

Stable isotope geochemistry and phase equilibria of coesite-bearing whiteschists, Dora Maira Massif, western Alps

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Abstract. Peak metamorphic temperatures for the coesite-pyrope-bearing whiteschists from the Dora Maira Massif, western Alps were determined with oxygen isotope thermometry. The $\delta^{18}\text{O}(\text{SMOW})$ values of the quartz (after coesite) ($\delta^{18}\text{O} = 8.1$ to 8.6‰ , $n = 6$), phengite (6.2 to 6.4‰ , $n = 3$), kyanite (6.1‰ , $n = 2$), garnet (5.5 to 5.8‰ , $n = 9$), ellenbergerite (6.3‰ , $n = 1$) and rutile (3.3 to 3.6‰ , $n = 3$) reflect isotopic equilibrium. Temperature estimates based on quartz-garnet-rutile fractionation are 700 – 750°C . Minimum pressures are 31 – 32 kb based on the pressure-sensitive reaction pyrope + coesite = kyanite + enstatite. In order to stabilize pyrope and coesite by the temperature-sensitive dehydration reaction talc + kyanite = pyrope + coesite + H_2O , the $a(\text{H}_2\text{O})$ must be reduced to 0.4 – 0.75 at 700 – 750°C . The reduced $a(\text{H}_2\text{O})$ cannot be due to dilution by CO_2 , as pyrope is not stable at $X(\text{CO}_2) > 0.02$ ($T = 750^\circ\text{C}$; $P = 30$ kb). In the absence of a more exotic fluid diluent (e.g. CH_4 or N_2), a melt phase is required. Granite solidus temperatures are $\sim 680^\circ\text{C}/30$ kb at $a(\text{H}_2\text{O}) = 1.0$ and are calculated to be $\sim 70^\circ\text{C}$ higher at $a(\text{H}_2\text{O}) = 0.7$, consistent with this hypothesis. Kyanite-jadeite-quartz bands may represent a relict melt phase. Peak P - T - $f(\text{H}_2\text{O})$ estimates for the whiteschist are 34 ± 2 kb, 700 – 750°C and 0.4 – 0.75 . The oxygen isotope fractionation between quartz ($\delta^{18}\text{O} = 11.6\text{‰}$) and garnet ($\delta^{18}\text{O} = 8.7\text{‰}$) in the surrounding orthogneiss is identical to that in the coesite-bearing unit, suggesting that the two units shared a common, final metamorphic history. Hydrogen isotope measurements were made on primary talc and phengite ($\delta\text{D}_{(\text{SMOW})} = -27$ to -32‰), on secondary talc and chlorite after pyrope ($\delta\text{D} = -39$ to -44‰) and on the surrounding biotite ($\delta\text{D} = -64\text{‰}$) and phengite ($\delta\text{D} = -44\text{‰}$) gneiss. All phases appear to be in near-equilibrium. The very high δD values for the primary hydrous phases is consistent with an initial oceanic-derived/connate fluid source. The fluid source for the

retrograde talc + chlorite after pyrope may be fluids evolved locally during retrograde melt crystallization. The similar δD , but dissimilar $\delta^{18}\text{O}$ values of the coesite-bearing whiteschists and hosting orthogneiss suggest that the two were in hydrogen isotope equilibrium, but not oxygen isotope equilibrium. The unusual hydrogen and oxygen isotope compositions of the coesite-bearing unit can be explained as the result of metasomatism from slab-derived fluids at depth.

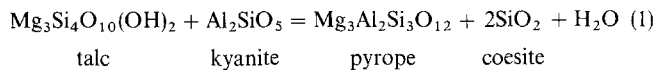
Introduction

The identification of coesite in whiteschists of the southern Dora Maira Massif by Chopin (1984) is certainly one of the more remarkable discoveries in metamorphic petrology in the last decade. The ultra-high pressures indicated by the coesite are far greater than previously documented and significantly expand our knowledge of the maximum depths from which tectonic exhumation of metamorphic material can occur. Chesnokov and Popov (1965) first alluded to the possibility of quartz pseudomorphs after coesite in regional metamorphic rocks, but it was the positive identification by Chopin that stimulated numerous additional discoveries of coesite or quartz pseudomorphs after coesite (Smith 1984; Smith and Lapin 1987; Okay et al. 1989; Wang et al. 1989; Yang and Smith 1989; Enami and Zang 1990; Tagiri and Bakirov 1990; Hirajima et al. 1991; Reinecke 1991; Schmädicke 1991). The discovery of diamond inclusions in metamorphic garnets (Sobolev and Shatsky 1990; Shutong et al. 1992) is even more remarkable. The presence of coesite and diamond in metamorphic rocks defines a new "ultra-high pressure" metamorphic facies. As these rocks represent the known depth limits of in situ metamorphic material now exposed at the Earth's surface, accurate determinations of the peak metamorphic pressure, temperature and fluid composition associated with the metamorphic event are essential for understanding metamorphic processes in the deepest crustal regimes.

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Coesite-bearing whiteschists from Dora Maira have been extensively studied (Vialon 1966; Chopin 1984, 1986, 1987; Rossman et al. 1989; Chopin et al. 1991; Monié and Chopin 1991; Kienast et al. 1991; Schertl et al. 1991; Tilton et al. 1991). Metamorphic pressures of these coesite-pyrope whiteschists are constrained by the preservation of coesite, the Si content in phengite (Massonne and Schreyer 1989), and the equilibrium assemblage pyrope + coesite in place of the lower pressure equivalent enstatite + kyanite (this study). The temperatures of metamorphism are more poorly constrained. The best temperature constraint comes from the univariant equilibrium:



Reaction (1) has been experimentally calibrated (Chopin 1985), but temperature estimates based on this reaction require an accurate knowledge of the H_2O activity [$a(\text{H}_2\text{O})$] attending metamorphism. Chopin (1984) proposed that temperatures were somewhere between 700 and 800 °C depending upon the H_2O activity. In this study, temperatures were estimated from oxygen isotope thermometry, a thermometric technique that is nominally independent of H_2O activity. The coesite-bearing assemblage is well suited for oxygen isotope thermometry and unlikely to have undergone retrograde reequilibration as (1) the mineral phases are refractory, (2) the rock was cooled rapidly and, as concluded in this study, (3) the $a(\text{H}_2\text{O})$ was low during peak and early retrograde metamorphism. The isotopic data not only allow P - T estimates to be made, but also can be used in conjunction with mineral equilibria data to constrain the composition of the fluid phase accompanying metamorphism.

