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THE ORIGIN OF FLUIDS ASSOCIATED WITH SERPENTINIZATION PROCESSES: EVIDENCE FROM STABLE-ISOTOPE COMPOSITIONS

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ABSTRACT

Values of δD for serpentine minerals from the Mesozoic Cassiar serpentinite in north-central British Columbia (δD from −196 to −103‰), and from several serpentinites from the Archean Abitibi greenstone belt in Ontario (δD from −147 to −54‰) are variable, low, and many are consistent with those expected from modern meteoric water, regardless of the probable age of serpentinization. In contrast, $\delta^{18}O$ values are relatively constant, although different for each area. Such a pattern of variable hydrogen but constant oxygen isotopic compositions would be expected from hydrogen-isotope exchange, rather than rock–fluid interaction with varying water:rock ratios. Exchange is greater near faults, where enhanced flow of fluid would be expected. Values of $\delta^{18}O$ correlate with mineralogy and texture (whereas δD does not), and the oxygen isotope thermometer gives temperatures consistent with those inferred from mineral assemblages (*e.g.*, 250 to 300°C). Antigorite has higher δD values than lizardite and chrysotile because antigorite forms impervious rocks, attains a greater grain-size, and has a greater degree of crystallinity relative to lizardite or chrysotile. Isotopic data from other studies of serpentinites show similar patterns and can be attributed to the same process of later hydrogen-isotope exchange. On the basis of data for antigorite from serpentinized komatiitic flows from the Abitibi belt, Archean seawater had δD values similar to those of modern seawater.

Keywords: stable isotopes, Archean seawater, antigorite, chrysotile, lizardite, isotope exchange, Abitibi belt, Ontario, Cassiar District, British Columbia.

SOMMAIRE

Les valeurs de δD des minéraux du groupe de la serpentine provenant de la serpentinite mésozoïque de Cassiar, dans la partie nord-centre de la Colombie-Britannique (δD entre −196 et −103‰), et de plusieurs exemples de serpentinites de la ceinture archéenne de roches vertes de l'Abitibi, en Ontario (δD entre −147 et −54‰), sont variables et faibles; dans plusieurs cas, elles concordent avec celles que l'on s'attend à trouver dans l'eau météorique moderne, quelle que soit l'âge probable de la serpentinisation. En revanche, les valeurs $\delta^{18}O$ sont relativement constantes, quoique différentes dans chaque région. On pourrait s'attendre à une telle distribution de données, avec les rapports isotopiques d'hydrogène variables mais avec les rapports isotopiques d'oxygène constants, suite à un échange d'isotopes d'hydrogène plutôt que d'une interaction roche–eau avec des rapports variables de roche à eau. L'échange est plus avancée près des failles, où il y a eu un flux plus important de phase aqueuse. Les valeurs de $\delta^{18}O$ montrent une corrélation avec la minéralogie et les textures (tandis que δD ne montre pas cette dépendance), et la géothermométrie fondée sur les rapports isotopiques de l'oxygène donne des températures concordantes avec celles qui sont prédites à partie des assemblages de minéraux (*e.g.*, 250 à 300°C). L'antigorite possède une valeur δD plus élevée que la lizardite et le chrysotile à cause de la tendance qu'ont les assemblages à antigorite de former des roches imperméables, à granulométrie plus grossière, et ayant un degré de cristallinité supérieur par rapport aux roches à lizardite ou à chrysotile. Les données isotopiques provenant des autres études de serpentinites indiquent des tendances semblables; on peut donc les attribuer au même processus d'échange tardif des isotopes d'hydrogène. D'après les données sur l'antigorite provenant de coulées komatiitiques serpentinisées de la ceinture de l'Abitibi, l'eau de mer archéenne aurait un intervalle de valeurs δD semblable à celui de l'eau de mer actuelle.

(Traduit par la Rédaction)

Mots-clés: isotopes stables, eau de mer archéenne, antigorite, chrysotile, lizardite, échange d'isotopes, ceinture de l'Abitibi, Ontario, district de Cassiar, Colombie-Britannique.

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INTRODUCTION

Interaction of hydrothermal fluids with ultramafic rocks commonly results in the formation of serpentine-group minerals with lesser quantities of chlorite, talc, tremolite, brucite, magnesite, and magnetite. The temperatures and isotopic compositions of the fluids involved in the formation of serpentinites are recorded in the hydrogen and oxygen isotopic compositions of these alteration products. As such, several studies on the origin of fluids associated with the serpentinization process have focused on the hydrogen and oxygen isotope systematics in serpentine minerals.

The first systematic study of the stable-isotopic compositions of serpentinites (Wenner & Taylor 1971) indicated that antigorite in oceanic environments forms from heated seawater near 235°C, whereas oceanic chrysotile and lizardite form at lower temperatures, in the range 130–185°C. In contrast, antigorite in most continental ophiolites has δD and $\delta^{18}O$ values compatible with formation from metamorphic fluids (Wenner & Taylor 1973, Sheppard 1980), whereas chrysotile and lizardite from ophiolites, which have δD values that parallel those of modern meteoric waters at each locality, are postulated to form at relatively shallow levels in the crust from hydrothermal meteoric waters or formational brines (Wenner & Taylor 1973, 1974).

Inherent in each of these studies is the assumption that serpentine-group minerals do not exchange isotopes with post-formational fluids. As Wenner & Taylor (1974) were concerned with the retention of the original δD values in the serpentines they studied, they examined the degree to which natural serpentines exchange hydrogen isotopes with water in laboratory experiments at 100 and 185°C for 6–8 weeks. Antigorite had only a few percent exchange, whereas chrysotile showed up to 18% exchange, depending primarily on grain size. Citing the difficulty in extrapolating these results to geological environments and the apparent retention of original δD values by some early-formed serpentines, Wenner & Taylor (1974) concluded that most serpentine-group minerals probably do not undergo significant amounts of post-formation exchange of hydrogen isotopes at low temperature.

In the present study, the hydrogen- and oxygen-isotope systematics of well-characterized serpentine minerals from the Archean Abitibi greenstone belt in the Superior Province of Ontario and the Mesozoic Cassiar serpentinite in northern British Columbia were examined. Serpentine minerals from the Abitibi were selected from serpentinized komatiitic flows and associated sills to examine both the origin of fluids associated with oceanic and possible continental serpentinization at 2.7 Ga and the possible extent of post-formation isotopic exchange. Antigorite from the komatiitic flows is used to constrain the hydrogen-isotope composition of Archean seawater, and all serpentine samples from the flows and sills were used to constrain the extent of post-formation exchange as a function of crystal structure, grain size and rock porosity. The Cassiar serpentinite in British Columbia was selected because the wide-ranging but consistently low δD values of serpentine minerals originally reported by Wenner & Taylor (1974) suggested the possible influence of several different fluids. Moreover, the paragenesis of this serpentinite has since been studied in detail (Wicks & O'Hanley 1988, O'Hanley & Wicks 1995).

ANALYTICAL TECHNIQUES

Samples of serpentinite were examined petrographically to identify the textures and the minerals that make up the textures. Representative textures were analyzed with a microbeam X-ray camera, Ni-filtered Cu*K*α X-radiation and a beam 40 μm in diameter, for 8–9 hours under vacuum (Wicks *et al.* 1995). Serpentine-group minerals and magnetite were separated from other minerals using flotation, magnetic separation, and hand-picking. All samples were treated with HCl to remove carbonate and examined using X-ray diffraction and SEM to verify purity and mineralogy. Grain size of the serpentine minerals was determined either petrographically or from the peak width at half height of the major (001) X-ray-diffraction peak using the Scherrer formula for peak broadening (West 1984). Antigorite from Cassiar and that from the serpentine body at Mt. Belvidere (Vermont) were used as a standard to determine the grain sizes of lizardite and chrysotile from the Cassiar mine and the Garrison deposit.

