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 δ¹⁸O(smow) values of the quartz (after coesite) (δ¹⁸O = 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 kbar based on the temperature-sensitive reaction pyrope + coesite = kyanite + enstatite. In order to stabilize pyrope and coesite by the temperature-sensitive dehydration reaction talc + kyanite = pyrope + coesite + H₂O, the a(H₂O) must be reduced to 0.4-0.75 at 700-750°C. The reduced a(H₂O) cannot be due to dilution by CO₂, as pyrope is not stable at X(CO₂) > 0.02 (T = 750°C, P = 30 kbar). In the absence of a more exotic fluid diluent (e.g. CH₄ or N₂), a melt phase is required. Granite solidus temperatures are ~680°C at a(H₂O) = 1.0 and are calculated to be ~70°C higher at a(H₂O) = 0.7, consistent with this hypothesis. Kyanite-jadeite-quartz bands may represent a relict melt phase. Peak P-T-f(H₂O) estimates for the whiteschist are 34 ± 2 kbar, 700-750°C and 0.4-0.75. The oxygen isotope fractionation between quartz and garnet (δ¹⁸O = 11.6%o) and quartz (δ¹⁸O = 8.7%) 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 (δD(smow) = -27 to -32‰), on secondary talc and chlorite after pyrope (δD = -39 to -44‰) and on the surrounding biotite (δD = -64‰) and phengite (δD = -44‰) 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 δ¹⁸O 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; Schmidtke 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, 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:

\[ \text{Mg}_3\text{Si}_4\text{O}_{10} \text{(OH)}_2 + \text{Al}_2\text{Si}_2\text{O}_5 = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{10} + 2\text{SiO}_2 + \text{H}_2\text{O} \]  

(1)

The reaction (1) has been experimentally calibrated (Chopin 1985), but temperature estimates based on this reaction require an accurate knowledge of the H\(_2\)O activity [a(H\(_2\)O)] attending metamorphism. Chopin (1984) proposed that temperatures were somewhere between 700 and 800 °C depending upon the H\(_2\)O activity. In this study, temperatures were estimated from oxygen isotope thermometry, a thermometric technique that is nominally independent of H\(_2\)O 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(H\(_2\)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 80 m in length and several tens-of-meters thick hosted in a phengite-biotite gneiss. The white schist 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 (Monie and Chopin 1991; Tilton et al. 1991). The white schist boudins can be divided into three types: a fine-grained quartzite with small pyrope porphyroblasts; a talc-phengite-kyanite-garnet assemblage and an olenkite and 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 ruffle (inclusions in garnet and matrix) and the new mineral ellenbergerite (inclusions in large garnets only). Chlorite is found as a relic 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:

\[ 6\text{K}_2\text{Mg}_3\text{Al}_2\text{Si}_2\text{O}_{10} \text{(OH)}_4 + 8\text{Al}_2\text{Si}_2\text{O}_5 + 10\text{SiO}_2 = \text{phlogopite} + \text{kyanite} + \text{coesite} \]

(2)

\[ 3\text{K}_2\text{Mg}_3\text{Al}_2\text{Si}_2\text{O}_{10} \text{(OH)}_4 + 5\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} = \text{phengite} + \text{pyrope} \]

Temperatures of metamorphism were constrained with reaction (1), although, as pointed out by Chopin, exact temperatures depend upon assumed H\(_2\)O 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\(_2\)O 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 none of the phengite may not have been included in the garnet. Sample PM-2 is 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 rotation of Chopin 1984) layer with small, coesite-bearing garnets. The garnet and the quartz matrix were analyzed. Sample AP-1 is 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 bimimeralic 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 Br\(_2\) 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 whitechis 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 whitechis 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 δ18Oquartz 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 Hofbauer et al. (1993) based on the increment method yield somewhat higher temperatures. The estimates of Hofbauer 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 Hofbauer et al. (1993). In addition to the fractionation factors published in Hofbauer et al. (1992), R. Hofbauer has kindly calculated the fractionation factor for ellenbergerite (113Oellenbergerite = 0.71 based on 60% bridging hydrogen, where 113Oquartz = 1.00; 1 = increment index of Hofbauer et al. 1993). The linear fit of the δ18O values for each mineral versus the temperature coefficient of fractionation a from the equation

\[
1000lnx = a \times 10^b \times T^{-2}
\]

