

Impure marbles from the UHP Brossasco-Isasca Unit (Dora-Maira Massif, western Alps): evidence for Alpine equilibration in the diamond stability field and evaluation of the $X(\text{CO}_2)$ fluid evolution

D. CASTELLI,^{1,2} F. ROLFO,^{1,2} C. GROppo¹ AND R. COMPAGNONI¹

¹Dipartimento di Scienze Mineralogiche e Petrologiche, Via Valperga Caluso 35, I-10125 Torino, Italy
(daniele.castelli@unito.it)

²Istituto di Geoscienze e Georisorse, CNR – Sezione di Torino, Via Valperga Caluso 35, I-10125 Torino, Italy

ABSTRACT Two impure ultrahigh-pressure (UHP) marbles, a calcite marble with the peak assemblage Grt + Phe + Cpx + Rt + (Arg) and a dolomite marble with the peak assemblage Crn + Chl + Rt + Dol ($\pm$ Arg), from the same lens from the polymetamorphic complex of the Brossasco-Isasca Unit (BIU) (southern Dora-Maira Massif) have been petrologically investigated and modelled by calculating P – T phase-diagram projections for H_2O – CO_2 mixed-volatile systems. Thermobarometric data obtained from the calcite marble suggest Alpine peak conditions in the diamond stability field (4.0 GPa at 730 °C), and allow reconstruction of the earlier portion of the Alpine retrograde P – T path, which is characterized by a significant decompression coupled with a moderate and continuous cooling to 650 °C at 2.50 GPa. The modelled fluid compositions at peak conditions point to $0.025 \leq X(\text{CO}_2) \leq 0.10$ and $X(\text{CO}_2) \leq 0.0012$ in the calcite marble and dolomite marble, respectively, suggesting fluid heterogeneity at the local scale and an internally buffered fluid evolution of the studied impure marbles. The lack of micro-diamond in the BIU marbles is explained by the very-low $X(\text{CO}_2)$ values, which favoured relatively high $f\text{O}_2$ -conditions, preventing the formation of diamond at the UHP peak metamorphic conditions.

Key words: Dora-Maira Massif, fluid evolution, marble, P – T – $X(\text{CO}_2)$ projection, UHP metamorphism

INTRODUCTION

Marbles associated with eclogite facies rocks may provide useful information for evaluating metamorphic processes and compositions of fluids associated with crustal subduction and exhumation. High-pressure (HP) marbles, which re-equilibrated in the quartz-eclogite stability field, have been described from the Voltri Massif (Cortesogno *et al.*, 1981) and Sesia-Lanzo Zone (Castelli, 1991) of the Italian western Alps, from the Zermatt-Saas Zone of the Swiss Alps (Ganguin, 1986), and from the Tauern Window of the Austrian Alps (Franz & Spear, 1983; Dachs, 1986). Ultrahigh-pressure (UHP) marbles, which re-equilibrated in the coesite-eclogite stability field, have been described from the Pan-African belt of Mali (Caby, 1994), from the Dabie Mountains of eastern-central China (Wang & Liou, 1993; Schertl & Okay, 1994; Zhang & Liou, 1996; Omori *et al.*, 1998) and from the Su–Lu terrane of eastern China (Kato *et al.*, 1997; Ogasawara *et al.*, 1998). UHP, diamond-bearing marbles have been reported from the Kokchetav Massif of northern Kazakhstan (Ogasawara *et al.*, 2000). Marbles are also associated with the granulite to eclogite

facies transitional rocks from the Bergen Arc System, western Norway (Boundy *et al.*, 2002).

The occurrence of relict aragonite, coesite and diamond, or their low- P , inversion polymorphs, has been used to infer HP to UHP peak metamorphic conditions in marbles (e.g. Wang & Liou, 1993; Ogasawara *et al.*, 2000; Ishida *et al.*, 2003), together with P – T estimates from thermobarometry and phase equilibria calculations (e.g. Franz & Spear, 1983; Wang & Liou, 1993; Ogasawara *et al.*, 1998; Omori *et al.*, 1998). Evaluations of fluid composition by modelled phase equilibria systematically suggest H_2O -dominated fluids during HP and UHP metamorphism of both calcitic and dolomitic impure marbles (e.g. Franz & Spear, 1983; Castelli, 1991; Wang & Liou, 1993; Kato *et al.*, 1997; Ogasawara *et al.*, 1998).

In the UHP Brossasco-Isasca Unit (in the following referred to as BIU) of southern Dora-Maira Massif, western Italian Alps, impure marbles occur in a coherent polymetamorphic complex which underwent both Variscan and Alpine tectonic and metamorphic cycles (e.g. Chopin, 1984; Chopin *et al.*, 1991; Compagnoni *et al.*, 1995; Compagnoni & Rolfo, 2003; with references therein). Most petrological studies (e.g.

Kienast *et al.*, 1991; Compagnoni *et al.*, 1995; Simon *et al.*, 1997; Rubatto & Hermann, 2001) suggest that the BIU peak-pressure conditions never exceeded the graphite–diamond equilibrium curve, in agreement with the results of a mineral inclusion study in zircon (Sobolev *et al.*, 1994) where only coesite was found. However, Hermann (2003a), combining experiments in the KCMASH model system with petrological information from whiteschist, metapelite and eclogite, obtained a petrogenetic grid suggesting for the BIU Alpine peak metamorphic conditions of $\sim 730^\circ\text{C}$ and $\sim 4.3\text{ GPa}$. A similar pressure estimate has been obtained from a BIU phengite–amphibole eclogite, by using conventional thermobarometry combined with pseudosection analysis (Groppo *et al.*, 2007).

In this contribution petrological data are presented for two marble samples selected from a lens within the BIU: a Grt–Cpx–Phe–Rt–Cal marble and a Spl–Crn–Chl–Dol–Cal marble (mineral abbreviations are from Bucher & Frey, 2002). Mineral assemblages and com-

positions together with thermobarometric estimates for the Grt–Cpx–Phe–Rt calcite marble suggest Alpine peak conditions in the diamond stability field and indicate the first portion of its retrograde P – T – t path towards the quartz–eclogite field. Modelling of phase equilibria by calculation of P – T phase-diagram projections for H_2O – CO_2 mixed-volatile systems (e.g. Carmichael, 1991; Connolly & Trommsdorff, 1991) in combination with the inferred Alpine P – T – t path allows estimation of the $X(\text{CO}_2)$ composition of UHP equilibrium fluid in both marbles, and suggests that very-low $X(\text{CO}_2)$ values favoured relatively high f_{O_2} -conditions, preventing the formation of diamond at peak UHP conditions.

GEOLOGICAL SETTING

The BIU is a UHP tectonic unit exposed in the southern Dora-Maira Massif, Penninic domain of the western Alps (Chopin, 1984; Compagnoni *et al.*, 1995) (Fig. 1).

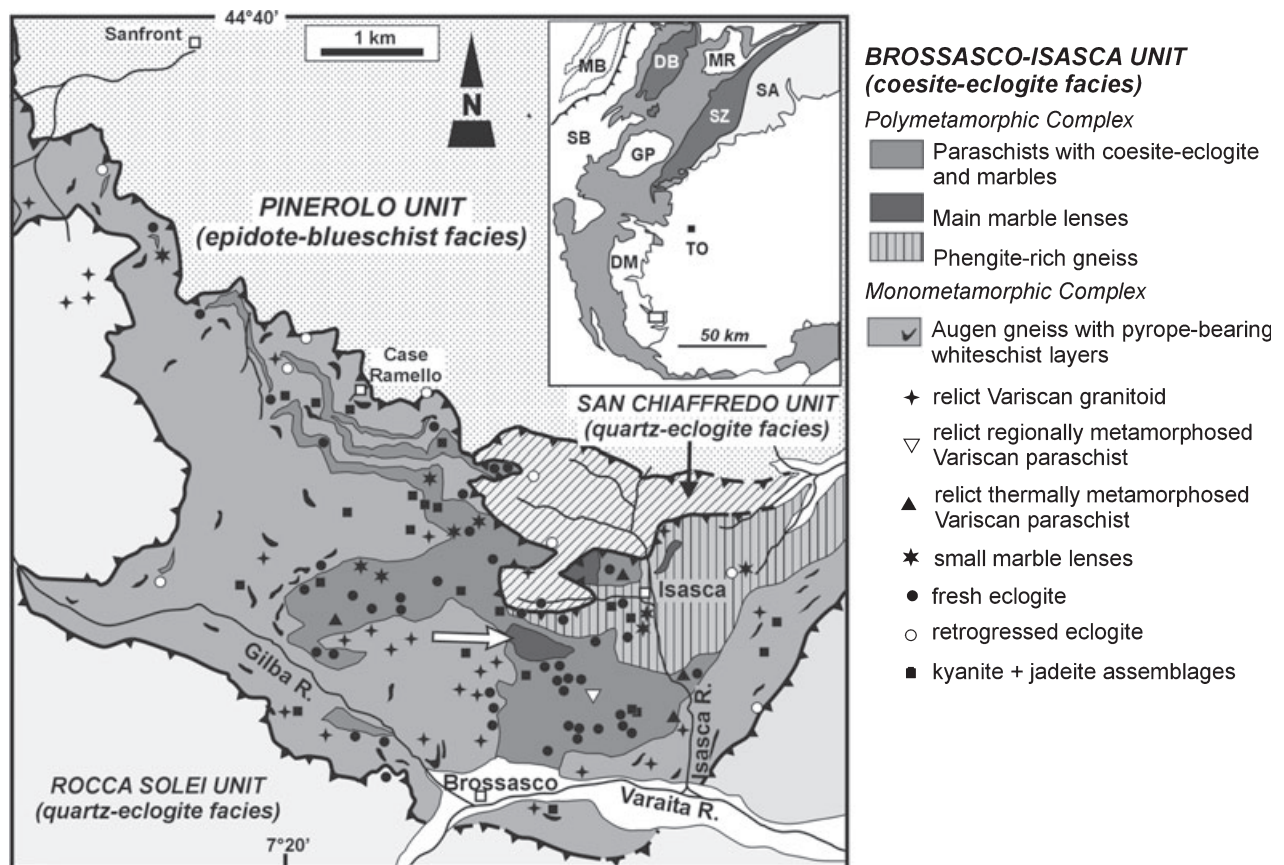


Fig. 1. Simplified geological map of the coesite-bearing Brossasco-Isasca Unit (BIU) (modified from Compagnoni & Rolfo, 2003; Compagnoni *et al.*, 2004). Undifferentiated units: graphite-rich schists and metaclastics of the epidote-blueschist facies 'Pinerolo Unit'; lower and upper tectonic units ('San Chiaffredo Unit' and 'Rocca Solei Unit', respectively) with pre-Alpine basement rocks overprinted by Alpine quartz–eclogite facies metamorphism. The white arrow shows location of the studied samples from the Costa Monforte marble lens. The inset shows location of the BIU within a simplified tectonic sketch-map of the Western Alps. Mont Blanc-Aiguilles Rouges (MB) of the Helvetic-Dauphinois Domain; SB: Grand St. Bernard Zone of the external Penninic Domain; Internal Crystalline Massifs of the Penninic Domain: Monte Rosa (MR), Gran Paradiso (GP), Dora-Maira (DM); Sesia-Lanzo Zone (SL) and Dent Blanche nappe (DB) of the Austroalpine Domain. SA: Southern Alps, TO: Town of Torino.