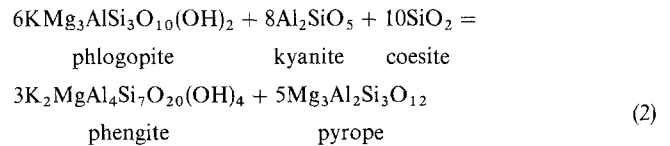
Geology and mineralogy of the coesite-bearing rocks

Coesite-bearing rocks and surrounding gneisses sampled in this study are from the Parigi outcrop, near Martiniana Po, Italy. This outcrop has been described in great detail (Vialon 1966; Chopin 1984; Chopin et al. 1991; Schertl et al. 1991), so that only relevant features are described in this section. The coesite bearing whiteschists are preserved as boudins up to 90 m in length and several tens-of-meters thick hosted in a phengite-biotite gneiss. The whiteschist is thought to have a protolith of Proterozoic age (Paquette et al. 1989; Tilton et al. 1989) and underwent high pressure metamorphism with a low geothermal gradient during the early Alpine orogeny (Monié and Chopin 1991; Tilton et al. 1991). The whiteschist boudins can be divided into three types: a fine-grained quartzite with small pyrope porphyroblasts; a talc-phengite-kyanite-quartz matrix with pyrope megacrysts and an occasional kyanite-jadeite-quartz-rich layer or vein.

A summary of the mineralogy of the Parigi rocks is given by Schertl et al. (1991), who listed over 20 minerals in the coesite-bearing unit. The modally abundant phases are quartz, kyanite, talc, pyrope, phengite, with minor rutile (inclusions in garnet and matrix) and the new mineral ellenbergerite (inclusions in large garnets only). Chlorite is found as a relict prograde mineral in pyrope megacrysts and as a late alteration product. Coesite is found most commonly as inclusions in the small pyropes in the quartzite layers and almost never in the groundmass. Phases notably absent include enstatite and phlogopite, the latter having been found only as an inclusion within a kyanite inclusion in pyrope (Schertl et al. 1991). The surrounding biotite-phengite gneiss is composed predominantly of quartz, plagioclase, microcline, biotite and phengite, with minor chlorite, garnet, epidote, tourmaline and sphene (Schertl et al. 1991).

Previous pressure-temperature estimates of Dora Maira whiteschists

Chopin (1984) was the first to document ultra-high pressures of regional metamorphism for the Dora Maira whiteschists based primarily on the presence of coesite. Chopin (1984) also recognized that the assemblage phengite + pyrope is the high pressure product of the reaction:



Temperatures of metamorphism were constrained with reaction (1), although, as pointed out by Chopin, exact temperatures depend upon assumed H_2O activity. Chopin (1984) concluded that water activities were above 0.2, temperatures were slightly higher than 700 °C, and pressures were greater than 28 kb. More recent temperature estimates range between 700 and 800 °C. Estimates of 700 °C have been proposed based on the lack of textural evidence for partial melting of the country rocks (Chopin 1987). The most recent P - T estimates are 37 kb and 800 °C, based on the intersection of the isopleth for the Si-content in phengite with reaction (1), and assuming unit H_2O activity (Schertl et al. 1991).

Sample description

Five samples from the coesite-bearing unit and one from the enclosing orthogneiss were analyzed. Two samples of pyrope megacrysts were analyzed. *Sample PM-1* was a 10 cm diameter megacryst that was crushed in order to separate the mineral inclusions quartz, rutile, kyanite, phengite, ellenbergerite and talc. A phyllosilicate rind existed on this garnet before crushing, so that some of the phengite may not have been included in the garnet. *Sample PM-2* was a 50–60 mm diameter garnet megacryst for which only the garnet was analyzed. *Sample GM-1* is a garnet megacryst layer. All mineral separates analyzed in this sample other than garnet were from the matrix. *Sample QZT-1* is a quartzite (coesite notation of Chopin 1984) layer with small, coesite-bearing garnets. The garnet and the quartz matrix were analyzed. *Sample AP-1* was a completely altered 30 mm diameter pyrope megacryst found in a stream bed. The sample is now a fine-grained greenish intergrowth of kyanite, talc and quartz after pyrope. *Sample AS-1* is a two-mica orthogneiss taken from the surrounding orthogneiss containing minor garnet.

Analytical methods

Rock samples were crushed, sieved and ultrasonically cleaned. Mineral separates were made with a combination of heavy liquid techniques, magnetic separation and final hand picking. Quartz was separated from feldspar in the gneiss sample AS1 by briefly reacting the biminerale concentrate in hydrofluoric acid. The product was gently ground to disintegrate the feldspar, leaving only pure quartz as a residual phase. Virtually pure mineral separates of 1–2 mg could be achieved by these methods.

Oxygen isotope values of mineral separates were determined with the laser-based extraction method (Sharp 1990; 1992). Analyses were made on ~1 mg of material. A maximum of 17 samples could be loaded simultaneously on a nickel sample holder and placed in the reaction chamber. Three to four standards were analyzed in each run. All samples were analyzed at least twice (except ellenbergerite, due to the rarity of this phase). Samples were heated with a CO_2 laser in a BrF_5 atmosphere to quantitatively liberate oxygen. The oxygen was separated from the excess reagent cryogenically and then passed over a mercury diffusion pump to remove traces of F_2 . The O_2 was converted to CO_2 by combustion with a heated graphite rod with a platinum catalyst and introduced directly into the mass spectrometer.

Hydrogen isotope ratios and water contents were determined on hydrous mineral separates following procedures of Vennemann and O'Neil (1993). Analyses were made by placing 20–40 mg of a purified mineral in a silica-glass tube. After evacuation, the samples were heated with a gas-oxygen flame until the minerals melted. All H₂O was collected on a cold trap during melting. Minor H₂ produced during heating was converted to H₂O by reaction with a CuO furnace at 550 °C. The two sources of H₂O were combined, cryogenically purified, and frozen into Pyrex tubes with excess zinc. The tubes were sealed and heated at 450 °C for 20 minutes, quantitatively reducing H₂O to H₂ by reaction with zinc. The δD value and the water content were determined with the mass spectrometer, the latter being determined from the mass 2 voltage for a constant volume.

Results

Oxygen and hydrogen isotopic values of mineral separates from the coesite-bearing whiteschist and the surrounding orthogneiss are given in Table 1. The δ¹⁸O values of all phases are homogeneous in hand sample and are nearly constant within the entire whiteschist body. Isotopic equilibrium was attained on a scale approaching > 100 m regardless of bulk composition. For example, the total range of garnet analyses is 5.45 to 5.81‰, and only 5.45 to 5.57‰ if sample PM-2 is excluded. The entire coesite-bearing unit has reached internal oxygen isotope equilibrium, but not with the surrounding orthogneiss. The δ¹⁸O_(quartz) value of the two-mica gneiss is 3‰ higher than in the coesite-bearing rocks.

Equilibrium temperatures based on the oxygen isotope fractionation between the minerals quartz, garnet and rutile were calculated with experimental, empirical and theoretical calibrations (Table 2). Temperature estimates for the coesite-bearing unit based on experimental calibrations range from 700–750 °C; those based on empirical calibrations have only a slightly larger temperature spread. The theoretical calibrations of Hoffbauer et al. (1993) based on the increment method yield somewhat higher temperatures. The estimates of Hoffbauer appear in some cases to yield excessively high temperatures (Sharp et al. 1992), and are not preferred. Temperature estimates for the garnet orthogneiss from the Δ(quartz-garnet) fractionations are identical to those of the coesite-bearing unit. Biotite in the orthogneiss is clearly out of isotopic equilibrium with the more refractory minerals quartz and garnet. This result is expected, as biotite is also out of textural equilibrium and most likely was crystallized in a later, low-pressure metamorphism (Monié and Chopin 1991).