Table 1. Oxygen and hydrogen isotopic composition of mineral separates

<table>
<thead>
<tr>
<th>Mineral</th>
<th>δ18O (SMOW)</th>
<th>Mass (mg)</th>
<th>Analysis Number</th>
<th>δD (SMOW)</th>
<th>Sample Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>8.42</td>
<td>1.03</td>
<td>S089-3</td>
<td>PM-1</td>
<td></td>
</tr>
<tr>
<td>Garnet</td>
<td>5.75</td>
<td>1.17</td>
<td>S090-4</td>
<td>PM-1</td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td>3.06</td>
<td>1.00</td>
<td>S089-8</td>
<td>PM-1</td>
<td></td>
</tr>
<tr>
<td>Kyanite</td>
<td>6.08</td>
<td>0.80</td>
<td>S093-12</td>
<td>GM-1</td>
<td></td>
</tr>
<tr>
<td>Phengite</td>
<td>6.33</td>
<td>2.15</td>
<td>S093-9</td>
<td>GM-1</td>
<td></td>
</tr>
<tr>
<td>Ellenbergerite</td>
<td>6.31</td>
<td>0.75</td>
<td>S089-11</td>
<td>PM-1</td>
<td></td>
</tr>
<tr>
<td>Talc</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–32</td>
<td>PM-1</td>
</tr>
<tr>
<td>Altered pyrope</td>
<td>4.51</td>
<td>1.09</td>
<td>S115-1</td>
<td>–42</td>
<td>AP-1</td>
</tr>
<tr>
<td>Enclosing orthogneiss</td>
<td>–</td>
<td>2.39</td>
<td>S115-2</td>
<td>AP-1</td>
<td></td>
</tr>
</tbody>
</table>

where 1000lnx ≈ δx – δy (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 relic 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 δ¹⁸O fractionations between coexisting phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental calibration</th>
<th>Empirical calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔQz-Gt</td>
<td>ΔQz-Ru</td>
</tr>
<tr>
<td>PM-1</td>
<td>710</td>
<td>740</td>
</tr>
<tr>
<td>GM-1</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>QZ-1</td>
<td>730</td>
<td>-</td>
</tr>
<tr>
<td>AS-1</td>
<td>720</td>
<td>-</td>
</tr>
</tbody>
</table>

Theoretical calibration

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔQz-Gt</th>
<th>ΔQz-Ru</th>
<th>ΔQz-Ph</th>
<th>ΔQz-Ky</th>
<th>ΔQz-El</th>
<th>ΔGt-Ru</th>
<th>ΔGt-Ky</th>
<th>ΔGt-El</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM-1</td>
<td>770</td>
<td>750</td>
<td>740</td>
<td>820</td>
<td>760</td>
<td>720</td>
<td>560</td>
<td>770</td>
</tr>
<tr>
<td>GM-1</td>
<td>820</td>
<td>760</td>
<td>870</td>
<td>900</td>
<td>-</td>
<td>700</td>
<td>460</td>
<td>-</td>
</tr>
<tr>
<td>QZ-1</td>
<td>780</td>
<td>-</td>
<td>-</td>
<td>900</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Sources of data: experimental ΔQz-Gt, Lichtenstein and Hoernes 1992; ΔQz-Ru, ΔGt-Ru, Matthews 1992. Empirical, ΔQz-Gt, ΔQz-Bi, ΔGt-Bi, Bottinga and Javoy 1975; ΔQz-Ru, Agrinier 1991; ΔGt-Ru, Bottinga and Javoy 1975; Agrinier 1991. Theoretical, Hoffbauer et al. 1993. Abbreviations: Bi, biotite; El, ellenergerite; Gt, garnet; Ph, phengite; Qz, quartz; Ru, rutile

Discussion

Comparison with phase equilibria—P-T-a (H₂O)

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 K₂O-MgO-Al₂O₃-SiO₂-H₂O.

