HT, pre-Alpine relics in a spinel-bearing dolomite marble from the UHP Brossasco-Isasca Unit (Dora-Maira Massif, western Alps, Italy)

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ABSTRACT. — A dolomite marble from the polymetamorphic complex of the UHP eclogite-facies Brossasco-Isasca Unit (southern Dora-Maira Massif), which preserves relics of a HT pre-Alpine, Spl-Dol-Ilm-bearing assemblage partially converted into a Crn + Chl + (Arg) + Rt UHP assemblage during the Alpine evolution, has been petrologically investigated. Its pre-Alpine P-T-X(CO$_2$) evolution is discussed using P-T phase diagram projections for H$_2$O-CO$_2$ mixed volatile systems.

The P-T-X(CO$_2$) modelling suggests that the Dol + Crn = Cal + Spl + F decarbonation reaction is the most likely spinel-producing reaction along the pre-Alpine prograde path. In the mixed-volatile model system, a X(CO$_2$) > 0.60 has been inferred as the equilibrium fluid composition of this univariant assemblage. Comparison of the P-T-X(CO$_2$) pre-Alpine and Alpine evolutions shows that CO$_2$-rich fluids involved in the pre-Alpine reactions are substantially different from the acqueous fluids produced during the UHP Alpine stage.

RIASSUNTO. — L'analisi petrologica di un marmo dolomitico proveniente dal Complesso Polimetamorfico dell'Unità Brossasco-Isasca (l'unità di altissima pressione del Massiccio Dora-

Maira meridionale) ha permesso di riconoscere una paragenesi relitta pre-alpina di alta temperatura e bassa pressione a Spl + Dol + Ilm, parzialmente sostituita dalla paragenesi alpina di altissima pressione a Crn + Chl + (Arg) + Rt. Le condizioni P-T-X(CO$_2$) pre-alpine sono state ricostruite mediante l'elaborazione di griglie petrogenetiche P-T-X(CO$_2$) che suggeriscono la formazione dello spinello secondo la reazione di decarbonatazione Dol + Crn = Cal + Spl + Fluido durante l'evoluzione prograda di bassa pressione. Nel sistema indagato, il fluido in equilibrio con questa paragenesi univariante è caratterizzato da un X(CO$_2$) > 0,60. Il confronto tra l'evoluzione P-T-X(CO$_2$) pre-alpina e quella alpina mostra che i fluidi pre-alpini, ricchi in CO$_2$, sono decisamente diversi rispetto a quelli acquosi liberati durante l'evento metamorfico di altissima pressione legato alla subduzione alpina.

KEY WORDS: *Dora-Maira Massif, dolomite marble, pre-Alpine evolution, P-T-X(CO$_2$) projection*

INTRODUCTION

In the western Alps polymetamorphic terranes, which underwent both pre-Alpine (Variscan) and Alpine tectono-metamorphic cycles, are

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widespread (see Desmons *et al.*, 1999 for a review). Pre-Alpine relict assemblages and structures are generally preserved in rock portions that escaped pervasive Alpine deformation and recrystallization (e.g. Compagnoni *et al.*, 1974; Dal Piaz *et al.*, 1983; Lardeaux and Spalla, 1991; Bouffette *et al.*, 1993; Compagnoni *et al.*, 1995).

To our knowledge, evidence of a polymetamorphic evolution is rarely recorded in metacarbonates. Franz and Ackermand (1980) described early or pre-Variscan regional to Variscan contact assemblages partly replaced by Alpine regional assemblages in Chl-Fo-Chu-Srp marbles from the western Tauern Area of Tyrol (abbreviations after Bucher and Frey, 2002). Castelli (1991) reported pre-Alpine augite and diopside relics at core of Alpine, HP pyroxenes in impure marbles from the Sesia-Lanzo Zone; Al, F-rich titanite in the same rocks also records evidence of a pre-Alpine to Alpine evolution (Castelli and Rubatto, 2002).

In this paper we study in detail the evolution of a relict pre-Alpine assemblage in a dolomitic marble from the Polymetamorphic Complex of the ultra-high pressure (UHP) Brossasco-Isasca Unit (BIU) of southern Dora-Maira Massif, shortly described by Compagnoni *et al.* (1995) and recently studied by Castelli *et al.* (2007) in the frame of its Alpine evolution. The pre-Alpine P-T-$X(CO_2)$ evolution of this polymetamorphic marble is discussed using P-T phase-diagram projections for H_2O-CO_2 mixed-volatile systems (e.g. Carmichael, 1991; Connolly and Trommsdorff, 1991) togheter with its inferred pre-Alpine P-T path (Compagnoni and Rolfo, 2003).

Geological setting

The coesite-bearing Brossasco-Isasca Unit is a small UHP tectonic unit (approximately 10x4x1 km) sandwiched between two HP tectonic units in the southern Dora-Maira Massif of Penninic domain, western Alps (Fig. 1) (e.g. Chopin 1984; Chopin *et al.*, 1991; Schertl *et al.*, 1991; Compagnoni *et al.*, 1995; Michard *et al.* 1995; Nowlan *et al.*, 2000; Rubatto and Hermann, 2001; Compagnoni and Rolfo, 2003; Hermann, 2003 Compagnoni *et al.*, 2004). Peak conditions of the UHP Alpine re-equilibration have been estimated

at $P \approx 4.0$ GPa and $T \approx 730°$C, i.e. in the diamond stability field (Hermann, 2003; Castelli *et al.*, 2007; Groppo *et al.*, 2007).