It is a small tectonic sliver, $\sim 10 \times 4 \times 1$ km, sandwiched between two HP tectonic units characterized by quartz–eclogite facies recrystallization peaking at ~ 550 °C and ~ 1.5 GPa (Chopin *et al.*, 1991; Schertl *et al.*, 1991; Sharp *et al.*, 1993; Compagnoni *et al.*, 1995; Matsumoto & Hirajima, 2000; Compagnoni & Rolfo, 2003; Hermann, 2003a). Regional geology, detailed petrographic descriptions of the various tectonic units exposed in the southern Dora-Maira Massif, and inferred P – T – t paths are given in a series of articles (e.g. Chopin, 1984; Chopin *et al.*, 1991; Schertl *et al.*, 1991; Compagnoni *et al.*, 1995; Michard *et al.*, 1995; Chopin & Schertl, 2000; Nowlan *et al.*, 2000; Rubatto & Hermann, 2001; Compagnoni & Rolfo, 2003; Groppo *et al.*, 2006, 2007).

Compagnoni *et al.* (1995) recognized two different complexes in the BIU: (i) a Polymetamorphic Complex, derived from Alpine recrystallization of a Variscan amphibolite facies basement, and mainly composed of kyanite–almandine–phengite–jadeite parashist with marble and eclogite intercalations; (ii) a Monometamorphic Complex, derived from Alpine reworking of late-Variscan granitoids intruded at *c.* 275 Ma (Gebauer *et al.*, 1997) into the Variscan metamorphic basement (Biino & Compagnoni, 1991, 1992), and composed of orthogneiss, usually with augen structure. Layers of pyrope-bearing whiteschist, derived from the metasomatic transformation of the granitoid protolith along ductile shear zones in the presence of a hydrous fluid phase (Compagnoni & Hirajima, 2001; Simon & Chopin, 2001), are locally included in the orthogneiss.

PETROGRAPHY AND MINERAL CHEMISTRY

The BIU marbles usually occur within the parashists of the Polymetamorphic Complex as lenses from a few metres to tens of metres long and from a few dm to several metres thick. The largest lens, ~ 800 m long and 70 m thick, is exposed at Costa Monforte (NNE of the Brossasco Village, Fig. 1). It is mainly embedded in kyanite–garnet–phengite $\pm$ jadeite micaschists with coesite relics of the Polymetamorphic Complex and is also in contact, to the west, with orthogneiss of the Monometamorphic Complex (Compagnoni & Rolfo, 2003; Compagnoni *et al.*, 2004). The Costa Monforte marble lens consists of both calcite- and dolomite-rich layers and locally retains thin (cm- to dm-thick) discontinuous interlayers of micaschist and boudins of eclogite. The fabric is generally medium- to coarse-grained, with a granoblastic polygonal to mortar microstructure; a very fine-grained mylonitic fabric occurs in decimetre-thick whitish shear zones. Main rock types include pure marbles and phengite marbles, with a weak foliation defined by medium-grained, subhedral to partly corroded and deformed phengite flakes (Ferraris *et al.*, 2005). Scattered and lens-shaped, dm-thick domains, which are set parallel to the foliation, are enriched in additional minerals. These

show highly variable abundance and include quartz, fine- to coarse-grained, reddish to brownish garnet, fine-grained Na-rich greenish clinopyroxene, epidote, Ca-amphibole, chlorite, biotite and accessory K-feldspar, titanite, rutile and zircon. Boundaries of these domains are poorly defined as they progressively grade into pure and/or phengite marble.

Two samples have been studied in detail: (i) a calcite marble with both coarse-grained (dark-red) and fine-grained (pinkish) garnet, deep-green pyroxene, phengite and rutile (hereafter referred to as calcite marble), and (ii) a chlorite, corundum, dolomite-rich marble with relics of bluish-green spinel (hereafter referred to as dolomite marble). The calcite marble is representative of the marble with the silicate-rich domains commonly found at the Costa Monforte marble quarry (Compagnoni *et al.*, 2004), where it was extensively exploited in the past. The dolomite marble is a unique sample collected from a different layer in the less-deformed, south-western portion of the same lens.

Minerals were analysed with a Cambridge SEM-EDS, operating at 15 kV accelerating potential and 50 s counting time. Natural and synthetic mineral and oxide standards were employed. End-members and Fe^{3+} ratios of Fe-bearing minerals were calculated according to Ulmer (1993). Representative mineral compositions are given in Tables 1 and 2.

The calcite marble

The calcite marble consists of calcite, garnet, pyroxene, highly celadonic phengite, minor epidote, titanite with relics of rutile and rare quartz. Silicates occur either as isolated idioblasts within the calcite matrix or as elongated aggregates arranged according to a very spaced foliation that runs parallel to the main regional foliation (Fig. 2).

Calcite, the main constituent of this marble, occurs as coarse-grained granoblasts in the rock matrix [$X_{\text{Cal}} = 0.96$, $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.49$] and as finer grained aggregates included in the porphyroblastic garnet. Two generations of garnet (Grt I & Grt II) are evident. Grt I occurs both as dark-red porphyroblasts up to 1 cm in diameter and as small pinkish idioblasts (Fig. 2a,b). It is mainly a grossular-almandine solid solution with low andradite component (Table 1 & Fig. 3a), and shows a weak zoning, with the almandine content progressively decreasing from core ($\text{Alm}_{52}\text{Grs}_{39}$) to rim ($\text{Alm}_{44}\text{Grs}_{40}$). A sharp Ca-increase (up to 54 mol.% Grs) was locally detected at the rim of the small pinkish idioblasts. Grt II occurs both as late and discontinuous rims around pinkish garnet (Grt I) and as small deep red idioblasts in the calcite matrix. It differs from Grt I for the higher almandine (53–57 mol.%) and andradite (14–23 mol.%) contents and for the lower grossular (16–26 mol.%) content (Table 1 & Fig. 3a). Garnet is partially retrogressed either to epidote or to a thin

Table 1. Representative analyses of selected minerals from the BIU calcite marble (DM1275).

	Grt I		Grt I		Grt II		Cpx		Phengite			Epidote		Titanite	
	core 17Grt27*	rim 17Grt28r*	core 17Grt45c	rim 17Grt46r	15Grt4c	15Grt5r	core 17Px29c*	rim 16Px55r*	core 13Wm18*	core 14Wm30*	rim A13Wm20r*	13Ep15	in Grt 0.38Ttn	after Rt a.1	
SiO ₂	38.97	38.47	38.08	38.68	37.23	36.96	54.35	53.98	55.31	56.52	49.89	39.60	30.85	30.36	
TiO ₂	—	—	—	—	—	—	0.17	0.01	0.34	0.31	0.44	0.15	37.59	35.43	
Al ₂ O ₃	21.02	20.71	20.83	20.78	16.79	17.46	3.12	2.20	21.55	20.96	26.81	27.27	1.55	3.11	
Fe ₂ O ₃	0.15	1.23	1.92	1.20	7.47	6.60	3.39	5.73	0.00	0.00	0.00	9.10	0.54	0.00	
FeO	24.31	22.97	22.90	22.52	23.73	25.28	7.84	6.29	2.93	2.44	2.83	0.00	0.21	0.00	
MnO	0.00	0.21	0.29	0.19	0.01	0.24	0.00	0.06	0.00	0.00	0.03	0.00	0.00	0.00	
MgO	2.51	2.62	2.69	2.67	1.32	1.51	10.02	9.90	5.23	5.23	3.44	0.00	0.00	0.00	
CaO	13.90	14.16	13.69	14.66	14.39	12.47	17.99	19.43	0.00	0.00	0.02	24.30	28.47	28.73	
Na ₂ O	—	—	—	—	—	—	3.39	3.38	0.10	0.00	0.31	0.10	0.00	0.00	
K ₂ O	—	—	—	—	—	—	0.22	0.00	11.10	10.92	10.91	0.00	0.00	0.00	
F	—	—	—	—	—	—	—	—	—	—	—	—	0.92	0.97	
Sum	100.86	100.37	100.40	100.70	100.93	100.52	100.50	100.98	96.55	96.38	94.68	100.52	100.13	98.60	
Si	3.032	3.009	2.982	3.011	2.983	2.973	2.007	1.993	3.651	3.715	3.374	3.017	1.006	0.996	
Ti	—	—	—	—	—	—	0.005	0.000	0.017	0.015	0.022	0.008	0.922	0.874	
Al	1.927	1.910	1.922	1.907	1.585	1.655	0.136	0.096	1.676	1.624	2.137	2.450	0.060	0.120	
Fe ³⁺	0.009	0.072	0.113	0.070	0.450	0.400	0.094	0.159	0.000	0.000	0.000	0.522	0.013	0.000	
Fe ²⁺	1.582	1.503	1.500	1.466	1.589	1.700	0.242	0.194	0.162	0.134	0.160	0.000	0.006	0.000	
Mn	0.000	0.014	0.019	0.013	0.001	0.017	0.000	0.002	0.000	0.000	0.002	0.000	0.000	0.000	
Mg	0.292	0.305	0.315	0.310	0.158	0.182	0.551	0.546	0.515	0.512	0.347	0.000	0.000	0.000	
Ca	1.159	1.187	1.149	1.223	1.235	1.074	0.712	0.769	0.000	0.000	0.001	1.984	0.994	1.010	
Na	—	—	—	—	—	—	0.243	0.242	0.013	0.000	0.041	0.015	0.000	0.000	
K	—	—	—	—	—	—	0.011	0.000	0.935	0.916	0.941	0.000	0.000	0.000	
F	—	—	—	—	—	—	—	—	—	—	—	—	0.095	0.101	
Sum	8.000	8.000	8.000	8.000	8.000	8.000	4.000	4.000	6.968	6.916	7.026	7.996	3.000	3.000	

Structural formulae are calculated on the basis of 8 cations and 12 oxygen for garnet, 4 cations and 6 oxygen for pyroxene, 11 oxygen and all Fe = Fe²⁺ for phengite, 12 oxygen and 1 OH-group for epidote, 3 cations and 10 charges – OH-group for titanite. Representative core and rim compositions of garnet, clinopyroxene and phengite used for the thermobarometric estimates of the peak and early retrogressive metamorphic stages are indicated with the asterisk.

Table 2. Representative analyses of selected minerals from the BIU dolomite marble (DM1171).

	Spinel		Ilmenite		Corundum		Chlorite I		Chlorite II		Högbomite		Margarite	
	core 1Spl56	rim 1Spl57r	Ilm I 1Ilm45	Ilm II 6Ilm24r	core 6Cor9	rim 6Cor3	11Chl74	11Chl70	6Hog43c	6Hog16r	Marg79	Marg82		
SiO ₂	0.48	0.24	0.34	0.22	0.00	0.00	30.88	27.98	0.03	0.03	31.69	33.80		
TiO ₂	0.00	0.00	56.18	53.50	0.11	1.01	0.00	0.42	9.53	11.10	0.07	0.03		
Cr ₂ O ₃	—	—	—	—	—	—	—	—	0.15	0.01	—	—		
Al ₂ O ₃	67.88	67.59	0.01	0.05	100.42	98.75	22.53	25.69	64.54	63.12	50.49	49.23		
Fe ₂ O ₃	1.33	0.00	0.00	1.94	0.01	0.19	0.00	0.00	0.00	0.00	0.00	0.00		
FeO	6.23	12.57	38.04	41.77	0.00	0.07	2.35	8.62	9.94	13.21	0.39	0.43		
MnO	0.00	0.13	0.22	0.28	0.00	0.10	0.10	0.00	0.14	0.00	0.00	0.00		
MgO	24.23	19.72	5.32	1.72	0.09	0.22	31.69	25.34	12.94	10.29	0.00	0.00		
CaO	0.13	0.06	0.00	0.36	0.12	0.04	0.15	0.18	0.05	0.16	11.46	10.17		
Na ₂ O	—	—	0.63	0.60	0.00	0.05	0.00	0.00	0.29	0.62	1.29	2.09		
K ₂ O	—	—	0.00	0.00	0.00	0.02	0.00	0.01	0.05	0.00	0.14	0.04		
Sum	100.28	100.29	100.73	100.44	100.75	100.45	87.70	88.24	97.66	98.54	95.54	95.79		
Si	0.012	0.006	0.008	0.006	0.000	0.000	5.779	5.394	0.001	0.001	4.165	4.414		
Ti	0.000	0.000	1.009	0.990	0.001	0.013	0.000	0.061	0.192	0.227	0.007	0.003		
Cr	—	—	—	—	—	—	—	—	0.003	0.000	—	—		
Al	1.952	1.992	0.000	0.001	1.994	1.974	4.968	5.837	2.042	2.019	7.819	7.578		
Fe ³⁺	0.024	0.000	0.000	0.036	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000		
Fe ²⁺	0.127	0.263	0.760	0.860	0.000	0.001	0.367	1.389	0.223	0.300	0.043	0.047		
Mn	0.000	0.003	0.005	0.006	0.000	0.001	0.015	0.000	0.003	0.000	0.000	0.000		
Mg	0.881	0.735	0.189	0.063	0.002	0.006	8.839	7.279	0.518	0.416	0.000	0.000		
Ca	0.003	0.002	0.000	0.010	0.002	0.001	0.031	0.038	0.001	0.005	1.614	1.424		
Na	—	—	0.029	0.029	0.000	0.002	0.000	0.000	0.015	0.033	0.328	0.529		
K	—	—	0.000	0.000	0.000	0.000	0.000	0.002	0.002	0.000	0.024	0.007		
Sum	3.000	3.000	2.000	2.000	2.000	2.000	20.000	20.000	3.000	3.000	14.000	14.000		