The degree of isotopic equilibrium between all phases in the coesite-bearing unit was assessed with the graphical method of Javoy et al. (1970) and the theoretical fractionation factors of Hoffbauer et al. (1993). In addition to the fractionation factors published in Hoffbauer et al. (1992), R. Hoffbauer has kindly calculated the fractionation factor for ellenbergerite ($I^{18}\text{O}_{\text{ellenbergerite}} = 0.71$ based on 60% bridging hydrogen, where $I^{18}\text{O}_{\text{quartz}} = 1.00$; I = increment index of Hoffbauer et al. 1993). The linear fit of the δ¹⁸O values for each mineral versus the temperature coefficient of fractionation a from the equation

$$1000\ln\alpha = a \times 10^6 \times T^{-2} \quad (3)$$

Table 1. Oxygen and hydrogen isotopic composition of mineral separates

Mineral	δ ¹⁸ O (SMOW)	Mass (mg)	Analysis Number	δD (SMOW)	Sample Name
Coesite-bearing unit					
Quartz	8.42	1.03	S089-3		PM-1
	8.65	1.14	S090-3		PM-1
	8.10	1.13	S092-4		GM-1
	8.30	1.70	S093-3		GM-1
	8.31	1.34	S099-6		QZT-1
	8.47	1.48	S099-7		QZT-1
	Garnet	5.57	1.17	S090-4	
5.80		1.39	S098-10		PM-2
5.81		1.46	S098-11		PM-2
5.55		1.13	S092-5		GM-1
5.45		1.49	S092-6		GM-1
5.48		1.60	S093-4		GM-1
5.54		1.64	S093-6		GM-1
5.50		1.23	S098-12		QZT-1
5.53		1.35	S098-13		QZT-1
Rutile		3.60	1.00	S089-8	
	3.50	1.96	S093-12		GM-1
	3.32	1.38	S093-13		GM-1
Kyanite	6.08	0.80	S089-7		PM-1
	6.12	1.52	S093-14		GM-1
Phengite	6.33	2.15	S089-5	–35	PM-1
	6.20	1.73	S089-6		PM-1
	6.41	1.19	S093-8		GM-1
Ellenbergerite	6.31	0.75	S089-11		PM-1
Talc	–	–	–	–32	PM-1
Altered pyrope ^a	4.51	1.09	S115-1	–42	AP-1
	4.73	2.39	S115-2		AP-1
Enclosing orthogneiss					
Quartz	11.46	3.20	S111-6		AS-1
	11.56	2.97	S112-3		AS-1
	11.88	1.79	S112-4		AS-1
	11.50	1.92	S112-5		AS-1
Garnet	8.85	1.24	S111-4		AS-1
	8.66	1.60	S111-5		AS-1
Biotite	6.78	1.59	S111-8	–64	AS-1
Phengite	–	–	–	–44	AS-1

^a Talc, kyanite and chlorite (reaction 3 in text)

where $1000\ln\alpha \approx \delta_x - \delta_y$ (phases x and y), indicates that all minerals have achieved and maintained isotopic equilibrium (Fig. 1). The slope of the best-fit line in Fig. 1 is proportional to the temperature of equilibrium by Eq. 3. Temperature estimates based on mineral inclusions in garnet megacrysts and groundmass minerals are identical, within experimental error. This result suggests that garnet megacrysts grew at or near peak metamorphic temperatures, or that complete equilibrium was attained by the process of intracrystalline diffusion at the peak of metamorphism. Ellenbergerite is also in apparent isotopic equilibrium with garnet and quartz, even though it is thought to be a prograde relict mineral, not stable at the peak of metamorphism (Chopin 1986). The uncertainties in the calculations for the fractionation factors are suffi-

Table 2. Temperature (°C) estimates based on the $\delta^{18}\text{O}$ fractionations between coexisting phases

Sample	Experimental calibration			Empirical calibration				
	$\Delta\text{Qz-Gt}$	$\Delta\text{Qz-Ru}$	$\Delta\text{Gt-Ru}$	$\Delta\text{Qz-Gt}$	$\Delta\text{Qz-Ru}$	$\Delta\text{Gt-Ru}$	$\Delta\text{Qz-Bi}$	$\Delta\text{Gt-Bi}$
PM-1	710	740	720	720	710	710	–	–
GM-1	750	750	700	760	720	680	–	–
QZ-1	730	–	–	740	–	–	–	–
AS-1	720	–	–	730	–	–	550	290
Theoretical calibration								
Sample	$\Delta\text{Qz-Gt}$	$\Delta\text{Qz-Ru}$	$\Delta\text{Qz-Ph}$	$\Delta\text{Qz-Ky}$	$\Delta\text{Qz-El}$	$\Delta\text{Gt-Ru}$	$\Delta\text{Gt-Ky}$	$\Delta\text{Gt-El}$
PM-1	770	750	740	820	760	720	560	770
GM-1	820	760	870	900	–	700	460	–
QZ-1	780	–	–	–	–	–	–	–

Sources of data: experimental $\Delta\text{Qz-Gt}$, Lichtenstein and Hoernes 1992; $\Delta\text{Qz-Ru}$, $\Delta\text{Gt-Ru}$, Matthews 1992. Empirical, $\Delta\text{Qz-Gt}$, $\Delta\text{Qz-Bi}$, $\Delta\text{Gt-Bi}$, Bottinga and Javoy 1975; $\Delta\text{Qz-Ru}$, Agrinier 1991; $\Delta\text{Gt-Ru}$, Bottinga and Javoy 1975; Agrinier 1991. Theoretical, Hoffbauer et al. 1993. Abbreviations: Bi, biotite; El, ellenbergerite; Gt, garnet; Ph, phengite; Qz, quartz; Ru, rutile

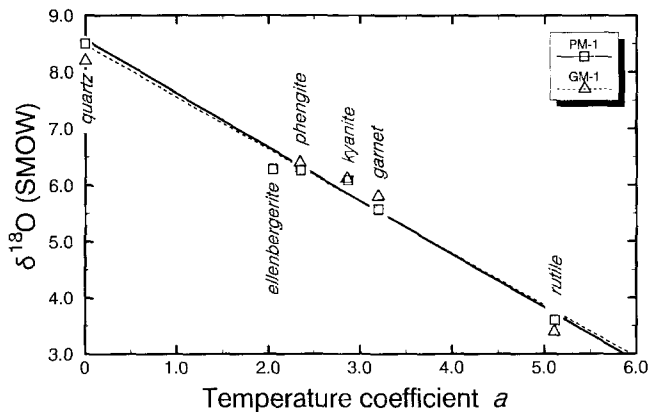


Fig. 1. A plot of the $\delta^{18}\text{O}$ values for mineral separates of samples PM-1 (pyrope megacryst and inclusions) and GM-1 (pyrope megacryst and groundmass) versus the fractionation temperature coefficient a (Eq. 3). The relationship between $\delta^{18}\text{O}$ and a must be linear if all phases are in equilibrium. (Fractionation coefficients from Hoffbauer et al. 1993)

ciently large so that the apparent peak-temperature equilibration may be fortuitous, although reequilibration at peak temperature by solid state diffusion is not unlikely.