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:

3MgSiO₃ + Al₂SiO₅ = Mg₃Al₂Si₃O₁₂ + SiO₂ (4)
enstatite kyanite pyrope coesite

Mg₃Si₄O₁₀(OH)₂ = 3MgSiO₃ + SiO₂ + H₂O (5)
talc enstatite coesite

2Mg₃Si₄O₁₀(OH)₁ + 4Al₂SiO₅ + 3Mg₃Al₂Si₃O₁₀(OH)₆ = 7Mg₆Al₃Si₃O₁₁ + 14H₂O (6)
talc kyanite chlorite pyrope

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

MgSiO₃ + Al₂SiO₅ = MgAl₂Si₆O₁₆ + SiO₂ (7)
enstatite kyanite MgTs coesite
reactions involving talc (Fig. 3). The phase equilibria relations for the high pressure mineral adjustment, but the substitution of the 2.42 Mb$^{-1}$ value 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; K$_y$, kyanite; l, liquid; Mag, magnesite; Mus, muscovite; OrH, KA$_3$Si$_3$O$_8$H$_2$O; Py, pyrope; Qz, quartz; Ta, talc

\[ 2\text{Mg}_2\text{SiO}_4 + \text{MgAl}_2\text{Si}_2\text{O}_8 \rightarrow \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_12 + \text{pyrope} \] (8)

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 curves can then be evaluated as a function of $a$(H$_2$O).

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$_2$O 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

\[ 3\text{KMgSi}_3\text{O}_10(\text{OH})_2 + 3\text{Al}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O} = \text{celadonite} + \text{kyanite} \] (9)

\[ 3\text{KAl}_2\text{Si}_3\text{O}_10(\text{OH})_2 + 2\text{Mg}_3\text{Si}_4\text{O}_11(\text{OH})_2 + 2\text{SiO}_2 = \text{muscovite} + \text{talc} + \text{coesite} \]
Phengites from the Dora Maira coesite-bearing unit have 3.55 Si per 12 oxygen (Chopin 1984). The experimental P-T location of the Si3.55 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(H2O) (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:

\[ 3\text{KMgAlSi}_3\text{O}_10(\text{OH})_2 + 2\text{Al}_2\text{SiO}_5 + \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_12 + 2\text{H}_2\text{O} = \]
\[ 3\text{KA}_3\text{Si}_3\text{O}_10(\text{OH})_2 + \text{Mg}_3\text{Si}_4\text{O}_10(\text{OH})_2 + \text{CO}_2 + \text{H}_2\text{O} \]

(10)

muscovite
talc

celadonite
kyanite
pyrope

(11)

muscovite

talc

(12)

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(H2O). In theory, the P-T conditions of the coesite-bearing rock must lie on reaction (12), the actual P-T depending upon the H2O activity. This P-T-a(H2O) 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 whitechists at Dora Maira and can be used in conjunction with the independent isotopic temperature estimates to constraint the a(H2O). 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(H2O) = 0.4–0.7 (Fig. 4). The best estimate of the peak metamorphic conditions for the coesite-bearing whitechists are T = 700–750 °C, P = 32–36 kb, a(H2O) = 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 whitechists. Graphite has been found in neighboring 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 H2O activity and still produce pyrope + coesite from the dehydration reaction (1), a fluid diluent, such as CO2 or a melt, must have been present during metamorphism. A likely fluid diluent is CO2, as low a(H2O) is commonly attributed to CO2 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 CO2-H2O fluid demonstrates that CO2 cannot, in fact, be the fluid diluent (Fig. 5). At \( X(\text{CO}_2) > 0.02 \) (\( T = 750^\circ \text{C} \)), pyrope is not stable. Magnesite is produced by the reaction

\[ 2\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_10 + 3\text{CO}_2 + \text{H}_2\text{O} = \]

pyrope

(13)

magnesite
kyanite

talc.

In the absence of an unusual fluid species (e.g. CH4, N2), the low a(H2O) 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(H2O) < 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 NaAlSi3-KAlSi3O8-SiO2-H2O (Huang and Wyllie 1975). The solidus determinations of Stern et al. (1975) for coesite-bearing granulites are \( T = 700–750^\circ \text{C}, P = 32–36 \text{kb}, a(\text{H}_2\text{O}) = 0.4–0.75 \). 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 whitechists. Graphite has been found in neighboring eclogite and marble units, but no diamond has yet been identified (Chopin personal communication 1992).
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(H₂O) = 1.0 is ~680°C and 30 kb and ~700°C at 35 kb (Fig. 6).