Structural formulae are calculated on the basis of 3 cations and 4 oxygen for Fe–Ti–Mg oxides, 2 cations and 3 oxygen for corundum and ilmenite, 20 cations and 28 oxygen and 16 OH for chlorite, 14 cations and 22 oxygen and 4 OH for margarite.

rim of bluish-green magnesiohornblende (Leake *et al.*, 1997).

The deep green, diopsidic Na-clinopyroxene occurs both as mm-sized porphyroblasts associated with

phengite and as small idioblasts in the matrix (Fig. 2a–c). It has low jadeite (5–14 mol.%) and aegirine (4–16 mol.%) contents and generally shows an increase in the aegirine component towards the rim

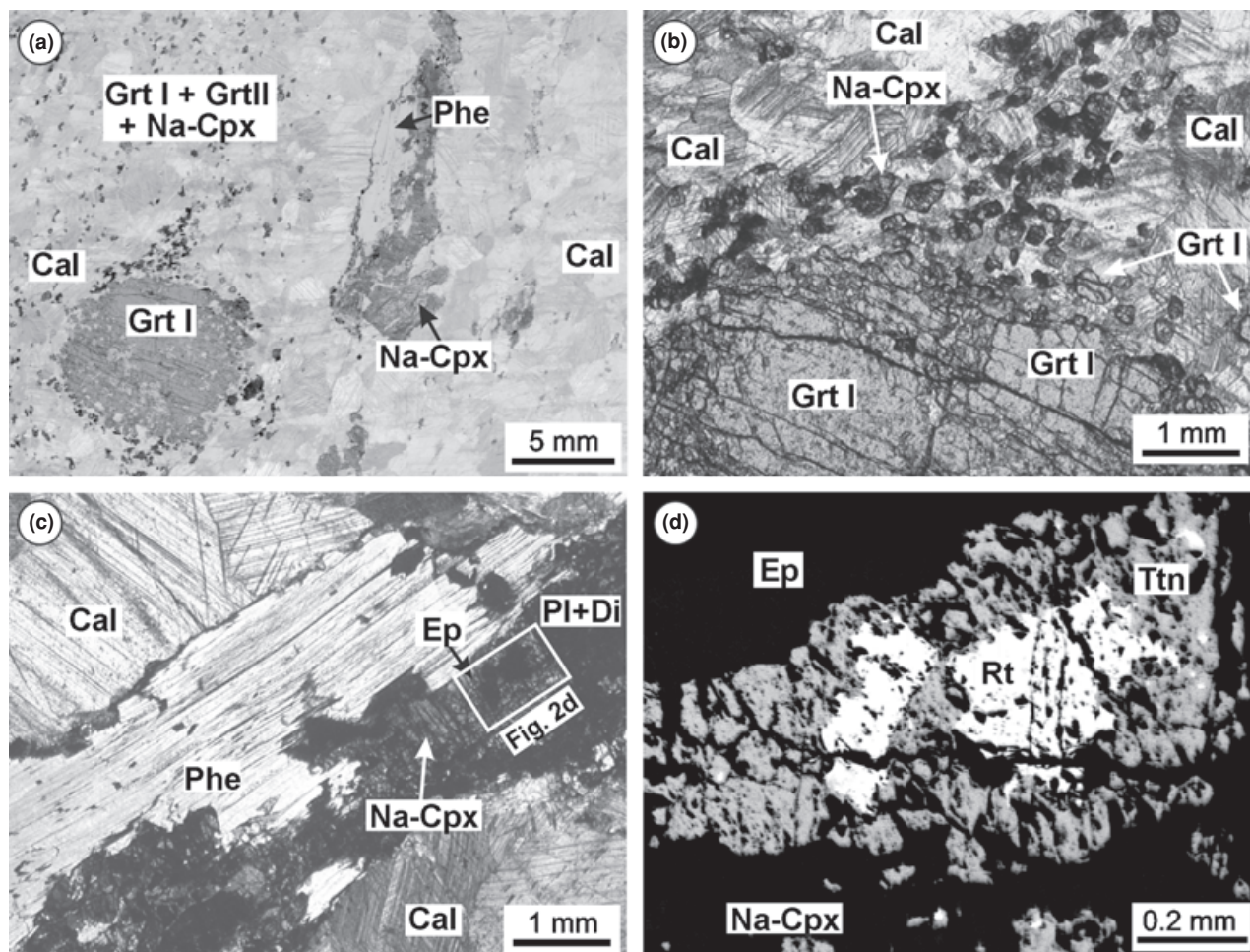


Fig. 2. Representative microstructures of the calcite marble (sample DM1275) as seen under optical and scanning electron microscope. (a) Overview of the marble which consists of garnet (Grt I and Grt II), clinopyroxene (Na-Cpx), highly celadonic phengite (Phe), Fe-epidote, and rutile partially replaced by titanite in a matrix of granoblastic calcite (Cal). Plane polarised light (PPL). (b) Porphyroblastic garnet (Grt I) surrounded by small idioblastic garnets (Grt I) in a matrix of granoblastic calcite (Cal) and small idioblasts of clinopyroxene (Na-Cpx) ± phengite. PPL. (c) Detail of the contact between calcite (Cal), phengite (Phe), Fe-epidote (Ep), clinopyroxene (Na-Cpx) and titanite with relict rutile in the core (see also the detail in Fig. 2d). Na-pyroxene is mostly replaced by a fine-grained symplectite of plagioclase + diopside (Pl + Di). Crossed polarizers (XPL). (d) Back scattered electron (BSE) image showing relict rutile (Rt) partially replaced by titanite (Ttn).

(Table 1 & Fig. 3b). It is partially replaced by a retrograde fine-grained diopside + sodic oligoclase symplectite (Fig. 2c).

Phengite occurs as millimetric flakes in equilibrium with garnet and clinopyroxene (Fig. 2a,c). It is strongly zoned, with the Si content ranging from 3.48 to 3.71 atoms p.f.u. (on the basis of 11 oxygen) in the core and from 3.29 to 3.35 a.p.f.u. in the outermost rim (Table 1 & Fig. 4). The silicon contents of the phengite cores are among the highest values ever reported from the BIU. Phengite from another marble from the same Costa Monforte lens, studied in detail by SEM/TEM-AEM (Ferraris *et al.*, 2005), revealed a complex mica core consisting of low-Si, most likely prograde, relict domains [Phe(a)] coexisting with high-Si nano-scale most likely UHP peak

domains [Phe(b)]. The high-Si Phe(b) described by Ferraris *et al.* (2005) shows a celadonite content comparable with that of the phengite core from the calcite marble (Fig. 4). Phengite is partially replaced by retrograde biotite [$\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.62$] at the rim and along cleavages.

Epidote occurs both as thin rims around garnet and scanty, medium-grained, unzoned crystals in contact with the pyroxene. Both types of epidote have similar and homogeneous composition, with $0.52 < \text{Fe}^{3+} < 0.66$ a.p.f.u. (Table 1). Relict rutile is partly replaced by titanite (Fig. 2d) that also occurs as rare fine-grained inclusions in garnet. Both titanite types display low Al ($0.06 < \text{Al} < 0.12$ a.p.f.u.) and F ($0.09 < \text{F} < 0.10$ a.p.f.u.) contents (Table 1).

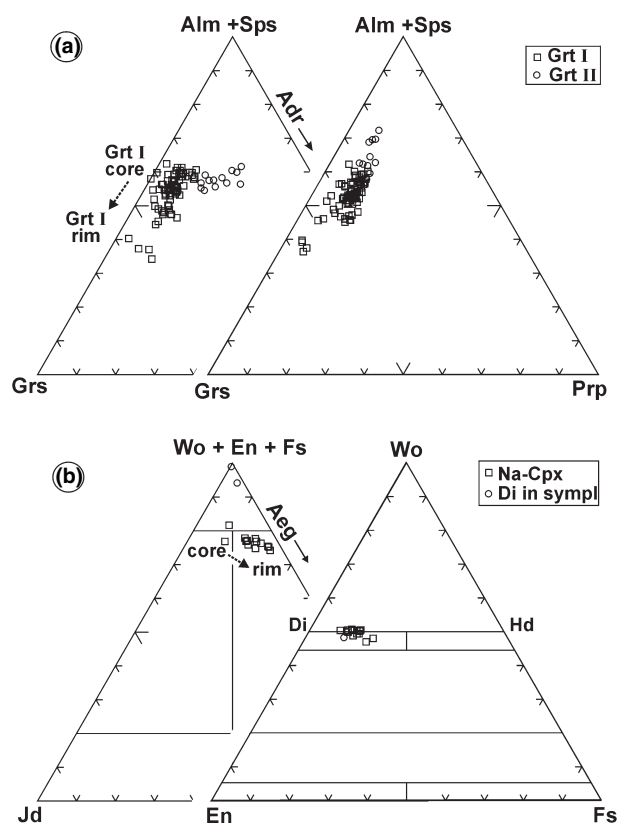


Fig. 3. Compositions of garnet (a) and pyroxene (b) from the calcite marble plotted in the Grs-(Alm + Sps)-Adr and Grs-(Alm + Sps)-Prp diagrams, and in the Jd-(Wo + En + Fs)-Aeg and En-Wo-Fs diagrams, respectively. Grt I is weakly zoned, with the almandine component decreasing from core to rim. Grt II shows higher almandine and andradite contents than Grt I; the sodic clinopyroxene shows an increase in the aegirine component towards the rim.

The dolomite marble

This marble consists of chlorite, corundum, dolomite, bluish-green spinel, calcite, minor margarite and accessory ilmenite, rutile and h  gbomite. The fabric is characterized by irregular to lens-shaped spinel + dolomite + corundum + chlorite $\pm$ calcite domains that are set in a matrix of fine- to medium-grained chlorite + calcite $\pm$ dolomite. These composite domains are aligned to define a poor foliation running parallel to the main regional foliation (Fig. 5).

The bluish-green spinel occurs as medium- to coarse-grained, fractured and corroded porphyroclasts that are moderately zoned from $\text{Spl}_{88}\text{Hc}_{12}$ in the core to $\text{Spl}_{74}\text{Hc}_{26}$ in the rim (Figs 5a,b & 6a; Table 2). The spinel locally includes roundish crystals of Mg-rich ilmenite (Ilm I, with 15–20 mol.% of geikielite component, Figs 5b & 6a; Table 2).

