Stable Isotope Geochemistry: A Tribute to Samuel Epstein
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Editors: H. P. Taylor, Jr., J. R. O'Neil and I. R. Kaplan

Retrograde exchange of hydrogen isotopes between hydrous minerals and water at low temperatures

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Abstract—Fine-grained hydrous silicates may undergo retrograde H-isotope exchange with meteoric waters at low temperatures (<100°C) in near-surface environments and along faults, in the absence of significant concurrent O-isotope exchange, thereby generating characteristic vertical trends in δD versus $\delta^{18}O$ plots. The mechanism involves exchange with OH-sites, and is distinct from the D/H changes that accompany recrystallization or neoformation, both of which are associated with changes in $\delta^{18}O$ values. Theoretical considerations and experimental data show that self-diffusion of hydrogen in clays is 100 times faster than for oxygen, and that a 2 μm clay mineral would completely re-equilibrate H isotopes at 25°C in a few million years, whereas H-isotope exchange in a 200 μm clay would be negligible. Selective δD shifts are documented in several U-deposits, serpentinites, authigenic clays, regoliths, shear zones, and gold deposits. In the Proterozoic Athabasca basin, fine-grained illite, chlorite, kaolinite, and dravite originally formed at about 1500 Ma and 200°C from basinal or basement fluids having high δD values. These minerals then subsequently exchanged intermittently with D-depleted ($\delta D = -180$), relatively modern meteoric fluids at low temperatures. Exchanged clays show no change of $\delta^{18}O$, chemical composition, or crystallinity, but in some illites the δD values and K-Ar ages decrease in concert. Serpentinized ultramafic rocks in the Archean Abitibi Greenstone Belt have $\delta^{18}O$ values of +3.4 to +4.7, reflecting synvolcanic seawater alteration; however, the δD values vary from −54 to −114, and the most D-depleted samples contain more of the fine-grained lizardite that preferentially exchanged H isotopes with modern meteoric waters especially in the environs of fault zones. Similarly, in the Cassiar serpentinized harzburgite, British Columbia, early coarse-grained antigorites are relatively D-enriched ($\delta D = -103$), whereas fine-grained lizardite has a uniform $\delta^{18}O$ but variable $\delta D \geq -196$. Mesothermal gold vein deposits of all ages are characterized by uniform $\delta^{18}O$ quartz values, and uniform $\delta^{18}O$ and δD of medium- to coarse-grained mica, chlorite, and tourmaline. Fine-grained micas, however, may be D depleted due to H-isotope exchange with late meteoric waters infiltrating the veins. Bulk extracts of H_2O from quartz are also variably D depleted, stemming from entrapment of the meteoric water in secondary fluid inclusions. If unrecognized, secondary H-isotope exchange may lead to invalid interpretations of the isotopic composition of fluids involved in primary formation of hydrous silicate minerals.

INTRODUCTION

HYDROGEN ISOTOPES IN hydrous minerals can be the most definitive indicator of the origin of aqueous fluids that have affected rocks, because the original oxygen isotopic composition of the fluid is commonly altered by exchange with the large reservoir of oxygen in rocks. In most geologic processes, water/rock ratios are usually high enough, and the hydrogen contents of most rocks and minerals low enough, that the D/H ratios of hydrous minerals are solely determined by the isotopic composition and temperature of the ancient fluid (*e.g.*, TAYLOR, 1974). However, in applying this technique, an assumption that must be made is that the D/H ratio of the mineral has remained unchanged since the mineral originally formed.

The assumption that most hydrous minerals retain their original hydrogen isotopic compositions is based primarily on a few studies of natural samples and limited experimental data. YEH and EPSTEIN (1978) concluded that the D/H ratio of detrital clay minerals from deep-sea sediments were unaffected by exchange with seawater for at least 2–3 Ma. HASSANIPAK and ESLINGER (1985) suggested that Cretaceous and Tertiary kaolin minerals from Georgia retained their original hydrogen and oxygen isotopic compositions, as did SHEPPARD *et al.* (1969), in their studies of Mesozoic and Tertiary porphyry copper deposits. Exchange experiments between serpentine minerals and water (WENNER and TAYLOR, 1974) and clay minerals and water (O'NEIL and KHARAKA, 1976) for durations of less than two years also indicate that exchange of hydrogen isotopes between hydrous minerals and water is very slow at temperatures less than 100°C.

The apparently slow rates of exchange of hydrogen isotopes between hydrous minerals and water at low temperatures make it difficult to design meaningful laboratory experiments. An obvious alternative to experiments is to use well-characterized natural samples that have been subjected over several million years to the influence of meteoric waters having radically different D/H ratios than the waters that originally equilibrated with the hydrous mineral. This study reviews data from previous studies pertinent to post-formational exchange of hydrogen isotopes, and also presents additional evidence based on clay minerals in a Proterozoic sedimentary basin, serpentine deposits in Canada, hydrous minerals in fault zones in the Alps, and hydrous minerals and fluid inclusions in mesothermal gold deposits. The possible mechanisms by which hydrogen isotopes in some minerals exchange with low-temperature meteoric waters are discussed, as are the geological implications of retrograde D/H exchange for isotope studies in high latitudes.

PREVIOUS STUDIES

Many hydrous minerals in terrestrial rocks have been, or currently are, residing in environments where they coexist with substantial quantities of meteoric waters. WENNER and TAYLOR (1974) were concerned with the extent to which serpentine minerals retain their original δD values in these low-temperature environments.

They examined the exchange of hydrogen isotopes between natural serpentines and water in laboratory experiments at 100 and 185°C for six to eight weeks. Although exchange for antigorite was found to be minimal, chrysotile exchanged up to 18 percent of its hydrogen with water, particularly for smaller grain sizes. WENNER and TAYLOR (1974) concluded from these results that most serpentine minerals probably do not undergo significant amounts of post-formation exchange at Earth-surface temperatures, but some exchange would be expected under conditions of high water/rock ratios and temperatures in excess of 100°C.

Other laboratory experiments indicate that differential exchange of hydrogen and oxygen isotopes between water and hydrous minerals can occur at temperatures below 100°C. O'NEIL and KHARAKA (1976) reported that the hydrogen isotopes in montmorillonite and kaolinite were exchanged up to 26% and 6%, respectively, with water at 100°C over a period of 265 days, whereas concurrent oxygen isotope exchange was negligible. They concluded that the D/H ratios of clay minerals could be altered by later exchange, especially for those clay minerals that contain interlayer water. Because of the drastically different rates at which hydrogen and oxygen in clay minerals exchange with water, O'NEIL and KHARAKA (1976) proposed that hydrogen isotope exchange occurs via proton exchange which, unlike oxygen isotope exchange, does not involve the breaking of strong Si-O and Al-O bonds.

Studies of well-characterized natural samples subjected to the influence of meteoric waters with substantially different δD values from those in the original hydrous mineral provide the most convincing evidence that some minerals can undergo differential isotope exchange. For example, biotites weathering at low temperatures in migmatites in Chad record shifts in δD values of up to 30 per mil regardless of the relative degree of alteration of the biotites as deduced from other changes in chemical composition (CLAUER *et al.*, 1982).

