Stable isotope variations (H, C, O) in a prograde metamorphic Triassic red bed formation, Central Swiss Alps

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Abstract

In the Swiss Central Alps, the Upper Triassic red beds range from unmetamorphosed Keuper sediments in the northern foreland to staurolite-grade pelites (Quartenschiefer) farther to the south. Individual stratigraphic sequences can be followed intermittently throughout the prograde metamorphic sequence, allowing for isotopic variations in hydrogen, carbon and oxygen to be traced in a single protolith that has undergone essentially a single Alpine metamorphic event. Samples were analyzed from each of four metamorphic grades: 1) unmetamorphosed sediments from the Lindau borehole in the Molasse Basin (MB), T $\approx$ 100 °C; 2) anchimetamorphosed sediments from the northern Glarus Alps (GA), T $\approx$ 200–250 °C; 3) epimetamorphic-grade (lower greenschist facies) sediments from the Urseren Zone (UZ), T $\approx$ 400 °C; 4) epi- and mesometamorphic pelites from the Lukmanier Pass are (LP), T $\approx$ 500–550 °C. The $\delta^{18}O$ (‰ vs SMOW) and the $\delta^{13}C$ (‰ vs PDB) values of the carbonate fraction, the $\delta^{18}O$ and δD values of the silicate residue (‰ vs SMOW) and the total wt% H_2O and wt% carbonate were measured for each sample. Averages and variability for each zone are given as follows:

Locality	wt% carbonate	wt% H_2O	$\delta^{13}C$ (carbonate)	$\delta^{18}O$ (carbonate)	$\delta^{18}O$ (silicate)	δD (silicate)
MB	36–59	1.9 ± 0.5 $2.3 \pm 0.4^*$	-4.2 ± 0.2	30.0 ± 1.3	19.2 ± 0.6	-73 ± 7 -68^*
GA	0–33	3.6 ± 0.7	-5.8 ± 0.5	23.5 ± 1.4	18.0 ± 1.1	-54 ± 4
UZ	1–12	3.5 ± 0.9	-9.9 ± 0.1	19.6 ± 0.1	18.0 ± 0.4	-51 ± 2
LP	0–1.4	2.4 ± 1.2	-4.8 ± 0.8	18.9 ± 3.3	18.5 ± 1.9	-60 ± 7

* not heated; all other samples heated to 150 °C for wt% H_2O and δD determinations

The silicates are the dominant oxygen reservoir at all but the lowest grades; hence the $\delta^{18}O_{silicate}$ values are essentially constant throughout the sequence. The $\delta^{18}O_{carbonate}$ values systematically decrease with increasing grade, approaching equilibrium with the silicates. The scattered $\delta^{13}C$ carbonate values may be due to varying degrees of decarbonation or interaction with organic matter (from adjacent black shales?). The δD values of the hydrous silicates initially increase, indicating interaction with deuterium-enriched pore waters, and then decrease at higher metamorphic grades due to the removal of water associated with dehydration reactions. The overall isotopic variations can be interpreted in terms of minor C–O–H fluid loss, with no external fluid input.

Keywords: stable isotopes, fractionation, Alpine metamorphism, red beds, Upper Triassic, Central Alps, Switzerland.

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Introduction

A significant proportion of the crustal fluid budget is derived from buried or subducted sediments. Sediments undergo a series of modifications during burial, including compaction and dewatering, mineral hydration reactions, and at higher metamorphic grades, mineral dehydration reactions. The liberated fluids can interact with adjacent lithologies and cause metasomatic and metamorphic reactions, and at high temperatures, partial melting. Stable isotope geochemistry may be used to trace the history of fluid movement and interaction if distinct isotopic signatures of different sources can be identified. In this study, the stable isotope variations (H, C and O) of a prograde metamorphic red bed sequence were measured in order to ascertain the isotopic modifications that attend metamorphism. The data are used to estimate the isotopic composition of fluids evolved at each successively higher metamorphic grade and to evaluate the degree of interaction with surrounding lithologies.

The Upper Triassic red bed formation in the Central Alps of Switzerland (the Keuper and Quartenschiefer lithologies) range from unmetamorphosed sediments in the Tabular Jura and Molasse Basin to amphibolite-grade metapelites southward in the Lepontine region (Fig. 1). Distinct lithologies have been identified across most of the metamorphic zones and have been examined petrographically in great detail (FREY, 1969; 1970; 1974). These well studied samples provide the unique opportunity to evaluate the isotopic changes that occur during progressive metamorphism of a rock type that undergoes nearly continual mineralogical modifications.

Previous isotopic studies

HOEFS and FREY (1976) measured the isotopic composition of carbonates and carbonaceous matter in an associated Liassic black shale unit. The $\delta^{13}C$ values of the carbonaceous matter was found to increase systematically from the unmetamorphosed value of -30 to $-25‰$ (PDB) to $-10‰$ at the highest metamorphic grade. The $\delta^{13}C$ values of the carbonates changed very slightly, from 0 to $-3‰$ in the unmetamorphosed sediments to -4 to $-6‰$ at the highest grades. Liberation of methane from the organic matter during maturation or interaction with the ^{13}C-enriched carbonates were proposed as explanations for the higher $\delta^{13}C$ values of the organic matter at the higher grades (HOEFS and FREY, 1976). The lowering of the $\delta^{13}C$ values of the carbonates may be explained by a concomitant interaction with the low $\delta^{13}C$ graphite.

HUNZIKER et al. (1986) analyzed the $\delta^{18}O$ and δD values of micas from the same sequence of rocks studied in the present work. The δD values of the micas increase from an initial unmetamorphosed value of -60 to $-70‰$ to -40 to $-53‰$ at intermediate grades and back down to values of -60 to $-80‰$ (with several outliers). The $\delta^{18}O$ values of the oxygen vary non-systematically from 18 to 22‰ in the Upper Triassic units. There is no isotopic variations associated with the transition from 1Md illite to $2M_1$ muscovite. HUNZIKER et al. concluded that the evolution from illite to muscovite involved a continuous lattice restructuring instead of a breaking and reforming of tetrahedral and octahedral bonds.

A few other studies have evaluated isotopic changes over a wide metamorphic grade. MORIKIYO (1986) measured the hydrogen and carbon isotope variations in graphite-bearing metapelites from unmetamorphosed to sillimanite-Kspar-bearing gneisses from Central Japan. Above 500 °C, the δD values of the muscovite and biotite increase with increasing temperature, from -80 to $-100‰$ at 500 °C to -75 to $-60‰$ at 650 °C. There is a strong correlation between the δD values of the micas and the presence or absence of graphite. The $\delta^{13}C$ values of graphite (and carbonaceous matter at low metamorphic grades) increases from -23 to $-22‰$ in weakly metamorphosed sediments to -19 to $-17‰$ in the highest grade samples. Morikiyo concluded that the observed variations and the spatial distribution with respect to graphite presence or absence is a result of methane-producing devolatilization reactions. Variations in the isotopic compositions of the organic matter and the carbonates are in response to a mixed volatile $CH_4–CO_2$ open system exchange.

ESLINGER and SAVIN (1973) determined $\delta^{18}O$ values of mineral separates from a high-grade diagenetic and low-grade metamorphic Precambrian metasedimentary sequence from Montana. The $\delta^{18}O$ values of the silicates decrease from 20‰ in the upper 500 meters to 12–15‰ at greater depths (maximum depth ~ 5500 meters). The quartz and illite appeared to be in isotopic equilibrium, whereas feldspar and carbonates are not in equilibrium with quartz and illite. It was concluded that the feldspar never achieved equilibrium and the carbonate underwent late isotopic reequilibration.