Spinel is extensively replaced (Fig. 5b,c) by fine-grained pseudomorphous aggregates of bluish corundum + chlorite (Chl I, clinocllore: $X_{\text{Mg}} = 0.97$, Fig. 6c & Table 2) + calcite. These pseudomorphs are

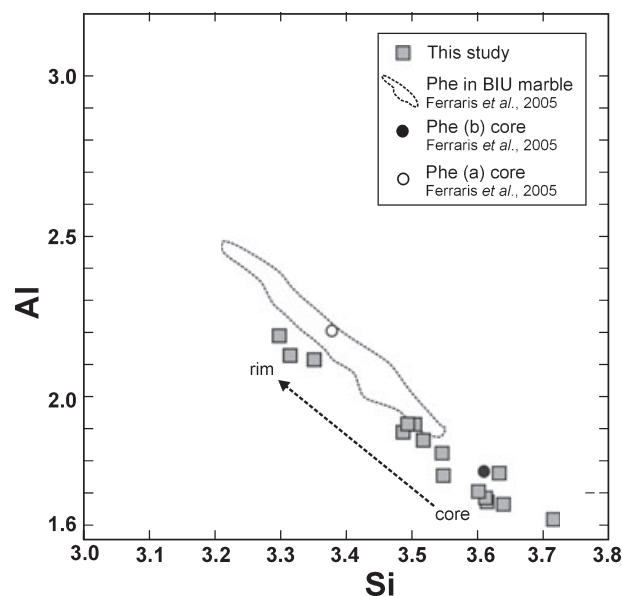


Fig. 4. Al v. Si content (a.p.f.u.) of phengite from the calcite marble. The dotted curve includes the compositions of phengite from the Costa Monforte marble studied by Ferraris *et al.* (2005). For comparison, compositions of prograde low-Si relict [Phe(a)] and UHP high-Si neoblastic domains [Phe(b)] preserved in the core of phengite flakes (Ferraris *et al.*, 2005) from the same marble lens are also reported.

rimmed by a different generation of coarser grained Fe-rich chlorite (Chl II, sheridanite: $0.83 < X_{\text{Mg}} < 0.85$; Figs 5c & 6c). Chl II also overgrows Chl I in the spinel + dolomite + corundum + chlorite $\pm$ calcite domains (Fig. 5d,e). Close to rutile, corundum also occurs as coarser-grained crystals that are slightly zoned (Fig. 5f & Table 2), with deeper-blue rims. Porphyroclastic dolomite is homogeneous in composition [$X_{\text{Dol}} = 0.98$, $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.98$] and does not display any calcite exsolution, being only partially replaced by almost pure calcite [$X_{\text{Cal}} = 0.98$, $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.80$ on average] at the rim and along fractures (Fig. 5d).

Some margarite occurs as nets of fine- to medium-grained, randomly oriented flakes at rim of the corundum + Chl I + calcite pseudomorphs after spinel. Single crystals display significant but variable amounts of Na, with up to 0.28 Na/(Na + Ca) (Fig. 6b & Table 2).

In thin section (Fig. 5f), h  gbomite [general formula $(\text{Mg,Fe,Ti})_2\text{O}_4$] occurs as small, deep-orange to brownish grains associated with spinel, bluish corundum, rutile and Ilm II (with lower Mg-content: 7–10 mol.% of geikielite, Table 2). H  gbomite crystals are almost unzoned, their $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratio ranging from 0.57 to 0.87 in different microdomains (Fig. 6a & Table 2). The Ti contents ($0.38 < \text{Ti} < 0.50$ a.p.f.u. on the basis of eight oxygen) are among the highest ever reported in the literature (e.g. Sengupta *et al.*, 2004, with references therein). A micro-Raman

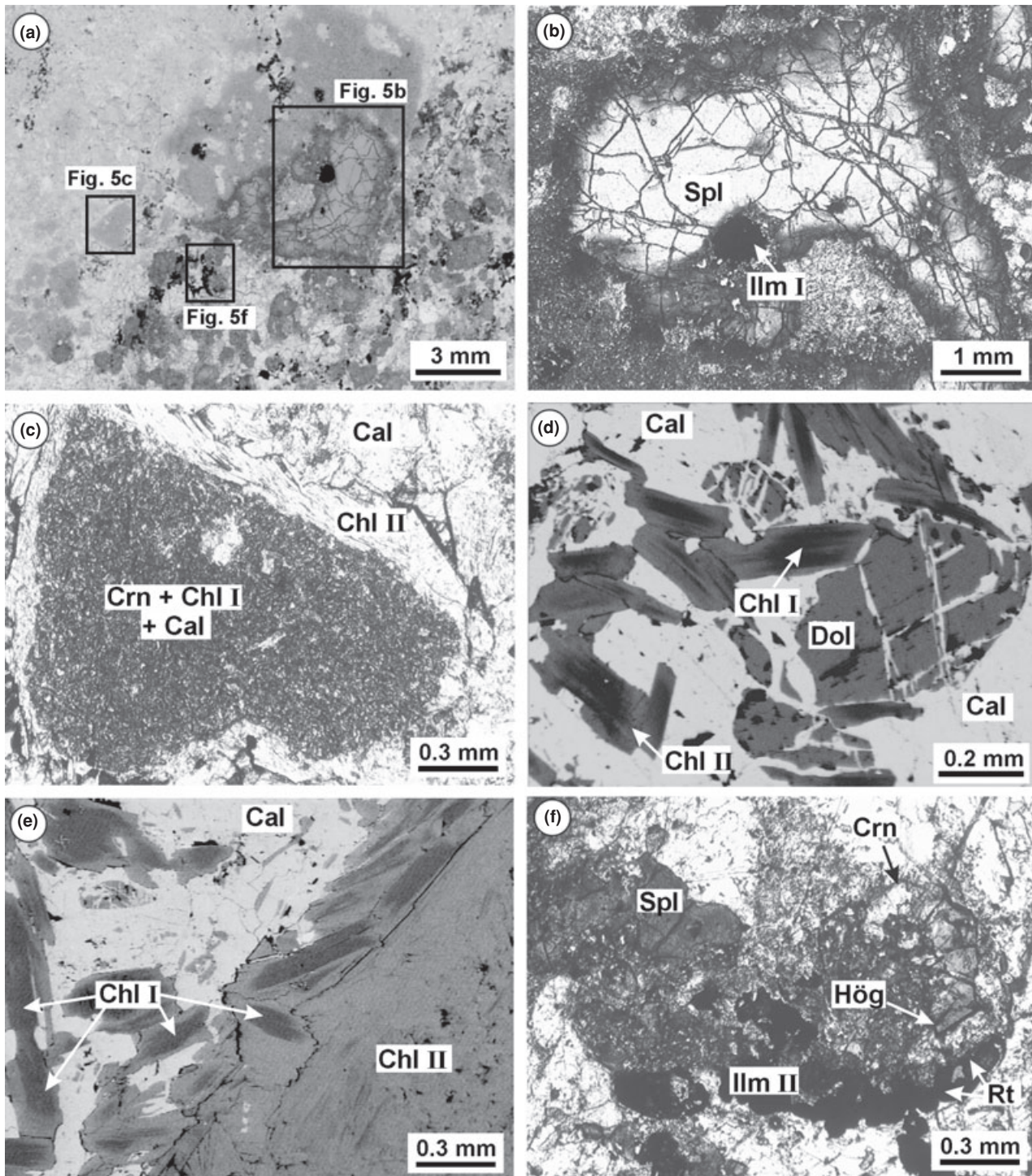


Fig. 5. Representative microstructures of the dolomite marble (sample DM1171) as seen under optical and scanning electron microscope. (a) Overview of a marble portion consisting of dolomite, Mg-chlorite, calcite, and rutile. PPL. (b) Relict greenish spinel (Spl) and ilmenite (Ilm I). Spinel is partially replaced by fine-grained corundum aggregates. PPL. (c) Fine-grained Alpine corundum (Crn) + Mg-chlorite (Chl I) + calcite (Cal) aggregates pseudomorphous after pre-Alpine spinel. PPL. (d) BSE image showing relict dolomite (Dol) partially replaced by calcite (Cal) along cleavages and relict Mg-rich chlorite (Chl I) preserved in the core of Fe-rich chlorite (Chl II). (e) BSE image showing relict Mg-chlorite (Chl I) partially replaced by a second generation of Fe-rich chlorite (Chl II). (f) Relict spinel (Spl) + rutile (Rt) and corundum (Crn) partially converted to lath-shaped hōgbomite (Hög) + ilmenite (Ilm II). PPL.

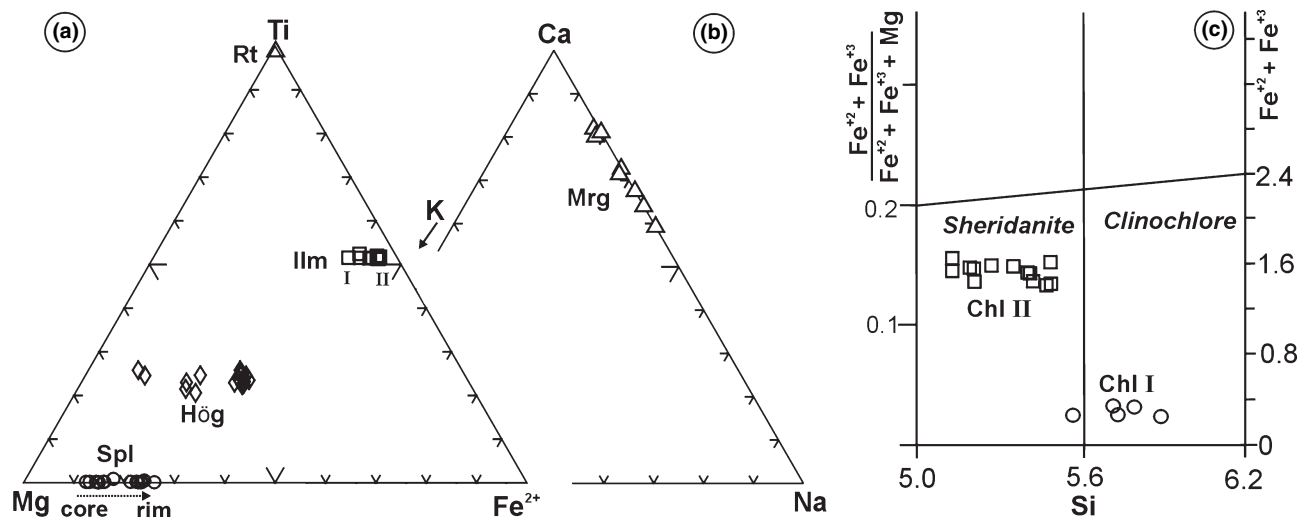


Fig. 6. Compositions of ilmenite, h  gbomite, rutile and spinel (a), margarite (b), and chlorite (c) from the dolomite marble plotted in the Mg–Ti–Fe²⁺ and K–Ca–Na diagrams, and the Si v. $X(Fe_{tot})$ and Fe_{tot} diagram (Hey, 1954), respectively.

spectrum acquired on an h  gbomite crystal with $Mg/(Mg + Fe^{2+}) = 0.59$ is comparable with that reported by Tsunogae & Santosh (2005).

METAMORPHIC EVOLUTION

Mineral assemblages and textural relationships described above indicate that the marbles preserve different portions of the polymetamorphic evolution experienced by the hosting parashists.