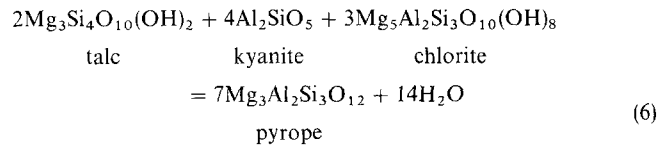
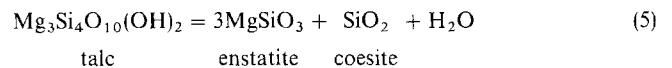
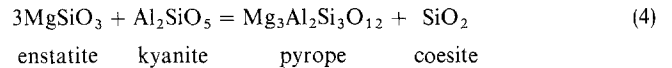
Several lines of evidence argue that the oxygen isotope temperatures were not partially reset during cooling. First, the temperature estimates are indistinguishable between the garnet megacrysts and the matrix. If either of these distinct micro-environments partially reset, then the temperature estimates would be different. Second, the diffusion rates in garnet, kyanite, and to a lesser extent in quartz are very slow, and oxygen diffusion rates are even slower under anhydrous conditions (e.g. Farver and Yung 1991). The rocks are also thought to have cooled rapidly (Monié and Chopin 1991), so that the possibility of retrograde exchange is minimized. Finally, all minerals appear to be in isotopic equilibrium (Fig. 1). As the diffusion rate for each phase is different, it is very unlikely that all phases would undergo partial reequilibration and still maintain apparent equilibrium.

Discussion

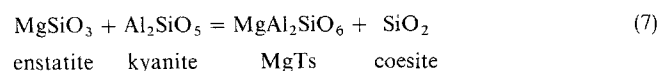
Comparison with phase equilibria– P - T - a (H_2O)

The oxygen isotope temperature estimates for the Dora Maira rocks are 700–750 °C. These data can be combined with phase equilibria constraints to estimate fluid fugacities and the probability of whether or not partial melting occurred. In order to make these comparisons, it is first necessary to develop an internally consistent thermodynamic data base for generation of a petrogenetic grid in the system $\text{K}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$.

Two large, internally consistent thermodynamic data sets have been generated that are applicable to metamorphic rocks (Berman 1988; Holland and Powell 1990). The stability fields of reactions (1) and the following three experimentally constrained reactions were calculated with these data bases:



The results from the two data sets are in excellent agreement but unfortunately do not reproduce the experimentally derived P - T locations for these reactions. The stability fields for reactions (1), (4), (5) and (6), calculated with the Holland and Powell data set and the computer program of Powell and Holland (1988), are plotted in Fig. 2 along with the experimentally determined reversals for these reactions. The agreement between the experimental and the computed univariant equilibria is poor. The discrepancy for reaction (4) is due to solid solution of Mg-Tschermak component (MgTs) in enstatite by the reaction



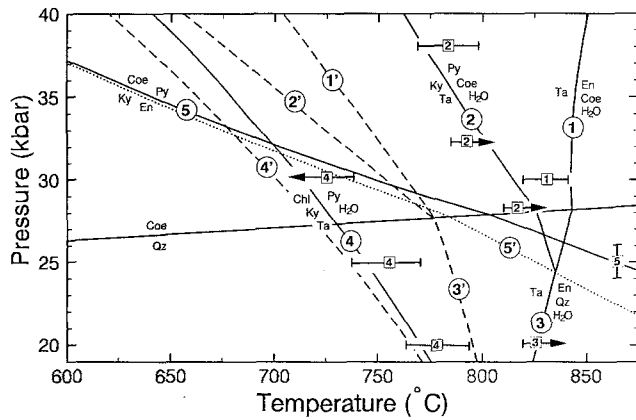
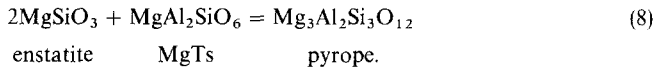


Fig. 2. Selected phase relations in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system calculated with talc compressibility factor (β) of 2.42 Mb^{-1} (solid lines, labels and numbers) and 1.69 Mb^{-1} (dashed lines and numbers followed by '). The β -value of 1.69 Mb^{-1} from Holland and Powell (1990) does not reproduce the experimental reversals. The value of 2.42 Mb^{-1} adequately reproduces all experiments involving talc. The solid curve for reaction 5 is corrected for the MgTs component in enstatite using the relationship of Gasparik and Newton (1984); the dotted curve is not. (Source of experiments: 1, 3, Kitahara et al. (1966); 2, 4, Chopin (1985); 5, Massonne (1983). Abbreviations for all figures *Cel*, celadonite; *Chl*, chlorite; *Coe*, coesite; *Dm*, diamond; *En*, enstatite; *Gr*, graphite; *Jd*, jadeite; *Ky*, kyanite; *l*, liquid; *Mag*, magnesite; *Mus*, muscovite; *OrH*, $\text{KAlSi}_3\text{O}_8\text{-H}_2\text{O}$; *Py*, pyrope; *Qz*, quartz; *Ta*, talc

and



Correction for the dilution of enstatite by MgTs buffered by pyrope was made with the experimental data for reaction (4) (Perkins et al. 1981; Gasparik and Newton 1984). The experiments for reaction (4) (Massonne 1983) and the calculated position of this reaction corrected for solid solution are in perfect agreement (Fig. 2).

All talc-bearing reactions are fit well with the Holland and Powell data set at pressures below 20 kb. Only the high pressure reactions are in poor agreement with the experimentally determined stabilities. The effect of pressure increases the discrepancy between the calculated and measured stability relations for talc, suggesting that the compressibility data for talc in the large data sets may be inappropriate for high pressure phase equilibria.

The compressibility of talc is expressed by Holland and Powell as a single variable. This unfortunately does not allow for second order effects to be considered in the computer program of Powell and Holland (1988), even though the compressibility of talc is strongly non-linear (Vaidya et al. 1973). Agreement between the high pressure experiments and calculated equilibria occurs if the compressibility (β) of talc is shifted to a value of 2.42 Mb^{-1} , higher than those given in either Berman (1988) or Holland and Powell (1990). Further compressibility experiments for talc are necessary to properly evaluate this adjustment, but the substitution of the 2.42 Mb^{-1} β value results in a data base that can be used to generate accurate phase equilibria relations for the high pressure mineral reactions involving talc (Fig. 3). The P - T shifts in these

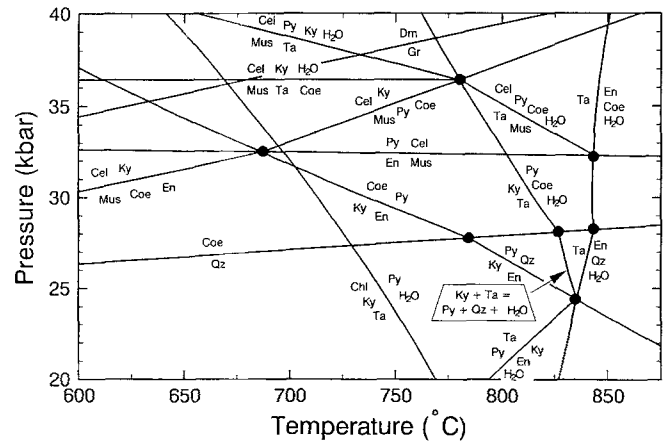


Fig. 3. Calculated phase diagram for selected reactions in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system with the compressibility factor of 2.42 Mb^{-1} for talc. Equilibria calculated for $a(\text{Cel}) = 0.62$, $a(\text{Mus}) = 0.38$ and $a(\text{En}) = 1.0$. Graphite-diamond transition also shown (Kennedy and Kennedy, 1976). Abbreviations given in Fig. 2.