Wenner & Taylor (1973) suggested that variable Cr content of magnetite in serpentinite indicates that the magnetite may not have reached isotopic equilibrium with the fluid that formed the coexisting serpentine minerals; variations in the chemical composition of magnetite were examined with a JEOL 8600 electron microprobe using wavelength-dispersion spectrometry (WDS). Only those samples determined to be chemically homogeneous were used for isotope geothermometry. Serpentine minerals were also analyzed to verify that their Fe contents, which can affect hydrogen-isotope fractionations (*e.g.*, Suzouki & Epstein 1976), are low.

Hydrogen-isotope compositions and H_2O contents of the serpentine-group minerals were determined using the uranium method of Godfrey (1962), as modified by Kyser & O'Neil (1984). Oxygen was extracted from the serpentines and magnetite using the BrF_5 technique (Clayton & Mayeda 1963). All hydrogen- and oxygen-isotope compositions are expressed in the familiar δ notation in units of ‰ relative to V–SMOW. Duplicate determinations indicate a reproducibility of ±0.2‰ and 3‰ for oxygen- and hydrogen-isotope compositions, respectively. A $\delta^{18}O$ value of 9.6‰ was measured for the NIST–28 quartz standard and a δD value of –65‰ was obtained for NIST–30 biotite standard using these techniques.

GEOLOGY, MINERALOGY, AND RESULTS

Abitibi greenstone belt

The Late Archean Abitibi greenstone belt of Canada represents the largest and youngest volcanic–plutonic terrane to have been accreted to the vast Superior Province of Canada. On the basis of lithological and chemical compositions, the belt has been divided into a Northern volcanic zone, Southern volcanic zone, and Southern granite–gneiss zone (Ludden *et al.* 1986). The Southern volcanic zone is further divided into three volcanic–sedimentary cycles: (1) submarine platform deposits of komatiitic through tholeiitic lavas overlain by (2) submarine to emergent complexes of calc-alkaline volcanic rocks and (3) local accumulations of sedimentary rocks (Pyke 1982, Dimroth *et al.* 1983, Jensen 1985). The series are intruded by coeval gabbro – anorthosite – ultramafic complexes and zoned diorite – tonalite – granodiorite plutons. The volcanic rocks range in age from 2693 to 2747 Ma (Corfu *et al.* 1990) and have been regionally metamorphosed to the prehnite–pumpellyite or greenschist facies (Jolly 1978, Dimroth *et al.* 1983). North–south compression accompanied the intrusion of late-stage granodiorites and porphyries at 2675–2693 Ma and potassic plutons at 2670–2680 Ma (Corfu *et al.* 1990). The Southern volcanic zone is cut into several blocks by east–west-trending faults related to movement between the Destor–Porcupine and Kirkland Lake – Larder Lake faults (Fig 1).

Serpentinized komatiitic flows, tholeiitic flows and associated ultramafic sills are abundant in the Southern volcanic zone (Fig. 1). Pyke (1982) divided the rocks around Timmins into the Deloro Formation and the overlying Tisdale Formation, which correspond to the second and third volcanic–sedimentary cycles, respectively, of the Southern volcanic zone. Serpentinized komatiitic pillow lavas and submarine flows from near Pyke's Hill (Fig. 1) are part of the Lower Tisdale Formation. The tholeiitic Dundonald sill and the sill-hosted Garrison chrysotile asbestos deposit also are part of the Tisdale Formation, whereas the sill-hosted Bowman chrysotile deposit (Fig. 1) is within the underlying Deloro Formation. The komatiitic flows, serpentinized

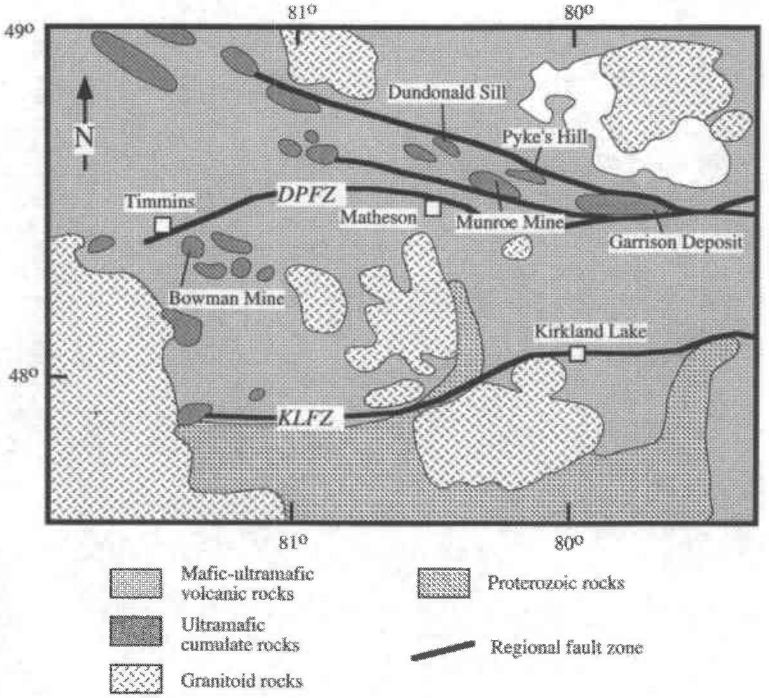

FIG. 1. Location of asbestos deposits and selected geological features of the Southern Volcanic Zone of the Archean Abitibi greenstone belt, Ontario and adjacent part of Quebec (Hubert *et al.* 1984, Ludden *et al.* 1986). Serpentinites in this study are from the Bowman asbestos mine, the Garrison asbestos deposit, a series of komatiite flows at Pyke's Hill that have been variably altered to serpentinite, and the Dundonald sill, which is a serpentinized tholeiitic intrusion. DPFZ: Destor–Porcupine Fault Zone, KLFZ: Kirkland Lake – Larder Lake Fault Zone.

ultramafic sills and every other rock type in the Abitibi belt are cut by unaltered Matachewan dikes that have a U–Pb age of 2450 Ma (Heaman 1989), indicating that serpentinization in the belt occurred prior to emplacement of the dikes.

The significance of different mineral assemblages and textures of serpentine from the Abitibi belt has been discussed by Wicks *et al.* (1983, 1984) and Kretschmar & Kretschmar (1986). The komatiitic submarine and subaerial flows and sills near Pyke's Hill have been extensively serpentinized to 90% serpentine, mainly antigorite, but relict olivine and, occasionally, pyroxene are present. Serpentinized flows usually consist of coarse-grained antigorite with a mesh texture pseudomorphic after olivine, as the earliest-formed alteration mineral (Table 1). Coarse-grained antigorite with a mesh texture is in some cases partly replaced around its rim by finer-grained mesh-texture lizardite, which is coeval with minor fine-grained, hourglass-texture lizardite in the groundmass of the flows (Table 1).

The earliest alteration event in the Dundonald sill and the Garrison and Bowman chrysotile asbestos deposits is recorded by relatively fine-grained, pseudomorphic mesh-texture lizardite (Table 1). This lizardite is similar in texture and grain size to mesh-texture lizardite in the flows, and is the predominant type of serpentine in the Dundonald sill (Table 1). The Bowman and Garrison serpentinites both contain later chrysotile ± antigorite with transitional textures (O'Hanley 1996) that replace the earlier mesh-texture lizardite. In the Bowman deposit, the early lizardite and the later chrysotile ± antigorite that replaced it are intimately associated and could not be separated for isotope analysis. Consequently, lizardite from the Bowman deposit includes serpentines from both stages of serpentinization. Chrysotile–asbestos veins cross-cut all earlier textures (Table 1). In the Bowman deposit, Schandl *et al.* (1990) measured homogenization temperatures of 290°C in fluid inclusions in diopside from rodingite that is contemporaneous with the formation of chrysotile ± antigorite.

