly, Wenner and Taylor (1974) conducted a H-isotopic exchange experiment between serpentines and water. Although antigorite shows negligible D-H exchange with water, they found that chrysotile does undergo 18% D-H exchange with water at 185°C during the 8-week experimental duration and lizardite shows a higher D-H exchange rate than chrysotile at 100°C. They also found that all serpentines undergo negligible D-H exchange with water at room temperature. These experimental results portray one possibility: that some continental lizardite-chrysotile might originally have formed in oceanic environment, and after or during their on-land emplacement these serpentines acquired their new latitude-correlated isotopic signatures (especially δD values) by being subjected to some geologic processes with temperatures higher than 150°C (e.g., on-land emplacement or low-grade metamorphism) and by being accessible to deep-circulated meteoric waters during Tertiary. Thirdly, the partial or complete merging of isotopic compositional fields of oceanic serpentines, continental antigorite, and continental lizardite-chrysotile (see previous discussion) supports the idea that some continental serpentines are only relics of recrystallized oceanic or pre-existing continental serpentines (Ikin and Harmon, 1983; Yui, 1984). Part of these arguments could also be applied to oceanic serpentines with the possibility that some of them originally formed through juvenile fluid, though there is no supporting evidence at the present time. Since serpentinization is a progressive process (Coleman, 1971, 1977; Ikin and Harmon, 1983; Yui, 1984), which might have continued through distinct geologic conditions and environments, the connotation of "preservation of isotopic compositions of serpentines" should therefore be noted with caution.

CONCLUSIONS

Stable isotopic studies concerning the isotopic compositional fields, the serpentinization temperatures, the serpentinization fluids and the serpentinization fluid/rock ratios of all kinds of serpentine minerals were initiated by Wenner and

Taylor (1971, 1973, 1974). Before 1980, all isotopic studies in these regards seemed to suggest that (1) the oceanic serpentines, the continental lizardite-chrysotile, and the continental antigorite show distinct H- and O-isotopic compositional fields; (2) antigorite always forms at temperatures higher than lizardite and chrysotile irrespective of their occurrences; (3) the serpentinization fluid for oceanic serpentines is mainly seawater, for continental lizardite-chrysotile is of meteoric water origin, and for continental antigorite is mainly metamorphic water; and (4) the fluid/rock ratios (in terms of oxygen) in all these serpentinizations might not be low. More recent research (Ikin and Harmon, 1983; Bonatti *et al.*, 1984; Yui, 1984), however, showed that some of the above conclusions may need revisions. For example, the isotopic compositional fields for different serpentines are partially of completely overlapped but not distinctly different, and the fluid/rock ratio for some continental antigorites might be quite low. It is also apparent that all these suggestions can only imply conditions/environments of the last geologic event to which the serpentinites have been subjected. Since serpentinization is a time-integrated result, the application of isotopic results to interpret the formation conditions of all serpentines must, therefore, be cautious.

Finally, in all the above discussions the H- and O-isotopic behaviors are assumed to be the same for all serpentines despite the small but distinct chemical and structural differences among them. This presumption, however, might be subjected to question, especially for hydrogen. The experimental work in this respect is therefore needed in the future.

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REFERENCES

Barnes, I., V.C. La Marche, and G. Himmelberg (1967). Geochemical evidence of present day serpentinization, *Science*, 156, 830-832.

Barnes, I. and J.R. O'Neil (1969). The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States. *Geol. Soc. Am. Bull.*, 80, 1947-1960.

Barnes, I., J.R. O'Neil, and J.J. Trescases (1978). Present day serpentinization in New Caledonia, Oman and Yugoslavia. *Geochim. Cosmochim. Acta,* 42, 144-145.

Bonatti, E. and J. Honnorez (1976). Sections of the earth's crust in the equatorial Atlantic. *J. Geophys. Res.*, 81, 4104-4116.

Bonatti, E. and P.R. Hamlyn (1981). Oceanic ultramafic rocks, in: *The Sea*, Vol. 7, Emiliani, C., Editor, Wiley-Interscience, New York, 241-283.

Bonatti, E., R. Lawrence, and N. Morandi (1984). Serpentinization of oceanic peridotites: temperature dependence of mineralogy and boron content. *Earth Planet. Sci. Lett.*, 70, 88-94.