Most other studies dealing with isotopic changes associated with metamorphism are confined to diagenetic conditions (see O'NEIL, 1987; LONGSTAFFE, 1987; SAVIN, 1980; and references
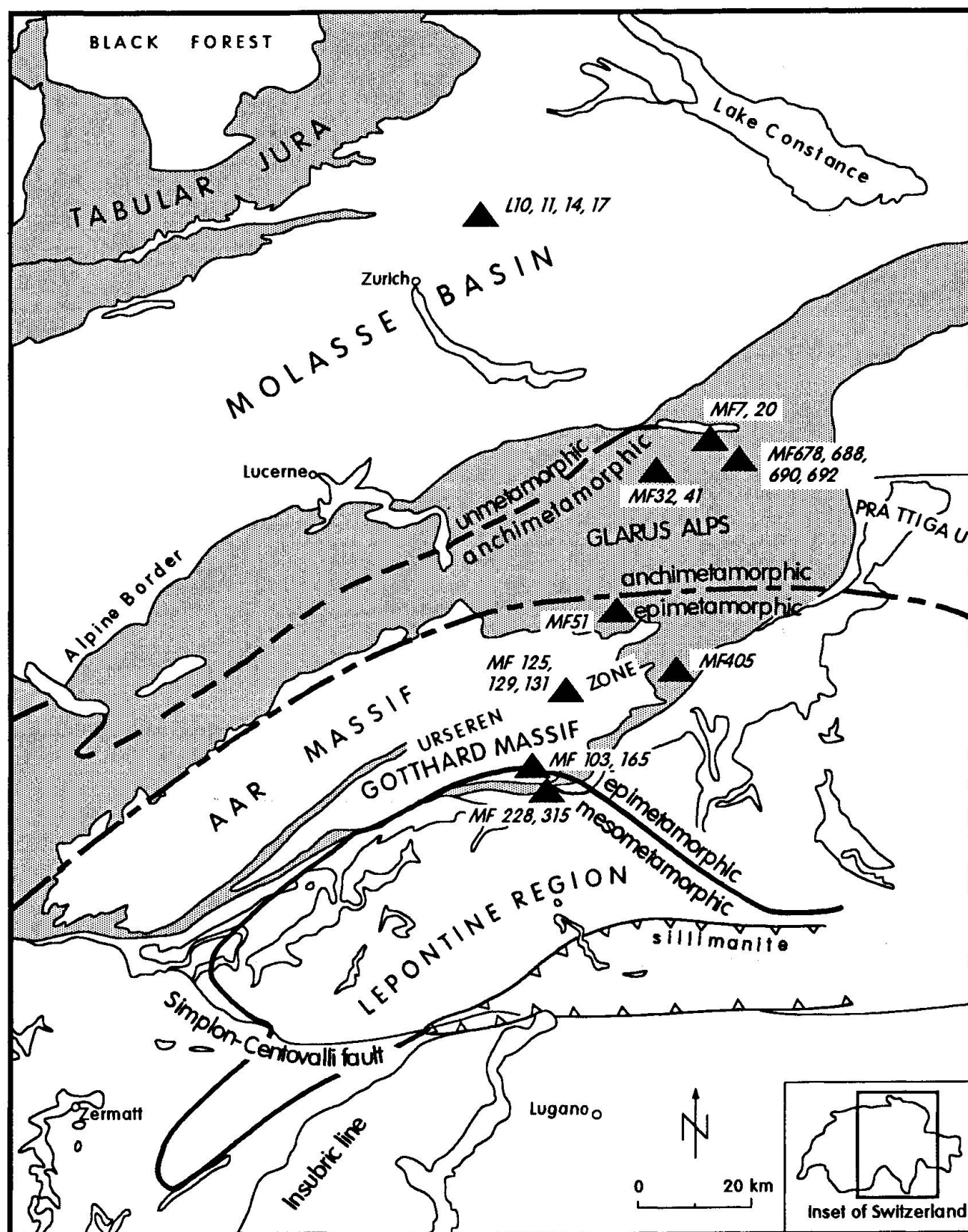
Fig. 1 Location map of samples analyzed in this study. Samples are divided into four groups: unmetamorphosed in the Molasse Basin, anchimetamorphic in the northern Glarus Alps, epimetamorphic in the southern Glarus Alps and in the Urseren Zone, and mesometamorphic in the Lukmanier Pass (LP) and Piora Zone (PZ). Modified from FREY (1974).

therein; YUI et al., 1993). Several fundamental observations have been made for diagenesis of marine sediments (equivalent to the protolith of the samples analyzed in the present study). In general, detrital clays have a $\delta^{18}O$ value of 16 to 18‰ while authigenic clays have $\delta^{18}O$ values of 26 to 31‰ (SAVIN and EPSTEIN, 1970 a, b). During burial diagenesis, the finest grain size clay portion undergoes both hydrogen and oxygen isotopic exchange (YEH and SAVIN, 1976; YEH and EPSTEIN, 1978). All diagenetic processes lead to a reduction in the $\delta^{18}O$ value of carbonates. The δD values of the clays are relatively light ($\approx$ -80‰) due to the contribution of a detrital component. During early diagenesis, the δD values increase due to interaction with deuterium-enriched pore waters (YEH, 1980). All size fractions of clays reach isotopic equilibrium during conversion from smectite to illite at $\approx$ 85 °C (YEH and SAVIN, 1977). The finest size fraction of quartz equilibrates with the clay at 100 °C, but quartz fractions > 20 μm remain out of equilibrium at 180 °C (YEH and SAVIN, 1977). Carbonate is not in equilibrium with the other phases due to continuing exchange with pore waters.

Geological setting

The samples analyzed in this study come from an Upper Triassic red bed formation of the Swiss Central Alps, investigated in detail by FREY (1969; 1970; 1974). The units consisted originally of marls, clays and dolostones that may have been transported in an alluvial fan from the Bohemian Massif in the northeast and deposited in shallow waters. Heterogeneities exist at an outcrop scale. The "red bed" formations range in thickness from 30 to 70 meters throughout the metamorphic sequence. Liassic black organic-rich shales were deposited over the Triassic red bed formations and have experienced the same metamorphic conditions (FREY, 1978). The entire Mesozoic sediments underwent only Alpine metamorphism. Although the Alpine orogeny consists of at least two separate events, the Mesozoic red beds were primarily affected by the high-temperature, low-pressure Eocene-Oligocene event (the Lepontine phase in the Central Alps). The metamorphic grade of the red bed formation ranges from essentially unmetamorphosed sediments in the Tabular Jura and below the Molasse Basin to staurolite-grade schists in the northern Gotthard massif (Fig. 1). The sediments under the Molasse basin are termed the Keuper sediments. They are covered by up to 5200 meters of Mesozoic and Tertiary cover and have present-

day borehole temperatures of 100 to 150 °C. The Alpine sequence is referred to as the Quartenschiefer. The entire sequence cannot be followed continuously from unmetamorphosed to high-grade rocks due to lack of exposure. Instead, samples from four different regions were collected. Essentially unmetamorphosed rocks were collected from the Lindau borehole in the Molasse Basin with estimated temperatures of 100 to 150 °C. Samples from the northern Glarus Alps are in the anchimetamorphic zone, corresponding to temperatures of 200–250 °C (FREY, 1986). Samples from the Garvera section (FREY, 1969) farther to the south, in the Urseren Zone are in the epimetamorphic zone. These rocks are near the chloritoid-in isograd, with temperature estimates of $\approx$ 400 °C. The highest-grade samples come from the Lukmanier Pass area at the border between the epimetamorphic and mesometamorphic zone. These rocks, at the staurolite-in isograd (NIGGLI and NIGGLI, 1965), reached peak temperatures of 500 to 550 °C.

Mineralogy

The mineralogy and mineralogical changes that occur are presented in FREY (1969; 1974). The mineralogy and approximate modal abundances of each phase for the samples in the present study are given in table 1. A general description of each zone is given in the following section.

DIAGENETIC ZONE

The samples from the Lindau borehole are distinguished by the presence of irregular illite/montmorillonite clays. The most important reactions in the diagenetic zone involve equilibration of the already-present phases. This equilibration is chemical (compositional homogenization and exclusion of incompatible elements), mineralogical (elimination of incompatible phases), and textural (formation of more regular grain boundaries and the increase in crystal size).