Serpentine minerals from variably serpentinized flows in the Abitibi belt have a restricted range in their $\delta^{18}O$ values, 3.3 to 4.7‰, but more varied δD values of –114 to –54‰ (Table 1, Fig. 2). The oxygen-isotope compositions do not vary systematically with the generations of serpentine minerals in the flows. Those serpentinites having the lowest δD values generally have a higher proportion of fine-grained lizardite relative to the more coarsely crystalline antigorite. One sample of antigorite (+ lizardite) from komatiite in the Abitibi belt falls within the field of modern oceanic antigorite defined by Wenner & Taylor (1973), whereas most other

TABLE 1. PARAGENESIS OF SERPENTINE MINERALS AND TEXTURES FROM THE ARCHEAN ABITIBI GREENSTONE BELT (KOMATIITE FLOWS FROM PYKE'S HILL, SILLS AND SERPENTINITES FROM THE BOWMAN MINE, GARRISON DEPOSIT AND DUNDONALD SILL) AND THE MESOZOIC CASSIAR SERPENTINITE, BRITISH COLUMBIA

Serpentine Texture	Mineral and Timing			
	Early			Late
Serpentine Paragenesis in the Abitibi Greenstone Belt				
komatiite flows				
mesh texture	Atg			
mesh and hourglass texture		Lz		
serpentinized sills				
mesh texture		Lz		
transitional texture				Ctl ± Atg
asbestos veins			Ctl	------------ Ctl
Serpentine Paragenesis in the Cassiar Serpentinite				
type-1 hourglass texture	Lz			
type-2 hourglass texture	Lz			
interpenetrating texture	Atg			
interlocking texture		Ctl and Atg		
asbestos veins			Ctl	------------ Ctl
carbonate – lizardite – magnetite vein				Lz

Symbols for the serpentine minerals. Atg: antigorite, Lz: lizardite, Ctl: chrysotile.

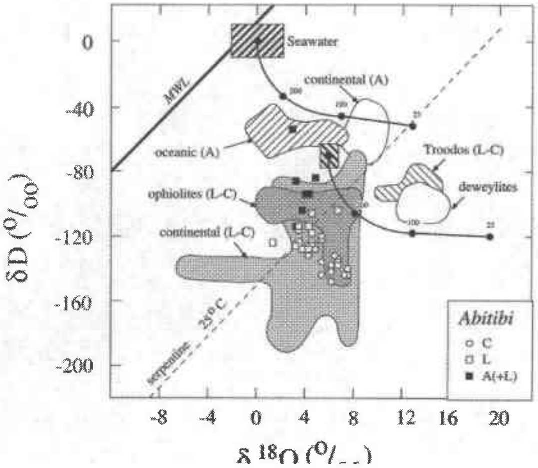

FIG. 2. Values of δD and $\delta^{18}O$ of serpentine-group minerals from the Abitibi greenstone belt relative to the field of values for serpentines from ophiolites, continental and oceanic areas, Troodos and deweylites as described by Wenner & Taylor (1973, 1974) and Margaritz & Taylor (1974). Also shown are the expected isotopic compositions of serpentine minerals in equilibrium with seawater having δD and $\delta^{18}O$ values of 0 and hydrothermal fluid having δD near –70‰, $\delta^{18}O$ of 6‰ (solid lines) at 200°C, 100°C, and 25°C. The compositions of serpentine expected from meteoric waters at 25°C using the meteoric water line (Craig 1961) and fractionation factors for serpentine – water extrapolated from Wenner & Taylor (1971) and Taylor (1974) are approximated by the serpentine 25°C line. Data from Table 1. Abbreviations for type of serpentine: A antigorite, C chrysotile, L lizardite.

samples of antigorite (+ lizardite) and of lizardite with mesh texture have lower δD values that fall within the field of continental lizardite–chrysotile (Fig. 2). Taken together, the "classic" interpretation of the isotope data from the flows indicates the presence of mixtures of a D-rich coarse-grained antigorite that may have formed from heated seawater and a more D-depleted fine-grained lizardite that may have formed from hydrothermal-meteoric fluids (Fig. 2). Both the seawater and the hydrothermal-meteoric fluids must have been Archean because all generations of serpentines in the flows were affected by emplacement of the Matachewan dikes at 2450 Ma.

Early-formed mesh-textured lizardite after olivine in the Garrison and the Dundonald sills have similar $\delta^{18}O$ values (3.3 to 6.7‰), but generally lower δD values (–128 to –105‰) than the mesh-texture lizardite from the serpentinized komatiitic flows (Table 1). In the "classic" interpretation, these data indicate that lizardite in both flows and sills may be related to the same fluid-circulation event. The late chrysotile in transitional textures and in asbestos veins in the Dundonald, Garrison and Bowman serpentinites is slightly more ^{18}O-rich (1.7 to 7.5‰) and more D-depleted (–145 to –115‰) relative to earlier-formed mesh-textured lizardite (Fig. 2), implying formation either from the same fluid (but at a different temperature) or from a fluid isotopically distinct from those associated with the earlier-formed serpentines. As with the serpentine minerals in the flows, the serpentines in the sills originally formed from Archean fluids prior to the emplacement of the Matachewan dikes.

Cassiar

The Cassiar serpentinite, in north-central British Columbia (59°40'N; Fig. 3), is an alpine-type serpentinite that hosts a major deposit of chrysotile. It occurs at

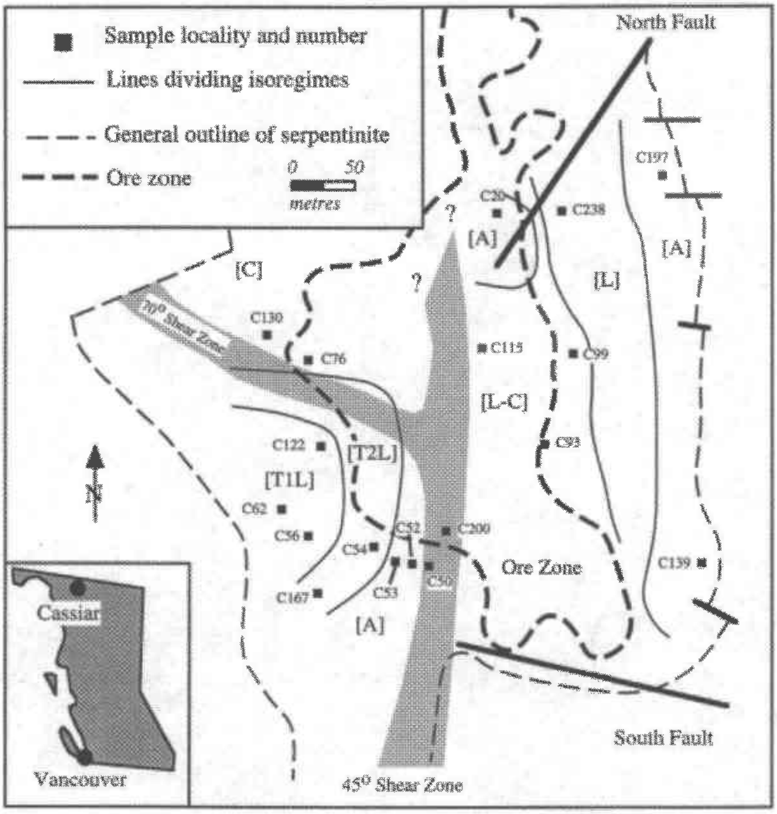

FIG. 3. Location and generalized geology of Cassiar serpentinite, British Columbia, showing sample locations, distribution of serpentine minerals and the orientation of the 70° and 45° shear zones. The hanging wall is east of the ore zone (from O'Hanley 1991). Abbreviations for serpentine minerals as in Figure 2; textures are T1: type 1, T2: type 2, interp.: interpenetrating, interl.: interlocking.

the base of the Sylvester Allochthon, which consists mainly of a 5000 m+ thick section of upper Paleozoic chert, argillite, and greenstone of island-arc and oceanic-crust affinity (Harms 1986, Nelson *et al.* 1993). Several fault-bounded ultramafic bodies of variable size and variable degree of serpentinization are scattered throughout the allochthon. During the Jurassic to mid-Cretaceous, the Sylvester Allochthon was thrust in a northeastly direction over autochthonous Precambrian to Mississippian shelf and platform deposits of limestone, shale and sandstone. Mesothermal gold mineralization was concurrent with tilting of all units into their present east-dipping orientation (Panteleyev & Diakow 1982). At 100 ± 10 Ma, quartz monzonite of the Cassiar batholith intruded the western part of the allochthon, producing metamorphism and deformation of the Cassiar serpentinite (O'Hanley 1991). The age of serpentine formation at Cassiar is further constrained from the age of undeformed lamprophyric dikes in the area, which were emplaced at about 67 Ma (Panteleyev 1985, Cooke & Godwin 1984, Nelson *et al.* 1993) along normal faults that offset all other types of faults and cross-cut the Cassiar serpentinite. The paleolatitude of Cassiar during Middle to Late Cretaceous time was about 50°N (Gabrielse 1985).