Preferential exchange of hydrogen isotopes between clay minerals and low-temperature meteoric waters has been proposed as a mechanism to explain the variable δD values but relatively constant $\delta^{18}O$ values and chemical compositions of some clay minerals. LONGSTAFFE and AYALAN (1990) suggested that Cretaceous authigenic kaolinites in sandstones of the Western Canadian Basin have aberrantly low δD values as a result of exchange with formation waters at <40°C, even though the $^{18}O/^{16}O$ ratios of the kaolinites are preserved. WILSON *et al.* (1987) and KOTZER and KYSER (1991) proposed that low δD values of less than −100 in illite, kaolinite, and chlorite associated with structures hosting unconformity-type uranium deposits in the Proterozoic Athabasca Basin resulted from the preferential retrograde exchange between the hydroxyl groups of clay minerals having original δD values of *ca.* −60 and late Cenozoic, low-D meteoric water at low temperatures (*e.g.* $T < 50°C$ and δD values as low as −180). BIRD and CHIVAS (1988, 1989) concluded that post-formational exchange of oxygen isotopes is negligible in kaolinite from Permian and post-Paleozoic regolith profiles in Australia, whereas hydrogen isotope exchange with D-rich meteoric waters has shifted the original δD values of about −160 to much higher values. In the first three studies, the D/H ratios of clay minerals were lowered as a result of differential isotope exchange, whereas in the latter study, the D/H ratios were increased, even though in all cases the $\delta^{18}O$ values remained relatively uniform.

THEORETICAL CONSIDERATIONS

The kinetics of isotopic exchange between minerals and fluids have been reviewed by COLE and OHMOTO (1986). Data for exchange of hydrogen isotopes between water and hydrous minerals via self-diffusion are available down to temperatures as low as 100°C. This compilation indicates that at low temperatures, rates of exchange as a result of self-diffusion are several orders of magnitude slower than the rates from recrystallization. Using the activation energies and pre-exponential coefficients calculated by COLE and OHMOTO (1986) and assuming that the reaction rates follow an Arrhenius relation down to low temperatures, we obtain the results shown in Fig. 1. The diffusion rate of hydrogen appears to be similar for most hydrous minerals, and the self-diffusion reaction rate at *ca.* 25°C for hydrogen in kaolinite is at least 100 times faster than for oxygen. The faster rate of exchange of $^{18}O/^{16}O$ for montmorillonite compared to kaolinite probably reflects a much faster rate of exchange of oxygen during recrystallization than during self-diffusion.

The self-diffusion rates at 25°C shown in Fig. 1 can be used to estimate the extent that a hydrous mineral such as kaolinite could, in theory, exchange with a meteoric water. The extent of isotopic exchange can be modelled using the relation $L = (Dt)^{1/2}$ where L = distance that hydrogen or oxygen diffuses into the mineral, D = diffusion coefficient, and t = time (Fig. 2). A more precise model is unwarranted because of the large uncer-

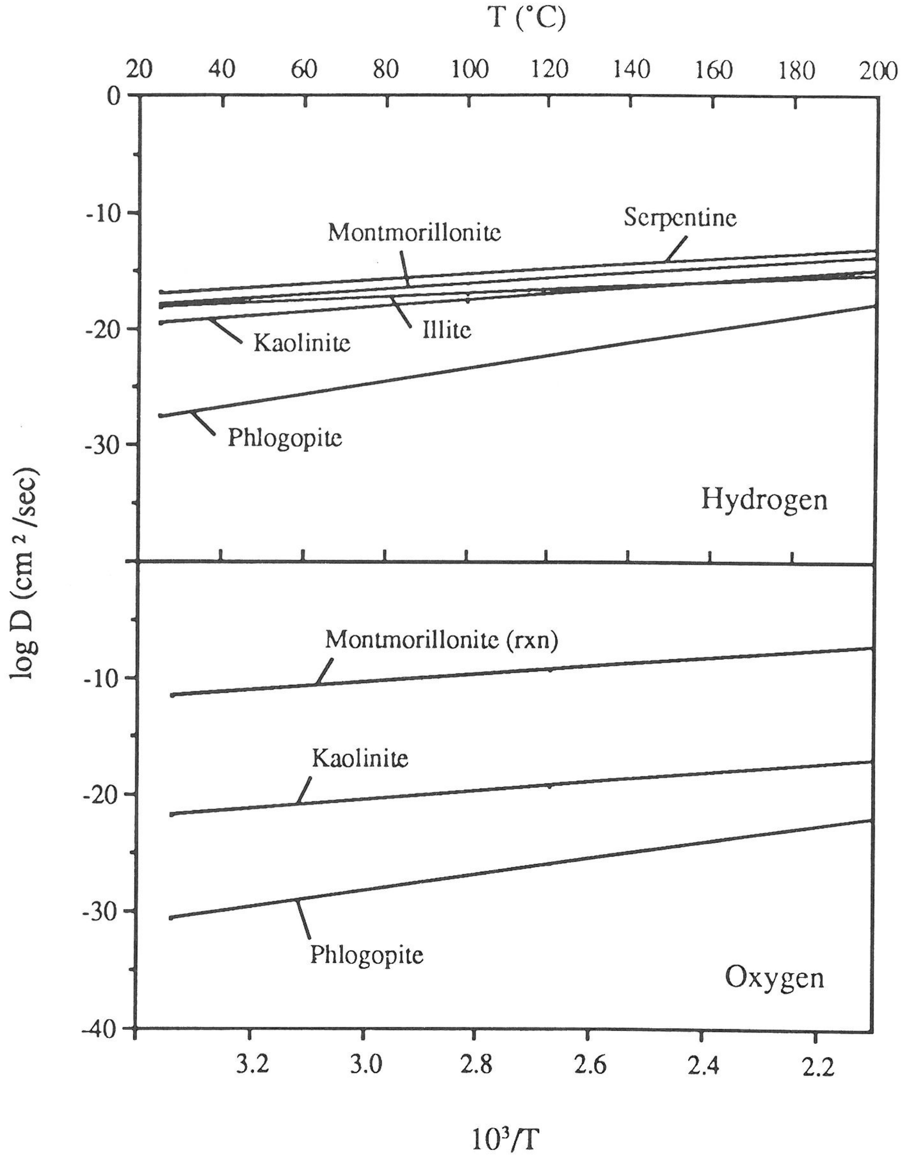

FIG. 1. Average self-diffusion rates of hydrogen and oxygen isotopes in various hydrous minerals, obtained from mineral-water exchange experiments as a function of temperature. With the exception of the values for phlogopite, which are extrapolated from 400°C, all rates are extrapolated from experimental results obtained between 100 and 200°C as compiled by COLE and OHMOTO (1986). The line for montmorillonite represents the rate of isotope exchange during recrystallization (rxn) in NaCl solution (O'NEIL and KHARAKA, 1976).

tainties associated with extrapolation of diffusion coefficients to low temperatures and the more general applicability of the results from the simple model to many different hydrous minerals. Given the self-diffusion rates from Fig. 1, the simple model predicts that a 2-micron kaolinite grain would completely exchange hydrogen isotopes with coexisting water in about 2 Ma, whereas only about ten percent of the oxygen will have exchanged. Larger grains, such as medium- to coarse-grained serpentines in hydrothermally altered basalt, or hydrothermal muscovite in quartz veins, should undergo little exchange over a geologically reasonable period of time (Fig. 2).

