Stable isotope composition of alteration fluids in low-grade Lower Palaeozoic Rocks, English Lake District

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ABSTRACT. A combination of hydrogen and oxygen isotope analyses and fluid inclusion studies has defined the composition of fluids involved in the metamorphism of Lower Palaeozoic rocks in the English Lake District. Three fluid fields have been defined from secondary phases: 1, syn-burial metamorphic D-enriched fluids from epidote and chlorite at a temperature between 250 and 350 °C; 2, D-depleted fluid measured from groundmass and quartz inclusions; 3, a mixed magmatic-meteoric fluid with an intermediate H-isotopic composition estimated from W/R granite data and calculated from illite.

KEYWORDS: metamorphism, stable isotopes, Palaeozoic rocks, Lake District, England.

THIS study investigates the nature and origin of fluids involved in low-grade metamorphism and hydrothermal alteration of Lower Palaeozoic igneous and sedimentary rocks of the English Lake District.

The Lake District succession represents the Lower Palaeozoic continental margin south of the Iapetus suture (Leggett *et al.*, 1983). Shales and silts of Tremadoc–Arenig age, the Skiddaw Slate Group, form the oldest part of the succession. These sediments are conformably overlain by the subduction-related Eycott Volcanic Group (Fitton and Hughes, 1970) of Arenig–Llanvirn age. Calc-alkaline lavas and tuffs of the Borrowdale Volcanic Group unconformably overlie the Skiddaw Slate and Eycott Volcanic Groups. Silts and greywackes of Ashgill–Downton age, here referred to as the Upper Ordovician and Silurian succession, lie with marked overlap on the Skiddaw Slate and Borrowdale Volcanic Groups. Both the Skiddaw Slate and Borrowdale Volcanic Groups show evidence of pre-Bala deformation (Moseley and Soper, 1978). The main deformation period was end-Silurian, producing polyphase deformation and cleavage development in less competent shale and tuff units.

The succession is intruded by high-level granitic plutons of Ordovician to end-Silurian age. Geophysical studies (Bott, 1974) suggest that a large batholith underlies the Skiddaw Slate and Borrowdale Volcanic Groups at relatively shallow depth. The general geology is summarized in fig. 1.

Base metal vein mineralization occurs in the roof regions of the postulated batholith suggesting a relationship between intrusion and mineralization (Firman, 1978). Isotope dating of mineralized veins gives Lower Devonian to Jurassic ages. A full account of Lake District geology is given by Moseley (1978).

Metamorphism. A detailed description of the burial metamorphism is given by Thomas in Bevins *et al.* (1984) and Oliver *et al.* (1984). Prehnite-pumpellyite facies metamorphism has been defined for the Eycott and Borrowdale Volcanic Groups from the co-existence of these mineral phases in basaltic to andesitic compositions. Epidote, chlorite, clinozoisite, prehnite, and pumpellyite are largely restricted to the more basic parts of the Eycott and Borrowdale Volcanic Groups. The more acidic volcanics contain a non-definitive assemblage of quartz $\pm$ chlorite $\pm$ carbonate and $\pm$ sericite. Taking a reasonable overburden (10 km) and using Schiffman and Liou's (1980) experimental data for prehnite and pumpellyite
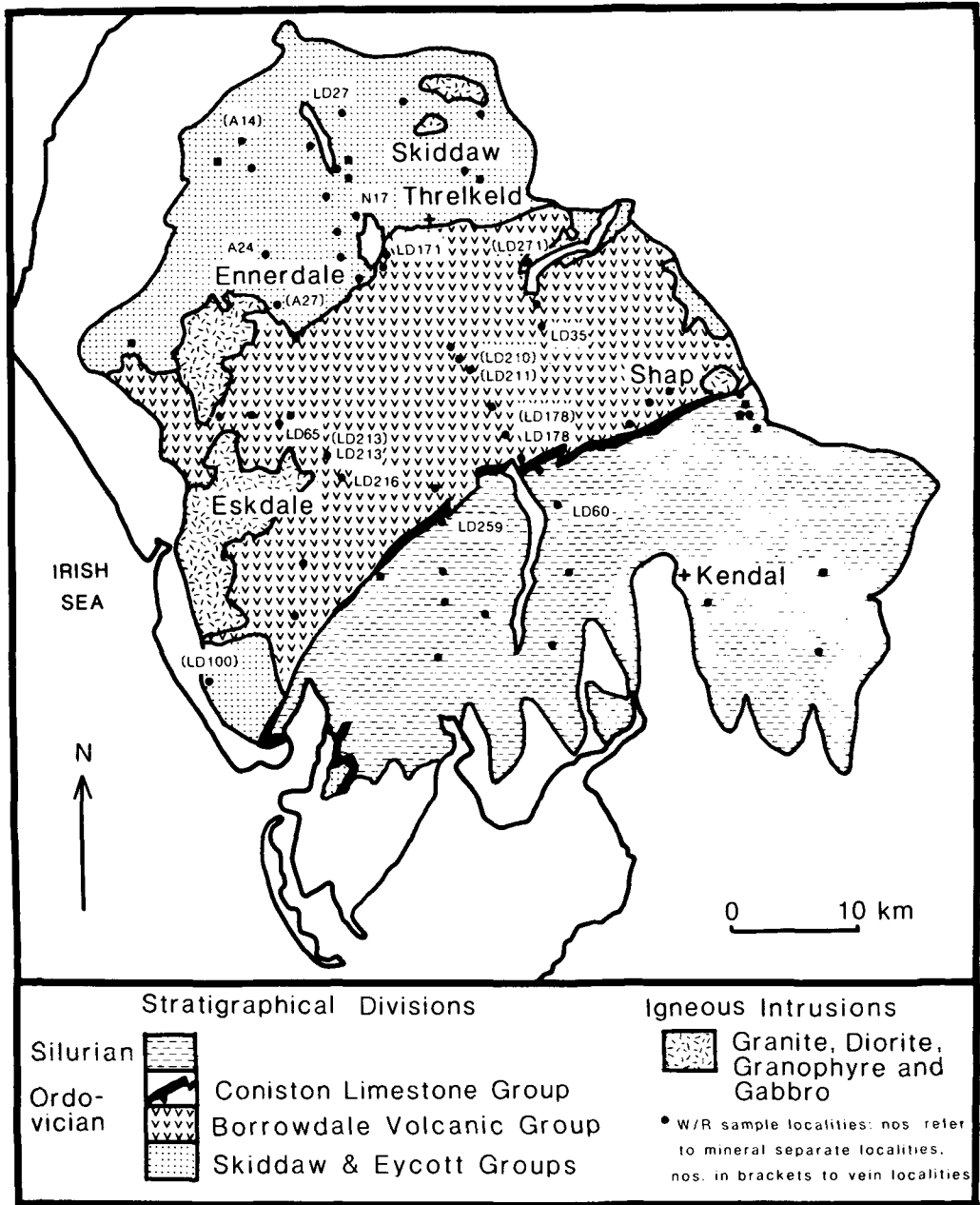
FIG. 1. Generalized geological map of the Lake District Lower Palaeozoic succession.