The Cassiar serpentinite originally was a harzburgite tectonite prior to serpentinization (Wicks 1984). Several distinct types of serpentinization have altered the harzburgite, resulting in replacement by lizardite, chrysotile and antigorite, and formation of veins of cross-fiber chrysotile asbestos and later veins of lizardite. The serpentinite is contained within a thrust sheet, and is enclosed by cherts and argillites on its footwall and by argillites and metavolcanic rocks on the hanging wall (Fig. 3). Several faults transect the serpentinite, with the 70° shear, which strikes ESE and dips 70°NE, and the 45° shear, which strikes NS and dips 70°E, being those most closely associated with formation of paragenetically late cross-fiber veins of chrysotile asbestos.

Wicks & O'Hanley (1988) and O'Hanley & Wicks (1995) divided the serpentine textures into four groups typical of the matrix and two other groups that typify vein textures (Table 1). The earliest-formed serpentine is Type-1 lizardite, having an hourglass-texture in the matrix of the serpentinite. Another hourglass-texture lizardite, Type 2, also occurs in the matrix and can be distinguished from Type 1 by the presence of crystallites that disrupt the Type-2 hourglass pattern of extinction. Petrographic relations indicate that Type-1 textures generally predate Type-2 textures (Table 1). Antigorite with an interpenetrating texture (with itself) that is coeval with the Type-2 lizardite textures is present in the matrix of the hanging-wall alteration zone, whereas chrysotile + antigorite with interlocking texture, most of which seems to postdate Type-2 textures, is present in the center of the serpentinite (Table 1, Fig. 3). With the exception of the antigorite serpentinite in the hanging-wall alteration zone, all of the above textural assemblages are cut by veins of cross-fiber chrysotile asbestos ± magnetite. The last generation of serpentine in the Cassiar serpentinite is carbonate – lizardite – magnetite veins that cross-cut all previous types of serpentine (Table 1).

TABLE 2. LOCATION, MINERALOGY, TEXTURE, $\delta^{18}O$ AND δD VALUES AND H_2O CONTENTS OF SERPENTINES FROM THE ARCHEAN ABITIBI GREENSTONE BELT, ONTARIO

Sample	Location	Mineralogy	Texture	$\delta^{18}O$	δD	H_2O
Abitibi flows						
AB1	Pike Hill Flow	Lz	mesh rim	3.5	−110	10.9
AB2	"	Atg (+Lz)	center	3.4	−86	8.0
AB4	"	Atg (+Lz)	center	3.5	−110	7.3
AB5	"	Lz	mesh rim	3.7	−102	10.9
AB6	"	Lz	mesh rim	4.4	−101	6.4
AB7	"	Atg	mesh center	4.5	−71	5.0
AB8	"	Atg (+Lz)	mesh center	3.3	−54	6.9
AB9	"	Atg (+Lz)	mesh center	4.7	−85	5.5
AB11	"	Atg (+Lz)	mesh center	4.4	−93	7.4
AB14a	"	Atg (+Lz)	mesh rim	3.4	−114	7.6
AB15	"	Atg (+Lz)	mesh rim	4.0	−93	6.8
Garrison Sill						
W70–572	Van Fibre Zone	Lz	mesh	4.1	−127	10.7
W71–251	"	Lz	"	4.6	−125	10.0
W82–151	"	Lz	"	4.9	−127	10.4
W82–152ba	"	Lz	"	4.7	−127	
W82–152bb	"	Lz	"	4.1	−128	9.7
W82–152bc	"	Ctl	veins	3.6	−115	9.2
W70–564c	North Fibre Zone	Lz	mesh	5.3	−121	10.4
W70–564cb	"	Lz	"	4.3	−108	10.4
W71–229	"	Lz	"	4.1	−114	9.8
W71–281a	"	Lz	"	6.7	−105	9.8
W70–564cc	"	Ctl	veins	4.3	−131	8.9
W71–240a	"	Ctl	"	7.5	−145	10.5
W71–240b	"	Ctl	"	5.9	−147	9.9
W82–149a	"	Ctl	"	5.9	−142	10.3
W82–149b	"	Ctl	"	7.1	−145	10.2
W70–573b	Bird Fibre Zone	Ctl	veins	5.7	−136	9.2
W70–573c	"	Ctl	"	5.6	−145	9.4
W71–233	"	Ctl	"	6.0	−139	10.2
W71–284	"	Lz	mesh	4.3	−118	9.5
W70–573a	"	Ctl	trans.	6.5	−134	10.2
W70–571	"	Ctl	"	6.4	−136	10.4
W71–224	"	Ctl	"	5.8	−120	10.6
W71–233a	"	Ctl	"	6.5	−137	10.8
W71–233b	"	Ctl	"	6.5	−139	10.2
W71–257a	SW Extension	Ctl	"	5.8	−140	10.8
W71–257b	"	Ctl	"	7.2	−140	9.4
W71–264a	"	Ctl	"	5.0	−128	10.2
W71–264c	"	Ctl	"	6.5	−131	11.0
Bowman Sill						
W70–505	Bowman mine	Lz (Ctl+Atg)	trans.	3.6	−129	9.6
W70–517	"	"	"	4.2	−126	9.7
W70–521	"	"	"	1.7	−124	8.6
W70–524	"	"	"	3.5	−115	9.7
Dundonald Sill						
W71–152	Dundonald Sill	Lz	mesh	3.5	−125	9.5
W71–153	"	Lz	"	3.3	−126	8.9

Symbols: Atg: antigorite, Lz: lizardite, Ctl: chrysotile; trans.: transitional. The values of $\delta^{18}O$ and δD are expressed in ‰, and the amount of H_2O is expressed in wt.%.

Replacement of lizardite to chrysotile + antigorite increases toward the 45° and 70° shear zones (Fig. 3).

TABLE 3. TEXTURE, MINERALOGY, $\delta^{18}O$ AND δD VALUES AND H_2O CONTENTS OF SERPENTINE MINERALS AND $\delta^{18}O$ VALUES OF MAGNETITE FROM THE CASSIAR SERPENTINITE

Sample	Mineralogy	Texture	$\delta^{18}O$	δD	H_2O	$\delta^{18}O$ Mgt	T°C
C–56	Lz	1–hourglass	9.7	–166	10.5		
C–62	Lz	1–hourglass	9.6	–169	10.1		
C–122	Lz	1–hourglass	9.7	–150	8.9		
C53B	Lz	2–hourglass	7.9	–177	9.6		
C54	Lz	2–hourglass	7.6	–174	10.3		
C130B	Lz	2–hourglass	8.2	–185	10.4		
C–139	Atg	interpenetrating	9.1	–103	9.1		
C–197	Atg	interpenetrating	8.8	–108	9.9		
C–115	Ctl+Atg	interlocking	8.8	–180	10.5		
C–76	Ctl+Atg	interlocking	8.9	–176	10.2		
C–50	Ctl+Atg	interlocking	8.2	–128	10.3		
C–52A	Ctl+Atg	interlocking	8.2	–161	10.0		
C–93A	Ctl+Atg	interlocking	8.2	–192	10.1		
C–99B	Ctl+Atg	interlocking	8.3	–177	10.2		
C–130C	Ctl+Atg	interlocking	8.5	–181	10.3		
C–20B	Ctl+Atg	interlocking	8.4	–185	10.4		
C–53A	Ctl	asbestos vein	7.9	–178	9.5	0.4	265
C93B	Ctl	asbestos vein	8.9	–175	10.0		
C–93C	Ctl	asbestos vein	8.9	–182	10.3	1.7	280
C–99A	Ctl	asbestos vein	9.1	–183	10.3	3.1	350
C–130A	Ctl	asbestos vein	9.2	–187	10.3		
C–167	Ctl	asbestos vein	8.2	–185	10.5		
C–200	Ctl	asbestos vein	7.7	–176	10.4		
C–238	Lz	carb–Srp–Mgt	6.8	–196	9.4	0.1	310

Temperature of isotopic equilibration of coexisting serpentine and magnetite is calculated using the empirical fractionation-factors developed by Wenner & Taylor (1971). Symbols: Atg: antigorite, Lz: lizardite, Ctl: chrysotile, Srp: serpentine, Mgt: magnetite, carb.: carbonate.