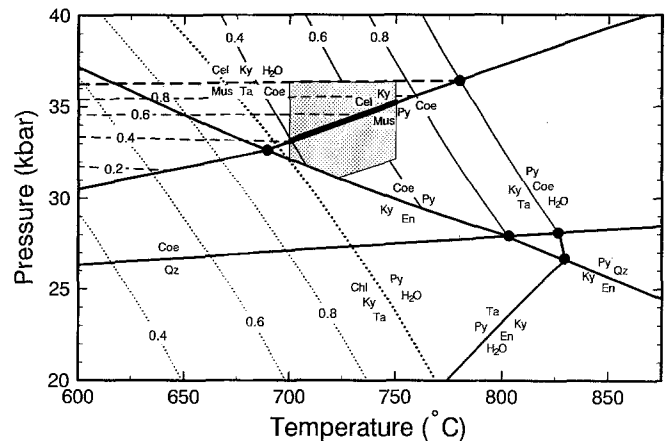
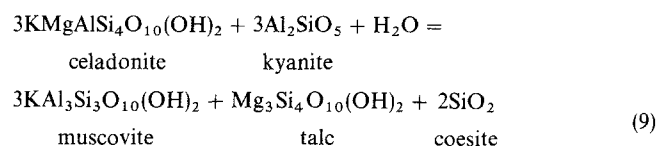


Fig. 4. Selected phase equilibria with contours for reduced water activity. Peak P - T - $a(\text{H}_2\text{O})$ estimates for the coesite-bearing white-schists are delineated by the shaded polygon. Temperatures are limited by oxygen isotope thermometry. The peak P - T must lie on the water-absent reaction 12 (shown as broad line between $700\text{-}750^\circ\text{C}$). Minimum pressure are constrained by reaction 4. The $a(\text{En})$ corrected for MgTs component, $a(\text{Cel}) = 0.62$, $a(\text{Mus}) = 0.38$. Abbreviations given in Fig. 2.

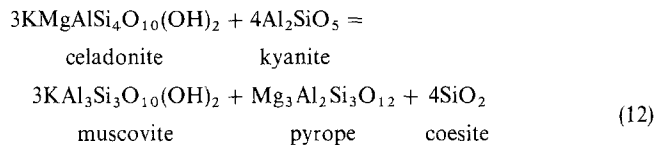
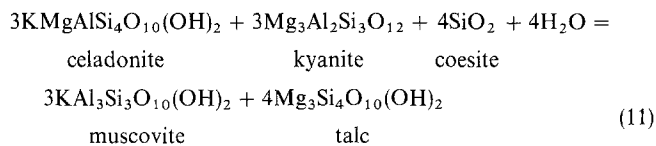
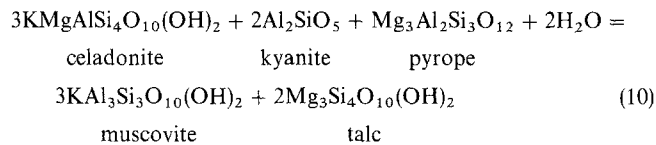
curves can then be evaluated as a function of $a(\text{H}_2\text{O})$ (Fig. 4).

The pressures of metamorphism are constrained by several reactions. The presence of coesite + pyrope and the absence of Al-enstatite requires minimum pressures of 28 kb at 800°C (reaction 4). This pressure constraint is significantly higher than coesite alone and is independent of the H_2O activity. A second pressure-constraining reaction is based on the Si-content in phengite coexisting with talc, kyanite and coesite (Massonne and Schreyer 1989). The Si-content in phengite is buffered by the reaction



Phengites from the Dora Maira coesite-bearing unit have 3.55 Si per 12 oxygen (Chopin 1984). The experimental P - T location of the $\text{Si}_{3.55}$ isopleth (Massonne and Schreyer 1989) can be fit with the thermodynamic data set of Holland and Powell (1990) if the assumed activities of celadonite and muscovite are 0.62 and 0.38, respectively. This is in fair agreement with the activities of celadonite and muscovite assuming an ideal molecular mixing model (0.55 and 0.45 respectively). By assuming activities of 0.62 and 0.38 for celadonite and muscovite, respectively, the P - T shift for reaction (9) can be calculated as a function of $a(\text{H}_2\text{O})$ (Fig. 4).

There are three other reactions that emanate from the invariant point defined by the intersection of reactions (1) and (9) (Fig. 3). These are the following:



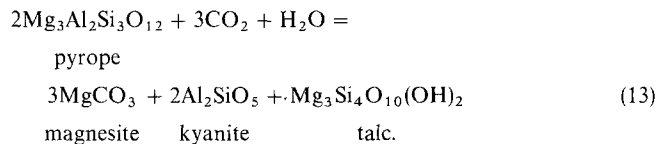
The invariant point defined by reactions (1), (9), (10) and (11) will move along the water-absent reaction (12) to lower P - T with decreasing $a(\text{H}_2\text{O})$. In theory, the P - T conditions of the coesite-bearing rock must lie on reaction (12), the actual P - T depending upon the H_2O activity. This P - T - $a(\text{H}_2\text{O})$ field is illustrated in Fig. 4. Unfortunately, the P - T location of reaction (12) is not well known. It is based on the invariant point defined by reactions (1) and (9). The stability field of reaction (1) has been determined experimentally (Chopin 1985), but reaction (9) is based on unreversed experiments and incompletely characterized run products (Essene 1989). Ideally, the P - T conditions of metamorphism must lie on reaction (12) within the temperature constraints defined by the oxygen isotope thermometric constraints (thick solid line segment in Fig. 4). A more conservative P - T estimate for the peak metamorphic conditions is illustrated by the shaded polygon in Fig. 4. It is based on a ± 2 kb uncertainty for reaction 12 coupled with the constraints that pressures must lie above the well-calibrated, anhydrous reaction (4) and below the experimentally determined reaction (9).