stability allows a maximum temperature for meta-morphism of about 350 °C. Metamorphism in the sedimentary succession has been defined by illite crystallinity (Hbrel index; Weber 1972); the measured values being compatible with prehnite-pumpellyite facies metamorphism (Weber 1972; Kisch 1974). The timing of metamorphism is un-known and may have developed independently for the various sequences during different burial episodes.

Experimental and theoretical background

Oxygen was extracted from separated silicate minerals using the fluorination procedure of Clayton and Mayeda (1963) adapted by Borthwick and Harmon (1982). Water was extracted from hydrous minerals and fluid inclusions following the method of Friedman (1953). Isotopic ratios were determined for purified H_2 and CO_2 gases on McKinney–Nier type mass spectrometers. Analytical precision is considered to be $\pm 0.2\%_0$ for $^{18}O/^{16}O$ ratios and ± 1–$2\%_0$ for D/H ratios.

Epidote-H_2O oxygen fractionation is empirical and derived using the method of Heaton (1976) and epidote-H_2O hydrogen fractionation factors are from Graham et al. (1980). Chlorite-H_2O oxygen fractionation factors have been empirically derived by Wenner and Taylor (1971) and those for hydrogen isotope exchange between chlorite and water have been given by Kuroda et al. (1976) and Marumo et al. (1980). Hydrogen isotope fractionation factors for illite-H_2O exchange have been taken from Marumo et al. (1980). Oxygen isotopic fractionations between quartz and water have been experimentally determined by Matsuhisa et al. (1979).

Isotopic data

Whole-rock isotopic analysis was carried out on a regional basis to define the spatial/stratigraphical variation of fluid–rock interaction and/or areas of enhanced fluid movement; particularly with respect to granite plutons. Because of the potential effects of granitic intrusions on sources of fluid and/or sources of heat for fluid convection, isotopic analyses of granite whole-rock samples have also been determined. Analysis of minerals, both from country rock and vein material, define the isotopic composition of the alteration fluids.

Whole-rock samples. Sediments: O-isotopic ratios were measured for metamorphosed shale, silt, and greywackes (see sample localities fig. 1). The isotopic values are given in Table I. Clayton et al. (1968) have shown that quartz is resistant to isotopic exchange at temperatures $< 340\,^\circ C$ (which is the upper limit for Lake District metamorphism, see above). However, isotopic zonation in the outer rims of detrital quartz grains undergoing diagenesis implies quartz-H_2O exchange at lower temperatures. However, the generally coarse-grain size of Lake District material appears to have inhibited the effectiveness of partial exchange; this is supported by the absence of spatial/stratigraphical correlation of $\delta^{18}O$ values (cf. Table I). Since quartz is the major ^{18}O reservoir in the sediments, the O-isotope ratios presumably reflect the composi-

tion of the protolith from which they were derived. The whole-rock D/H ratios for the two sedimentary successions are very similar (Table I) and show no spatial/stratigraphical variation. The major source of hydrogen in both sequences is from neo-formed illite and chlorite, and thus D/H ratios provide an indication of the H-isotope composition of the fluid phase present during hydrothermal alteration.

O-isotope ratios (Table I) for the Lake District meta-volcanic are enriched in ^{18}O relative to the fresh unaltered volcanic rocks (Taylor, 1968); an enrichment presumably resulting from fluid-rock exchange during metamorphism (see below). The D/H ratios of the volcanics derive entirely from secondary hydrous phases present in them, and therefore define the isotopic composition of alteration fluids. Chlorite and sericite are the most common hydrous phases and the whole-rock values are primarily controlled by $\Delta_{chlorite-H_2O}$ and $\Delta_{illite-H_2O}$. The observed variation in D/H ratios may reflect a range of chlorite Fe/(Fe + Mg) ratios which effectively controls the magnitude of $\Delta_{chlorite-H_2O}$ (Kuroda et al., 1976; Marumo et al., 1980).