A dense, tough antigorite rock with an interpenetrating texture is most common in the hanging-wall alteration zone, whereas alteration in the footwall of the ore zone is characterized predominantly by a much less competent, porous serpentinite composed of Type-1 and Type-2 lizardite in an hourglass texture. In conjunction with the paragenesis of the serpentine minerals (Table 1), these textural relations indicate that there is a continuum in development of the serpentinite wherein lizardite with a pseudomorphic texture (Type 1) is replaced first by lizardite (Type 2), but then lizardite became unstable near major shear zones and was replaced by chrysotile + antigorite with interlocking textures in association with veins of chrysotile asbestos. Lizardite again became stable in the very late stages as carbonate – lizardite veins cross-cut all other textures.

The mechanical properties of the various serpentinites are significantly different. The antigorite serpentinite along the hanging wall is an extremely competent and impervious rock that is very difficult to break and resists fracturing and shearing. The lizardite hourglass and chrysotile – antigorite serpentinites are mechanically much less competent and much more porous than the antigorite serpentinite. They are the focus of fracturing, major shear zones and fluid migration. Most of the cross-fiber, chrysotile-asbestos veins are composed of uncemented chrysotile fibers that have high porosity and can be easily disaggregated.

Rodingites occur throughout the deposit. Fluid inclusions in grossular, diopside and clinozoisite from within the 45°N shear and the ore zone (Schandl *et al.* 1990, O'Hanley *et al.* 1992) have homogenization temperatures of 250–350°C and salinities of 4–10 wt% NaCl equivalent.

All the serpentine minerals from the Cassiar deposit have $\delta^{18}O$ values from 7.6 to 9.7‰, but different generations of serpentine have distinct values (Table 3, Fig. 4). For example, the earliest generation of serpentine, the Type-1 lizardite with an hourglass texture, tends to be the most ^{18}O-rich, with values near 9.7‰. The last generation of serpentine, as represented by lizardite from a carbonate – lizardite – magnetite vein, has the lowest $\delta^{18}O$ value, 6.8‰. The $\delta^{18}O$ values of chrysotile asbestos veins range from 7.7 to 9.2‰ (Table 3), and encompass the range of values for chrysotile from the asbestos pit at Cassiar (Wenner & Taylor 1974).

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‰ (Table 3, Fig. 4). Samples of coarse-grained antigorite from the hanging wall are the most D-rich serpentine (–108 and –103‰) whereas lizardite from the late carbonate – lizardite – magnetite veins has the lowest δD value (–196‰). As a group, the serpentines form a trend (Fig. 4) similar to that observed in the flows from the Abitibi, in which the $\delta^{18}O$ values are relatively constant, but the δD values are between those of the coarse-grained antigorite and the fine-grained lizardite in the carbonate – lizardite – magnetite veins. Serpentine min-

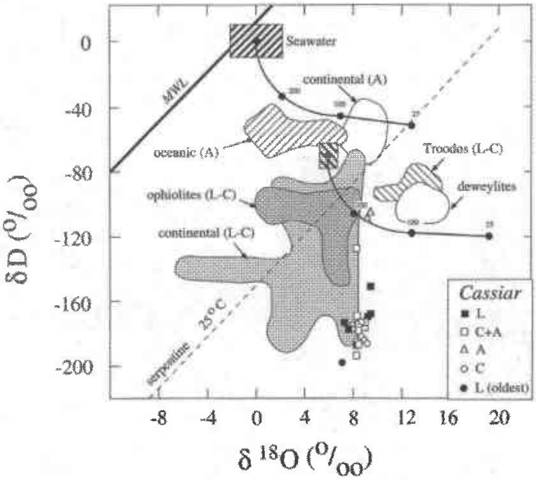

FIG. 4. Relationship between δD and $\delta^{18}O$ values of serpentine-group minerals from the Cassiar serpentinite, British Columbia. Fields of values for various serpentinites and other symbols are described in Figure 2. Data are from Table 3.

erals from the Cassiar are among the most D-depleted minerals measured; they have low δD values, which eliminates the possibility of formation from heated seawater, and high $\delta^{18}O$ values, which precludes formation from low-temperature meteoric waters. All the serpentines (including the antigorite) fall within or near the field of continental lizardite – chrysotile (Fig. 4), in part because Wenner & Taylor (1974) used their own values from Cassiar to define this field.

Differences between the $\delta^{18}O$ values of chrysotile and coexisting magnetite from the asbestos veins give apparent temperatures of equilibration of 300 ± 50°C (Table 3) using the empirical isotope geothermometer of Wenner & Taylor (1973). These temperatures are similar to those obtained from homogenization temperatures (250–350°C) of fluid inclusions in contemporaneous rodingites from within the 45° shear and the ore zone. Lizardite – magnetite oxygen-isotope fractionations give an apparent equilibration temperature of 300°C for minerals in the late carbonate – lizardite – magnetite veins (Table 3), which is evidence that much of the serpentinization process at Cassiar was isothermal.

DISCUSSION

Abitibi greenstone belt

Antigorite from the Abitibi belt has widely variable δD but much more restricted $\delta^{18}O$ values that form a near-vertical trend in a plot of δD *versus* $\delta^{18}O$ (Fig. 2). The most D-rich samples of antigorite plot within or near the field of modern oceanic antigorite and have petrographic characteristics, morphology and grain size similar to oceanic antigorite. This similarity implies that some of the antigorite samples may record the isotopic composition of Archean seawater. Temperatures at which the antigorite in the Abitibi formed can be constrained from three factors: (1) in the Bowman serpentinite, rodingites associated with the formation of chrysotile ± antigorite that postdate and did not affect the pseudomorphic antigorite in the flows have homogenization temperatures of fluid inclusions near 300°C, (2) modern oceanic antigorite forms at temperatures above 235°C (Wenner & Taylor 1971), and (3) experimental and theoretical results indicate that antigorite is stable at temperatures above 250°C at $P(H_2O)$ less than 2000 bars (Berman 1988). Assuming 300°C as the temperature of formation of Abitibi antigorite, the sample with the highest δD value was in equilibrium with a fluid having a δD value of about –20‰ and a $\delta^{18}O$ value of +3‰ (Fig. 5a). Inasmuch as field evidence and analogies to modern oceanic antigorite suggest that this fluid was mainly heated seawater at *ca.* 2700 Ma, a δD value of about –20‰ indicates that the hydrogen-isotope composition of Archean seawater was similar to that of modern seawater. The δD value of –20‰ is a minimum for Archean seawater because any contribution to the serpentinizing fluid from other waters or any later exchange of hydrogen isotopes would only lower the D/H ratio. Antigorite from the Abitibi provides the first evidence that the hydrogen-isotope composition of late Archean seawater was similar to that of modern seawater.