Reaction (1) is the most temperature sensitive reaction applicable to the coesite-bearing whiteschists at Dora Maira and can be used in conjunction with the independent isotopic temperature estimates to constraint the $a(\text{H}_2\text{O})$. Reaction (1) is located at 800 °C at 30 kb, well above the 700–750 °C temperature estimates from oxygen isotope thermometry. The univariant assemblage defined by reaction (1) will be stable at 700–750 °C, 30–35 kb at $a(\text{H}_2\text{O}) = 0.4$ –0.7 (Fig. 4). The best estimate of the peak metamorphic conditions for the coesite-bearing white-

schist are $T = 700$ –750 °C, $P = 32$ –36 kb, $a(\text{H}_2\text{O}) = 0.4$ –0.75. The P - T estimates are within a few kb of the stability field of diamond (Fig. 3), although no carbon phase has yet been identified in the Dora Maira whiteschists. Graphite has been found in neighbouring eclogite and marble units, but no diamond has yet been identified (Chopin personal communication 1992).

Fluid and melt composition

In order to maintain a reduced H_2O activity and still produce pyrope + coesite from the dehydration reaction (1), a fluid diluent, such as CO_2 or a melt, must have been present during metamorphism. A likely fluid diluent is CO_2 , as low $a(\text{H}_2\text{O})$ is commonly attributed to CO_2 streaming in granulite-facies terranes (e.g. Touret 1971; Janardhan et al. 1979). An examination of the stability of talc and kyanite in a mixed CO_2 - H_2O fluid demonstrates that CO_2 cannot, in fact, be the fluid diluent (Fig. 5). At $X(\text{CO}_2) > 0.02$ ($T = 750$ °C), pyrope is not stable. Magnesite is produced by the reaction



In the absence of an unusual fluid species (e.g. CH_4 , N_2), the low $a(\text{H}_2\text{O})$ could only have been maintained by the presence of a melt. A melt would provide a sink for fluids evolved by the dehydration of talc. Reaction (1) could proceed with $P(\text{fluid}) < P(\text{total})$ and $a(\text{H}_2\text{O}) < 1$ (e.g. Valley et al. 1990). Experimental determination of the high pressure solidus have been made for natural granites (Boettcher and Wyllie 1968; Stern et al. 1975) and for bulk compositions in the system $\text{NaAlSi}_3\text{-KAlSi}_3\text{O}_8$ - SiO_2 - H_2O (Huang and Wyllie 1975). The solidus determinations of Stern et al. (1975) for coesite-

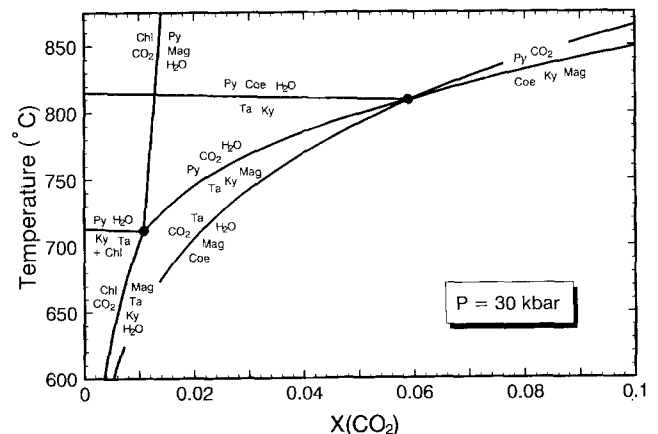


Fig. 5. Temperature- $X(\text{CO}_2)$ phase diagram at 30 kb, assuming $P(\text{fluid}) = P(\text{tot})$ for selected phases in the $\text{MgO-Al}_2\text{O}_3$ - SiO_2 - H_2O - CO_2 system. The stability field of pyrope and chlorite are limited to very low $X(\text{CO}_2)$, indicating that the $X(\text{CO}_2)$ must have been extremely low during prograde and retrograde conditions. Abbreviations given in Fig. 2

jadeite-kyanite-H₂O are identical to the results of Huang and Wyllie (1975) for jadeite-coesite-KAlSi₃O₈·H₂O-H₂O), while the data of Boettcher and Wyllie give solidus temperatures that are 30 °C higher. The solidus curve for $a(\text{H}_2\text{O}) = 1.0$ is $\sim 680^\circ\text{C}$ and 30 kb and $\sim 700^\circ\text{C}$ at 35 kb (Fig. 6).

The granitic solidus will be displaced to higher temperatures with decreasing $a(\text{H}_2\text{O})$. There are no reliable relationships between the wt.% H₂O versus $a(\text{H}_2\text{O})$ for granitic melts at pressures > 20 kb, but a crude estimate for the effect of $a(\text{H}_2\text{O})$ on the high pressure solidus was made based on the relationship between wt.% H₂O versus $a(\text{H}_2\text{O})$ for the NaAlSi₃O₈-H₂O system between 0 and 10 kb (Eqs. 16-4; Burnham 1979). Applying Burnham's equation to granite melts at 30 kb, the expected temperature shifts in the liquidus for $a(\text{H}_2\text{O}) = 0.7$ and 0.5 are ~ 70 and $\sim 120^\circ\text{C}$, respectively, based on the estimates of water-undersaturated liquidus surfaces for rhyolite (Stern et al. 1975). The solidus will also be shifted by 70–120 °C for $a(\text{H}_2\text{O}) = 0.5$ –0.7, if the solidus- $a(\text{H}_2\text{O})$ relations are similar to those for the liquidus. These estimates are not without large uncertainties, but they support our proposal that a melt phase was present during metamorphism.

Evidence for partial melting is preserved as the kyanite-jadeite-almandine quartz layers in the coesite-bearing units. These layers have a much higher Fe and Na content than the surrounding coesite-bearing units, and approximate the eutectic composition for granite melts at high pressures. A partial melt origin for these layers has been proposed (Schreyer et al. 1987), although a source of the water for melting was not indicated. The H₂O required for the melting of these units would be derived locally by the dehydration reaction (1). During cooling, the melts would crystallize and expel water back to the system. This water may be manifest in the occasionally observed altered pyrope megacrysts by reaction (6). Retrograde fluids could not have been pervasive, or all of the pyrope would have been hydrated. The stable isotope data support a local origin for the retrograde fluid. The $\delta^{18}\text{O}$

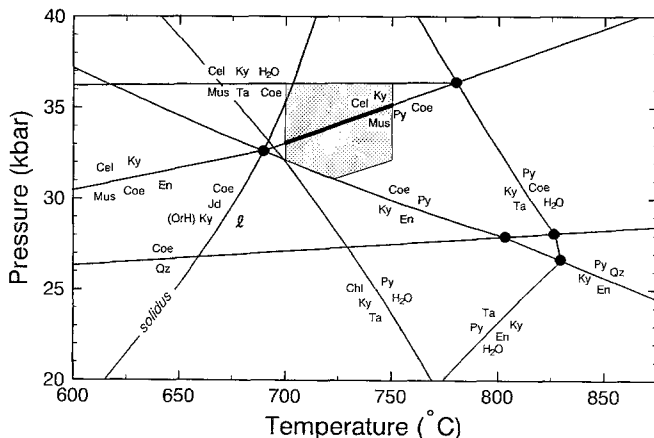
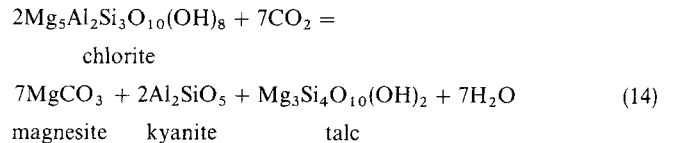