Lake District granite O-isotope ratios (Table I) are enriched relative to normal granitic rocks (Taylor, 1968). The role of crustal assimilation and interaction with crustal metasomatic fluids in the enrichment of the $\delta^{18}O$ values has been discussed by Halliday (1984). The D/H ratios (Table I) are generally enriched relative to fresh igneous rocks (Taylor, 1968).

Widespread alteration of the granites is manifest in the chloritization of biotites and sericitization of feldspars and D/H ratios are therefore not primary but reflect the isotopic composition of post-crystallization fluid.

Mineral separates. Fluid compositions (see below) are defined from the secondary mineral phases epidote, chlorite, illite, and quartz (mineral values given in Table I). Analysis of secondary phases eliminates the inherent problem of potential isotopic equilibration of primary phases in low-temperature systems. Isotopic data from quartz and contained fluid inclusions is problematical and has to be interpreted with reference to possible multiple generations of quartz growth and the temporal relationship between host quartz and fluid inclusions.

Groundmass quartz in sedimentary samples shows no textural indication of secondary development and the O-isotope ratios are presumed to be primary detrital values. A large proportion of quartz in the Borrowdale Volcanic Group however, occurs in microveins and discrete segregations which are suggestive of secondary development and/or recrystallization. Much of the groundmass

TABLE I. *Hydrogen and oxygen data for Lake District whole rocks and minerals*

Sample No	δD^*	$\delta^{18}O^\ddagger$	Sample No	δD^*	$\delta^{18}O^\ddagger$	Sample No	δD^*	$\delta^{18}O^\ddagger$
WHOLE ROCK DATA						**MINERAL SEPARATE DATA**		
Skiddaw Slate Group			*Borrowdale Volcanic Group*			*Epidote*		
A24	-52	+10.3	LD189	-42	+ 9.4	LD213 (V)	-30**	+ 4.0
LD51	-48	+11.7	LD67	-51	na	LD216 (V)	-29	+ 5.1
F3	-50	+ 9.6	LD223	-48	na	LD171 (V)	-30	+ 5.5
LD7	-46	+12.9	LD216	-54	+ 8.9			
B1	na	+14.7	LD118	-41	+ 6.2			
LD8DR	-42	+14.3	LD112	-43	+ 8.5	*Chlorite*		
LD23DR	-37	+11.2	J1	-42	+ 7.7			
LD16DR	-46	na	LD86	-46	+ 8.5	LD65 (V)	-50	+ 5.4
N6	-41	na	LD87	-47	+ 8.2	LD178 (V)	-56	+ 8.1
N15	-49	na	LD65	-54	+ 6.7	LD216 (V)	-48	+ 4.0
N17	-47	+13.5	LD185	-48	na	LD259 (S, UOSS)	-54	+ 8.0
N5	-39	na	HW1	-41	na			
LD27	-52	+13.7	HW2	-46	na			
LD127	-49	+13.6	LD178	-56	+10.9	*Illite*		
LD137	-48	+13.5	LD43	-37	+ 9.3			
MAT6	-52	+13.5	LD209	-47	+ 9.9	LD178 (V)	-50	na
MAT9	-57	na	LD171	-45	na	LD60 (S, UOSS)	-49	na
			LD172	-47	+ 6.9	A24 (S, SSG)	-44	na
			LD183	-50	+10.7	LD27 (S, SSG)	-32	na
Upper Ordovician and Silurian succession			LD35	-47	+ 7.5	N17 (S, SSG)	-43	na
			LD33	-42	+ 7.3			
LD256	-49	+14.0	LD213	-50	+ 9.0			
LD257	-43	+14.4				*Groundmass quartz*		
LD258	-37	+12.9						
LD259	-49	+14.7	*Granites*			N17 (S, SSG)	na‡‡	+14.7
LD204	na	+16.5				LD7 (S, SSG)	na	+16.1
LD232	-41	+13.0	C1 (Th)	-54	+11.1	LD60 (S, UOSS)	na	+15.6
LD247	na	+13.8	B1115 (En)	-49	+ 9.4	LD259 (S, UOSS)	-52	+16.3
LD242	-50	+13.5	B1128 (Es)	-41	+10.9	LD65 (V)	-53	+12.0
LD230	-49	na	B1107 (Sk)	-51	na	LD213 (V)	-37	+12.8
LD60	-43	+13.1	B1148 (Sh)	-48	+10.4	LD216 (V)	-44	+14.8
LD48	-53	+16.2	B1126 (Es)	-45	+10.7	LD178 (V)	-45	+16.3
MIS3	-54	+13.7	B1121 (En)	-50	+10.1	LD35 (V)	-40	+11.8
SHA7	-46	+13.0	B1102 (Sk)	na	+ 9.7			
SHA6	na	+13.9						
SHA5	-44	+14.0				*Vein quartz*		
SHA1	-48	+12.3						
LD250	-44	+13.3				LD100 (S, SSG)	-37	+ 7.8
						A14 (S, SSG)	-55	+17.1
						A27 (S, SSG)	-44	+10.2
						LD271 (S, SSG)	na	+14.0
						C25 (V)	-45	+16.1
						LD178 (V)	-37	+13.9
						LD211 (V)	-38	+13.9
						LD213 (V)	-48	+ 8.9
						LD210 (V)	-40	+11.8
						LD201 (V)	-33	+11.6