Homogenization temperatures of fluid inclusions in rodingite from the Bowman deposit indicate that the chrysotile and antigorite that replaced the earlier mesh-texture lizardite (Table 1) in the serpentinites formed near 300°C (Schandl *et al.* 1990). Using 300°C as the temperature at which the lizardite – chrysotile – antigorite assemblages in the Abitibi formed, the fluids calculated to be in equilibrium would have $\delta^{18}O$ values of 1–6‰, wide-ranging δD values of –125 to –70‰, and overlap those fluids calculated to be in equilibrium with the earlier antigorite (+ lizardite) from the komatiitic flows (Fig. 5a). The low δD values of these assemblages (Fig. 2) and of the fluid phase from which they formed (Fig. 5a) indicate that the isotopic composition of these serpentines do not reflect Archean seawater. Their relatively constant $\delta^{18}O$ values are consistent with an isothermal process and make a change in temperature to produce the variations of up to 55‰ in the δD values of the lizardite highly unlikely.

Variable δD values of the fluids associated with the lizardite – antigorite – chrysotile assemblages in the Bowman, Dundonald and Garrison sills could result either from metamorphism of isotopically distinct sources, which would require periodic release of fluids from a variety of protoliths, or from mixing of a metamorphic fluid having a high δD value of *ca.* –75‰ and hydrothermal meteoric water having a low δD value of *ca.* –120‰. Within the Abitibi belt, the majority of rocks are volcanic–plutonic or volcaniclastic, such that significant variations in the δD value of fluids released from different protoliths during metamorphism are unlikely. Furthermore, the lowest δD values of the lizardite – chrysotile – antigorite assemblage would necessitate metamorphism of rocks having hydrous minerals with very low δD values because the fluid released is enriched in D relative to either the parent or residual daughter mineral. Such minerals normally form only in environments of high altitude or latitude, both of which are unlikely for the Abitibi, and for which there is no evidence in any pre-Mesozoic rocks from the Canadian Shield (*e.g.*, Kyser & Kerrich 1991). Hydrothermal meteoric water could have the same $\delta^{18}O$ value as a metamorphic fluid, provided the water:rock ratio was very low (Fig. 5a), but the low δD value of the water also requires that serpentinization occurred at high latitude, if the temperature was *ca.* 300°C.

Interpretation of the stable-isotope data from the serpentine minerals in the Abitibi flows illustrates the quandary that many have had with detailed studies on the isotope systematics of complex serpentinites. Although certain isotopic reservoirs (*e.g.*, Archean seawater for the coarse-grained antigorite from the flows) can be

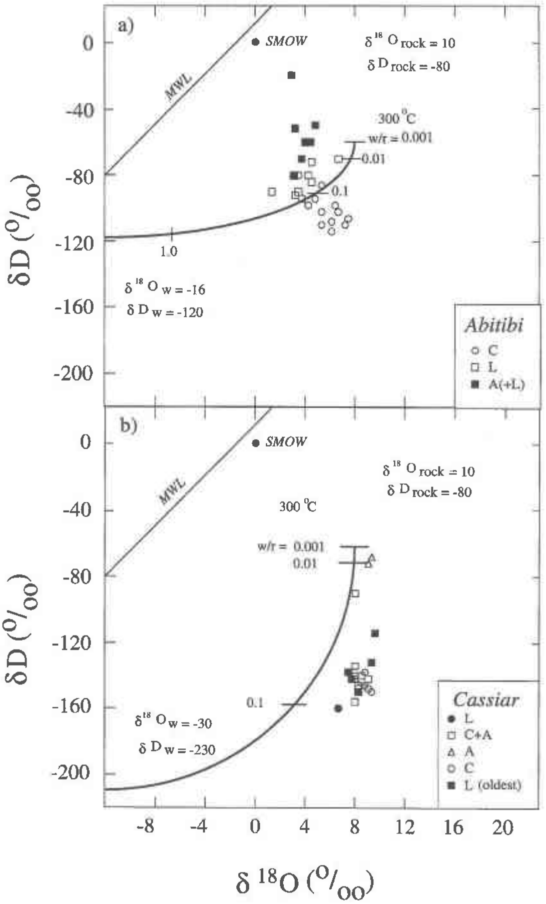

FIG. 5. Calculated δD and $\delta^{18}O$ values of fluids in equilibrium with serpentines from (a) the Archean Abitibi greenstone belt, and (b) the Mesozoic Cassiar serpentinite, assuming all formed at 300°C. Also shown are the water:rock ratios for open-system exchange between a precursor rock ($\delta^{18}O$ 10‰, δD –80‰) and modern meteoric waters in each area.

delineated from the high δD values and geological relations, many paragenetically distinct types of serpentine-group minerals have a significant range of δD values, but relatively constant (albeit in some cases distinct) $\delta^{18}O$ values. Moreover, the lowest δD values for each generation of serpentine tend toward those of serpentine in equilibrium with modern meteoric waters, despite geological evidence that the serpentines formed in a different environment.

In their survey of the stable-isotope composition of continental serpentinites, Wenner & Taylor (1974) showed that lizardite and chrysotile exhibit a progressive range in δD values parallel to that of modern meteoric waters, whereas $\delta^{18}O$ values do not. Consequently, they concluded that these minerals formed from meteoric hydrothermal fluids during emplacement of the ultramafic bodies. However, results of subsequent studies indicate that many generations of serpentine-group minerals in serpentinites show similar trends in δD, regardless of their paragenesis. For example, Yui *et al.* (1990) concluded that the range in δD values from –70 to –45‰ and constant $\delta^{18}O$ values in metamorphic antigorite from the Fengtein ophiolite, Taiwan, resulted from variable water:rock ratios to produce the antigorite, culminating in late chrysotile having low δD (but similar $\delta^{18}O$) values. However, constant $\delta^{18}O$ values for all generations of serpentine from the Fengtein ophiolite require that integrated water:rock ratios be small, and the source, homogeneous (*i.e.*, rock-dominated), whereas variable δD values require variable water:rock ratios or heterogeneous sources.

Burkhard & O'Neil (1988) reported similar results for greenschist-facies antigorite in the Alps. High values of δD (–42 to –34‰) suggestive of seawater-induced serpentinization occur in the eastern part of Valmalenco in the Alps, whereas antigorite has much lower values (–93 to –60‰) in the west. They proposed that the antigorite in the west has low $\delta^{18}O$ and δD values as a result of an incomplete overprint by magmatic and meteoric fluids associated with contact metamorphism caused by a large granitic intrusion. However, the δD and $\delta^{18}O$ values of the antigorite seem unrelated to the intrusion, in contradiction of their model.

In another study of alpine ophiolites in the Alps, Fruh-Green *et al.* (1990) reported that lizardite – chrysotile serpentinites in the South Pennine nappes have relatively high and constant $\delta^{18}O$ values (from 6 to 10‰), but variable δD values, from –146 to –30‰. Serpentines from clast- and matrix-dominated ophicalcites have higher δD values (typical of oceanic serpentinites) than spatially related massive and fractured serpentinites, and the lower δD values require interaction with a fluid dominated by modern meteoric water (*e.g.*, Wenner & Taylor 1971 1973, Burkhard & O'Neil 1988). However, as is the case for serpentines from the Abitibi and serpentinites in many ophiolites, geological and mineralogical evidence indicates that much of the serpentinization in these Alpine serpentinites occurred prior to, or early in, the accretionary history. Evidence for regional metamorphism of the serpentines by fluids with a meteoric water component is made apparent only by the range in δD values, and rarely by the geological histories, mineralogical compositions, $\delta^{18}O$ values or other isotope systematics (*e.g.*, Stille *et al.* 1989).

If the serpentines from the Abitibi have retained their original isotopic compositions, several serpentinization events for each serpentine mineral are required, most of which would have had a significant "modern" component of meteoric water. Such a result is in direct conflict with the petrographic and geological evidence that antigorite, lizardite and chrysotile formed early in the history of these serpentinites. Unless Archean meteoric waters in the Abitibi area had isotopic compositions similar to those of modern meteoric water, the participation of greater volumes of relatively modern water is required.