The consequences of differential isotopic exchange in contrast to complete isotopic equilibrium

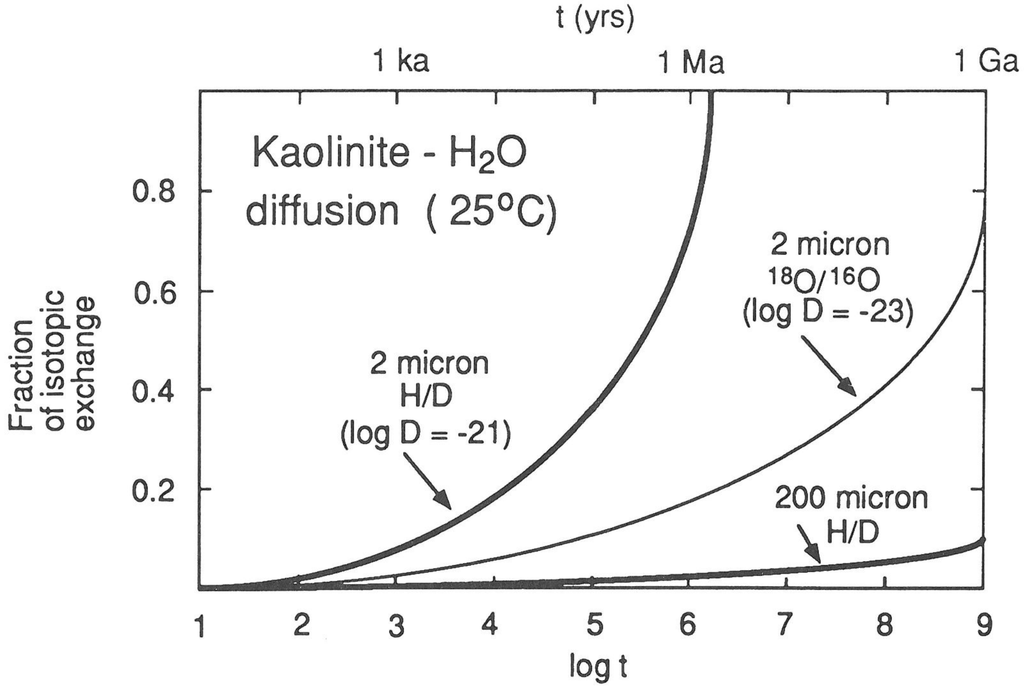

FIG. 2. Plot of fraction of exchange of hydrogen and oxygen isotopes vs. time (log scale) for a 2 micron diameter kaolinite grain and a large reservoir of water at 25°C, assuming self-diffusion coefficients of $D = 10^{-21}$ for hydrogen and 10^{-23} cm^2/sec for oxygen. Also shown is the extent of hydrogen isotope exchange in a kaolinite of 200 micron diameter.

with a later fluid can be evaluated by considering a kaolinite that originally formed at 200°C from a fluid having a δD of −40 and a δ^{18}O of 0 (fluid A; Fig. 3). The isotopic composition of this fluid is typical of meteoric-hydrothermal fluids in near-coastal or low-latitude environments (*e.g.* see TAYLOR, 1974). The kaolinite formed would have a δD of −40 and a δ^{18}O of +10 (kaol A; Fig. 3). If this hydrothermal kaolinite later underwent low-temperature exchange with local meteoric waters, it would shift toward kaol A′ (Fig. 3). However, if the terrane were later tectonically transported into higher latitudes or uplifted, differential isotopic exchange with new kinds of meteoric waters, for example with δD of −180 and δ^{18}O of −24 (fluid B), would result in the systematics shown in Fig. 3. Moreover, the apparent "temperature" of formation from anything other than a specific ^{18}O-shifted hydrothermal fluid would be unreasonably low. In contrast, neoformation or recrystallization of kaolinite at 25°C from the high-latitude or high-altitude meteoric water would result in a kaolinite with very low δD and δ^{18}O values (kaol B; Fig. 3); thus, most samples would have isotopic compositions between those of the new kaolinite and the original kaolinite. The trends in Fig. 3 should apply to all hydrous minerals, indicating that, in general, preferential exchange of hydrogen isotopes in hydrous minerals should be distinct from the effects observed in neoformed or recrystallized hydrous minerals.

ATHABASCA BASIN

One of the best studies showing that hydrogen isotopes in hydrous minerals exchange preferentially relative to oxygen isotopes at low temperature is that by WILSON *et al.* (1987) on the mid-Proterozoic Athabasca Basin. These basin sediments are dominantly quartz-sandstones deposited in a shallow shelf environment, and they are host to many unconformity-type uranium deposits and diagenetic clay minerals that display petrographic, chemical, and isotopic relationships indicative of several distinct fluid events (WILSON *et al.*, 1987; WILSON and KYSER, 1987; KOTZER and KYSER, 1991). The Athabasca Basin originally formed at about 1700 Ma in a near-coastal, low-latitude environment, but during the Cenozoic it has been inland at a latitude of 60°N where the meteoric waters have much lower δD values. Illite, kaolinite, chlorite, and the Mg-

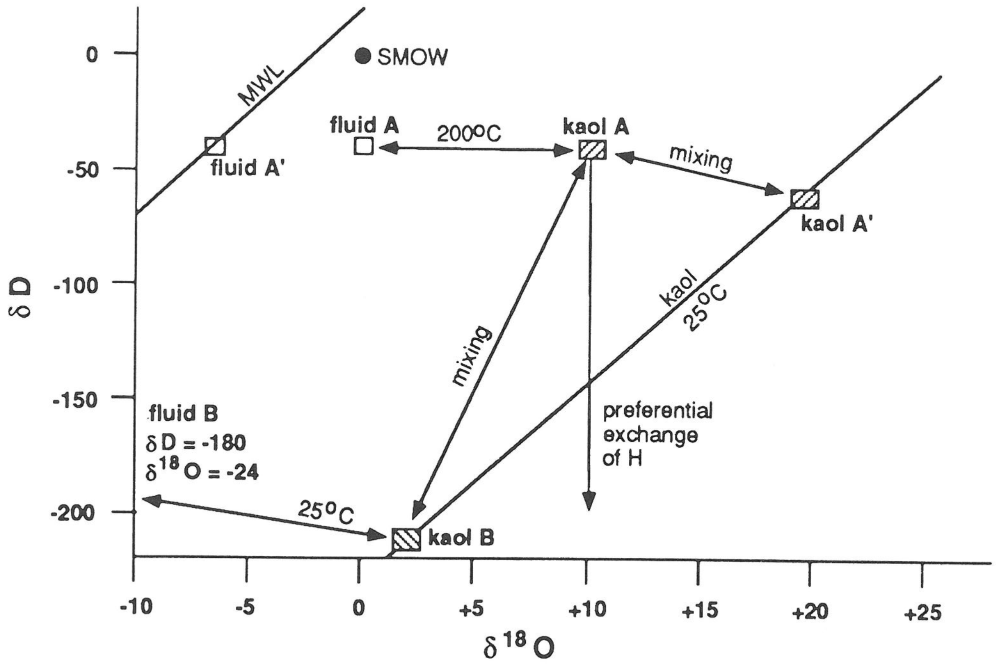

FIG. 3. Variations in the δD and $\delta^{18}O$ values of kaolinite formed from different fluids. A low latitude environment with meteoric water of fluid A′ produces a hydrothermal fluid having the composition of fluid A, which at 200°C will form kaol A. Subsequent preferential exchange of hydrogen isotopes with meteoric water having the composition of fluid B at 25°C in a high latitude environment will result in a vertical trend that can extend below the kaolinite 25°C line as shown. Neoformed kaolinite from fluid B at 25°C will have the composition of kaol B. Kaol A′ represents kaolinite in equilibrium at 25°C with the meteoric water of fluid A′. Also shown is the meteoric water line (MWL) and standard mean ocean water (SMOW). Fractionation factors for kaolinite-water are from LAMBERT and EPSTEIN (1980), LIU and EPSTEIN (1984), and LAND and DUTTON (1978).