In the silicates, the most prominent reactions are typically the precipitation of quartz cements or overgrowths, the consumption of feldspars (albite possibly faster than potassium feldspar), the formation of illite from smectite and feldspars, the formation or consumption of kaolinite (depending upon the local aluminum content), chlorite formation, and the formation of the paragonite precursor. Glauconite may be present in some samples. Dolomite cements are common

Tab. 1   Mineralogy and modal abundance of samples analyzed in this study. Abbreviations: montm = montmorillonite. Data compiled from FREY (1969, 1970). Wt%. carb. from acid digestion weight loss.

| Sample	Swiss Coordinates	Illite	Phengite	Paragonite	Illite/Montm.	Chlorite	Quartz	Potassium Feldspar	Plagioclase	Dolomite	Calcite	Chloritoid	Biotite	Staurolite	Kyanite	Hornblende	Garnet	Epidote	Ilmenite	Hematite
L10	692.815/255.100				30-35	<5	7	<1	3	54.7										
L11	692.815/255.100				40	<5	9	1	3½	39.2										
L14	692.815/255.100				30	<5	9	1	2½	24.3	25.8									2-3
L17	692.815/255.100	25-30					4		2½	60.5	3.0									3-5
MF7	735.800/218.400	15-20				20-25	29	2	2	5.2	11.0									3-4
MF32	729.050/211.025																			3-4
MF41	725.525/210.725																			3-4
MF51	~714.6/185.4																			3-4
MF678	742.050/214.300		71			7	22													3-5
MF688	742.050/214.300		55	10		28				6										3-5
MF690	742.050/214.300		29			12	20			12	26									3-4
MF692	742.050/214.300		24	7		13	25				30									
MF405	731.200/179.900		35-40			5-10	37		1	6.6										5
MF125	711.625/172.400		25-30	5		5-10	51		1	3.6										4
MF129	711.625/172.400		25-30			25-30	29		2		14.2	0.3								
MF131	711.625/172.400		20-25			15-20	43		2½		1.9	14								
MF103	704.600/159.970		50			7	33		3				5							
MF165	706.350/157.000																		1	
MF228	706.840/154.140					3	17		21				10	trace	6	30	11	½	½	
MF315	707.650/153.950		10	10-15		1	24		5				1	40	trace		5		2	

and calcite is commonly found in late? veins. Hematite is present in all but the highest (mesometamorphic) grade rocks.

ANCHIZONE

Most of the silicates have equilibrated both chemically and mineralogically. Kaolinite has been consumed to form chlorite, pyrophyllite, muscovite and/or paragonite. Smectite has been consumed to form phengitic muscovite. Mafic elements participate in the formation of chlorite. More than one type of chlorite may be present in any one sample. TEM, SEM and electron microprobe analyses indicate that tri-octahedral chlorites, di,tri-chlorites and di-chlorites may all exist (LIVI, 1994). In the anchizone, anatase has inverted to rutile.

EPIZONE

By the time the epizone is reached, textures are more typically "metamorphic". Reactions and mineral stabilities depend on the bulk composition, mainly on the availability of aluminum. Chloritoid and chlorites are formed, partly at the expense of carbonates. FREY (1974) proposes the reaction

Al-rich chlorite + Ti-bearing hematite =
chloritoid + ripidolite + rutile + H_2O + O_2 1)
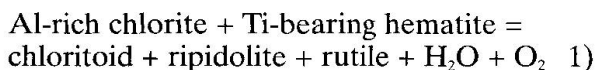
Ilmenite may form in the Quartenschiefer. Rare-earth phosphates and apatite have reacted with silicates (possibly carbonates) to form epidote and allanite. Pyrite is converted to pyrrhotite in sulfide-rich rocks. Kyanite appears in the upper epimetamorphic zone, but not in the lithologies from this study. In stratigraphically adjacent black-shale layers, organic matter is converted to graphite at the anchizone-epizone boundary.

MESOMETAMORPHIC ZONE

Biotite, staurolite, kyanite, hornblende and garnet appear in the mesometamorphic zone. Biotite is common both in the marly and pelitic Quartenschiefer. Feldspar changes from albite north of the Lukmanierpass to oligoclase south of the pass. FREY (1969) proposes the following kyanite-forming reaction:

muscovite + chlorite =
quartz + kyanite + biotite + H_2O 2)
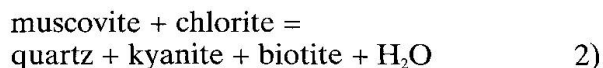
FREY (1974) presents textural arguments for the formation of alternating amphibole-rich and biotite-rich layers at Camperio, at the eastern end of the Piora Zone (Fig. 1). From lower-grade rock equivalents, it is supposed that dolomite was involved in amphibole formation, and that there has been a great loss of CO_2.

Experimental methods

Sample analyses were made on finely ground whole-rock powders dried at 110 °C before weighing. The carbonate fraction in the whole rock powder was determined using the conventional phosphoric acid-extraction method (McCREA, 1950). The weight% carbonate was determined manometrically on the evolved CO_2 gas. The carbonate fraction was removed for δD and $δ^{18}O$ determinations of the silicate fraction by reaction with dilute HCl followed by repeated rinsing in distilled water. The hydrogen isotope composition of the hydrous phases and weight% water of the silicate residue (related to wt% H_2O in the whole rock) were determined with the zinc extraction technique (VENNEMANN and O'NEIL, 1993). Approximately 30 to 50 mg of powder was loaded into an 6 mm quartz tube and evacuated at 150 °C overnight. The samples were heated with a gas-oxygen flame until the sample melted. Evolved water was transferred to Pyrex tubes preloaded with 50 mg of zinc metal. Any H_2 gas produced during heating was converted to H_2O with a CuO furnace heated to 550 °C. In this manner, all of the hydroxyl H_2 was collected in the Pyrex tubes in the form of H_2O. The Pyrex tubes were sealed, and placed in a furnace at 480 °C for 30 minutes in order to quantitatively convert H_2O to H_2 gas. The quantity of hydrogen was determined from the mass 2 voltage on the mass spectrometer for a fixed volume. Water contents were determined to within 0.1 wt% and δD values were reproducible to ±3‰. The effect of the preheating was evaluated by determining the δD values and water content of selected samples that were degassed under vacuum overnight, but were not preheated (Tab. 2). The δD values of the unmetamorphosed samples (those that contained significant illite-montmorillonite clays) were 10‰ higher than for the heated samples, and the water content was significantly higher. The preheating treatment had no effect on higher grade samples (MF688). The preheat treatment apparently caused water loss in the montmorillonite-bearing samples. Savin and EPSTEIN (1970 a, b) demonstrated that adsorbed and interlayer water in clays is exchangeable with the atmosphere in a

Tab. 2   Isotopic composition, wt% carbonate and wt% water of samples analyzed in this study. Wt% calcite determined manometrically.

T(°C)	Sample	$\delta^{13}C$ (PDB) carbonate	$\delta^{18}O$ (SMOW) carbonate	Wt% carbonate	$\delta^{18}O$ (SMOW) silicate	δD (SMOW) silicates	Wt%H₂O (w/o carb)	Wt%H₂O (total)
100	L10	–4.31	31.4	54	19.9	–72	2.9	1.3
				not preheated →		–63	4.3	1.9
	L11	–4.04	30.5	36	19.4	–82	3.7	2.4
				not preheated →		–72	4.3	2.8
	L14	–4.10	28.5	45	18.8	–72	3.9	2.1
	L17	–4.31	29.5	59	18.6	–65	3.5	1.4
						–68	HUNZIKER et al., 1986)	
200–250	MF7	–7.93	22.5	19	18.3			
	MF32	–3.33	32.3	61	24.5			
	MF41	–3.36	28.7	47	20.1			
	MF51	–2.44	28.1	41	18.8			
	MF678	–2.12	23.6	0.1	15.9	–61	3.1	3.1
	MF688	–5.95	24.0	2	18.2	–50	4.2	4.1
				not preheated →		–51	4.5	4.4
	MF690	–6.64	22.7	33	18.7	–50	4.4	2.9
	MF692	–5.70	25.4	< 0.1	18.6	–54	4.4	4.4
	MF20					–45	0.6–2 µm	
						–45	2–6 µm	
						–43	6–20 µm	
350–450	MF405	–5.55	21.7	4	18.4	–57	3.6	3.5
	MF125	–9.89	19.5	4	18.1	–52	2.6	2.5
	MF129	–9.89	19.6	19	19.5			
	MF131	–9.90	19.6	2	17.3	–50	4.3	4.2
500–550	MF103	–5.78	15.2	< 0.1	18.3	–48	3.2	3.2
	MF165	–4.31	21.6	0.4	17.4	–53	3.5	3.5
	MF228	–4.38	20.0	3	17.4	–66	0.9	0.9
	MF315	–	–	0	21.2	–63	1.6	1.6

matter of hours. The adsorbed and interlayer water is removed by heating at 150 °C under vacuum. Although the water contents of the unheated samples may be more representative of the untreated rock, the δD values of the heated samples are accepted as those of the original clay mineral.