In the calcite marble, the garnet I–clinopyroxene–phengite–rutile assemblage, typical of high-pressure conditions and arranged according to the main regional foliation, can be unquestionably referred to the Alpine eclogite facies stage(s). Particularly, core compositions of garnet I, clinopyroxene and phengite (Table 1) are interpreted as representative of the UHP Alpine metamorphic stage dated at *c.* 35 Ma (Gebauer *et al.*, 1997; Rubatto & Hermann, 2001). On the contrary, rim compositions of the same minerals (garnet I, clinopyroxene and phengite), and small neoblastic garnet (Grt II) and their breakdown products (epidote and blue-green amphibole after garnet I, diopside + oligoclase symplectite after clinopyroxene, biotite after phengite) record different stages of the BIU exhumation history (Table 3). Accordingly, calcite and the rare quartz are interpreted as retrograde phases replacing former HP to UHP aragonite and coesite, respectively. Based on microstructural relationships (Fig. 2d), rutile is interpreted as a UHP peak phase, armoured by titanite. This titanite is, therefore, a retrograde phase unlike the zoned titanite from a calc-silicate rock from the same marble lens, used by Rubatto & Hermann (2001) to date the whole Alpine (UHP and retrograde stages) history. However, the presence of different titanite generations and the stability of rutile v.

Table 3. Pre-Alpine and Alpine parageneses in the studied samples.

	Pre-Alpine assemblage	Alpine UHP assemblage	Alpine retrograde assemblage*
Calcite marble		(Arg) Na-Cpx Grt I Phe Rt (Cs) Crn + Chl I	Cal Di + Pl symplectite Grt II ± Ep ± Mg-Hbl Bt Ttn Qtz
Dolomite marble	Spl Ilm I (Cal) [Ca-Pl] Dol	Rt (Arg) [Zol] Dol	Chl II, Na-Mrg, Cal, H��g, Ilm II

Minerals in brackets were present but are completely replaced during retrogression; phases in square brackets are inferred from petrological arguments.

*Rim compositions of Na-Cpx, Grt I and Phe are also included in the early retrograde Alpine re-equilibrations.

titanite can be hampered by difference in the bulk and/or $X(CO_2)$ composition (see below).

In the dolomite marble microstructural relationships and phase compositions indicate that three main mineral assemblages can be envisaged (Table 3) giving additional information on the metamorphic history, complementary to the evolution recorded in the calcite marble. The oldest recognized assemblage (i) consists of spinel + Ilm I + dolomite ± calcite; it is pre-kinematic with respect to the main foliation that in the calcite marble is defined by the UHP minerals. The replacement of spinel by fine-grained aggregates of bluish corundum + Chl I (Fig. 5c) and of Ilm I by rutile therefore can be referred to the UHP Alpine stage, with an assemblage of Crn + Chl I + Rt + Dol + Arg (ii). The later re-equilibration developed, at the expense of both assemblages (i) and (ii), a third assemblage (iii), including calcite inverted

from aragonite, h  gbomite and ilmenite (Ilm II) after the spinel + corundum + rutile domains, a chlorite overgrowth (Chl II) around Chl I, and the late growth of margarite.

We interpret the spinel-bearing assemblage (i) in the dolomite marble as a pre-Alpine assemblage that could be referred either to the regional amphibolite facies event of Variscan age (recorded in the BIU parascists: Figs 1 & 7, and Compagnoni *et al.*, 1995), or to the contact metamorphic event linked to the intrusion of late-Variscan granitoids as also tentatively suggested by Compagnoni *et al.* (1995). Both assemblages (i) and (ii) probably included additional Al-rich silicates (such as plagioclase and/or zoisite: Table 3) that participated in the chlorite-forming reactions. A similar polymetamorphic evolution was described in a clinohumite-chlorite-serpentine marble from the western Tauern, Austria (Franz & Ackermann, 1980).

H  gbomite is not frequently observed in marble and its stability field is still uncertain (e.g. Petersen *et al.*, 1989; Grew *et al.*, 1990; Sengupta *et al.*, 2004). However, microstructural relationships in the dolomite marble suggest that h  gbomite formed at the expense of spinel (as observed elsewhere: e.g. Gier  , 1986; Rammlmair *et al.*, 1988; Petersen *et al.*, 1989; Sengupta *et al.*, 2004) with the involvement of rutile as suggested by its high Ti content. Following Petersen *et al.* (1989) who discussed the pressure-independent reactions $\text{Spl} + \text{Rt} + \text{Crn} + \text{H}_2\text{O} \rightarrow \text{H  g}$, and $\text{Spl} + \text{Rt} + \text{H}_2\text{O} \rightarrow \text{H  g} + \text{Ilm}$, with h  gbomite stable on the low temperature side, we consider that h  gbomite formed as a retrograde phase, together with fine-grained Chl II, Ilm II and Na-rich margarite (Table 3).

ALPINE P - T - $X(\text{CO}_2)$ CONDITIONS IN THE CALCITE MARBLE

Reconstruction of the P - T path

P - T conditions of the Alpine UHP and retrograde stages have been estimated using the garnet-clinopyroxene-phengite assemblage in the calcite marble. The calibration of Ravna & Terry (2004) was used, which combines the reaction $6\text{Di} + 3\text{Ms} = 2\text{Grs} + 1\text{Prp} + 3\text{Cel}$ with the garnet-clinopyroxene Fe-Mg thermometer of Ravna (2000). According to Ravna & Terry (2004), the estimated standard deviations are $\pm 45^\circ\text{C}$ in temperature and $\pm 0.3\text{ GPa}$ in pressure.

In order to obtain the peak- P conditions, as suggested by Carswell *et al.* (2000) and Ravna & Paquin (2003), the garnet with maximum $(a_{\text{grs}})^2 a_{\text{prp}}$, omphacite with minimum a_{di} and correspondingly maximum X_{jd} , and phengite with maximum $a_{\text{Al-cel}}$ (maximum Si content) were chosen. These compositions occur in the core of porphyroblastic Grt I, in the core of the deep green clinopyroxene, and in the core of phengite, respectively (Table 1). The phengite isopleths, calculated for the highest Si content

($3.64 \leq \text{Si} \leq 3.71$ a.p.f.u.), intersect the Grt-Cpx thermometric curves at different temperatures, depending on the solution model used for both garnet and clinopyroxene (Fig. 7). In order to assess the best temperature estimate, the fluid-absent equilibrium $\text{Rt} + \text{Grs} + \text{Di} = \text{Prp} + \text{Ttn}$ was also modelled, using the measured core compositions of Grt I ($\text{Grs}_{40-38}\text{Prp}_{8-10}$) and clinopyroxene ($\text{Di}_{55}\text{Jd}_{12}$),

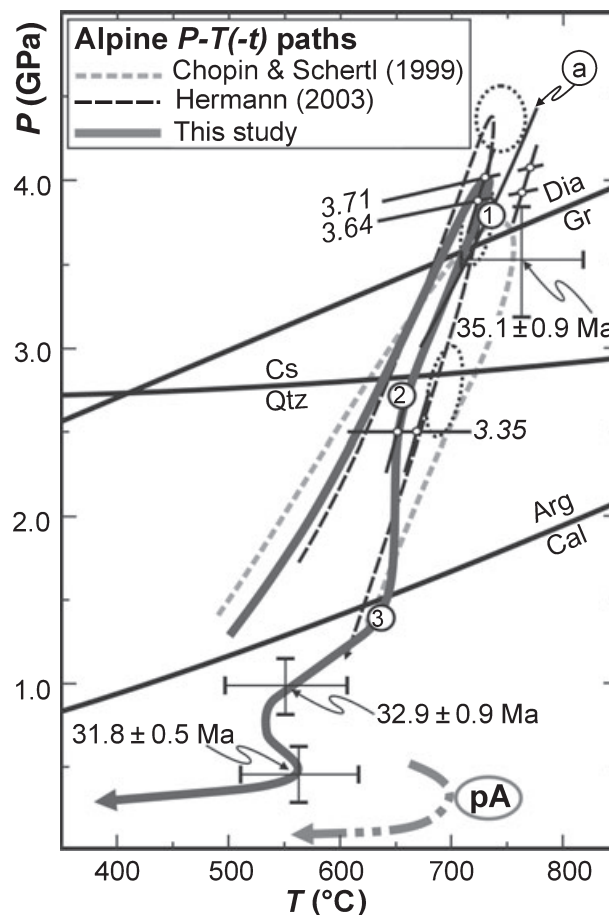


Fig. 7. Estimated P - T conditions of peak UHP and retrograde Alpine stages in the calcite marble from Costa Monforte and synopsis of selected Alpine P - T estimates and inferred Alpine and pre-Alpine P - T paths for the BIU polymetamorphic complex. Numbers in italics refer to different Si contents of phengite. The $\text{Rt} + \text{Grs} + \text{Di} = \text{Prp} + \text{Ttn}$ equilibrium (a) has been used to discriminate intersections at different temperatures between the Grt-Cpx thermometry and the calculated Si-isopleths of phengite, as a function of different garnet and clinopyroxene solution models. Open circles (labelled 1–3) refer to peak and retrograde P - T estimates from Groppe *et al.* (2007); dotted ellipses are the P - T conditions of peak and retrograde stages of the BIU estimated by Hermann (2003a). The error bars are the P - T estimates within 2σ errors of the UHP and two, lower- P , Alpine stages dated by Rubatto & Hermann (2001). The solid, black curve is the new Alpine P - T path suggested for the BIU; see text for discussion. The dotted-dashed path (pA) is the pre-Alpine P - T path of the BIU from Compagnoni *et al.* (1995). The Arg-Cal, Qtz-Cs and Gr-Dia equilibrium curves have been calculated using the thermodynamic data of Holland & Powell (1998, revised version 2002).

and titanite. This equilibrium was calculated following the approach of Connolly (1990) and using the internally consistent thermodynamic data set and equation of state for H₂O of Holland & Powell (1998, revised 2002). Solid solution models for garnet, clinopyroxene and phengite were taken from Holland & Powell (1996, 1998). Following Tropper *et al.* (2002), the titanite thermodynamic parameters were recalculated for an $a_{\text{Ttn}} = 0.88$, in order to ideally simulate its X_{Al} content (Table 1). The resulting equilibrium curve [curve (a) in Fig. 7] clearly shows that only the lower- T intersections are compatible with the occurrence of rutile in the peak paragenesis. As a consequence, 4.02 GPa and 732 °C were estimated for the UHP peak of the calcite marble. The early-retrograde metamorphic conditions, estimated from garnet, clinopyroxene and phengite rim compositions (Table 1), point to intersections at 2.50 GPa and 652 or 668 °C, according to the solution model used for garnet and clinopyroxene (Ravna, 2000). It is noteworthy that the intersection at 652 °C overlaps the P – T estimate of retrograde stage (2) from Groppo *et al.* (2007).

These peak estimates, which point to UHP re-equilibration of the BIU within the diamond stability field, are in very good agreement with those inferred from the experiments in the KCMASH system by Hermann (2003a) and with the UHP peak conditions (circle 1 in Fig. 7) obtained from the petrological study of a phengite–amphibole eclogite by Groppo *et al.* (2007), combining conventional thermobarometry and pseudosection analysis. Also the retrograde P – T evolution estimated for this marble is consistent with the data of Hermann (2003a) and Groppo *et al.* (2007), thus confirming that the common Grt–Cpx geothermometers used for eclogite compositions may also be applied to UHP marbles with grossular-rich garnet. The resulting P – T path consists of a relatively steep decompression associated with a significant cooling from 732 °C at 4.02 GPa to 652 °C at 2.50 GPa. In order to supplement the Alpine P – T –(t) path (Fig. 7), the prograde portion was taken from Chopin & Schertl (2000), Hermann (2003a) and Compagnoni & Rolfo (2003). The late exhumation history of the BIU marbles down to 1.4 GPa was inferred from the data of Hermann (2003a) and Groppo *et al.* (2006, 2007; circle 3 in Fig. 7), and for a pressure of <1.4 GPa from Rubatto & Hermann (2001). In Fig. 7, for comparison, the pre-Alpine P – T path proposed by Compagnoni *et al.* (1995) is also reported.