tourmaline, dravite, are ubiquitous hydrous minerals in the basin. The earliest fluid event recorded by these minerals occurred *ca.* 1500 Ma, and involved basinal fluids or basement fluids having high δD values and temperatures of about 200°C. The mineral paragenesis and fluid history of the basin is discussed by KOTZER and KYSER (1991).

Unconformity-type uranium deposits, which form in fracture systems at the unconformity between crystalline basement rocks and the overlying sandstones, yield a spectrum of U-Pb ages from 900 to 1500 Ma. The variable ages are interpreted as resulting from retrograde interactions of uraninite with basinal fluids. Subsequent to the formation of the uranium deposits, the Athabasca Basin experienced episodic influxes of meteoric waters that had substantially lower D/H and $^{18}O/^{16}O$ ratios than the original basinal fluids. Late-stage kaolinite and dravite were formed in fractures (Fig. 4). However, all of the clay minerals and dravite in the environs of fracture systems throughout the basin exhibit aberrantly low δD values without any apparent changes in their $\delta^{18}O$ values or crystal structure (Fig. 4). In some minerals that formed early in the paragenesis the only changes observed are in the D/H ratios; these minerals are not altered even on the scale of XRD, SEM, and TEM analysis (KOTZER and KYSER, 1991). The trends towards low δD values are consistent with preferential retrograde exchange of hydrogen isotopes.

Other subtle changes occur in the chemical compositions of some of the changed hydrous minerals in the Athabasca Basin. The most notable change is a slight increase in the water content of the dravite and all of the clay minerals that correlates with decreasing δD value, despite the fact that there is no apparent change in the crystallinity of the minerals (WILSON *et al.*, 1987; WILSON and KYSER, 1987; KOTZER and KYSER, 1991). Fe/Mg ratios are slightly higher in the exchanged chlorites and dravites, and the K_2O contents and K-Ar ages of illites decrease with increasing water contents and decreasing δD values. These subtle changes in the hydrous minerals in the Athabasca Basin cannot be

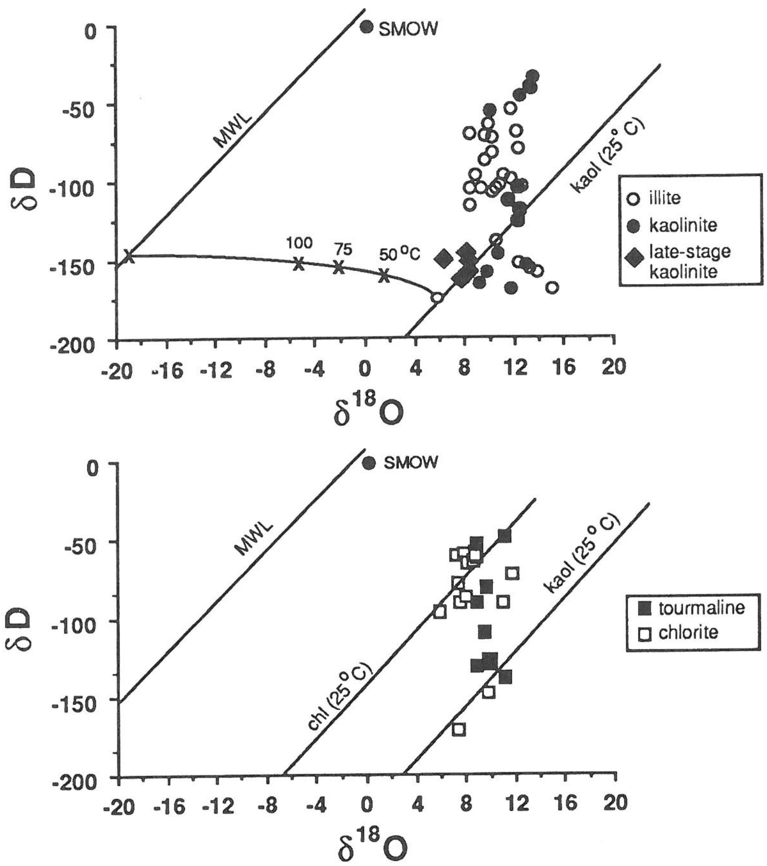

FIG. 4. δD and $\delta^{18}O$ values of clay minerals and dravite (Mg-tourmaline) from fracture zones in the Athabasca Basin, Canada. The late-stage kaolinite formed along fractures from relatively modern low-D meteoric water. All other minerals have crystallinity and paragenesis compatible with formation from low-latitude basinal brines at 900–1500 Ma. Also shown are the meteoric water line (MWL), the isotopic "lines" for chlorite (chl) and kaolinite (kaol) in equilibrium with meteoric waters at 25°C, and the isotopic composition of kaolinite in equilibrium with modern meteoric water in the basin at 100, 75, 50, and 25°C using the fractionation factors listed in Fig. 3 for kaolinite and extrapolation of data in WENNER and TAYLOR (1971) and TAYLOR (1974) for chlorite.

attributed to increasing proportions of neoformed minerals, but represent retrograde alteration of the minerals by low-temperature meteoric waters in a high water/rock environment near fracture systems. The earliest and most clear-cut signature of this retrograde process is the record of preferential exchange of hydrogen isotopes in the minerals; the other geochemical effects become evident only as retrograde alteration continues. Because illite in the basin records in its K-Ar and Rb-Sr isotope systematics the timing of the chemical changes that occur during this retrograde process, KOTZER and KYSER (1991) proposed a series of steps wherein meteoric water enters the interlamellar sites, exchanges hydrogen isotopes with the hydroxyl groups, and eventually displaces K^+ ions, affecting the K-Ar ages of the illites. In the most advanced stages of retrograde alteration, oxygen isotopes in the hydroxyl groups are also affected, although even here the crystallinity is not affected. Eventually the illite is recrystallized, resulting in $\delta^{18}O$ values compatible with formation from high-latitude, meteoric water at low temperatures. Similar processes are presumed to operate for all the micron-sized clay minerals and dravite in the basin.