Abbreviations: S = sediment; V = volcanic; SSG = Skiddaw Slate Group; UOSS = Upper Ordovician and Silurian succession; Th = Threlkeld microgranite; Es = Eskdale granite; SK = Skiddaw granite; Sh = Shap granite; En = Ennerdale granophyre. *, precision of $\pm 2\,\permil$, ‡ = accuracy of $\pm 0.2\,\permil$; **, mean of repeat analyses, ‡‡ = fluid inclusion data, precision of $\pm 5\,\permil$. All data reported in $\permil$ (per mil) relative to SMOW as defined by Craig (1961).

quartz displays textures indicative of recrystallization, i.e. sutured boundaries, subgrain development and undulose extinction. The groundmass quartz fluid inclusions show possible decrepitation textures (in microveins) and migration towards grain boundaries indicative of the destruction of early (?primary) inclusions by recrystallization (Kerrich, 1976). Fractures and enhanced weaknesses due to these processes themselves provide pathways for later fluid migration into the quartz grain and the D values of the inclusion fluids (Table I) may therefore not be related to the greater proportion of the host quartz, but instead represent late-stage or post-alteration fluids entrapped during recrystallization.

The formation ages of the quartz veins are unknown. However, quartz veins A14 (Skiddaw Slate Group) and C25 (Borrowdale Volcanic Group) are folded about the cleavage and are therefore clearly of at least pre-end Silurian age (Moseley and Soper, 1978). There is no distinction between the oxygen and hydrogen isotopic ratios (Table I) for veins in sedimentary host-rocks and those in volcanic host rocks. With the exception of A14 and C25, the veins show no evidence of recrystallization; the D/H ratios of the inclusions presumably relate directly to the $^{18}O/^{16}O$ ratio of the host quartz grain. D/H ratios of the vein inclusion samples lie in the same range as those of groundmass quartz fluid inclusions (see Table I).

Composition of alteration fluids

The isotopic composition of alteration fluids has been calculated for the temperature range 150–350 °C using appropriate mineral–water H- and O-isotope fractionation factors (method of calculation discussed by Sheppard, 1977). Fluid inclusion studies (unpublished data) indicate vein fluid salinities of 1M NaCl and the quartz-H_2O O-isotope fractionation data have been calculated using corrections for 1M NaCl solution (Truesdell, 1974). Other mineral-H_2O fractionations for which the fluid salinities are unknown, have been calculated for pure water.

Fluids in equilibrium with epidote and chlorite. Calculated fields for the isotopic composition of waters in equilibrium with epidote and chlorite are shown on fig. 2. The similarity of calculated water compositions for the various epidote samples suggests equilibration with fluids of similar composi-

tions. Only the general field, rather than fields for individual samples, is plotted. The calculated D/H and $^{18}O/^{16}O$ compositions of the fluids in equilibrium with individual chlorite samples cover a relatively wide range, suggestive of diverse fluid sources.

At temperatures < 250 °C, calculated δD values of epidote fluids are depleted relative to those of chlorite, suggesting the possibility of retrograde epidote-H_2O isotopic exchange. The closure temperature range for hydrogen isotope exchange with epidote has been estimated at 175–250 °C (Graham *et al.*, 1980). Retrograde isotopic exchange between epidote and water at temperatures < 250 °C is therefore possible, but would indicate (1) the presence during cooling of a D-depleted fluid and (2) higher closure temperatures for chlorite-H_2O exchange. For one sample only (LD 216) could both epidote and chlorite separates be obtained. The calculated H-isotope fluid compositions for
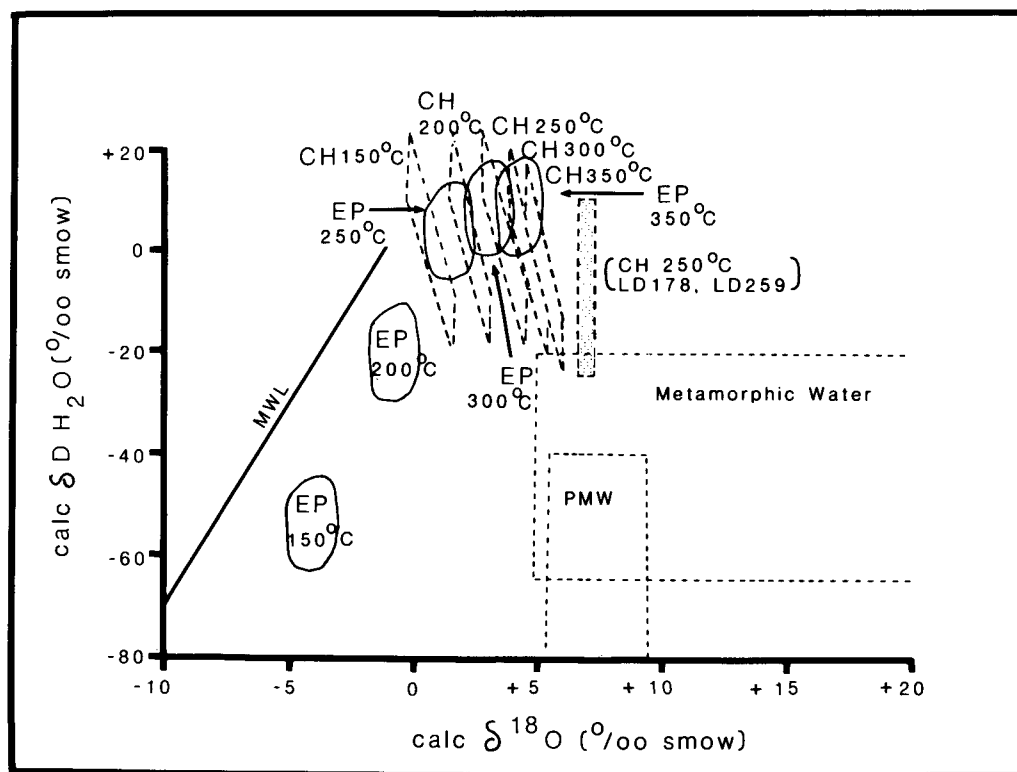