The $\delta^{18}O$ values of the silicate fraction were determined with the conventional fluorination method (CLAYTON and MAYEDA, 1963). Samples were degassed at 150 °C for several hours and re-acted at 550 °C for 12 to 15 hours in the presence of BrF_5. The oxygen was cryogenically separated from the halogen fluorides and converted to CO_2 by reaction with graphite heated with a platinum resistance furnace. The $\delta^{18}O$ values are reproducible to ± 0.2‰.

Results

All isotopic results, as well as wt% carbonate and wt% water in rock, are presented in table 2. Data are relative to standard values for calcite (NBS-19), quartz (NBS-28), hydrogen (NBS-30) and graphite (NBS-21) reported in HUT (1987) and COPLEN et al. (1983) and $\delta^{18}O$ (SMOW) = $1.03091 \cdot \delta^{18}O$ (PDB) + 30.91 (COPLEN et al., 1983).

OXYGEN

The $\delta^{18}O$ values of the silicates, 18.9 ± 1.7‰ are typical for ocean sediments and are at the upper limit for shales (SAVIN and EPSTEIN, 1970a). A
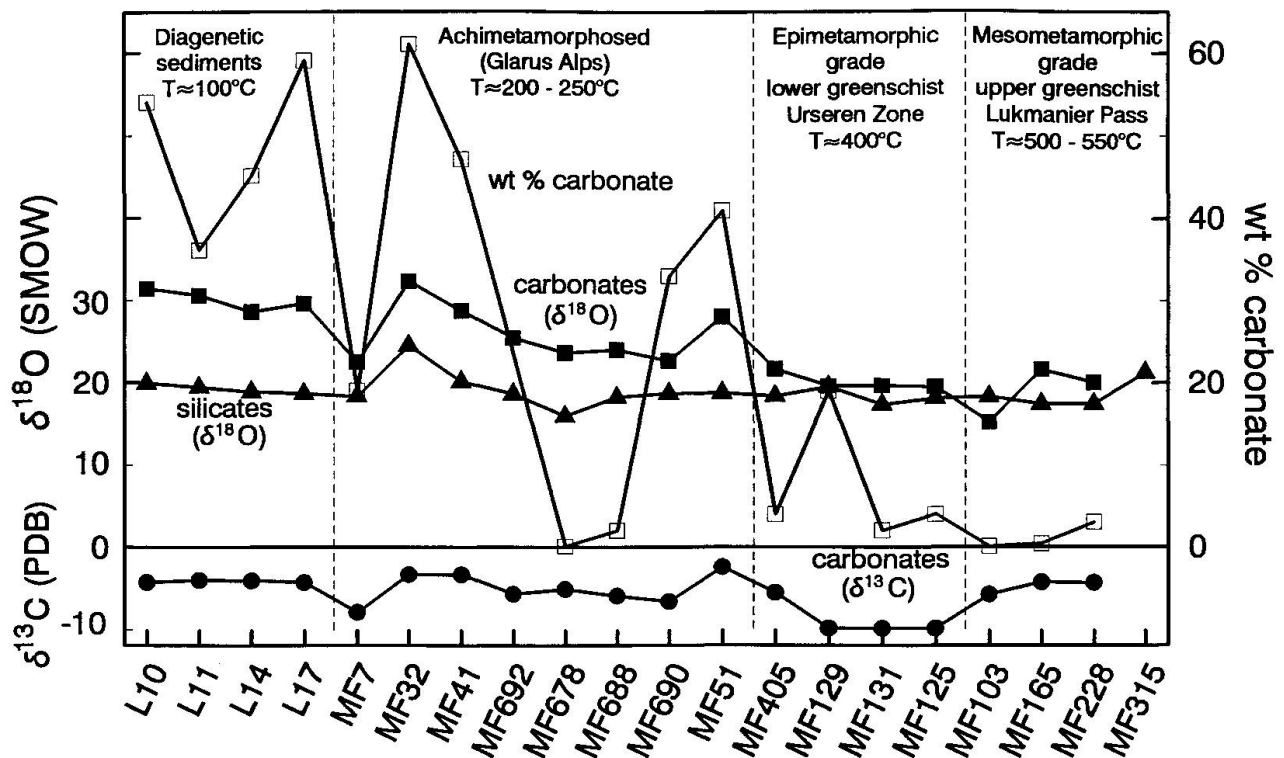
Fig. 2 Isotopic compositions and wt% carbonate of samples plotted against increasing metamorphic grade. The $\delta^{18}O$ values of the unmetamorphosed carbonates are typical marine values. Between 250 and 400 °C, the carbonates come into isotopic equilibrium with their silicate hosts. The $\delta^{18}O$ value of the silicates remains relatively constant, as the silicates are the main oxygen reservoir of the system. The constant $\delta^{18}O$ values imply closed system behavior. The $\delta^{13}C$ values of the carbonates do not vary systematically. The low $\delta^{13}C$ values for samples MF7 and especially MF125, 129, 131 may have been inherited from the protolith or they could be explained by Rayleigh distillation during decarbonation. If decarbonation was important, then the higher-grade rocks should have the same low $\delta^{13}C$ values. The higher values measured in these rocks requires infiltration of a carbon-bearing fluid phase from the surrounding black shale units.

$\delta^{18}O$ value of 18 to 20‰ for the silicate fraction is best explained as a mixture of detrital and authigenic sediments. The $\delta^{18}O$ value is independent of metamorphic grade. The $\delta^{18}O$ values of the unmetamorphosed carbonates (28.5 to 31.4‰) are typical for normal marine carbonates. There is a slight decrease down to values of 23‰ in the anchimetamorphosed zone. This small decrease is commonly observed in diagenetically altered samples (e.g., O'NEIL, 1987). At higher metamorphic grades, the $\delta^{18}O$ values of the carbonates decrease further, as equilibrium with the silicate hostrock is approached (Fig. 2). This equilibration occurs between the anchimetamorphic (250 °C) and epimetamorphic (400 °C) grades. The relatively constant isotopic value for the silicate fraction is expected from mass balance considerations. The silicate fraction comprises the bulk reservoir of oxygen in all but the lowest grade samples, so that as equilibrium between the carbonate and silicate fractions is approached, the $\delta^{18}O$ value of the carbonate changes. Overall, the $\delta^{18}O$ of the whole rocks are

quite constant. Small variations are probably due to heterogeneities in the protolith composition. The constancy of the whole rock $\delta^{18}O$ values indicates that there were no incursions of large amounts of externally derived fluids in isotopic disequilibrium.