Estimate of the equilibrium fluid composition

As to the modelling of the equilibrium fluid composition in the BIU marbles, it is essential to point out that subduction-zone fluids are rich in H₂O relative to other volatiles, such as CO₂, because of its greater abundance and favourable partitioning into the fluid phase, and the low thermal stability of hydrated silicates (e.g.

Kerrick & Connolly, 2001; Manning, 2004). Silica and alkalis are the dominant solutes in these highly dilute fluids, with significant Al and Ca and low Mg and Fe (e.g. Manning, 2004). At UHP conditions, these solutes become significant components of fluid/melt phase(s) as reported for example from the Saxonian Erzgebirge (Hwang *et al.*, 2001; Massonne, 2003), the Kokchetav massif (Korsakov & Hermann, 2006) and the southern Sulu (Frezzotti *et al.*, 2007). Being impossible at this stage to model such complex fluid compositions, our calculations are limited to binary volatile species of H₂O and CO₂ (see e.g. Omori *et al.*, 1998; Ogasawara *et al.*, 2000), and should be regarded as the first step for assessment of the fluid evolution in the BIU marbles.

The Grt–Cpx–Phe peak and retrograde assemblages in the calcite marble do not provide information on the equilibrium fluid composition. However, given the estimated P – T conditions for the UHP Alpine peak stage of the calcite marble and the retrograde P – T path discussed above, the composition of coexisting H₂O–CO₂ fluid may be inferred from the coexistence of rutile and garnet in the peak assemblage.

The stability field of rutile as a function of $X(\text{CO}_2)$ has been modelled after the decarbonation reaction $\text{Rt} + \text{Cal}/\text{Arg} + \text{Qtz}/\text{Cs} = \text{Ttn} + \text{CO}_2$, using the approach of Connolly (1990) and the thermodynamic mineral data and the equation of state for H₂O–CO₂ fluids of Holland & Powell (1998, revised version 2002). In the calculation, aragonite, calcite, quartz, coesite and rutile were treated as pure phases, whereas titanite was considered as either pure end-member or actual ($a_{\text{Ttn}} = 0.88$) composition. In Fig. 8(a), the calculated P – T sections at constant fluid composition are projected together with the above estimated Alpine P – T – t path. Considering the actual titanite composition a moderate shift of the $\text{Rt} + \text{Cal}/\text{Arg} + \text{Qtz}/\text{Cs} = \text{Ttn} + \text{CO}_2$ reaction towards lower temperatures is produced, as also predicted by Tropper *et al.* (2002) for low X_{Al} titanite. Due to the location of the prograde P – T path and the peak UHP stage, a $X(\text{CO}_2) \geq 0.025$ is required to stabilize rutile within the diamond stability field.

The occurrence of garnet (instead of epidote) at UHP peak conditions sets the upper limit of $X(\text{CO}_2)$ in the coexisting fluid by considering selected T – $X(\text{CO}_2)$ phase relationships in the TiCMASHC system among aragonite, dolomite, coesite, garnet, clinopyroxene, epidote, rutile and titanite. In addition to the fluid-absent reaction $\text{Rt} + \text{Gr}_{\text{ss}} + \text{Di}_{\text{ss}} = \text{Pr}_{\text{ss}} + \text{Ttn}_{\text{ss}}$ [previously used to constrain the geothermometric estimates; curve (a) in Fig. 7], two garnet–epidote-bearing reactions occur in the T – $X(\text{CO}_2)$ section at 4.0 GPa of Fig. 8(b). As the reaction $\text{Ep}_{\text{ss}} + \text{Cs} + \text{Dol} = \text{Pr}_{\text{ss}} + \text{Arg}$ occurs in the Mg-richer subsystem and involves dolomite (never observed or inferred as either ‘product’ or ‘reactant’ in the studied sample), the reaction $\text{Ep}_{\text{ss}} + \text{Cs} + \text{Arg} = \text{Gr}_{\text{ss}}$ can be used to

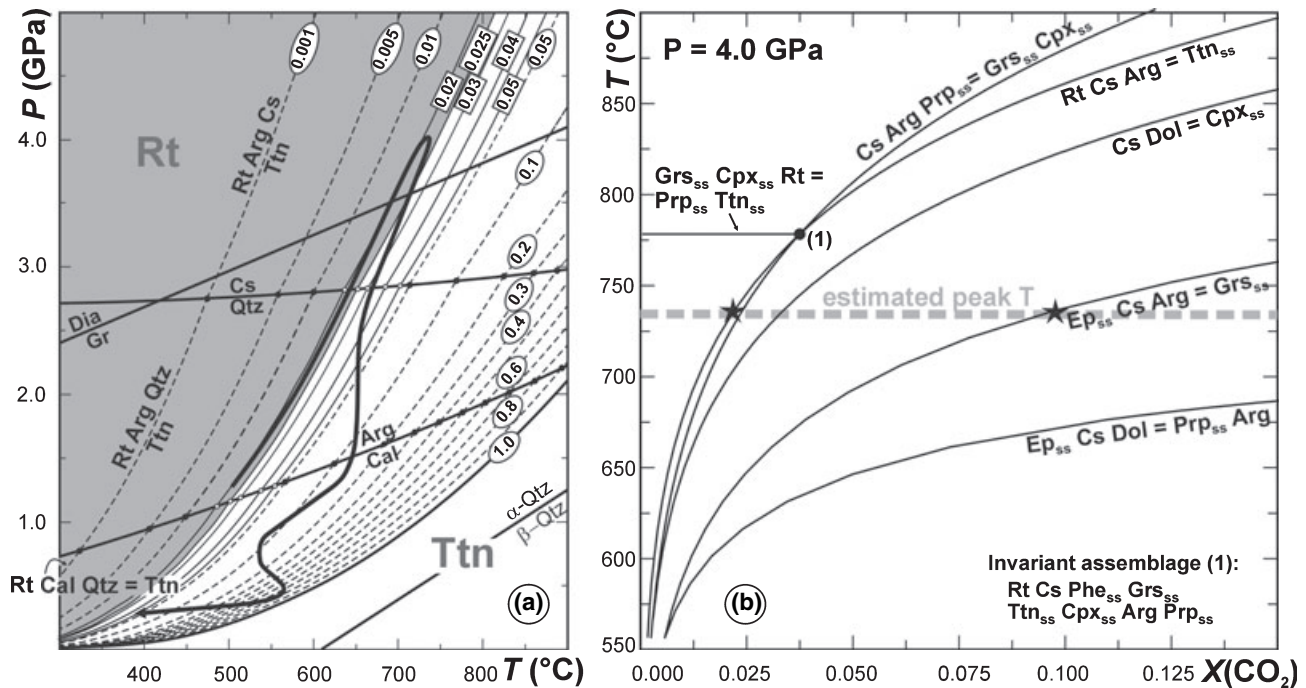


Fig. 8. (a) P - T loci of selected equilibria in the $\text{CaO-TiO}_2\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ model system. Dashed curves show the shift of the $\text{Rt} + \text{Arg/Cal} + \text{Qtz/Cs} = \text{Ttn}$ equilibrium for different compositions of the coexisting $\text{H}_2\text{O-CO}_2$ fluid phase; encircled numbers are $X(\text{CO}_2)$ values. Thin, solid curves show the shift of the same equilibrium when considering the actual composition of titanite at $X(\text{CO}_2) = 0.02, 0.025, 0.03, 0.04$ and 0.05 , respectively. The grey field outlines the stability field of rutile with respect to titanite in the calcite marble at $X(\text{CO}_2) \leq 0.025$. The Qtz-Cs and Gr-Dia equilibria and the Alpine P - T path are from Fig. 7. See text for discussion. (b) T - $X(\text{CO}_2)$ section at 4.0 GPa in the $\text{CaO-TiO}_2\text{-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ model system. The grey dashed line shows the UHP peak temperature estimated on the basis of geothermometry. Black stars constrain the $X(\text{CO}_2)$ range of the peak fluid. The lower $X(\text{CO}_2)$ value [$X(\text{CO}_2) = 0.025$] is constrained by the occurrence of rutile in the peak assemblage (see also Fig. 8a); the upper $X(\text{CO}_2)$ limit [$X(\text{CO}_2) = 0.10$] is constrained by the occurrence of garnet in the peak paragenesis. Activities of solution phases have been calculated at peak P - T conditions assuming ideal $a = X$ relationships. All reaction equations are written such that the high- T assemblage is on the right side.

constrain at $X(\text{CO}_2) \leq 0.10$ the composition of coexisting fluid at the estimated peak temperature.

The inferred range of $X(\text{CO}_2)$ [$0.025 \leq X(\text{CO}_2) \leq 0.10$] at $\sim 730^\circ\text{C}$ and 4.0 GPa is fully consistent with the stability of phengite (with respect to K-feldspar) as suggested by the calculated T - $X(\text{CO}_2)$ phase relationships in the KCMASHCO₂ subsystem.

ALPINE P - T - $X(\text{CO}_2)$ CONDITIONS IN THE DOLOMITE MARBLE

Although no geothermobarometric estimates can be directly obtained from the dolomite marble because the peak mineral assemblage is incompletely preserved, it is evident that both samples followed the same Alpine evolution. Therefore, the P - T path reconstructed for the calcite marble (Fig. 7) should be also the same for the dolomite marble. Particularly, we will focus here on the Alpine P - T - $X(\text{CO}_2)$ evolution.

In addition to the information available from isothermal and isobaric phase diagram sections, the changes in both fluid composition and mineral assemblages of metacarbonates may be also predicted

by projecting volatile variable compositions along univariant equilibria of a P - T phase diagram (Baker *et al.*, 1991; Carmichael, 1991; Connolly & Trommsdorff, 1991; Omori *et al.*, 1998). Phase equilibria in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$ (CMASHC) system were therefore calculated using the computational approach of Connolly (1990) and Connolly & Trommsdorff (1991) and the thermodynamic mineral data and the equation of state for $\text{H}_2\text{O-CO}_2$ fluids of Holland & Powell (1998, revised version 2002). The following, solid end-members were considered: An, Arg, Cal, Chl (clinochlore), Crn, Dol, Dsp, Mrg, Spl, Zo. Anorthite and zoisite were included to account for the presence of Al-bearing phases (chlorite, corundum and margarite) at different stages of the decompressional evolution (Table 3); quartz was excluded because of the occurrence of spinel. Variable composition of the equilibrium $\text{H}_2\text{O-CO}_2$ fluid phase has been modelled by 29 pseudocompounds (Connolly & Kerrick, 1987), using a logarithmic compositional spacing that is symmetrical about $X(\text{CO}_2) = 0.5$ in order to provide better resolution of fluid composition near the two $X(\text{CO}_2)$ extremes. In the modelled petrogenetic grid (Fig. 9), 23 fluid-present and five fluid-absent