Bottinga, Y. and M. Javoy (1973). Comments on oxygen isotope geothermometry. *Earth Planet. Sci. Lett.*, 20, 250-265.

Cann, J.R. (1968). Geological processes at mid-ocean ridge crests. *Jour. Geophys.*, 15, 331-341.

Christensen, N.I. (1970). Composition and evolution of the oceanic crust. *Marine Geol.*, 8, 139-154.

Clayton, R.N., I. Friedman, D.L. Graf, T.K. Mayeda, W.F. Meents, and N.F. Shimp (1966). The origin of saline formation waters: I. isotopic composition. *J. Geophys. Res.*, 71, 352-373.

Coleman, R.G. (1971). Petrologic and geophysical nature of serpentinites. *Geol. Soc. Am. Bull.*, 82, 897-918.

Coleman, R.G. (1977). *Ophiolites*, in Minerals and Rocks, Vol. 12, Springer-Verlag, Berlin, 229 pp.

Craig, H., G. Boato, and D.E. White (1956). Isotope geochemistry of thermal waters, in *Proc. Second Conf. on Nuclear Processes in Geol. Settings. Nat. Acad. Sci., Nat. Res. Council Publ.*, 400, 29.

Dungan, M.A. (1974). The origin, emplacement and metamorphism of the Sultan Mafic-Ultramafic Complex, Northern Cascades, Snohomish County, Washington, Ph.D. Dissertation, University of Washington, Seattle, Wash.

Evans, B.W., W. Johannes, H. Oterdoom, and V. Trommsdorf (1976). Stability of chrysotile and antigorite in the serpentine multi-system, Schweiz. *Min. Pet. Mitt.*, 56, 79-93.

Graham, C.M., S.M.F. Sheppard, and T.H.E. Heaton (1980). Experimental hydrogen isotope studies: I. systematics of hydrogen isotope fractionation in the systems epidote-H_2O, zoisite-H_2O and AlO(OH)-H_2O. *Geochim. Cosmochim. Acta,* 44, 353-364.

Heaton, T.H.E. and S.M.F. Sheppard (1977). Hydrogen and oxygen isotope evidence for seawater hydrothermal alteration and ore deposition, Troodos Complex, Cyprus, in *Volcanic Processes in Ore Genesis. Inst. Mining Metal. and Geol. Soc. London*, 42-57.

Hess, H.H. (1955). Serpentines, orogeny, and epiorogeny, in Polderraart, Aarie, Editor, Crust of the Earth-A Symposium. *Geol. Soc. Am. Spec. Paper,* 62, 391-407.

Hess, H.H. (1965). Mid-ocean ridges and tectonics of the sea-floor, in *Submarine Geology and Geophysics* – Closton Research Soc. Symposium, 17th, Bristol England 1965, Proc. Whittard, W.F., Editor, Butterworths, London, 317-332.

Hoernes, S., H. Friedrichsen, and H.H. Schock (1978). Oxygen- and hydrogen-isotope and trace-element investigations on rocks of DSDP Hole 395A, Leg 45. *Initial Reports of Deep Sea Drilling Project*, Vol. XLV, Washington, 541-550.

Ikin, N.P. and R.S. Harmon (1983). A stable isotope study of serpentinization and metamorphism in the Highland Border Suite, Scotland, U.K. *Geochim. Cosmochim. Acta,* 47, 153-167.

Kunze, G. (1958). Die gewellte Struktur des Antigorits, II. *Z. Krist.*, 110, 282-320.

Magaritz, M. and H.P. Taylor, Jr. (1974). Oxygen and hydrogen isotope studies of serpentinization in the Troodos Ophiolite Complex, Cyprus. *Earth Planet. Sci. Lett.*, 23, 8-14.

Matsuhisa, Y., J.R. Goldsmith, and R.N. Clayton (1979). Oxygen isotopic fractionation in the system quartz-albite-anorthite-water. *Geochim. Cosmochim. Acta,* 43, 1131-1140.

Nitsch, K.H. (1971). Stabilitatsbeziehungen von prehnite und pumpellyithaltigen paragenesen. *Contrib. Mineral. Petrol.*, 30, 240-260.

Sakai, H. and M. Tsutsumi (1978). D/H fractionation factors between serpentine and water at 100° to 500°C and 2000 bar water pressure and the D/H ratios of natural serpentines. *Earth Planet. Sci. Lett.*, 40, 231-242.