CARBON

The carbonates have nearly constant $\delta^{13}C$ values of –5‰ (PDB) below the epimetamorphic grade. In the epimetamorphic samples, the $\delta^{13}C$ values decrease to –10‰ and then increase back to –5‰ in the mesometamorphic zone. The decrease in the $\delta^{13}C$ values in the epimetamorphic zone could be due to premetamorphic heterogeneities or may be related to ^{13}C loss during metamorphic decarbonation. The percentage of carbonate in the metasediments decreases with increasing metamorphic grade from a high of 60% carbonate down to completely decarbonated samples at the highest metamorphic grades (Fig. 2). The
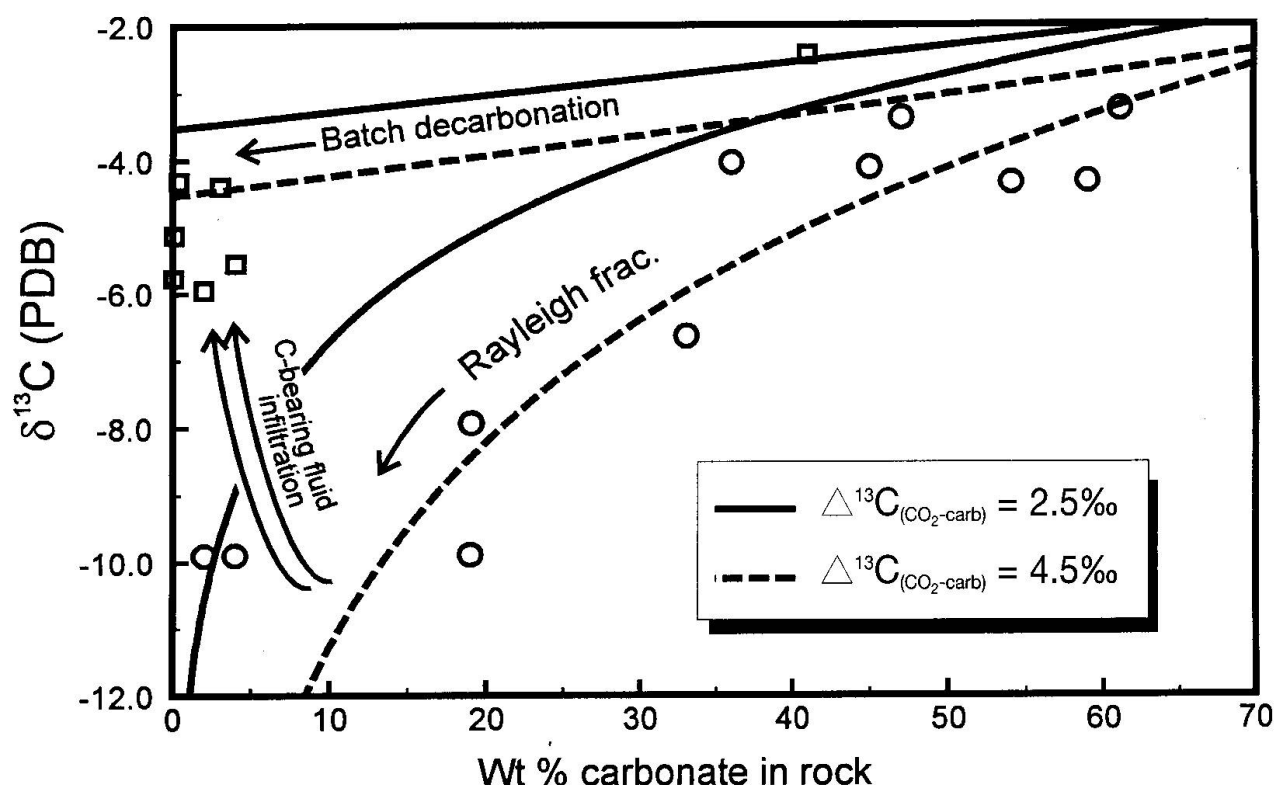
Fig. 3 $\delta^{13}C$ values vs wt% carbonate in whole rock. The calculated effects of batch and Rayleigh decarbonation are shown for $\Delta^{13}C_{(CO_2\text{-}carb)}$ = 2.5‰ and 4.5‰. Samples indicated by open circles are consistent with open-system Rayleigh volatilization. The samples indicated by open squares fall off the calculated Rayleigh fractionation trend. These samples are best explained by either batch devolatilization (for the low-grade metamorphic samples) or infiltration by a C-bearing fluid (highest-grade samples).

change in the $\delta^{13}C$ values as a function of decarbonation progress depends on the mechanism of decarbonation. The two endmember cases are closed system (or batch decarbonation) and open system (or Rayleigh fractionation) (e.g., VALLEY, 1986). A plot of wt % carbonate vs $\delta^{13}C$ values is presented along with calculated bulk and Rayleigh decarbonation curves (Fig. 3). Most of the samples follow a Rayleigh-type behavior, although some can only be explained by batch decarbonation.

The highest grade samples (mesometamorphic) appear to have undergone batch decarbonation while the epimetamorphic samples followed a Rayleigh distillation behavior. It is difficult to explain why the higher grade samples would not have followed the same geochemical pathways as the lower-grade equivalents. Perhaps the permeability in the higher grade samples was fortuitously lower than in the lower-grade ones. Alternatively, the carbonates in the high grade samples may have undergone the same decarbonation behavior as the epimetamorphic samples and then had their $\delta^{13}C$ values raised to less negative values during mesometamorphic condi-

tions. The increase in the $\delta^{13}C$ values can be caused by fluid infiltration from adjacent units. The carbonate $\delta^{13}C$ values of adjacent black shales are very similar to the mesometamorphic samples in the red beds of the present study (HOEFS and FREY, 1976 and Fig. 4). Considerable amounts of carbon-bearing gases (fluids) are released during the coalification of the organic matter. Equilibrium between all of the carbon-bearing phases (carbonate, graphite, methane and CO_2) probably only occurs at the highest metamorphic grades, where the rates of equilibration are most rapid. The carbon-bearing fluid in the highest grade black shales was in equilibrium with a carbonate having a $\delta^{13}C$ value of ~ –5‰ (Fig. 4). If this fluid infiltrated the red beds of this study, they could cause an increase in the $\delta^{13}C$ values from –10‰ in the decarbonated samples to –5‰ in the highest-grade metamorphic samples.

HYDROGEN

The δD values of the hydrous phases in the unmetamorphosed sediments are approximately
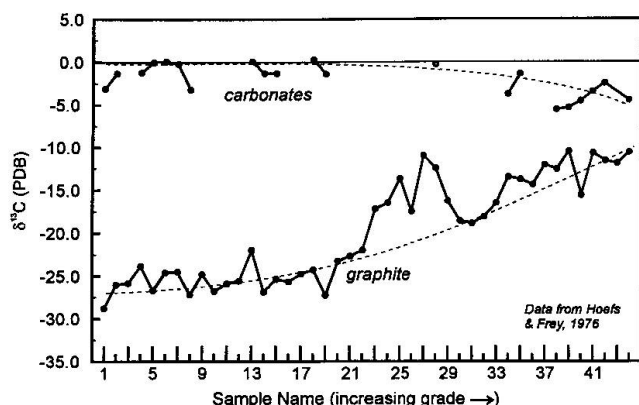
Fig.4 Carbon isotope data for coexisting carbonates and organic matter (graphite at higher grades) from a Liassic black shale formation (HOEFS and FREY, 1976). The two phases approach isotopic equilibrium at the highest grades and correspond to a temperature of 500 to 600 °C for a fractionation between 5 and 7‰ using the calibration of DUNN and VALLEY (1992). A fluid in equilibrium with the highest-grade samples is in equilibrium with a carbonate that has a $\delta^{13}C$ value of –5‰.

–70 to –80‰ (Fig. 5). These are in the normal range for marine sediments and, like the oxygen data, are best explained as a mixture of detrital and authigenic sediments (SAVIN and EPSTEIN,

1970a; YEH, 1980; KUSAKABE et al., 1989). In the anchizone sediments, the δD values increase to –50 to –60‰. The change is probably due to equilibration with pore waters. The formation of new hydrous silicates (chlorites, pyrophyllites and muscovites at the expense of kaolinite and smectite) facilitates exchange with pore waters. In near-surface ocean sediments, the δD values of pore waters are similar to modern seawater (FRIEDMAN and HARDCASTLE, 1988; KUSAKABE et al., 1989; LAWRENCE, 1989; FRANCE-LANORD and SHEPPARD, 1990). With increasing depth, the δD values of the porewaters decreases due to interaction with the hydrous phases (and meteoric water). The porewater-hydrous silicate interaction is manifest by the increase in δD values of the anchizone samples.