FIG. 2. Calculated hydrogen and oxygen compositions of waters in equilibrium with epidote and chlorite at 150–350 °C. EP = epidote, CH = chlorite. Epidote fields defined by solid lines, chlorite fields by dashed lines. Stippled field shows the calculated (enriched $\delta^{18}O$) fluid composition for chlorite samples LD178 and LD259. For simplicity the field at 250 °C is shown. δD values for LD259 lie within the depleted part of the field. Fields of primary magmatic water (PMW) and metamorphic water and the meteoric water line (MWL) are shown for reference; since SW lies at around $\delta D = 0‰$, $\delta^{18}O = 0‰$, the MWL is defined for values < $\delta D = 0‰$ only.

epidote and chlorite in this sample are similar over the temperature interval of 250–350 °C, indicating that epidote and chlorite in this rock exchanged either with the same fluid or fluids of different origin having the same H-isotope composition.

Coincidence of calculated fluid compositions for epidote and chlorite in the temperature range 250–350 °C is interpreted as defining the isotopic composition of the metamorphic fluid. Presumably isotopic exchange was terminated above the mineral closure temperatures by loss of the fluid phase.

The calculated fluid $\delta^{18}O$ values for epidote and chlorite samples are also coincident in the temperature range 250–350 °C, with the exception of two chlorite samples, LD 178 from the top of the Borrowdale Volcanic Group and LD 259 from the overlying sedimentary sequence. The calculated $\delta^{18}O$ chlorite fluid compositions for LD 178 and LD 259 indicate enrichment relative to the other samples for exchange at temperatures of 250–350 °C (fig. 2) (see discussion below).

Fluid in equilibrium with quartz. Volcanic groundmass quartz: much, if not all, of the volcanic quartz appears to be recrystallized and/or of secondary origin. Calculated fluid isotopic compositions for co-existing quartz and chlorite from two of the volcanic samples (LD 65 and LD 178, fig. 3) indicate possible equilibrium at temperatures of 300 °C and 250 °C respectively. The calculated O-isotope fluid compositions for quartz and chlorite in LD 216 and quartz and epidote in LD 213 are not coincident over the relevant temperature range. It is possible that quartz was the last secondary mineral phase to form, and as such may have been precipitated at lower temperatures during cooling. The temperature differential for chlorite and quartz formation is unknown and, depending on the magnitude, the quartz fluid may have had a similar O-isotope composition or been depleted in ^{18}O relative to the fluid in equilibrium with chlorite. If closure temperatures for isotopic exchange for epidote and chlorite in the Lake District system were 200–250 °C, then quartz may have been precipitated from residual fluids or fluids introduced at lower temperatures without affecting chlorite and epidote O-isotope values.

Measured δD values for fluids in groundmass quartz fluid inclusions lie in the range -53 to -37 ‰ (fig. 4). Repeat analyses of inclusion fluids
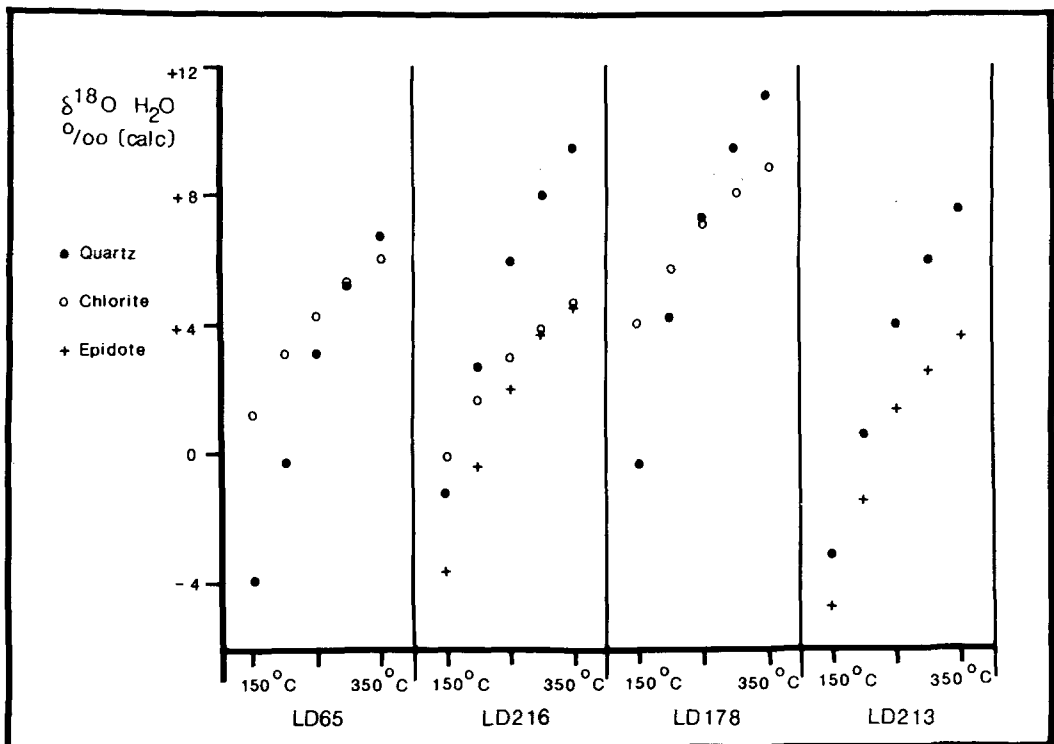

FIG. 3. Comparison of calculated oxygen compositions of fluids from coexisting quartz-chlorite and quartz-epidote mineral pairs at 150–350 °C. Intermediate temperature calculated fluid values indicated for 50 °C intervals.

had a precision of $\pm 5\%$; the inclusions presumably representing a single generation of trapped fluids. Since textural evidence suggests destruction of primary inclusions (see above), δD values of the inclusion fluids may not relate to the O-isotope values of the best quartz grain.