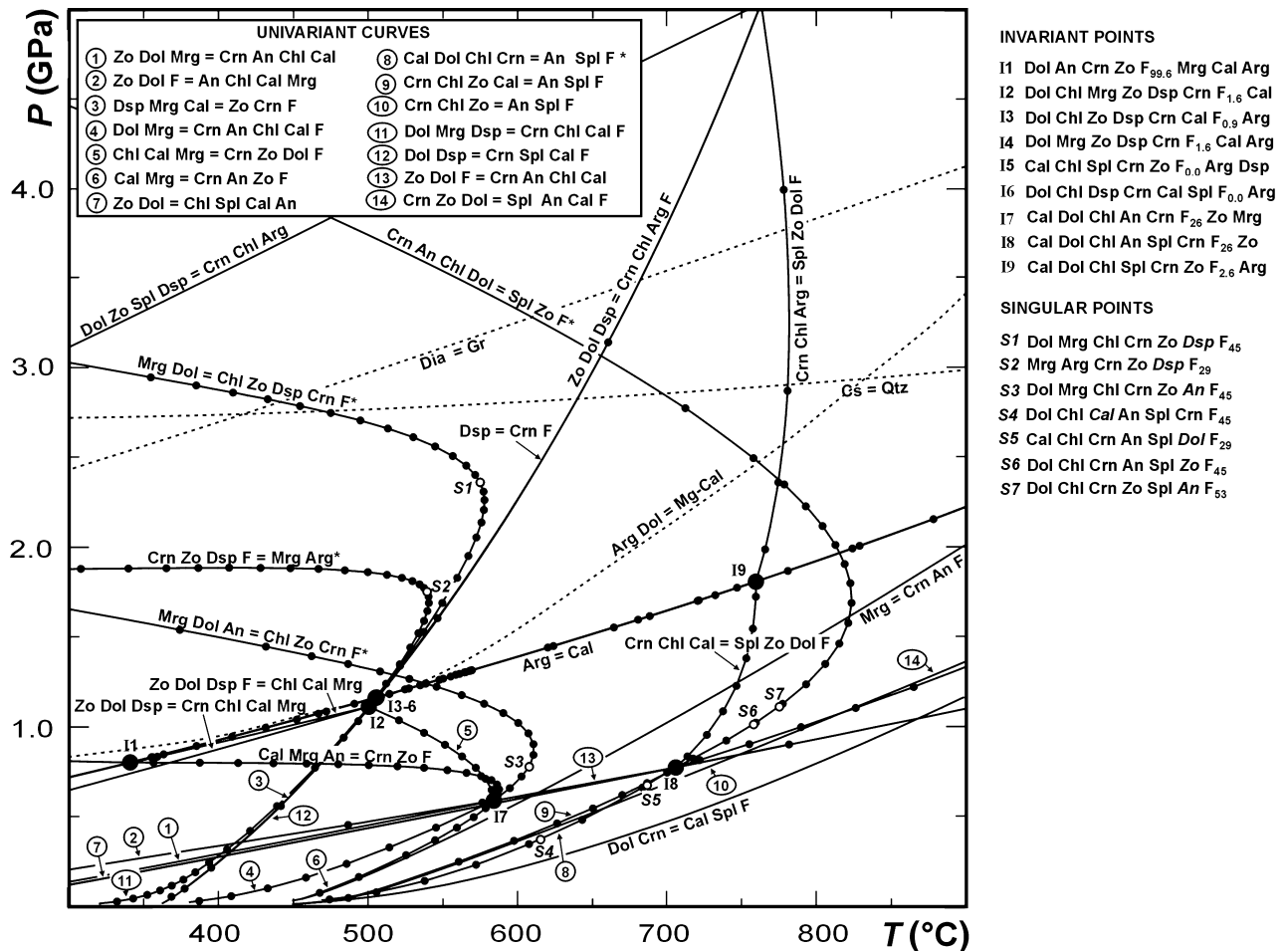


Fig. 9. Calculated P - T projection for the Qtz-absent, CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂ model system, the phases An, Arg, Cal, Chl, Crn, Dol, Dsp, Mrg, Spl, Zo, and a H₂O-CO₂ fluid phase (F) of variable composition. Large filled circles (11–19) are true invariant assemblages; small filled circles are pseudo-invariant assemblages due to approximation by discrete steps of the continuous compositional variation of the fluid phase along univariant equilibria. All reaction equations are written such that the high- T assemblage is on the right side. Small empty circles (S1–S7) are singular points occurring along univariant equilibria marked by asterisks. Approximate compositions (mol.% CO₂) of the equilibrium fluid phase at the invariant and singular assemblages are given at right of the figure (phases whose coefficients vanish at singular points are given in *italics*). Pseudo-univariant curves extending from pseudo-invariant points and singular curves extending from singular points are omitted for clarity. The Qtz-Cs and Gr-Dia equilibria from Fig. 7 are shown as reference; the Arg + Dol = Mg-Cal reaction curve is from Ogasawara *et al.* (2000). See text for discussion.

univariant assemblages occur, generating nine, fluid-present, invariant assemblages. Out of the 23 fluid-present univariant curves, two display two singular points (along the Crn-Chl-Dol-An-Cal-Spl-F and the Crn-An-Chl-Dol-Spl-Zo-F equilibria, respectively) and three display one singular point, at which fluid attains a composition such that the stoichiometric coefficient of one phase vanishes (e.g. Baker *et al.*, 1991; Carmichael, 1991; Abart *et al.*, 1992). Singularities are listed in Fig. 9, and their significance will not be discussed in detail as they mostly do not interfere with the ensuing discussion.

None of the fluid-absent univariant reactions (the aragonite/calcite transformation excluded) is of interest in modelling mineral assemblages and reactions in the dolomite marble. On the contrary, strong varia-

tions in the Clapeyron slopes of the fluid-present univariant reactions occur both along individual curves and among different curves, and dissect the P - T space into relatively narrow regions. Two of these regions, relevant to peak and retrograde Alpine P - T - X (CO₂) conditions, will be discussed in detail hereafter, assuming end-member composition of all phases but spinel. Only the standard-state thermodynamic properties of spinel (Holland & Powell, 1998, revised version 2002) have been modified to match the real composition (Table 2) in order to ideally model the changes in its P - T - X (CO₂) stability field. Modelling of other solid solutions has been disregarded for the following reasons: (i) the measured compositions are close to end-member compositions (such as for chlorite and carbonates); (ii) the lack of internally consistent

thermodynamic data and solution models (such as for margarite–ephesite solution); (iii) the lack of any compositional data for the inferred original phase (such as for anorthite and zoisite). As Mg–calcite has not been included in the calculations, the modelled reactions should apply only to the aragonite + dolomite stability field (Fig. 9; Goldsmith & Newton, 1969; Ogasawara *et al.*, 2000; Hermann, 2003b) that covers most of the prograde, peak and early-retrograde Alpine P – T path experienced by the BIU dolomite marble.

Alpine UHP and retrogression stages

Phase equilibria from the petrogenetic grid of Fig. 9, encompassing the Alpine P – T estimates for the UHP and early retrogression stages in the calcite marble, are shown in Fig. 10(a). Particularly, at UHP peak conditions (~ 730 °C at ~ 4.0 GPa, i.e. within the diamond stability field), the Arg + Crn + Chl + fluid (F hereafter) peak assemblage in the dolomite marble (see also Table 3 & Fig. 5) is constrained by the pseudo-compound approximation at $X(\text{CO}_2) \leq 0.002$. For the same system, the T – $X(\text{CO}_2)$ section, calculated at

4 GPa considering the actual composition of spinel (Fig. 10b), shows the numerically exact fluid compositions at true invariant points, and helps in better constraining the fluid composition in equilibrium with the Arg + Crn + Chl + F peak assemblage at $X(\text{CO}_2) \leq 0.0012$.

Although the growth of rutile in the dolomite marble is also driven by ilmenite-consuming reaction(s), an additional, consistent constraint on the equilibrium fluid composition at the UHP stage is given by the occurrence of rutile in the Alpine peak assemblage of dolomite marble (Table 3 & Fig. 5f). Mineral equilibria, controlling the stability of rutile with respect to titanite, which have been calculated by adding the TiO_2 component to the quartz-free CMASHC system (see inset of Fig. 10b), show that the modelled stability field of the Arg + Crn + Chl + Rt + F assemblage is fully consistent with the above inferred P – T – $X(\text{CO}_2)$ conditions.

As to the first portion of the retrograde P – T path, the modelled Arg + Crn + Chl + F assemblage (Fig. 10a) appears to be stable during the early history, which occurred first in the coesite and later in the quartz stability fields; a slightly increasing $X(\text{CO}_2)$ of

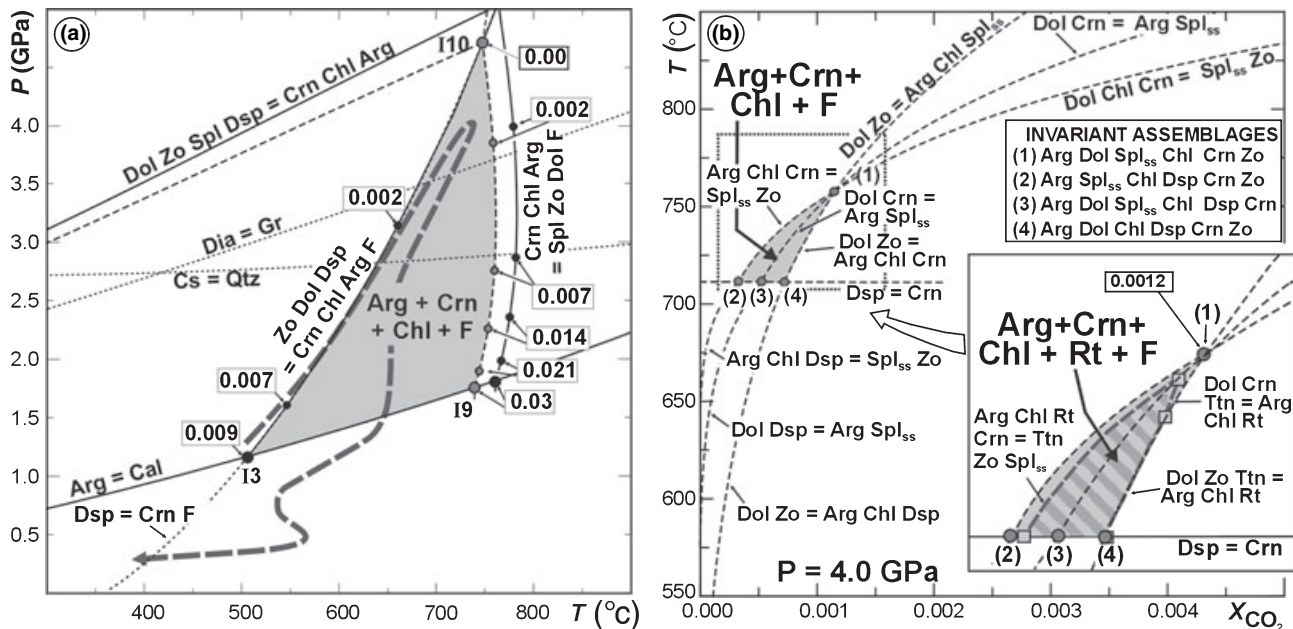


Fig. 10. (a) Selected fluid-present and fluid-absent equilibria from the P – T projection of Fig. 9 limiting the stability field of the Alpine UHP assemblage Arg + Crn + Chl + F (pale-grey field) in the dolomite marble. Numbers in boxes are $X(\text{CO}_2)$ values of coexisting H_2O – CO_2 fluid at pseudo-invariant points (small filled circles) and at true invariant points (large filled circles). Dashed curves and grey circles locate the shift of univariant and (pseudo-)invariant, Spl-bearing assemblages with the actual composition of spinel. The shift produces the additional invariant assemblage Dol–Zo–Spl_{ss}–Dsp–Crn–Chl–Arg–F_{0.0} (I10). The dotted curve is the Dsp–Crn–F equilibrium, which extends through the whole P – T range of the phase diagram and overlaps the Zo–Dol–Dsp–Crn–Chl–Arg–F equilibrium curve. The Alpine (long-dashed, arrowed curve) P – T path, and the Cs–Qtz and Dia–Gr equilibria are from Fig. 7. (b) Isobaric T – $X(\text{CO}_2)$ section showing the stability field of the same UHP Arg + Crn + Chl + F assemblage in the dolomite marble (pale-grey field) at $P = 4.0$ GPa, i.e. the average pressure estimated by the Grt–Cpx–Phe geothermobarometry in the companion calcite marble. Reaction equations are written such that the high- T assemblage is on the right side; dashed curves and grey circles as in (a). The equilibrium fluid compositions for the invariant assemblages are: (1) = 0.0012, (2) = 0.0003, (3) = 0.0005, (4) = 0.0007 $X(\text{CO}_2)$, respectively. The inset shows the stability field of Arg + Crn + Chl + Rt + F (pale-grey field with dark-grey pattern) as modelled in the TiCMASHC system for P – T – $X(\text{CO}_2)$ conditions of the UHP stage. See text for discussion.