There is no change in the δD values or wt% water in the epimetamorphic or even lower mesometamorphic zone samples (Fig. 5). Although numerous mineralogical changes occur over this interval, the constancy of hydrogen isotope ratios and water contents indicates that the metasediments behaved as a closed system with respect to hydrogen during prograde mineralogical reorganization. Probably all of the pore waters had been eliminated by early- to mid-anchimetamorphic conditions. If this were not the case, the δD
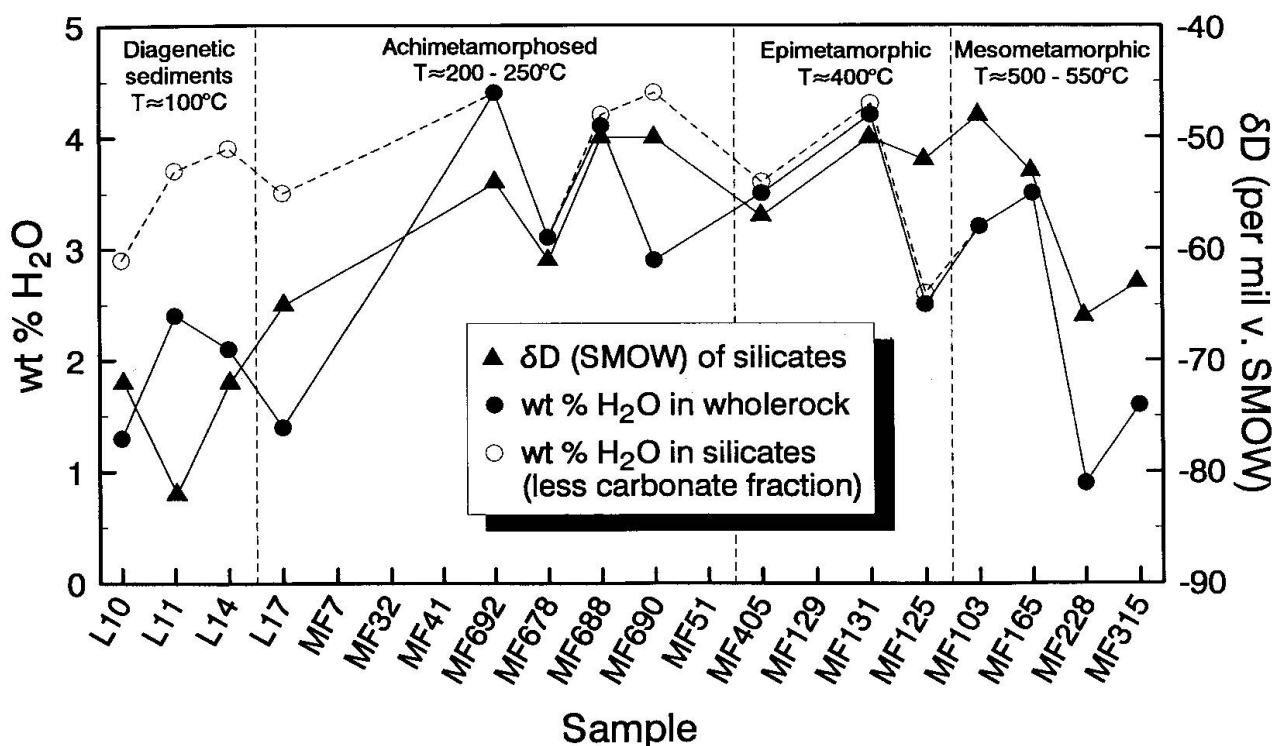
Fig. 5 Hydrogen isotope data and wt% H_2O in corresponding samples. The wt% water is calculated for the wholerock fraction and the silicate fraction. There is an excellent correspondence between the wt% H_2O in the wholerock fraction and $\delta D_{wholerock}$ value. The $\delta D_{wholerock}$ values increase in the anchimetamorphic zone due to exchange with high deuterium pore waters. The $\delta D_{wholerock}$ decrease at the highest grades is due to batch volatilization.

values would be expected to change as interaction with pore waters continued.

There is a drop in the wt% water and δD values at the highest metamorphic grades due to water release during dehydration. Release of water in the highest grade rocks accompanies the breakdown of chlorite and muscovite. A typical reaction would be

$$3\ (Fe_{0.4}Mg_{0.6})_5Al_2Si_3O_{10}(OH)_8 +$$
chlorite
$$5\ KAl_3Si_3O_{10}(OH)_2$$
muscovite
$$= 5\ K(Fe_{0.4}Mg_{0.6})_3AlSi_3O_{10}(OH)_2 +$$
biotite
$$8\ Al_2SiO_5 + SiO_2 + 12\ H_2O \qquad 3)$$
kyanite   quartz
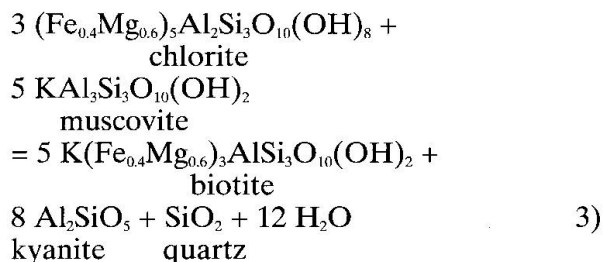
The change in δD values as a function of reaction progress was modeled for batch volatilization and a Rayleigh type distillation behavior (Fig. 6 and Appendix). The $\delta D_{wholerock}$ values for the two highest-grade samples (MF228 and MF315) fit the batch model of devolatilization perfectly. This result implies that fluid, generated during the dehydration of chlorite and muscovite, did not leave the system as it was formed. There were no open channelways for fluid escape. Instead, the small amounts of fluid generated during dehydration were retained in the rock at least until reaction (4) (or its equivalent) went to (near) completion.

Fig. 6 A plot of the reaction progress vs $\delta D_{wholerock}$ for the devolatilization reaction 3).

The $\delta D_{wholerock}$ values are calculated for batch and Rayleigh fractionation devolatilization. For the batch devolatilization mechanisms, the system is considered to be closed throughout the devolatilization process. The $\delta D_{wholerock}$ value remains constant until the reaction reaches the desired reaction progress. Then a new $\delta D_{wholerock}$ value is calculated on the basis of the solid hydrous phase compositions (i.e., the water has left the system). The batch devolatilization lines are not straight due to the fact that hydrogen is present in both the product and reactant phases. The $\delta D_{wholerock}$ values for Rayleigh fractionation are calculated with an iterative method following RUMBLE et al. (1982). Both procedures are explained in appendix 1. The two highest grade samples (MF228 and MF315) are consistent with closed-system devolatilization indicating that during dehydration, the H_2O-rich fluid did not leave the system until the devolatilization was essentially complete.

Conclusion

The isotopic variations observed in the Central Alpine red beds preserve a record of the physiochemical changes that occurred during the prograde metamorphism of these rocks. The isotopic changes are illustrated in figure 7. Carbon, oxygen and hydrogen isotope data are presented for appropriate phases as a function of metamorphic grade. The gaps, where no outcrop can be found, are presented as boxes with information of the mineralogical changes that separate the metamorphic grades on either side of the gap. The conclusions that we have made using the isotopic data are summarized in the following discussion for each metamorphic field.