Vein quartz: the textures and fluid inclusions of most vein quartz samples, by contrast to the groundmass quartz, show little indication of recrystallization and the fluid inclusion δD values are therefore probably directly related to the O-isotope composition of the quartz-forming fluid. The general lack of recrystallization and grain deformation in the quartz veins, relative to the groundmass quartz, suggests a later, post-deformational age.

Fluid inclusion studies of vein quartz have given homogenization temperatures generally in the range 125 to 280 °C. Since the amount of overburden cannot be estimated accurately, pressure corrections have been applied for between 1-9 km

of lithostatic load (Potter, 1977). Hydrostatic loads (because of their effectively lower pressures) require smaller temperature corrections and, therefore, are encompassed within the corrected temperature range for lithostatic load. The calculated fluid $\delta^{18}O$ values for the estimated temperatures are also shown on fig. 3. The fluid compositions for the pressure corrected homogenization temperatures (i.e. estimated trapping temperatures for 1-9 km) for 5 quartz veins lie in a similar range and encompass the calculated O-isotope composition of sample LD 100 ($+3.2\%$, Th $= 350$ °C) which shows textural (inclusion) evidence of boiling during formation (Roedder, 1979) and therefore, requires no pressure correction (Roedder, 1981). The two pre-deformation (folded) quartz veins, A14 and C25, yield significantly higher $^{18}O/^{16}O$ ratios in the range $+7$ to $+17.1\%$. The range of measured δD values (-55 to -33%) shows no apparent relation to calculated $\delta^{18}O$ compositions.
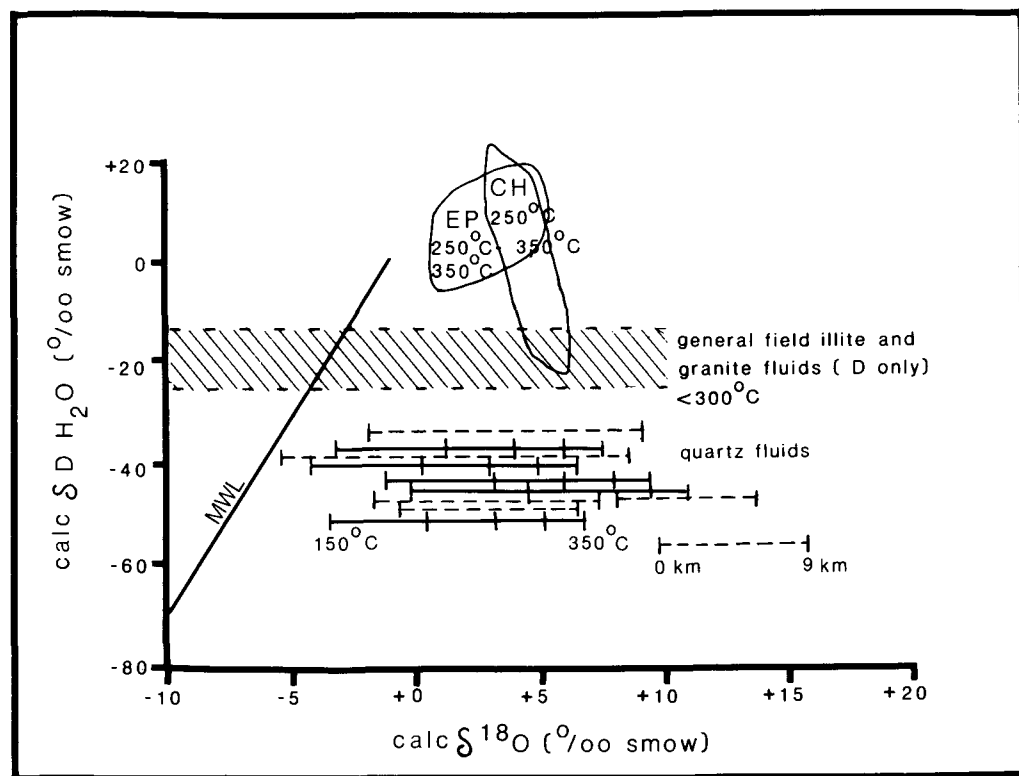

FIG. 4. Calculated hydrogen compositions of waters in equilibrium with illite, estimated hydrogen field for granites and measured hydrogen (fluid inclusion) and calculated oxygen values for groundmass and vein quartz. Solid lines represent groundmass quartz; dashed lines, vein quartz. Oxygen values for vein quartz calculated using corrected homogenization temperatures for 1-9 km overburden (see text). Vertical bars for groundmass quartz indicate calculated oxygen isotopic compositions at 150-350 °C. Intermediate bars at intervals of 50 °C. Also shown are simplified calculated water fields for epidote and chlorite at 250-350 °C.