SERPENTINIZATION

General statement

The interaction of hydrothermal fluids with mafic and ultramafic rocks often results in the formation of serpentine minerals and lesser quantities of chlorite, talc, tremolite, brucite, magnesite, and magnetite. Recorded in the isotopic compositions of these alteration products are the temperatures and isotopic compositions of the fluids involved in the formation of the serpentinite. The first systematic stable isotopic study of the serpentinites was by WENNER and TAYLOR (1971). They showed that the fractionation of oxygen isotopes between coexisting antigorite and magnetite is invariably smaller than between coexisting chrysotile-lizardite and magnetite. These relationships are observed in both continental and oceanic environments, and they imply that the antigorite formed at higher temperatures than lizardite or chrysotile. The distinct hydrogen and oxygen isotopic compositions and formation temperatures of the serpentine minerals led WENNER and TAYLOR (1973) to suggest that serpentines in oceanic environments form predominantly from heated seawater, under conditions of high water/rock ratios. Antigorites in most continental ophiolites have δD and $\delta^{18}O$ values compatible with formation from metamorphic fluids (WENNER and TAYLOR, 1973; SHEPPARD, 1980), whereas chrysotiles and lizardites from ophiolites, which have δD values that parallel those of modern meteoric waters at each locality, most likely form at relatively shallow levels in the crust in the presence of hydrothermal meteoric waters or formational brines (WENNER and TAYLOR, 1973, 1974). Most of the more recent studies on the isotopic systematics of serpentinites have confirmed the results of WENNER and TAYLOR (1971, 1973, 1974), although recent studies on some serpentinites where the paragenesis is known (*e.g.* IKIN and HARMON, 1983; BURKHARD and O'NEIL, 1988; YUI *et al.*, 1990) have revealed that some serpentine minerals in continental areas have hydrogen and oxygen isotope systematics that differ from those reported by WENNER and TAYLOR (1973, 1974).

Abitibi serpentines (Archean)

The Late Archean Abitibi Greenstone Belt of Canada represents the largest and youngest volcano-plutonic terrane to be accreted to the vast Superior Province of Canada. Serpentinized komatiitic and tholeiitic flows and associated ultramafic sills are abundant in the Southern Volcanic Zone. The komatiitic flows, serpentinite sills, and other rock types in the Abitibi Belt are cut by Matachewan dikes, dated at 2450 Ma (HEAMAN, 1989), indicating that serpentinization probably occurred during the Late Archean.

The ultramafic flows are fractured and consist of variably serpentinized samples of up to 90% serpentine, predominantly antigorite pseudomorphic after olivine. The restriction of antigorite only to certain flows and the pseudomorphic texture after olivine is compatible with the idea that serpentinization in part occurred shortly after eruption during alteration by heated seawater. The rims of some antigorite grains are partially replaced rims by finer-grained lizardite, and the earliest alteration event in the serpentinized sills is recorded by pseudomorphic lizardite, similar in texture and grain size to the lizardite in the serpentinized komatiitic flows. Chrysotile asbestos veins postdate the lizardite in some bodies and SCHANDL *et al.* (1990) measured homogenization temperatures of 290°C for fluid inclusions in diopside in rodingite that is contemporaneous with the formation of this chrysotile.

Serpentine minerals from variably serpentinized flows in the Abitibi Belt have a restricted range of $\delta^{18}O$, +3.4 to +4.7, but more variable δD values of −114 to −54 (Fig. 5). Neither the hydrogen nor oxygen isotopic compositions vary systematically with the stage of serpentinization, except that those serpentinites having the lowest δD values also have

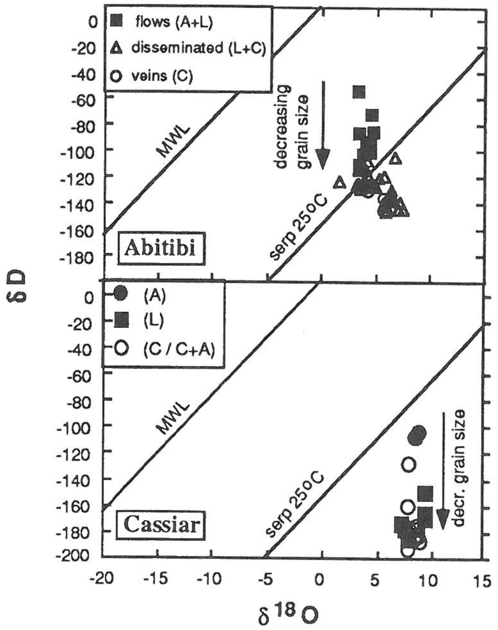

FIG. 5. δD and $\delta^{18}O$ values of serpentine minerals from the Archean Abitibi Greenstone Belt, Canada, and the Cassiar serpentine, British Columbia. Abbreviations are A = antigorite, L = lizardite, C = chrysotile. The arrow depicts the change in isotopic composition with generally decreasing grain size of serpentines in both areas. Also shown is the meteoric water line (MWL) and the approximate line depicting serpentine in equilibrium with meteoric waters at 25°C (KYSER, 1987).

a higher proportion of fine-grained lizardite relative to more coarsely crystalline antigorite. One antigorite sample from the Abitibi komatiites falls within the field of oceanic antigorites as defined by WENNER and TAYLOR (1973), compatible with the δD value of Archean seawater being similar to that of modern seawater. However, most of the other antigorites and the lizardites have lower δD values, suggestive of preferential exchange of the hydrogen isotopes with relatively modern meteoric waters having low δD values. The late chrysotiles in asbestos veins in the serpentinite sills tend to be more ^{18}O rich and D depleted relative to earlier formed lizardite.

Cassiar serpentinite (Cretaceous)

The Cassiar serpentinite, located in north-central British Columbia at 59°40′N, is a low-grade alpine-type serpentinite that originally was a harzburgite tectonite prior to serpentinization. The age of serpentine formation at Cassiar is constrained from the age of undeformed lamprophyric dikes in the area, which were emplaced at ages $>$ 67 Ma (O'HANLEY, 1990) along normal faults that offset all other types of faults and crosscut the Cassiar serpentinite. The paleolatitude of Cassiar during Middle to Late Cretaceous time was about 50°N (BUTLER *et al.,* 1988). Several faults transect the serpentinite and some are associated with formation of chrysotile asbestos veins.

The mineralogy, composition, and texture of serpentine minerals from the Cassiar serpentinite are described by WICKS and O'HANLEY (1988). The earliest-formed serpentine is lizardite in the matrix of the serpentinite. A later antigorite is present in the matrix of the hangingwall alteration zone, whereas an interlocking texture of lizardite, chrysotile ± antigorite ± chlorite is present in the center of the serpentinite body. All of the above textures, with the exception of the hangingwall alteration zone, are cut by chrysotile asbestos ± magnetite veins. Rodingites throughout the deposit are related to the formation of the late chrysotile asbestos veins and have fluid inclusion homogenization temperatures of 250–300°C and salinities of 4–10 wt.% NaCl equivalent (SCHANDL *et al.,* 1990).