Preservation and alteration of the Abitibi serpentinites

Why do some serpentine-group minerals in the Abitibi (and elsewhere) have low δD values that trend toward those of modern meteoric water in the area? The geological evidence in most areas argues against meteoric water as a serpentinizing agent. An alternative possibility is that in many cases, serpentine-group minerals have not retained their original δD values. Wenner & Taylor (1973, 1974) cited four major aspects of their data that implied that the isotopic compositions of serpentines are preserved: (1) both the δD and $\delta^{18}O$ values of lizardite and chrysotile from serpentinized ultramafic intrusions in southeastern Alaska are unusually low, indicating that heated groundwater can be the serpentinizing fluid; (2) some lizardite and chrysotile in Precambrian dikes and sills have low δD values, but not as low as would be expected from modern meteoric water, thereby indicating that their values have been preserved, at least in part; (3) antigorite normally has a much higher δD value than coexisting lizardite and chrysotile, even where the latter have low δD values and are proximal to the antigorite; (4) limited experimental results and similarity in the structures of the serpentine minerals suggest that antigorite, lizardite and chrysotile of the same grain-size should exchange at the same rate, but in many cases, coexisting serpentine-group minerals have heterogeneous δD values. Although the data from the Alaskan serpentinites do support the contention that meteoric water can be a serpentinizing fluid, the remaining three aspects can be attributed to hydrogen-isotope exchange processes.

There are at least three possible factors that must be considered in isotope-exchange processes. These are, in order of decreasing importance, (1) the porosity and permeability of the rock, (2) the grain size of the minerals that make up the rock, and (3) the crystal structures of the mineral grains in the rock.

If a rock is impermeable, the exchange of hydrogen isotopes cannot take place because H_2O cannot reach the interior of the rock. Antigorite serpentinites form at high temperatures relative to lizardite and chrysotile, normally in a metamorphic regime of elevated temperature and pressure. The relatively coarse, interpenetrating blades of antigorite form a dense, impervious rock of very low porosity and great structural strength. In sharp contrast, lizardite serpentinites and chrysotile serpentinites normally form at lower temperatures and confining pressures and, as a result, are porous. Compared to antigorite serpentinites, they are much less competent rocks, and readily fracture and shear. The porosity and incompetence of lizardite and chrysotile serpentinites permit flow of fluids, particularly meteoric water, which enhances the opportunity for hydrogen-isotope exchange. Serpentinites composed of antigorite + lizardite, or antigorite + chrysotile, have intermediate porosities and permeabilities, and intermediate potential for hydrogen-isotope exchange. Antigorite in these serpentinites will have a greater opportunity for exchange than in serpentinites composed solely of antigorite.

Antigorite usually forms coarse grains relative to lizardite and particularly chrysotile. Fine grains have greater surface-area, relative to their mass, than coarse grains, so that exchange is enhanced and can occur more rapidly in fine grains. Thus, the greater surface-area of chrysotile and lizardite, relative to antigorite, make them more susceptible to hydrogen-isotope exchange.

In terms of crystal structure and chemical composition, most antigorite occurs as well-ordered, large crystals with fewer defects and less stacking disorder than lizardite (Wicks & O'Hanley 1988). In contrast, lizardite commonly occurs as disordered, fine-grained crystals in complex pseudomorphic textures. Chrysotile occurs as fibers that are much longer than wide and have a hollow core 400–500 nm in diameter that would facilitate hydrogen-isotope exchange.

Chrysotile asbestos fibers occur over a fairly restricted range of 1500 to 3000 nm (Yada 1971). However, polygonal serpentine is a common habit of serpentine in serpentinites. Polygonal serpentine may or may not have a central core of a single chrysotile fiber, but it always has an outer polygonal zone, approximately 20,000 nm in diameter, of 15 or 30 sectors of various polytypes of lizardite (Baronnet *et al.* 1994). Groups of polygonal serpentine and bundles of chrysotile fibers may be cemented to adjacent polygonal serpentine or chrysotile fibers, respectively, to decrease their intergranular or interfiber porosity and to increase their effective grain-size. Such an arrangement would not be conducive to hydrogen-isotope exchange and is an example of the many variables that must be considered in assessing conditions for exchange.

The H_2O content of serpentine calculated from the ideal formula is *ca.* 13 wt%. The H_2O is present as OH groups at specific sites in the structure. Hydroxyl groups and Mg atoms are systematically omitted at the planes of inversion in the modulated structure of antigorite (Guggenheim & Eggleton 1988), so that antigorite has a lower-than-ideal H_2O content that varies systematically with the wavelength of the antigorite structure (Kunze 1961). Relative to antigorite, lizardite and chrysotile usually have higher than ideal H_2O contents (Wicks & O'Hanley 1988) because of H_2O on the external surfaces of the minerals, within the hexagonal rings of the sheet of basal atoms of oxygen, or within the hollow axial cores of chrysotile fibers. This H_2O is weakly bound, as it is released from both structures below 300°C, a considerably lower temperature than the 700–800°C for release of structural OH groups. In addition to their overall smaller grain-size and distinct habit of the crystals relative to antigorite, this weakly bonded H_2O in lizardite and chrysotile is relatively mobile and would facilitate hydrogen-isotope exchange with OH groups in much the same way as that proposed for illite and other 1:1 layered silicates (Wilson *et al.* 1987, Bird & Chivas 1989, Longstaffe & Ayalon 1990, Kotzer & Kyser 1991, 1995).

Antigorite serpentinites, and the antigorite within them, have different mechanical properties, coarser grains, and different crystal-chemical properties in comparison with lizardite and chrysotile serpentinites. This combination of physical properties of the serpentinites and crystal-chemical factors of the serpentine minerals means that antigorite serpentinites have much less potential for interaction with H_2O and hydrogen-isotope exchange than lizardite and chrysotile serpentinites. Serpentinites that are mixtures of antigorite with lizardite or chrysotile (or both) will have properties intermediate between antigorite serpentinites and lizardite or chrysotile serpentinites. This explains why antigorite has higher δD than proximal lizardite or chrysotile.

Although it is difficult to systematically assess all the factors that control hydrogen-isotope exchange, we have been able to assess the effect of grain size. Figure 6 shows the relationships between grain size, determined by X-ray diffraction, and δD and $\delta^{18}O$ values for Garrison and Cassiar serpentinites. These results show that those serpentinites with the highest δD values, usually antigorite, have the coarsest relative grain-size, and those with the lowest δD values, the smallest grain-size. Values of $\delta^{18}O$ vary less regularly with grain size. All these factors and our results suggest that serpentines can exchange hydrogen isotopes with later fluids, but antigorite much less so than lizardite and chrysotile.

In the Abitibi, the antigorite is paragenetically the oldest and, therefore, most susceptible to resetting by later fluids. However, not only does antigorite have the most ordered structure of the serpentine-group minerals, the antigorite samples in the Abitibi suite are also the serpentine with the largest grain-size, as is normally the case for antigorite in many serpentinites (Fig. 6). Therefore, the exchange should be less substantial for the antigorite than for the finer-grained lizardite and chrysotile. Given that the Abitibi antigorite usually is contaminated with some lizardite (Table 2), some exchange may be expected and, in fact, antigorite hosts the largest range in δD values, the lowest of which trend toward the values in lizardite and chrysotile. Consequently, some of the antigorite-bearing samples have retained their original values, and others have been partially exchanged, but all the finer-grained serpentine minerals have been more extensively affected by later meteoric fluids. Furthermore, the relatively constant $\delta^{18}O$ values of each type of serpentine mineral require either that the water:rock ratios in the hydrothermal meteoric water system were vanishingly small or that hydrogen isotopes have been preferentially exchanged, because the original $\delta^{18}O$ values were not affected.