Fluid in equilibrium with illite. Contamination of illite separates by quartz and feldspar precluded the determination of their O-isotope compositions. The calculated H-isotope compositions of fluids in equilibrium with the illites at temperatures below 300 °C are shown in fig. 4. Most D values lie in the range -26 to $-16\%_0$, with the illite fluid compositions depleted in D relative to calculated epidote and chlorite fluids, but enriched in D relative to quartz inclusion fluids.

The closure temperature for hydrogen isotope exchange with illite is unknown, but may be quite low. O'Neil and Kahara (1976) have suggested that the rapid isotope exchange observed experimentally between smectite and water is due to the intimate relationship between interlayer water and structural OH groups. While illite contains much less interlayer water than smectite, it is capable of retaining a small amount (Deer et al., 1962; p. 221) which could facilitate rapid exchange between an external fluid and the OH groups, effecting H-isotope exchange to relatively low temperatures.

Estimated H-isotope compositions of fluids involved in granite alteration. Interpretation of the whole rock granite δD values using the hydrous mineral assemblage allows estimation of possible H-isotope compositions of alteration fluids. Sample LD 121 from the Ordovician Ennerdale Granophyre contains secondary epidote as the only hydrous phase. The Δ_{rock-H_2O} value is therefore equivalent to the epidote-H_2O fractionation, so that the calculated fluid δD range is $-42\%_0$ at 200 °C and -18 to $14\%_0$ at 250–350 °C.

If chlorite were the sole hydrous phase in the granitic rocks the whole rock δD values would be indicative of exchange with a fluid enriched in D having a δD value of -25 to $0\%_0$ at < 250 °C and -31 to $3\%_0$ at 300–350 °C. Since most granite samples are affected by partial or total sericitization in addition to chloritization, the smaller magnitude of $\Delta_{sericite-H_2O}$ would effect a reduction in total Δ_{rock-H_2O} values; fluid compositions are estimated in the range $\delta D = -30$ to $-20\%_0$ (see fig. 4).

Discussion

Calculated δD values of fluids in equilibrium with mineral phases suggest that three distinct waters have played a role in hydrothermal alteration in the Lake District: (i) a D-enriched fluid ($\delta D \approx -10$ to $+10\%_0$) responsible for epidote and chlorite alteration, (ii) D-depleted fluid ($\delta D \approx -60$ to $-40\%_0$) present in inclusions in recrystallized groundmass and vein quartz, and (iii) a fluid of intermediate H-isotope composition ($\delta D \approx -20\%_0$) involved in granite alteration and recorded by illite. In order to determine the origin of these

different fluids and to construct a model for fluid-rock interaction, it is necessary to consider the isotopic compositions of fluids which may have been involved in Lake District rock-H_2O exchange.

Isotopic compositions of potential fluid sources. The marine character of the Lake District sedimentary sequences suggests the involvement of sea water in the alteration process. The isotopic composition of modern sea water lies in the range $\delta D = -7$ to $+5\%_0$ and $\delta^{18}O = -1.0$ to $+0.5\%_0$ (Sheppard, 1977), and is considered to have been more or less constant throughout Phanerozoic time. Uplift and erosion could permit the introduction of meteoric water into the sedimentary succession. Large thicknesses of Borrowdale Volcanic Group are water-lain tuffaceous deposits (Moseley, 1978) and, in the absence of diagnostic fossil assemblages, may represent fresh water lacustrine or marine environments. The isotopic compositions of all unmodified meteoric waters lie along the meteoric water line (Craig, 1961) labelled MWL in fig. 2. The position of a meteoric water on the MWL is a function of its geographic position and the temperature of precipitation. The Palaeozoic altitude of the Lake District is unknown, but the latitude has been estimated as 25 °S to 5 °N (Fallen and Briden, 1978). Within 30° of the equator the effect of latitude has been estimated to be small, so that most meteoric waters in tropical and subtropical latitudes have δD values of -20 to $-10\%_0$. Friedman et al. (1964) have determined that precipitation in low latitudes at altitudes below 300 m has δD values $< -60\%_0$. Therefore, the estimated composition of Lake District Palaeozoic meteoric water is $\delta D = -60$ to $-20\%_0$.

The intrusion of granitic plutons into the Lake District sedimentary sequence suggests the possible involvement of primary magmatic water (defined by Sheppard, 1977; Taylor, 1974; labelled PMW in fig. 2), in Lake District hydrothermal alteration (Sheppard et al., 1969; Sheppard, 1977). The involvement of PMW in mineralization has been recognized in a number of hydrothermal ore deposits (summarized by Sheppard, 1977), but PMW is not generally considered to be involved in large-scale regional alteration because it is volumetrically restricted to a few stock diameters of an intrusion (Taylor, 1974). The field of metamorphic waters (defined by Sheppard, 1977; Taylor, 1974), which could be produced by dewatering lower in the sedimentary pile, is shown on fig. 2. Like PMW, the volume of metamorphic water available is likely to be very small by comparison to the amount trapped in pore fluids within the sedimentary sequence. Therefore the two waters most likely to have been available in sufficient quantities for large

scale rock-H_2O interaction in the Lake District system are seawater and meteoric water.

Isotopic evolution of fluids during exchange. The isotopic composition of a fluid can be modified during rock–water exchange, the magnitude of the modification depending on the initial isotopic composition of the rock and the water, the relative amounts of exchangeable element in both (water/rock ratio) and the temperature of exchange (Ohmoto and Rye, 1974).

Relative to water, rocks contain a far greater reservoir of oxygen and the effect of oxygen isotopic exchange is therefore to shift the water value closer to that of the rock. Although the proportion of hydrogen contained in the rock is small by comparison with water, at very low water/rock ratios, or during hydration, as in exchange with anhydrous volcanic rocks, the D/H ratio of the fluid will be similarly affected.