In contrast to the relatively restricted range in their $\delta^{18}O$ values, the δD values of the serpentines from Cassiar vary significantly from -196 to -103 (Fig. 5). Coarse-grained antigorites are the most D-rich serpentines whereas lizardites from the late carbonate-serpentine-magnetite veins have the lowest δD values. On a plot of δD versus $\delta^{18}O$, the serpentines as a group form a trend similar to that observed in the Abitibi flows; namely, the $\delta^{18}O$ values are relatively constant but the δD values are intermediate between those of the coarse-grained antigorite and the fine-grained serpentine minerals. Differences between the $\delta^{18}O$ values of coexisting chrysotile and magnetite yield apparent equilibration temperatures of 300 ± 50°C using the empirical isotope geothermometer of WENNER and TAYLOR (1973). These temperatures are comparable to those obtained from homogenization temperatures of fluid inclusions in the rodingites. Lizardite-magnetite oxygen isotope fractionations yield an apparent equilibration temperature of 300°C for the late lizardite-carbonate-serpentine veins.

Summary

There are several aspects of the isotope systematics of the serpentine minerals from the Abitibi and Cassiar that favour a mechanism of retrograde hydrogen isotope exchange rather than neoformation to explain the coexistence of variable δD but constant $\delta^{18}O$ values. Serpentines from the Abitibi display $\delta^{18}O$ values that correlate with textural changes, and hence with paragenesis, the δD values do not vary with texture. Most of the data from paragenetically different generations of serpentines from both localities display variable δD values at relatively constant $\delta^{18}O$ values, with the finest-grained serpentines showing the most substantial shifts in δD. The coarse serpentines, which are early-formed antigorites in the Abitibi flows or the later-stage antigorites at Cassiar, generally have the highest δD values. In addition to the correlation with mineralogy and grain size, those serpentines most closely associated with fractures and faults along which meteoric waters can infiltrate also have the lowest δD values. There is no apparent relation between the δD values and $\delta^{18}O$ values, and serpentine-magnetite isotopic temperatures are similar to those obtained from fluid inclusions in associated rodingites, implying that oxygen isotopes in the serpentines have probably not been altered. Finally, WENNER and TAYLOR (1974) noted that the δD values of serpentinites from North America vary directly with their present latitude and the δD values of local meteoric waters, whereas $\delta^{18}O$ values in general do not (Fig. 6). In effect, δD values of serpentinites throughout North America vary directly with the δD value of modern meteoric water despite different apparent ages of the serpentinites (Fig. 6).

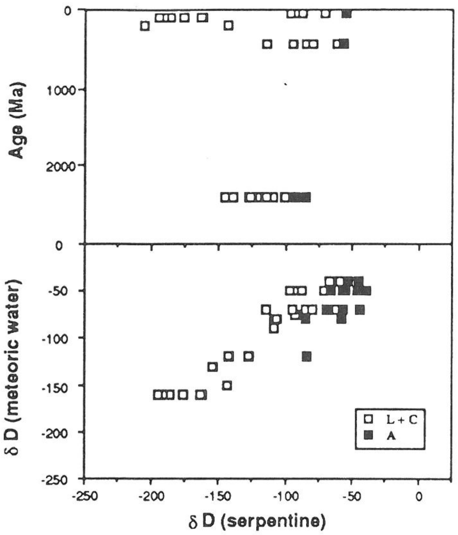

FIG. 6. Variation in the δD values of serpentine minerals from serpentines throughout North America with age of serpentinite (as determined from geologic relations) and the estimated δD value of meteoric water presently in the area of the serpentine using data from TAYLOR (1974). Data are from this study and WENNER and TAYLOR (1971, 1973, 1974). Abbreviations as in Fig. 5.

ALPINE OVERPRINTING

This section addresses stable and radiogenic isotope resetting that accompanied the Alpine orogeny in Europe, with specific reference to retrograde shifting of δD values. Stable isotope and petrologic studies in the European Alpine belt have revealed pronounced differences between basement and cover tectonic units, in terms of metamorphic temperatures, effects of overprinting, scale of isotope exchange, and fluid regimes. In general the basement units (Penninic nappes and thrust sheets) are pre-Mesozoic in age and polymetamorphic, whereas the Mesozoic cover has experienced only Alpine tectonism and metamorphism.

Localized isotopic effects of Alpine overprinting on Hercynian basement gneisses have been identified. Maximum Alpine metamorphic temperatures in the Monte Rosa area derived from oxygen isotopic compositions of coexisting minerals were *ca.* 460°C (FREY *et al.*, 1976). Some biotites retain oxygen isotopic temperatures indicative of Permian metamorphism, but have K-Ar systems reset to Alpine ages.

Biotite and muscovite in the pre-Alpine basement gneisses are characterized by a restricted range of δD values, independent of rock type. Biotite δD values cluster at −35 to −60 in the Otztal-Stubai Alps, at −40 to −80 in the Monte Rosa area, and −60 to −65 in the Swiss Central Alps (although the total range here is −50 to −140). Pre-Alpine phengites in the Sesia Zone have δD between −30 and −45 (DESMONS and O'NEIL, 1978). HOERNES and FRIEDRICHSEN (1978, 1980) attributed the narrow range of δD values to pervasive exchange with magmatic fluids in a pre-Alpine metamorphic event. However, δD values of biotite in equilibrium with most "magmatic fluids" would be somewhat more D depleted (−60 to −80 per mil) than the observed values. An alternative explanation for δD values as enriched as −35 was proposed by FREY *et al.* (1976), who suggested that D-enriched connate fluids originally affected the rocks. A similar suggestion was advanced by WICKHAM and TAYLOR (1985) for the Hercynian metamorphic rocks of the Pyrenees. The presence of such fluids would also account for the widespread oxygen-isotope homogenization observed in the Austrian basement gneisses.

In Mesozoic metasedimentary cover rocks, δD values of biotites are inherently more variable, and extend to lower values, than those in the basement gneisses. For example, the δD values of biotite are −40 to −95 in the Otztal-Stubai Alps, −60 to −130 in the Swiss Central Alps, and −134 to −157 at Monte Rosa (Fig. 7). The two processes proposed to explain the populations of most D-depleted biotites ($\delta D = -80$ to -157) involve either infiltration of an external, D-depleted aqueous fluid during Alpine metamorphism (FREY *et al.*, 1976; HOERNES and FRIEDRICHSEN, 1978, 1980) or loss of water enriched in D accompanying metamorphic recrystallization (HOERNES and FRIEDRICHSEN, 1978). There are difficulties in accounting for the most depleted biotites ($\delta D = -140$) by the second mechanism, given that most mineral-water fractionations are less than 60 per mil at all temperatures (*e.g.* SUZUOKI and EPSTEIN, 1976). The contrast between uniform biotite δD values throughout the Penninic basement gneisses ($\delta D = -57 \pm 3$), and larger dispersions in the Mesozoic cover ($\delta D = -60$ to -90), rules out extensive fluid exchange between basement and cover during Alpine tectonism.