Satake, H. and S. Matsuo (1984). Hydrogen isotopic fractionation factor between brucite and water in the temperature range from 100°C to 510°C. *Contrib.*

Mineral. Petrol., 86, 19-24.

Seyfried, W.E., Jr. and W.E. Dibble, Jr. (1980). Seawater-peridotite interaction at 300°C and 500 bars: implications for the origin of oceanic serpentinites. *Geochim. Cosmochim. Acta*, 44, 309-321.

Suzuoki, T. and S. Epstein (1976). Hydrogen isotope fractionation between OH-bearing minerals and waters. *Geochim. Cosmochim. Acta*, 40, 1229-1240.

Taylor, H.P., Jr. (1974). The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.*, 69, 843-883.

Taylor, H.P., Jr. (1977). Water/rock interactions and the origin of H_2O in granitic batholiths. *J. Geol. Soc. London*, 133, 509-558.

Taylor, H.P., Jr. and S. Epstein (1962). Relationship between O^{18}/O^{16} ratios in coexisting minerals of igneous and metamorphic rocks. Part I: Principles and experimental results. *Geol. Soc. Am. Bull.*, 73, 461-480.

Thompson, G. and W.G. Melson (1970). Boron contents of serpentinites and metabasalts in the oceanic crust: implications for the boron cycle in the oceans. *Earth Planet. Sci. Lett.*, 8, 61-65.

Vdovykin, G.P. and L.V. Dmitriyev (1968). Organic matter in ultramafic rocks of the Mid-Indian ridge. *Geochim. Internat.*, 5, 828-831.

Wenner, D.B. and H.P. Taylor, Jr. (1971). Temperatures of serpentinization of ultramafic rocks based on O^{18}/O^{16} fractionation between coexisting serpentine and magnetite. *Contrib. Mineral. Petrol.*, 32, 165-185.

Wenner, D.B. and H.P. Taylor, Jr. (1973). Oxygen and hydrogen isotope studies of serpentinization of ultramafic rocks in oceanic environments and continental ophiolite complexes. *Am. J. Sci.*, 273, 207-239.

Wenner, D.B. and H.P. Taylor, Jr. (1974). D/H and O^{18}/O^{16} studies of serpentinization of ultramafic rocks. *Geochim. Cosmochim. Acta*, 38, 1255-1286.

Whittaker, E.J.W. and J. Zussman (1956). The characterization of the serpentine minerals by X-ray diffraction. *Mineral. Mag.*, 31, 107-126.

Whittaker, E.J.W. and F.J. Wicks (1970). Chemical differences among the serpentine "polymorphs": a discussion. *Am. Mineral.*, 55, 1025-1047.

Wicks, F.J. and E.J.W. Whittaker (1975). A reappraisal of the structure of the serpentine minerals. *Can. Mineral.*, 13, 227-243.

Yui, T.F. (1984). Stable isotope studies on serpentinites and nephrite deposits in the Fengtien area, Hualien, Taiwan, Ph.D. Dissertation, Inst. of Geology, Natl. Taiwan University, Taipei, Taiwan, R.O.C.

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蛇紋岩與蛇紋石化作用之氫、氧同位素研究

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摘　　要

超基性岩石之蛇紋石化作用通常產生細蛇紋石，纖蛇紋石及／或葉蛇紋石。穩定同位素在這方面的研究顯示海洋型蛇紋石、大陸型葉蛇紋石及大陸型細—纖蛇紋石具有相互重疊之氫、氧同位素成份範圍，這指示了「大陸型葉蛇紋石」及「大陸型細—纖蛇紋石」兩個名詞應不具任何成因上的含意。氧同位素地質溫度計顯示葉蛇紋石之形成溫度要較細、纖蛇紋石者為高。根據這些同位素資料，參與海洋型蛇紋石化作用之溶液應主為海水源，參與大陸型細—纖蛇紋石化作用之溶液主為天水源，而參與大陸型葉蛇紋石化作用之溶液則為變質水源。值得注意的是，所有這些基於穩定同位素資料所推論而得的形成條件與環境，應只能適用於解釋蛇紋岩體所歷經的最後一次地質作用。

蛇紋石礦物間化學成份與結晶構造上的差異對其穩定同位素分化性質的影響尚不清楚，這方面的實驗工作對深入切實了解蛇紋石化作用是非常須要的。