The isotopic data for the unmetamorphosed sediments give an indication of the rock type and origin. The carbonates have typical marine sediment $\delta^{13}C$ and $\delta^{18}O$ values. The δD values of the hydrous silicates are in the range of typical detrital argillaceous sediments, as are the $\delta^{18}O$ values of the silicate fraction.
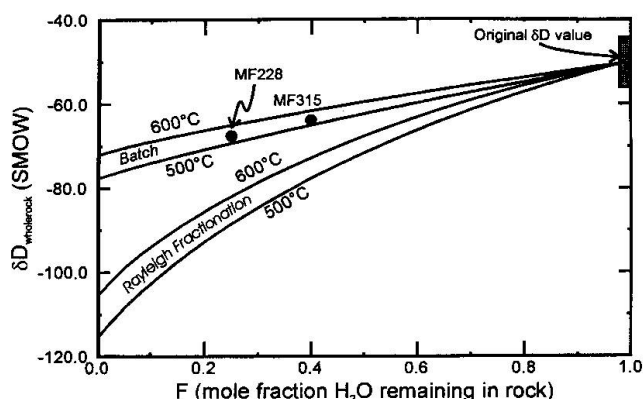
There is no change in the $\delta^{13}C$ value of the carbonates across the gap separating the unmetamorphosed sediments from the anchimetamorphosed rocks. The wt% carbonate is variable, but generally unchanged from the lower grade samples. Variations in the wt% carbonate probably reflect initial bulk rock heterogeneities as opposed to loss of carbonate by any mineral reactions. The $\delta^{18}O$ values of the carbonates is unchanged across the gap, but begin to decrease as the samples approach epimetamorphic grade, in response to the beginning of oxygen isotope equilibration with the silicates. The δD values of the hydrous silicates jump from $-80‰$ to $-60‰$ as the hydrous phases (during mineralogical reorganization) equilibrate with the sedimentary pore fluids. The oxygen isotope composition of the silicates is unchanged throughout the entire metamorphic sequence. This is not surprising, as they are the dominant reservoir for oxygen in the sediments.
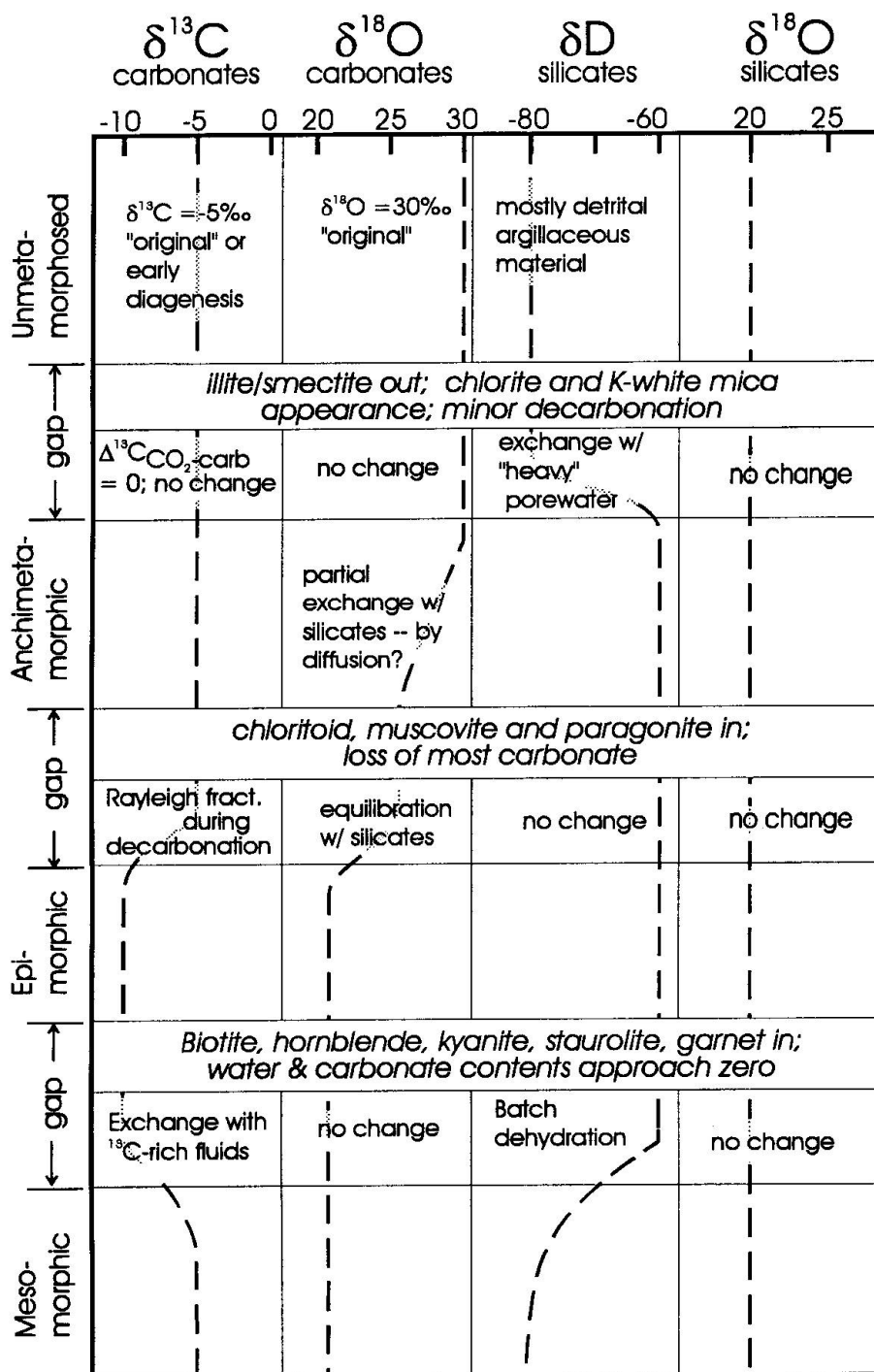
	$\delta^{13}C$ carbonates	$\delta^{18}O$ carbonates	δD silicates	$\delta^{18}O$ silicates
scale	-10 -5 0	20 25 30	-80 -60	20 25
Unmetamorphosed	$\delta^{13}C = -5‰$ "original" or early diagenesis	$\delta^{18}O = 30‰$ "original"	mostly detrital argillaceous material	
gap — illite/smectite out; chlorite and K-white mica appearance; minor decarbonation				
Anchimetamorphic	$\Delta^{13}C_{CO_2\text{-}carb} = 0$; no change	no change	exchange w/ "heavy" porewater	no change
		partial exchange w/ silicates -- by diffusion?		
gap — chloritoid, muscovite and paragonite in; loss of most carbonate				
Epimorphic	Rayleigh fract. during decarbonation	equilibration w/ silicates	no change	no change
gap — Biotite, hornblende, kyanite, staurolite, garnet in; water & carbonate contents approach zero				
Mesomorphic	Exchange with ^{13}C-rich fluids	no change	Batch dehydration	no change

Fig. 7   A general overview of the isotopic changes that accompany prograde metamorphism of the Central Alpine red beds. The "gaps" are regions where no outcrop can be found; mineralogical changes that occur in these gaps are described in the boxes in the gap sections. Average isotopic data and the mechanisms that control the changes in the isotopic ratios are described in the figure and in detail in the text.

The gap separating the anchimetamorphic from epimetamorphic samples involves the generation of chloritoid, muscovite and paragonite and the loss of most of the carbonate. Isotopic modifications occur only in the carbonate fraction. The $\delta^{13}C$ values of the carbonate drop from

$-5‰$ in the anchimetamorphic zone to $-10‰$ in the epimetamorphic zone. The preferential loss of ^{13}C during decarbonation is expected, and can be modeled by a simple Rayleigh decarbonation mechanism. (We cannot rule out the possibility that the lower $\delta^{13}C$ values in the epi-

metamorphic samples are due to pre-metamorphic modification, although there is no evidence to support this). The $\delta^{18}O$ values of the carbonates also drop across the boundary, but the isotopic change is too large to be explained by decarbonation alone (VALLEY, 1986). Instead, the carbonates have come into isotopic equilibrium with the silicates which make up the major oxygen reservoir in the rock.

The gap between the epimetamorphic and mesometamorphic samples represents the zone of biotite, hornblende, kyanite, and staurolite formation. Dehydration and decarbonation approach completion; water contents of less than 1% are found in the highest grade samples. Decarbonation reactions should lead to a decrease in the $\delta^{13}C$ values of the carbonates. Instead, the $\delta^{13}C$ values *increase* relative to those found in the epimetamorphic samples. Two explanations are proposed. The first is that the $\delta^{13}C$ values are not modified by any metamorphic processes, but rather, the anomalously low $\delta^{13}C$ values in the epimetamorphic zones are pre-metamorphic features. Alternatively, the epimetamorphic values are indicative of Rayleigh fractionation processes that have affected all samples that crossed the epimetamorphic boundary. In this case, the carbon isotope composition in the mesometamorphic samples has been raised by the influx of a ^{13}C-rich fluid. The source of such a fluid can be found in the immediately adjacent lithologies. FREY (1974) proposed that a carbon-bearing fluid infiltrated the red bed lithologies from the adjacent Liassic black shales. The isotopic composition of such a fluid must have been in equilibrium with a carbonate with a $\delta^{13}C$ value of -4 to $-5‰$ (Fig. 4). Carbon isotope exchange between the fluid and carbonate would have been facilitated by reactivity of the carbonate accompanying decarbonation reactions.