Hydrogen and oxygen isotopic compositions of biotites and muscovites are not correlated in the population of low-δD micas (Fig. 7), compatible with the micas having preferentially undergone H-isotope exchange with meteoric water at relatively low temperatures, while at the same time remaining far from isotopic equilibrium with oxygen in the water. This interpretation is consistent with evidence from calcite-filled fractures for infiltration of low $\delta^{18}O$ fluids during buoyant rise of the Alpine

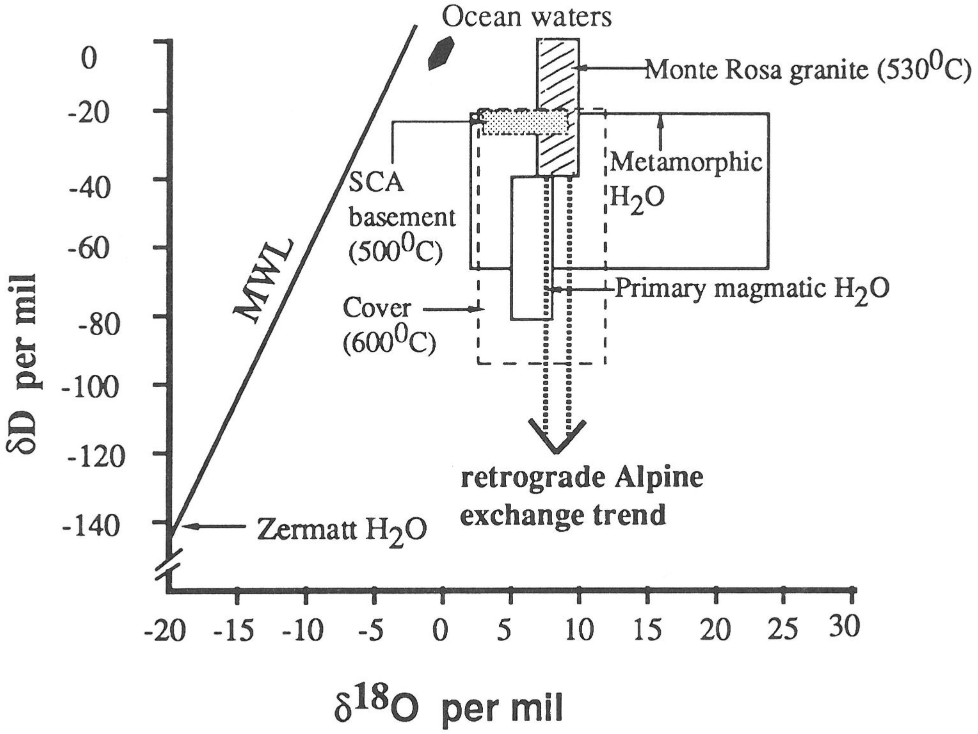

FIG. 7. Calculated hydrogen and oxygen isotope compositions of waters in equilibrium with basement (stippled) and cover (dashed field) tectonic units of the Alpine orogenic belt. Also shown is the trend of δD values of biotites in the Mesozoic metasedimentary cover rocks, as well as the values for modern meteoric waters at Zermatt. Sources of data: Monte Rosa, FREY *et al.* (1976); Swiss central Alps (SCA), HOERNES and FRIEDRICHSEN (1978). Ocean water, meteoric water line (MWL), metamorphic and primary magmatic fields after TAYLOR (1974).

mountain belt (BURKHARD and KERRICH, 1988). Micas in the Alpine cover units are finer grained than their basement counterparts, which may in part explain the observed preferential D depletion in the Mesozoic cover.

GOLD-QUARTZ VEINS

The origin of Mother Lode–type mesothermal gold-quartz vein systems is enigmatic. These veins may have vertical and lateral extents of several kilometers, are generally restricted to greenschist- or amphibolite-facies metamorphic rocks, and occur near regional structures that have been interpreted as major terrane boundaries. Examples include the Kirkland Lake–Cadillac fault zone in the Archean Abitibi Belt of Ontario, the Jurassic Melones fault in the Foothills Metamorphic Belt in California, and the Cretaceous-Tertiary Coast Range Megalineament near Juneau, Alaska.

Irrespective of age, or the relative proportions of supracrustal lithologies, the vein systems and associated mesothermal precious metal deposits share a number of common features at a variety of scales including: association with the brittle-ductile transition; uniformly low fluid inclusion salinities (≤ 3 wt.% NaCl equivalent) with CO_2 contents of 5–30 mole %; a paragenesis dominated by quartz, carbonate, mica, chlorite, pyrite, scheelite, and tourmaline; vertical extents of up to 2 km and a lack of zoning; restricted ranges of O, C, Sr, and Pb isotopic compositions within vein systems, albeit with a geographic provinciality; and late-kinematic timing (WYMAN and KERRICH, 1988; KERRICH and WYMAN, 1990). These common features support the view that all such vein systems formed by similar genetic processes, whatever their age. The origin of the ore-forming fluids is controversial. Here, we critically consider the H-isotope evidence on which a meteoric water model is based.

The majority of Archean and Proterozoic mesothermal gold deposits are characterized by relatively uniform $\delta^{18}O$ values of vein quartz and temperature (280–340°C). Ore-forming fluids have estimated $\delta^{18}O$ (H_2O) = +5 to +11, and δD (H_2O) = −20 to −80, where δD was determined on medium- to coarse-grained (0.1–2 mm) micas or chlorite (Fig. 8). Based on this and other lines of evidence, the ore-forming fluids have been interpreted as being metamorphic in origin by KERRICH (1989). Phanerozoic mesothermal deposits similarly feature uniform $\delta^{18}O$ values of quartz and temperature (280–360°C), albeit with somewhat larger inter-deposit variations of $\delta^{18}O$ (quartz); and the calculated $\delta^{18}O$ values of the ore-forming fluids range from +5 to +14 (Fig. 8D), whereas the calculated δD values of the hydrothermal fluids range from −15 to −70, based on analyses of coarse-grained hydroxy-silicates (Fig. 8).

NESBITT *et al.* (1986) proposed that the Mother Lode–type mesothermal quartz vein systems and precious metal deposits in the Cordillera formed in response to deep circulation of meteoric water along transcurrent faults under conditions of low water/rock ratios. They have extended this model to Archean mesothermal veins (NESBITT, 1988; NESBITT and MUEHLENBACHS, 1989). The meteoric water model stems from the observation that the δD values of H_2O, obtained by decrepitating fluid inclusions from some vein quartz, become lighter at higher latitudes. Uniform $\delta^{18}O$ quartz values at each deposit, but a spread of δD values, define a vertical band in δD_{H_2O} versus $\delta^{18}O_{H_2O}$ coordinates (Fig. 8D). On the other hand, for Cordilleran mesothermal deposits in Alaska, PICKTHORN *et al.* (1987) and GOLDFARB *et al.* (1991) measured δD values of −75 to −53 on hydrothermal micas, giving calculated δD values for the hydrothermal fluids of −35 to −20; these are interpreted to be metamorphic in origin. Data for the Proterozoic Homestake and Jurassic Mother Lode deposits also plot as vertical bands in δD_{H_2O} versus $\delta^{18}O_{H_2O}$ coordinates, defined