There is no geological evidence for hydrothermal groundwaters in the Abitibi area since the Neoproterozoic (Kerrich & Kamineni 1987), and only recent groundwaters have the low δD values appropriate for those in the lizardite, chrysotile and some of the antigorite. Therefore, the original $\delta^{18}O$ values may have been preserved in the serpentines from the Abitibi, but the δD values have not. Hydrogen-isotope exchange seems most pronounced in serpentines that are fine-grained and less ordered, such as the lizardite and chrysotile, or those associated with faults and fractures, such as the chrysotile, where integrated water:mineral ratios should be the highest. If there has been preferential hydrogen-isotope exchange, the original δD values of the lizardite and chrysotile would have been greater than the highest δD values, *i.e.*, >–108 and >–115‰, respectively (Table 2).

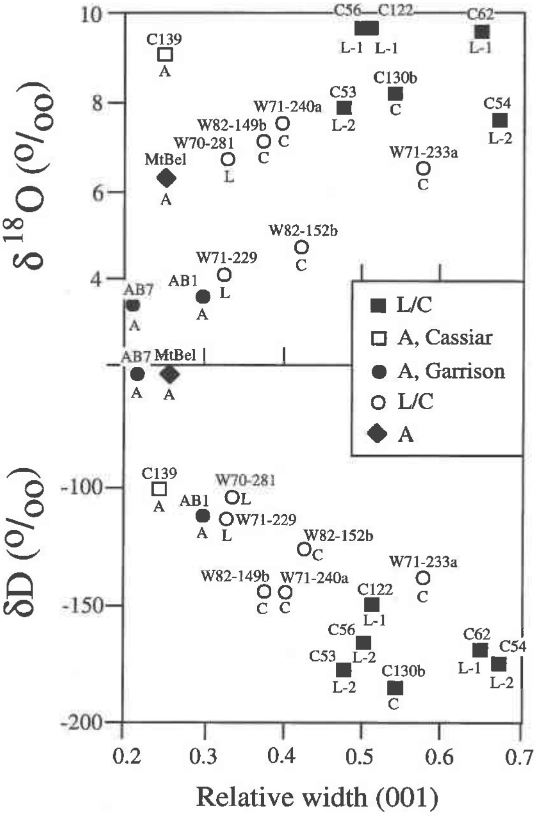

FIG. 6. Relation between grain size (width in 2θ at 1/2 height of 001 peak) and δD or $\delta^{18}O$ for serpentine minerals from the Archean Garrison and Mesozoic Cassiar serpentinites. One specimen of coarse-grained antigorite from Mt. Belvidere, Vermont, is included for comparison. Abbreviations for type of serpentine: A antigorite, C chrysotile, L lizardite.

The large variations in the δD values of some generations of serpentines from Taiwan and the Alps may also result from preferential (but differential) exchange of hydrogen isotopes with relatively modern meteoric waters, although detailed grain-size or geological relations are usually lacking. However, in a study of Alpine ophiolites in the Alps (Früh-Green *et al.* 1990), where geological relations indicate that serpentinization occurred prior to accretion, serpentines in the fractured serpentinite have more variable and lower δD values than samples of ophicalcite, probably because the former had higher integrated water:mineral ratios than the ophicalcite.

Cassiar

The low δD values of the Cassiar serpentines require that the dominant fluid was meteoric water, as was first suggested by Wenner & Taylor (1973). However, the significantly higher δD values of the antigorite relative to all other generations of serpentine imply that another water, such as a metamorphic fluid, also was involved. In the "classic" interpretation, for a constant temperature of 300°C, the serpentinizing fluids would have started with low δD values of *ca.* –160‰, gone to significantly higher values of *ca.* –70‰ when antigorite formed, and then dropped again to *ca.* –160‰ with the later generations of chrysotile and fracture-filling lizardite (Fig. 5b). The $\delta^{18}O$ values of the fluids were constant throughout this process.

Although meteoric waters could have been serpentinizing agents in the Cassiar serpentinite, several factors support (1) an origin by metamorphic fluids for the serpentines, and (2) subsequent hydrogen-isotope exchange with meteoric waters. The δD values vary with grain size (Fig. 6), as is the case with the Abitibi serpentines. Serpentines closest to fault zones, where the integrated water:rock ratios have been highest owing to higher porosity and permeability, tend to have the lowest δD values regardless of their paragenesis (Table 2). In addition, as with the Abitibi serpentinites, only the $\delta^{18}O$ values correlate with serpentine texture; δD values do not. The antigorite that occurs in the most impervious rock and has the largest grain-size relative to all other serpentines also has the highest δD values. It most likely has retained its original composition because meteoric water could not penetrate. Earlier-formed lizardite and later-formed chrysotile have variable δD values that range between those of the coarser antigorite and modern meteoric water. This is expected from differential hydrogen-isotope exchange, but not from formation from similar fluids, at decreasing temperatures or from low-temperature meteoric water. None of the serpentines plot at high water:rock ratios, as would be expected in hydrothermal systems involving meteoric water. Moreover, serpentine – magnetite isotope geothermometry is still valid regardless of the δD values of the serpentine at Cassiar.

We suggest that both the isotopic compositions and temperatures of all the serpentinizing fluids were similar at Cassiar, and were metamorphic in origin. Later influx of meteoric waters, particularly along shear zones and through the porous serpentinites and abestos veins, effected preferential hydrogen-isotope exchange. As suggested by O'Hanley & Wicks (1995), early-formed lizardite was replaced by antigorite and chrysotile assemblages from the same fluid, implying that the isotopic compositions of the fluids did not evolve by mixing with meteoric water. In effect, all of the serpentines could have originally had δD values similar to those of the coarser, impervious, hanging-wall antigorite and formed from metamorphic fluids having δD and $\delta^{18}O$ values of –70 and +9‰, respectively. Meteoric water participates only in late, low-temperature hydrogen-isotope exchange processes in the porous serpentinites and asbestos veins.

SUMMARY

Serpentines can form from a multitude of fluids, as originally proposed by Wenner & Taylor (1971, 1973), but the role of heated meteoric water in forming serpentines in most ophiolites may be less significant than previously proposed. Seawater and metamorphic fluids seem to be the dominant serpentinizing agents, whereas meteoric water participates in post-formational hydrogen-isotope exchange processes. Although there may be some exceptions, such as some Alpine serpentinites in Alaska (Wenner & Taylor 1973), most detailed studies suggest that preferential hydrogen-isotope exchange may be ubiquitous in parts of most serpentinites, provided the serpentinites are porous, modern fluxes of meteoric water are significant, and grain sizes are small. Kyser & Kerrich (1991) modeled the post-formational exchange of hydrogen and oxygen isotopes between kaolinite and water and concluded that hydrogen-isotope exchange can be geologically rapid (*i.e.,* within a few million years) provided integrated water:rock ratios are high.

Not only is exchange theoretically possible, but the evidence from the serpentines studied here, in conjunction with other results, supports a process by which the variable δD values of many serpentines occur. This evidence includes:

(1) Antigorite often retains its original δD value because antigorite serpentinites are normally impervious and antigorite has greater grain-size and greater crystallinity relative to lizardite and chrysotile.

(2) There is a correlation between the δD values of modern meteoric waters and some serpentines in Alpine serpentinites and ophiolites, despite geological evidence that the serpentines formed in the distant past and in a different environment.

(3) Retrograde exchange of hydrogen isotopes has been observed in 2:1 and other 1:1 layered silicates.

(4) Values of $\delta^{18}O$ in most serpentinites correlate with serpentine texture, whereas δD values do not.

(5) In a plot of δD *versus* δ^{18}O, the vertical shift in the δD values of many serpentines is more consistent with hydrogen-isotope exchange rather than formation from a single fluid with decreasing temperatures or from low-temperature meteoric waters. In addition, no serpentine samples plot at high water:rock ratios, as would be expected in hydrothermal systems involving meteoric water.

Hydrogen-isotope exchange in serpentine-group minerals probably is enhanced in specific environments where the integrated water:mineral ratios are greatest. Not all the serpentine present will be affected by this process, but the effect may be more pronounced from areas with meteoric waters isotopically distinct from metamorphic or ocean waters. Some serpentinites may have recorded the isotopic composition of ancient seawater or metamorphic water, but are overprinted by hydrogen-isotope exchange with modern meteoric waters.

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