The granitic solidus will be displaced to higher temperatures with decreasing a(H₂O). There are no reliable relationships between the wt. % H₂O versus a(H₂O) for granitic melts at pressures > 20 kb, but a crude estimate for the effect of a(H₂O) on the high pressure solidus was made based on the relationship between wt. % H₂O versus a(H₂O) 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(H₂O) = 0.7 and 0.5 are ~70°C and ~120°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(H₂O) = 0.5–0.7, if the solidus-a(H₂O) 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 the water for melting was not indicated. The partial melting 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 δ¹⁸O values of the altered pyrope (AP-1) are only 1‰ lighter than the non-hydrated pyropes. In contrast, the surrounding orthogneiss is enriched in ¹⁸O relative to the coesite-bearing rocks by 3‰. If the fluids responsible for pyrope retrograde hydration had been from the surrounding orthogneisses, then the δ¹⁸O 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(⟨CO₂⟩) to very low values. The stability field of chlorite at high pressure is restricted to extremely low X(⟨CO₂⟩) (Fig. 5). If the X(⟨CO₂⟩) was greater than 0.01 (at 30 kb) or 0.04 (at 20 kb, <700°C), chlorite would break down by the reaction

\[
2\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_10(\text{OH})_8 + 7\text{CO}_2 = 7\text{MgCO}_3 + 2\text{Al}_2\text{Si}_3\text{O}_5 + \text{Mg}_3\text{Si}_4\text{O}_9(\text{OH})_2 + 7\text{H}_2\text{O} \quad (14)
\]

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) isochronous 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; Vrina 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 δ¹⁸O values of the coesite-bearing whiteschists from Dora Maira (δ¹⁸O = 8.1–8.7%) are in the normal range for charnockites/anorthosites and amphibolites/metabasites (Fig. 7). They are at the ¹⁸O-depleted end of metamorphic granitic rocks and orthogneisses and at the extreme lower limit for metapelites (Fig. 7). Other rock types, such as
closed, then the observed $\delta^{18}O$ values are far better matched by a hydrothermally altered or metasomatized fluid. If the system remained essentially in isotopic equilibrium with the coexisting phengite (Suzuoki and Epstein 1976). Other rocks that have equivalent $\delta D$ values are (1) Alpine rocks that have undergone ecologitization 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). The proposed source of the high $\delta D$ values from Alpine samples in previous studies is connate waters, presumably of oceanic affinity (Frey et al. 1976). The $\delta D$ 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 $\delta D$ values from the coesite-bearing and surrounding units demonstrates large-scale hydrogen isotope equilibrium during metamorphism. In contrast, the $\delta^{18}O$ 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 $\delta D$ values in both units indicate that both shared a common fluid source at some point in their metamorphic history. The whiteschist has attained inter-

**Fig. 7.** Published $\delta^{18}O_{quartz}$ 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, 1977, 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 Morteani 1979; Hoernes and Hoffer 1979; McNaughton and Wilson 1979; O'Neil and Hay 1973; Savin 1980). The $\delta^{18}O$ values of the coesite-bearing unit are not matched by a mudstone or saponitic protolith. Normal prograde metamorphic effects do not lower the $\delta^{18}O$ 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 $\delta^{18}O$ values are far better matched by a hydrothermally altered or metasomatized igneous rock protolith. In contrast to the whiteschist, the surrounding orthogneisses have a typical granite isotopic signature, and is clearly not in equilibrium with the whiteschist boudins it hosts.

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

**Fig. 8.** Published $\delta D$ values of in metamorphic rocks and $\delta D_{(phengite)}$ 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 Morteani 1979; Hoernes and Hoffer 1979; Hoernes and Friedrichsen 1978, 1980; Pineau et al. 1981; Thomas et al. 1985; Morikijo 1986; Huebner et al. 1986; Wickham and Taylor 1985; McCaig et al. 1990
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 is unusual. The isotopically light $^{18}$O and heavy $^2$H 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 metamorphism 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 whiteschists with the host orthogneiss 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). Dehydration metasomatism could provide 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 $f$(O$_2$) buffers in the Dora Maira whiteschists, but other whiteschists contain hematite-rich layers indicative of high $f$(O$_2$) conditions (McKie 1959; Vrana 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 host 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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