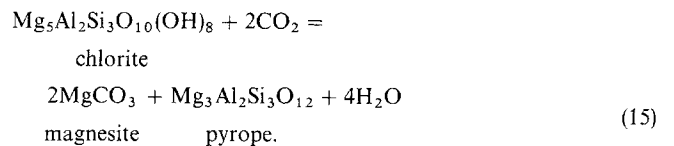
Fig. 6. Phase diagram with P - T - $a(\text{H}_2\text{O})$ estimate (shaded polygon) and the water-saturated solidus for Coe + Jd + Ky (Stern et al. 1975) and Coe + Jd + OrH (Huang and Wyllie 1975). These two melting curves are identical within error. The $a(\text{En})$ corrected for MgTs component, $a(\text{Cel}) = 0.62$, $a(\text{Mus}) = 0.38$. Abbreviations given in Fig. 2

values of the altered pyrope (AP-1) are only 1‰ lighter than the non-hydrated pyropes. In contrast, the surrounding orthogneiss is enriched in ^{18}O relative to the coesite-bearing rocks by 3‰. If the fluids responsible for pyrope retrograde hydration had been from the surrounding orthogneisses, then the $\delta^{18}\text{O}$ values for the altered samples would be higher, not lower, than those of the unaltered pyrope.

The presence of prograde and retrograde chlorite constrains the prograde and retrograde $a(\text{CO}_2)$ to very low values. The stability field of chlorite at high pressure is restricted to extremely low $X(\text{CO}_2)$ (Fig. 5). If the $X(\text{CO}_2)$ was greater than 0.01 (at 30 kb) or 0.04 (at 20 kb, < 700 °C), chlorite would break down by the reaction



or, at higher temperatures,



As chlorite is found as both prograde inclusions in garnet and retrograde products of pyrope hydration, it is clear that CO₂ was never an important fluid component.

Rock protolith and fluid origin

The coesite-bearing quartzites are assumed to be higher grade equivalents of whiteschists (Schreyer 1977; Chopin 1984). Whiteschists consist almost exclusively of components in the MgO-Al₂O₃-SiO₂-H₂O system with very low Ca, Na and concentrations and a very low Fe/Mg ratio. Several protoliths have been proposed for this unusual bulk chemistry. McKie (1959) suggested three possibilities: (1) a tectonic mixture of quartz with an ultrabasic rock, (2) magnesium metasomatism of an argillaceous sandstone, and (3) isochemical metamorphism of a saponitic bentonite. The first two scenarios do not adequately explain the Ca and Al contents of the whiteschists. The third possibility could involve weathering and/or leaching of basic pyroclastic rocks. Other authors have proposed hydrothermal alteration of basic to ultrabasic rocks or sedimentary rocks as the mechanism for whiteschist formation (Vallance 1967; Vrána 1975; Munz 1990; Hoernes and Van Reenen 1992). Schreyer (1977) argued that some of the whiteschists may be high-grade equivalents of metamorphosed mudstones associated with evaporites.

Stable isotope data from whiteschists can be used to limit the possible origin for these rocks. The $\delta^{18}\text{O}_{(\text{quartz})}$ values of the coesite-bearing whiteschists from Dora Maira ($\delta^{18}\text{O} = 8.1$ –8.7‰) are in the normal range for charnockites/anorthosites and amphibolites/metabasites (Fig. 7). They are at the ^{18}O -depleted end of metamorphic granitic rocks and orthogneisses and at the extreme lower limit for metapelites (Fig. 7). Other rock types, such as

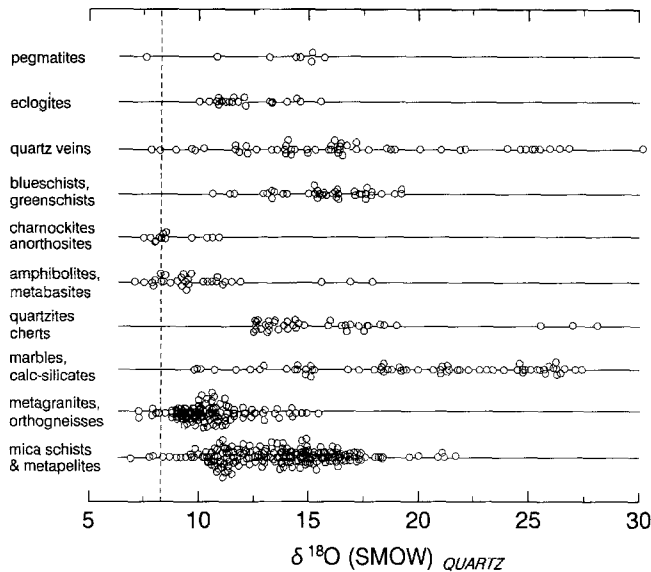


Fig. 7. Published $\delta^{18}\text{O}_{(\text{quartz})}$ values for metamorphic rocks and average value for the Dora Maira samples (vertical dashed line). Sources of data: Taylor and Epstein 1962; Taylor et al. 1963; Garlick and Epstein 1967; Taylor and Coleman 1968; Wilson et al. 1970; Schwarcz et al. 1970; Wilson and Green 1971; Perry and Tan 1972; Fourcade and Javoy 1973; Black 1974; Hoernes and Friedrichsen 1974, 1978, 1980; Honma and Sakai 1975; O'Neil and Ghent 1975; Frey et al. 1976; Margaritz and Taylor 1976; Rye et al. 1976; Desmons and O'Neil 1978; Rumble 1978; Friedrichsen and Morteanni 1979; Hoernes and Hoffer 1979; McNaughton and Wilson 1980; Pineau et al. 1981; Brown and O'Neil 1982; Matthews and Schliestedt 1984; Valley and O'Neil 1984; Whelan et al. 1984; Robert et al. 1985; Thomas et al. 1985; Wickham and Taylor 1985; Huebner et al. 1986; Jiang et al. 1988; Sharp et al. 1988; Burkhard and Kerrich 1988; Baker 1990; Hoffbauer et al. 1992; Vennemann and Smith 1992

pegmatites, eclogites, blueschists and greenschists, quartzites, quartz veins, marbles and calc-silicates have $\delta^{18}\text{O}$ values that are significantly higher than those of the Dora Maira whiteschists. Sediments, particularly those of authigenic origin, have a much higher $\delta^{18}\text{O}$ value than the whiteschists from Dora Maira (e.g. Savin and Epstein 1970; O'Neil and Hay 1973; Savin 1980). The $\delta^{18}\text{O}$ values of the coesite-bearing unit are not matched by a mudstone or saponitic protolith. Normal prograde metamorphic effects do not lower the $\delta^{18}\text{O}$ value of a rock by more than 1–2‰ (e.g. Schwarcz et al. 1970; Desmons and O'Neil 1978; Valley 1986); if the whiteschist is of sedimentary origin, it must have undergone massive exchange with an isotopically light fluid. If the system remained essentially closed, then the observed $\delta^{18}\text{O}$ values are far better matched by a hydrothermally altered or metasomatized igneous rock protolith. In contrast to the whiteschist, the surrounding orthogneiss has a typical granite isotopic signature, and is clearly not in equilibrium with the whiteschist boudins it hosts.