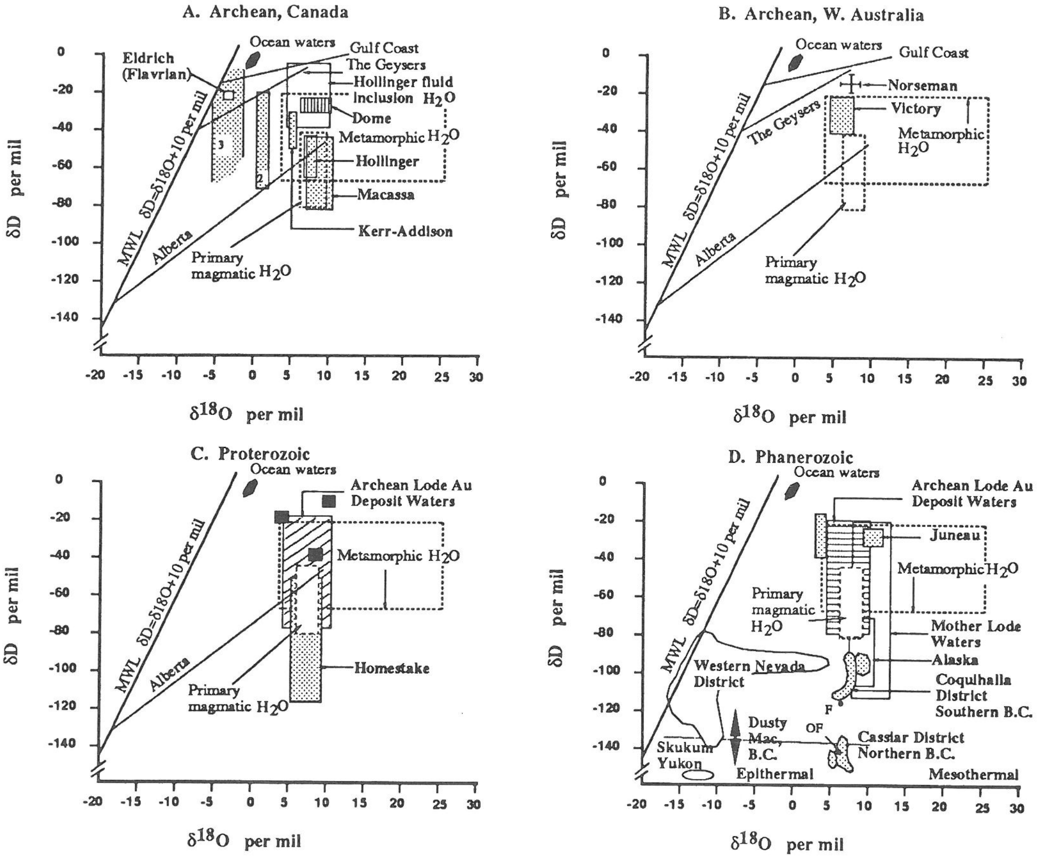

FIG. 8. Calculated isotopic compositions of ore-forming fluids associated with Archean (A, B), Proterozoic (C), and Phanerozoic (D) mesothermal gold deposits. Note that the D-depleted trend from Homestake (C) and the Cordilleran mesothermal deposits (D) are exclusively based on bulk extraction of fluid inclusion waters (modified after KERRICH, 1989). F and OF (D) are the adjacent Fairview and Oro Fino deposits in southern British Columbia (after ZHANG *et al.*, 1989).

by uniform $\delta^{18}O_{quartz}$ values, but a spread of δD_{H_2O} values from bulk extraction of fluid inclusions (Fig. 8C,D). There is clearly a discrepancy between D-depleted values obtained from bulk extraction of fluid inclusions and the D-enriched values obtained from co-existing medium- to coarse-grained (0.1 to 2 mm) micas.

As suggested by PICKTHORN *et al.* (1987), the δD results from bulk extraction of fluid inclusions may not reflect the primary ore-forming hydrothermal solutions, but rather secondary inclusions formed in the presence of surface meteoric waters infiltrating down the vein. In a detailed study, GOLDFARB *et al.* (1991) showed that bulk extracted fluid inclusion waters from vein quartz of the Juneau mesothermal deposits exhibit a wide range of δD values from −48 in relatively undeformed quartz to −110 in deformed counterparts. This span reflects decrepitation of variable proportions of two end-member fluid inclusion populations: a D-enriched ore-forming fluid in primary inclusions and a D-depleted meteoric water trapped in secondary inclusions along fractures. Significant spreads of δD values from bulk extraction of fluid inclusion waters are also evident in the data of ZHANG *et al.* (1989) and NESBITT and MUEHLENBACHS (1989). For example, it is not clear why the Fairview ($\delta D = -121$) and Oro Fino ($\delta D = -148$) mesothermal gold deposits, which share a common geographic and altitudinal position in southern British Columbia, should have such disparate bulk fluid inclusion δD values, if these are indeed all primary.

Numerous lines of evidence indicate that late infiltration of meteoric water does indeed occur along such vein-hosting structures. WEIR and KERRICK (1987) showed that late vuggy vein quartz was precipitated from such meteoric waters in the Mother lode, and O'HANLEY *et al.* (1989) reported that serpentine was shifted to low δD values along faults in the Cassiar district, British Columbia. In the Canadian Shield, the $\delta^{18}O$ values of calcite and ferroan dolomite paragenetically associated with vein quartz were isotopically reset by exchange with later meteoric water (KERRICH, 1989), even though the quartz was not affected. A problem also arises with the NESBITT *et al.* (1986) meteoric-water model, because of the magnitude of the ^{18}O-shifts required in the most northerly deposits. Under the conditions of low fluid/rock ratio and moderate temperatures (300–500°C) required for the pronounced ^{18}O-shifts in the fluids, the δD values of meteoric waters might also be expected to evolve off the meteoric water line with significant positive δD shifts (TAYLOR, 1974; OHMOTO, 1986). Finally, the meteoric water model does not account for the observation that mesothermal vein systems are restricted to terrane boundary structures and their splays. The model would predict mesothermal veins in any large transcurrent fault with the appropriate attributes of fluid infiltration, thermal structure, and permeability; this does not seem to be the case (KERRICH, 1989).

In summary, we interpret the δD values determined by NESBITT *et al.* (1986) and NESBITT and MUEHLENBACHS (1989) on bulk extracted fluid inclusion waters from quartz as consonant with other examples of late meteoric water infiltration, such as in the Alps (Fig. 7). Such terranes are characterized by pronounced shifts in δD values but minor changes in $\delta^{18}O$ values, and the hydrogen isotopic overprinting is indicative of a secondary process superimposed upon the primary hydrothermal regime. Primary fluid inclusion waters from undeformed quartz and coarse-grained hydrothermal micas yield mutually consistent D-enriched values for the ore-forming fluids. This interpretation implies that a major re-setting of the secondary fluid inclusions in such quartz veins is common, and that this occurs without any significant re-setting of the δD values of the coarse-grained hydrous minerals. If this interpretation is valid, it shows clearly that the medium- to coarse-grained hydrous minerals can preserve their D/H ratios, whereas an earlier discussion has demonstrated that micron-sized hydrous minerals under similar conditions do not preserve their original δD values.

CONCLUSIONS

Preferential exchange of hydrogen isotopes relative to oxygen isotopes during hydrous mineral-water exchange at low temperatures is supported by theoretical considerations of experimental results and, most importantly, by detailed studies of natural samples. Environments in which preferential alteration of δD values in micron-sized hydrous minerals are enhanced include reactivated fracture systems that permit the influx of meteoric waters having substantially different D/H ratios than the minerals. These environments may also enhance entrapment of the meteoric waters as secondary fluid inclusions along microfractures, and under these conditions some medium- to coarse-grained hydrous minerals seem to almost perfectly preserve their D/H ratios. These effects of grain-size and mineralogy on D/H exchange require a great deal more study.

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