The modification of fluid compositions during exchange, particularly under hydration, may complicate the identification of fluid sources. At low water/rock ratios (< 0.1) the process of hydration would effect D-enrichment of the fluid phase such that the calculated fluids may have been derived from low latitude meteoric waters. In the absence of independent evidence for effective water/rock ratios, the sources of recorded fluids are equivocal. However, the position of the volcanic sequence on the southern side of the Iapetus Ocean, with marine sequences both above and below, and the tectonically unstable arc environment suggests both proximity to, and entry mechanisms for, seawater.

Timing of fluid events and models of fluid–rock interaction. The diverse fluid compositions calculated from the volcanic and sedimentary sequences may represent actual differences in fluid origin or reflect the different isotopic evolution of fluids within the two successions. Chlorite and quartz separates from a Borrowdale Volcanic Group tuffaceous unit (sample LD 178), situated close to the base of the overlying sedimentary sequence are enriched in ^{18}O relative to the other volcanic samples (fig. 2). The chlorite $\delta^{18}O$ value is, however, similar to that obtained from the Upper Ordovician and Silurian chlorite separate LD 259 (fig. 2). It is possible that the ^{18}O enrichment at the top of the volcanic pile resulted from exchange with an ^{18}O-enriched pore fluid derived from the overlying sedimentary sequence. However, the δD value of chlorite from LD 178 is D-enriched relative to the sedimentary chlorite LD 259. If the volcanic units were anhydrous prior to exchange with sedimentary-derived pore fluids, D-enrichment of the fluid phase would result, in addition to the retention of an inherited ^{18}O enrichment. The δD values of fluids calculated from illite separates from

the volcanic sample LD 178, are also very similar and depleted in D by about 24‰ relative to the volcanic chlorite. This suggests the influence of a second fluid phase in the volcanic group at a temperature below closure for chlorite–water H-isotope exchange (possibly 175–250 °C by analogy with epidote). The δD values of fluids from groundmass quartz in volcanic rocks are -55‰ to -33‰ and distinct from the other fluids. The fluid inclusions are probably secondary, recording the presence of an additional fluid phase. Illite may therefore have experienced partial exchange with the fluid preserved in inclusions, or partial or total exchange with a later fluid. The destruction of primary fluid inclusions in the Borrowdale Volcanic Group groundmass quartz is clearly deformation related, the secondary inclusions recording post-deformation, possibly end-Silurian, fluids.

The entry and pervasive circulation of these later, post metamorphic fluids through the succession may have been initiated by heat flow from intrusion of the end-Silurian batholith. Evidence for large fluid circulation systems around plutons has been described by Sheppard (1977) and Taylor (1977).

Sheppard (1977) has suggested that the δD values of fluids associated with tin-tungsten mineralization in the Carrock Fell area of the Lake District ($\delta D = -40$‰) are indicative of a pure meteoric-hydrothermal system. From ^{18}O values of quartz associated with the Carrock Fell deposits ($+3$‰ to $+5$‰) Shepherd *et al.* (1980) concluded that the quartz was precipitated from a mixed magmatic-meteoric hydrothermal fluid. The δD composition of alteration fluids in the Lake District granites has been estimated in the present study as -30‰ to -20‰. It is suggested that the similarity of this value to those calculated from illite separates (-34 to -12‰) rather than to the fluids recorded by vein and groundmass quartz fluid inclusions (-56 to -33‰) indicates late stage exchange with a pure meteoric fluid. The more D-depleted vein and groundmass quartz inclusion fluids may relate to the initial stage of pluton-associated fluid circulation, representing mixing between magmatic and meteoric waters, the range of δD values being a function of variation in component mixing.

Summary

On the basis of calculated fluid D/H ratios, three fluids are inferred to have played a role in alteration of the Lake District succession.

(i) D-enriched syn-metamorphic fluids calculated from epidote and chlorite. Coincidence of epidote and chlorite fields suggests that isotopic exchange was terminated during metamorphism by loss of

the fluid phase at 250-350 °C. Exchange with seawater or modified low-latitude meteoric water could produce the calculated isotopic compositions, but the environmental setting of the volcanic succession suggests exchange with seawater to be the more likely.

(ii) D-depleted post-metamorphic fluids measured from groundmass and vein quartz fluid inclusions. Destruction of primary fluid inclusions in secondary groundmass quartz suggests that the recorded inclusion fluids are later than the metamorphic event. Preservation of primary inclusions in vein quartz indicates a later, post-deformational age for vein development. The similarity of D/H ratios of both groundmass and vein quartz may be explained by pervasive movement of vein fluids through the host rocks, with entrapment of the fluid inclusions in deformed groundmass quartz.

(iii) Intermediate D-compositions calculated from illite and estimated from granite whole-rock data. Lake District granites are pre- or syn-deformation and the recorded alteration fluids are therefore clearly of at least end-Silurian age. Coincidence of estimated granite and calculated illite D fluid compositions suggests equilibration with similar fluids.

The post-deformational age of the quartz, illite, and granite fluids allows for the influence of intrusion-related circulation of both magmatic and contemporary pore fluids. It is suggested that early expulsion of magmatic water and mixing with circulating meteoric water, giving D-depleted fluid, is recorded in groundmass and vein quartz, the subsequent stage of hydrothermal circulation, recorded by intermediate δD illite and granite whole rock values, involving a more pure meteoric water.

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