The δD values of the talc ($\delta\text{D} = -32\text{‰}$) and phengite ($\delta\text{D} = -35\text{‰}$) in the coesite-bearing unit are at the extreme upper limit for metamorphic rocks (Fig. 8; Taylor 1974). The surrounding orthogneisses have similar $\delta\text{D}_{(\text{phengite})}$ values as do the hydrated pyrope megacrysts

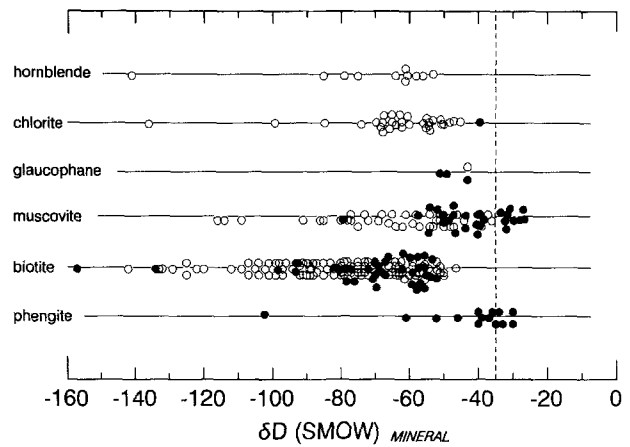


Fig. 8. Published δD values of in metamorphic rocks and $\delta\text{D}_{(\text{phengite})}$ value from this study (vertical dashed line). The filled circles are Alpine samples. Sources of data: O'Neil and Ghent 1975; Frey et al. 1976; Margaritz and Taylor 1976; Rye et al. 1976; Desmons and O'Neil 1978; Friedrichsen and Morteanni 1979; Hoernes and Hoffer 1979; Hoernes and Friedrichsen 1978, 1980; Pineau et al. 1981; Thomas et al. 1985; Morikiyo 1986; Huebner et al. 1986; Wickham and Taylor 1985; McCaig et al. 1990

(Table 1). The $\delta\text{D}_{(\text{biotite})}$ value of -64‰ in the orthogneiss are in isotopic equilibrium with the coexisting phengite (Suzuki and Epstein 1976). Other rocks that have equivalent δD values are (1) Alpine rocks that have undergone eclogitization at some point in their metamorphic history (Frey et al. 1976; Desmons and O'Neil 1978; G. Früh-Green personal communication), (2) rocks that have experienced extensive hydrothermal seawater interaction (Wickham and Taylor 1985) and (3) altered/metamorphic sea-floor basalts (Kawahata et al. 1987; Kusakabe et al. 1989; Stakes 1991). The proposed source of the high δD values from Alpine samples in previous studies is connate waters, presumably of oceanic affinity (Frey et al. 1976). The δD values for the Dora Maira rocks are, therefore, indicative of an oceanic source, but do not constrain the time at which the fluid-rock interaction took place. The fluids could be connate or introduced at a later point in their metamorphic history from dewatering of underlying altered oceanic rocks in a downgoing slab.

The similarity of the δD values from the coesite-bearing and surrounding units demonstrates large-scale hydrogen isotope equilibrium during metamorphism. In contrast, the $\delta^{18}\text{O}$ values of the coesite-bearing rocks and the surrounding orthogneisses are out of equilibrium, although oxygen isotope equilibrium was attained in all samples of the whiteschist. Large-scale hydrogen isotope equilibrium has previously been observed in the Alps (Frey et al. 1976; Desmons and O'Neil 1978), and is not unexpected. First, the rates of exchange for hydrogen are far more rapid than for oxygen (O'Neil and Kharaka 1976; Graham 1981), and second, hydrogen tends to be buffered by a fluid phase, whereas oxygen is rock buffered. The mutually high δD values in both units indicate that both shared a common fluid source at some point in their metamorphic history. The whiteschist has attained inter-

nal oxygen isotope equilibrium on a 10 to 100 m scale, but not with the surrounding orthogneiss. The mechanism responsible for oxygen isotope homogenization in the whiteschist was not shared with the present-day host rock.

The combined oxygen and hydrogen isotope geochemistry for the Dora Maira whiteschists are very unusual. The isotopically light $\delta^{18}\text{O}$ and heavy δD values are similar to high-temperature sea floor metamorphosed basalts (Kawahata et al. 1987; Kusakabe et al. 1989; Stakes 1991), but different from almost all other rock types. Metamorphosed oceanic rocks could either be the protolith for the Dora Maira whiteschists, or could have supplied the fluids responsible for the generation of the whiteschists. In the first case, the basalts would be subducted to depths in excess of 100 km and undergo metasomatism without extensively altering their stable isotope composition. In the second case, the dehydration of a metamorphosed, hydrated oceanic crust in the downgoing slab would provide a fluid source for metasomatism of an overlying layer. The intercalation of the orthogneiss with the whiteschist has recently been reinterpreted as a pre- or early Alpine hydrothermal metasomatic transformation of the hosting orthogneiss/granite along shear zones (Chopin et al. 1991). Dehydrating metabasalts could be the fluid source for this metasomatism.

Dehydration of a downgoing slab begins at shallow levels, but will continue to depths in excess of 100 km (e.g. Tatsumi 1989; Kesson and Ringwood 1989). Fluids evolved from the breakdown of hydrous phases could cause melting of an overlying, hot eclogite, with an initial partial melt that is up to 60–65% SiO_2 (Kesson and Ringwood 1989). The fluid generated from phlogopite dehydration experiments (Massonne and Schreyer 1986) is highly enriched in potassium and magnesium (Schreyer et al. 1987). Metasomatism of the orthogneisses along shear zones by such K-Mg-Si-rich fluids/partial melts would partly explain the unusual chemistry of the whiteschists. The very low Fe/Mg ratio may be explained by metasomatism in an oxidizing environment. The different geochemical behaviour of Fe^{+++} and Mg would explain the strong Mg-Fe partitioning accompanying metasomatism. There are no $f(\text{O}_2)$ buffers in the Dora Maira whiteschists, but other whiteschists contain hematite-rich layers indicative of high $f(\text{O}_2)$ conditions (McKie 1959; Vrána and Barr 1972; Munz 1990) that could explain the preferential metasomatic depletion of iron. Metasomatism of the orthogneiss protolith by a slab-derived fluid can therefore explain (1) the unusual hydrogen and oxygen isotope composition of the whiteschists, (2) the enigmatic and intimate structural relationship between the whiteschists and the hosting orthogneiss, (3) the depletion in the Fe-content of the rock and (4) the enrichment of Mg in the whiteschists. Further experimental studies that reproduce the metasomatic activity proposed here are necessary to substantiate or discredit this hypothesis of whiteschist formation.

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