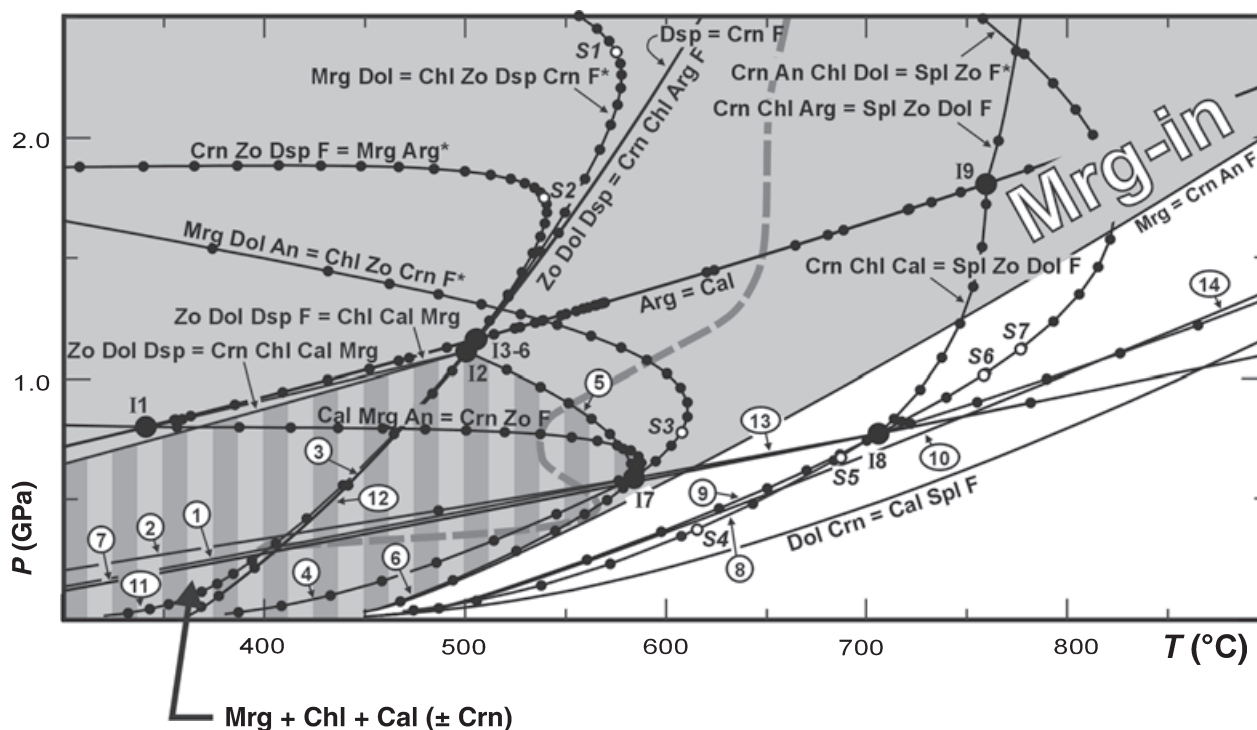


Fig. 11. Univariant equilibria from the P - T projection of Fig. 9 that are relevant to the late-Alpine retrograde stages of the BIU. Symbols and labels of equilibria as in Fig. 9. The pale-grey field encompasses the stability field of margarite, whilst the stability of $\text{Mrg} + \text{Crn} + \text{Cal}$ (pale-grey field with dark-grey pattern) is restricted to the lower P - T region of the phase diagram. The Alpine (long-dashed, arrowed curve) P - T path is from Fig. 7. See text for discussion.

equilibrium fluid compositions is modelled at decreasing pressure.

The lack of low-pressure, equilibrium assemblages in the dolomite marble and limitations of the petrogenetic grid discussed above hamper the exact modelling of the $X(\text{CO}_2)$ fluid composition during the later portion of the Alpine retrograde path within the calcite stability field. Nevertheless, the modelled assemblage $\text{Mrg} + \text{Chl} + \text{Cal}$ (Fig. 11) is coherent with both the late growth of margarite and Chl II (Table 3) and with the low-pressure portion of the BIU P - T path.

DISCUSSION

The Alpine P - T path

Thermobarometric estimates from the calcite marble combined with petrological modelling of mineral assemblages and reactions in both the calcite and dolomite marbles from Costa Monforte provide significant information on the Alpine metamorphic evolution of metacarbonates from the UHP BIU of southern Dora-Maira Massif. Such evolution is coherent with that recorded in other lithologies of the BIU (e.g. Chopin *et al.*, 1991; Schertl *et al.*, 1991; Hermann, 2003a; Groppo *et al.*, 2007; with references therein).

Grt-Cpx-Phe core compositions from the calcite marble point to UHP Alpine peak conditions within the diamond stability field, based on the highest celadonite contents of phengite, and in agreement with data from Hermann (2003a) and Groppo *et al.* (2007). Given the lack of an *ad hoc* study of phengite at the TEM scale, these celadonite contents may either correspond to a pure UHP end-member or represent a mixture of prograde and peak phengite nanodomains as observed by Ferraris *et al.* (2005); therefore, our pressure estimates could either refer to the actual peak pressure conditions or be an underestimation.

Thermobarometry on Grt-Cpx-Phe rim compositions from the same sample are also in agreement with the estimates of Groppo *et al.* (2007) and allows reconstruction of the first portion of the Alpine retrograde P - T -(t) path, characterized by a significant decompression coupled with a moderate cooling (Fig. 7). The different slopes of the first (between UHP peak and the coesite to quartz transition) and of the second (down to the aragonite to calcite transition) part of the retrograde path is documented in the calcite marble and is consistent with the modelled evolution of eclogite from the same unit (Groppo *et al.*, 2007). This Alpine P - T path is consistent with a rapid exhumation to shallow levels as suggested by the available geochronological data (e.g. Duchêne *et al.*, 1997; Gebauer

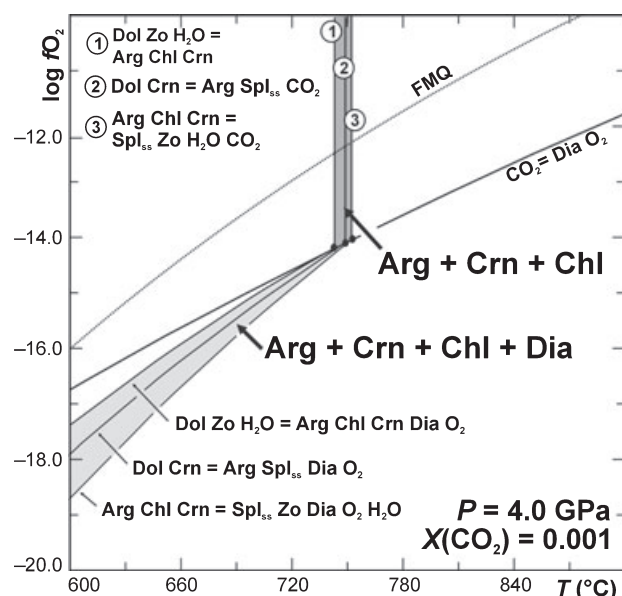


Fig. 12. Projection of $\log f_{\text{O}_2}$ - T selected phase relationships in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-C-O}_2\text{-H}_2\text{O}$ system at different $X(\text{CO}_2)$ values encompassing the UHP conditions in the BIU dolomite marble. FMQ is the fayalite-magnetite-quartz buffer. Reaction equations are written such that the high- T assemblage is on the right side. Grey field corresponds to Arg + Crn + Chl field of Fig. 10b and pale grey refers to the same assemblage in the $\log f_{\text{O}_2}$ - T diamond stability field.

et al., 1997; Rubatto & Hermann, 2001; Di Vincenzo *et al.*, 2006).

The Alpine $X(\text{CO}_2)$ fluid evolution

From the P - T - $X(\text{CO}_2)$ projections, the two samples derived from the same marble lens were characterized by slightly different composition and evolution of the equilibrium fluids, suggesting internally buffered systems during Alpine metamorphism. On the basis of meso- and microstructures, together with the suitable petrological data (Compagnoni *et al.*, 1995; Ferraris *et al.*, 2005), the inherited mineralogical heterogeneities and the polyphase Alpine deformation controlled the scale of these local systems ranging from the nanoscale (i.e. the nano- to micro-scale phengite zoning described by Ferraris *et al.*, 2005) to the centimetre-decimetres scale which is the size of the silicate-rich domains occurring in both the studied samples and the whole Costa Monforte marble lens. Such different Alpine fluid evolution for relatively small, independent closed systems fits the available studies on stable isotopes and fluid inclusions. These studies show that most UHP and HP rocks evolved as a closed system, and that limited aqueous fluids with limited mobility were available only locally and episodically (e.g. Philippot & Rumble, 2000, with references therein).

Similar to other HP to UHP marble occurrences (e.g. Franz & Spear, 1983; Castelli, 1991; Wang & Liou, 1993; Kato *et al.*, 1997; Ogasawara *et al.*, 1998;

Omori *et al.*, 1998; Manning, 2004), the modelled equilibrium fluid at peak conditions has very low $X(\text{CO}_2)$. This finding suggests that at UHP conditions (corresponding to sub-arc depth) most of the volatile content of deeply subducted carbonate rocks can be retained and that carbonate rocks would undergo little devolatilization upon subduction (e.g. Kerrick & Connolly, 2001), or that devolatilization may not necessarily imply, at least locally, a significant increase of $X(\text{CO}_2)$ in internally buffered systems.

The stability of diamond in the BIU marbles

Thermobarometric estimates from the calcite marble point to Alpine peak UHP metamorphic conditions within the diamond stability field; however, in the samples, neither diamond nor graphite have been observed so far. Hermann (2003a) already suggested that the absence of diamond in other lithologies of the BIU might be due to the low temperature of metamorphism (and consequently of the slow element diffusion), the absence of a free fluid phase in the metapelites and a short residence time of the BIU in diamond facies conditions.

However, considering the Arg + Crn + Chl peak assemblage of the dolomite marble, the calculated T - $\log f_{\text{O}_2}$ relationships for the CMAS system of Fig. 10 (in equilibrium with a C-O-H fluid at $X(\text{CO}_2) \leq 0.0012$) show that, at the inferred P - T conditions, the $\text{Dia} + \text{O}_2 = \text{CO}_2$ reaction occurs at about $\log f_{\text{O}_2} = -14$ (i.e. ~ 2 log units below the FMQ buffer) hampering the formation of diamond in the peak assemblage (Fig. 12). Therefore, the lack of diamond could be explained, at least in the dolomite marble, by the relatively high oxidizing conditions. This hypothesis is in agreement with the results of Ogasawara *et al.* (1997, 2000) who suggested that very-low $X(\text{CO}_2)$ values favour higher f_{O_2} -conditions, preventing the formation of either diamond at UHP peak conditions, or graphite during exhumation.

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