Dehydration and concurrent water loss across the epimetamorphic-mesometamorphic isograd result in a drop in the $\delta D_{wholerock}$ values. The drop can be modeled very well with a simple batch volatilization mechanism; the Rayleigh fractionation model does not fit the data as well. Apparently, fluid that was generated during dehydration was not able to escape during formation, and remained until the dehydration was nearly complete. There did not seem to be interconnected fluid channelways allowing for simultaneous fluid generation and fluid release. It must be pointed out that there is enough uncertainty in these calculations so that a distillation mechanism is possible, but our best estimates suggest otherwise.

The results of this work demonstrate that a number of mineralogical-chemical modifications which accompany metamorphic processes are reflected in their isotope signatures. The overall "closed system" oxygen isotope behavior is clear. It has been proposed that geological homogeneity over a large scale requires massive fluid fluxes (e.g., SHIEH and SCHWARCZ, 1977). There are clearly examples of such processes occurring during metamorphism, but, as this study demonstrates, dehydration of an initially high water content pelite is not sufficient to change the wholerock $\delta^{18}O$ value.

The hydration/dehydration systematics in metamorphic rocks can be monitored by hydrogen isotope variations. To our knowledge, no evidence for Rayleigh fractionation of hydrogen isotopes during high-grade metamorphism has been seen. Perhaps hydrous fluids can only be released in pulses or are not generated in sufficient quantities to allow for continuous expulsion from the host rock? Further studies will no doubt help to address this question.
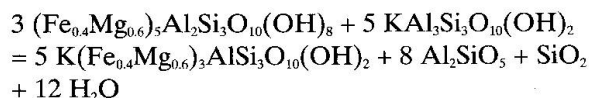
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Appendix

The change in δD as a function of reaction progress for reaction (3)

$$3\ (Fe_{0.4}Mg_{0.6})_5Al_2Si_3O_{10}(OH)_8 + 5\ KAl_3Si_3O_{10}(OH)_2$$
$$= 5\ K(Fe_{0.4}Mg_{0.6})_3AlSi_3O_{10}(OH)_2 + 8\ Al_2SiO_5 + SiO_2$$
$$+ 12\ H_2O$$

was modelled for batch devolatilization and Rayleigh devolatilization mechanisms. In the batch devolatilization, water does not leave the system until the devolatilization reaction reaches the desired degree of reaction progress (ξ). Because there are solid hydrous phases in both the reactants and products, the standard batch volatilization equation (e.g., VALLEY, 1986) does not adequately express the batch volatilization mechanism (although it is a very good approximation). Batch devolatilization for reaction (3) is not lin-

ear in terms of (ξ) vs $\delta D_{wholerock}$ because hydrogen is present in both the products and reactants (Fig. 7). Hence, the fractionation between water and the solid phases changes as a function of the relative proportions of the solids. At the point where the desired degree of reaction progress is reached, the equilibrium δD value of one phase is computed on the basis of the following algorithm: 1) The δD value of any solid hydrous phase is computed from the initial $\delta D_{wholerock}$ value (it is arbitrary which phase is chosen, in this example, we use chlorite). 2) A new wholerock δD value is computed by summing the δD contributions of the hydrous solids in their relative proportions at the degree of reaction progress ξ, with the water phase excluded. In effect, the δD value of a phase is determined from the original composition, the water is removed from the system, and the new $\delta D_{wholerock}$ value is computed from the remaining solids. The basic equation for the $\delta D_{wholerock}$ is the following:

$$\delta D_{wholerock}^{initial} = \sum_i \{X_i(1-\xi)(\delta D_{chlorite} - \Delta(chlor-i))\}_{reactants} +$$
$$+ \sum_j \{X_j(\xi)(\delta D_{chlorite} - \Delta(chlor-i))\}_{products} +$$
$$+ \{X_{H_2O}(\xi)(\delta D_{chlorite} - \Delta(chlor-H_2O))\}$$

Rearranging the above reaction, the $\delta D_{chlorite}$ is calculated from the equation

$$\delta D_{chlorite} = \delta D_{wholerock}^{initial} + (1 - \xi) \sum_i \{X_i \cdot \Delta (chlor-i)) +$$
$$(\xi) \left[\sum_j (X_j \cdot \Delta(chlor - i)) + X_{H_2O} \cdot \Delta (chlor - H_2O)) \right]$$

The final $\delta D_{wholerock}$ value after the water leaves the system is then determined from the expression

$$\delta D_{chlorite}^{initial} = \frac{\begin{array}{l} \sum_i \{X_i(1-\xi)(\delta D_{chlorite} - \Delta (chlor-i))\}_{reactants} + \\ \sum_j \{X_j(\xi)(\delta D_{chlorite} - \Delta (chlor-j))\}_{products} \end{array}}{(1 - \xi)\sum_i X_i + \xi \sum_j X_j}$$

Terminology is given as follows: (ξ) is reaction progress. ξ ranges from 0 before the reaction commences to 1 at which point all of the reactants are completely consumed; X_i refers to the mole fraction oxygen of the reactant i, where

$$\sum_i^m X_i = 1$$

for m reactants; the same expression holds for products j where

$$\sum_j^n X_j + X_{H_2O} = 1$$

for n product phases; $\Delta(chlor-i)$ is the equilibrium hydrogen isotope fractionation between chlorite and phase i (or j).

Rayleigh fractionation behavior for reaction (4) was calculated using the iterative method described by RUMBLE et al. (1982). In this process, reaction (4) is allowed to proceed in a small increment, and the equilibrium values for all phases are calculated assuming a closed system (constant $\delta D_{wholerock}$ value). Then, the small fraction of water generated in the increment is removed from the system and a new $\delta D_{wholerock}$ value is calculated on the basis of the solid water-bearing phases. Then new equilibrium δD values are calculated for each of the solid phases with the new $\delta D_{wholerock}$ value and the process is repeated until the desired degree of reaction progress is achieved.

The two process are described by the following mathematical treatment. The $\delta D_{chlorite}$ value at a new step is obtained by the following equation in terms of the $\delta D_{wholerock}$ value from the previous step

$$\delta D_{chlorite} = \frac{\begin{array}{l} \delta D_{wholerock}^{n-1}\left((1-\frac{n}{N}) + \frac{n}{N}\sum_j X_j + (\frac{1}{N})X_{H_2O}\right) + (1-\frac{n}{N})\sum_i X_i\Delta(chlor-i) + \\ (\frac{n}{N})\sum_j X_j\Delta(chlor - i) + (\frac{1}{N})X_w\Delta(chlor - H_2O) \end{array}}{(1-\frac{n}{N}) + \frac{n}{N}\sum_j X_j + \frac{1}{N}X_{H_2O}}$$

where n is the number of the step and N is the total number of steps (100 is sufficient) and $\delta D_{wholerock}^{n-1}$ is the $\delta D_{wholerock}$ value from the previous step. The new δD value $\delta D_{wholerock}^{n}$ is then determined from the expression

$$\delta D_{wholerock}^n = \frac{\begin{array}{l} (1-\frac{n}{N})\sum_i \{X_i(\delta D_{chlorite} - \Delta(chlor - i))\}_{reactants} + \\ (\frac{n}{N})\sum_j \{X_j(\delta D_{chlorite} - \Delta(chlor - j))\}_{products} \end{array}}{(1-\frac{n}{N}) + \frac{n}{N}\sum_j X_j}$$

The procedure is continued from 1 to n, where n/N is the degree of reaction progress (ξ) and N is the total number of steps for the reaction to go to completion.

In the above calculations, it was assumed that the initial water content was 4 wt%. The following fractionation factors were used (SUZUOKI and EPSTEIN, 1976):

	500 °C	600 °C
Δ(chlorite – biotite)	– 5‰*	– 5‰*
Δ(chlorite – muscovite)	–36.6‰	–36.6‰
Δ(chlorite – H$_2$O)	–43.9‰	–35.8‰

*where the (chlorite – biotite) value is a result of the addition of brucite layers in the chlorite.