Two lithostratigraphic complexes have been distinguished in the BIU: a "Monometamorphic Complex" and a "Polymetamorphic Complex" (Compagnoni *et al.*, 1995). The "Monometamorphic Complex" mainly consists of orthogneiss derived from the Alpine tectono-metamorphic reworking of late-Variscan granitoids, intruded at ca. 275 Ma (Gebauer *et al.*, 1997) into the Variscan metamorphic basement (Fig. 2), i.e. the "Polymetamorphic Complex" (Biino and Compagnoni, 1991, 1992). Undeformed granitoid relics are locally observed. 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 and Hirajima, 2001; Simon and Chopin, 2001), are locally found within the orthogneiss. The "Polymetamorphic Complex", derived from the Alpine tectono-metamorphic reworking of a Variscan amphibolite-facies metamorphic basement, mainly consists of kyanite-almandine-phengite ± jadeite paraschist with marble and eclogite intercalations (Fig. 2). In the "Polymetamorphic Complex", Variscan structures and assemblages are in places well preserved: relics of pre-Alpine amphibolite-facies paraschists and of intrusive contacts have been locally found between granitoids and metamorphic basement (Biino and Compagnoni, 1992; Compagnoni *et al.*, 1995). On the basis of these pre-Alpine mineralogical and structural relics, two distinct pre-Alpine events have been recognised: (i) a pre-Alpine medium- to low-P regional metamorphic event, which reached the upper amphibolite facies and developed a garnet + biotite + K-feldspar + sillimanite assemblage, and (ii) a pre-Alpine low-pressure static recrystallization, most likely related to the thermal metamorphism connected to the intrusion of the late Variscan granitoids, which led to the widespread development of contact biotite, andalusite and cordierite (Compagnoni *et al.*, 1995; Compagnoni and Rolfo, 2003). The occurrence of quartz-feldspar lens-like aggregates (metatects) in paraschists suggests that during the regional Variscan metamorphism temperature exceeded that of the wet granite solidus ($T \approx 700°$C at $P \approx$ 0.3 GPa: Compagnoni *et al.*, 1995).
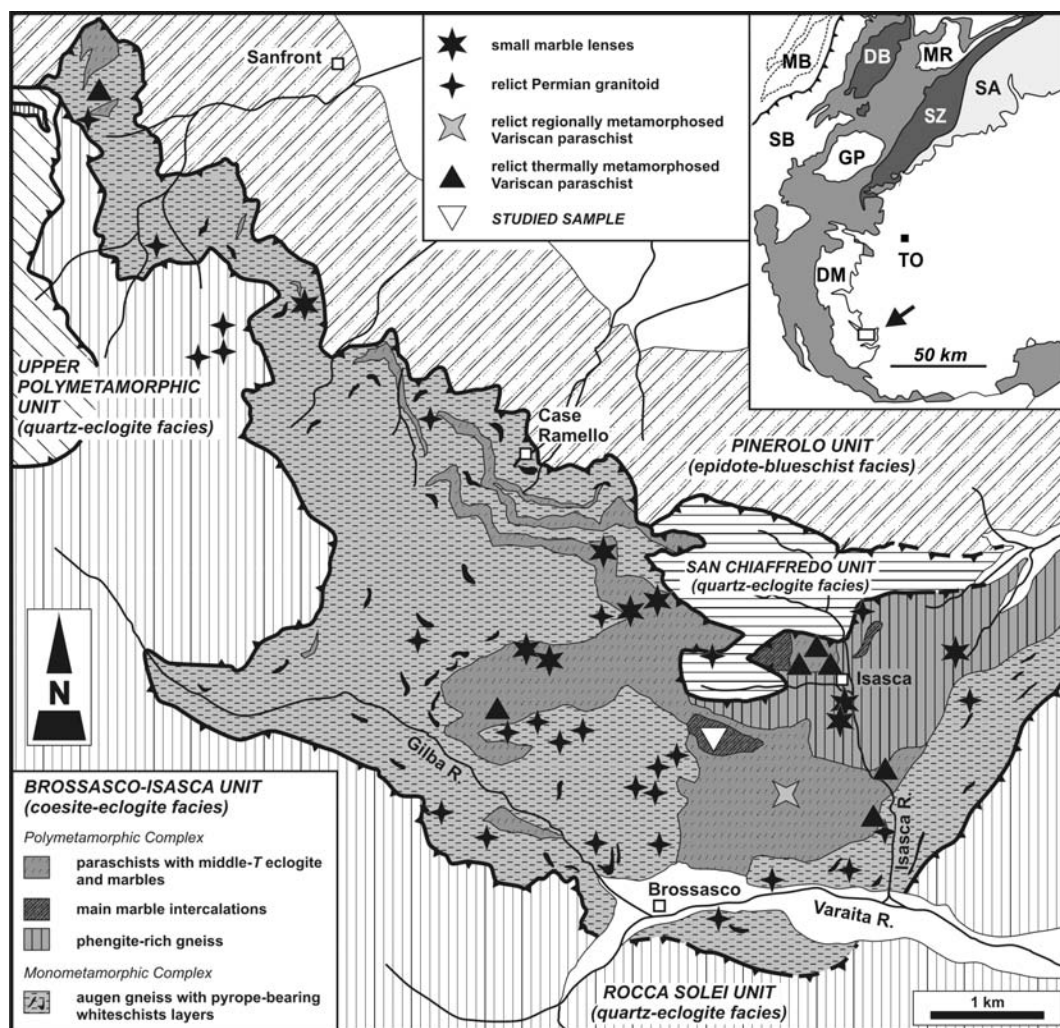
Fig. 1 – Simplified geological map of the coesite-bearing "Brossasco-Isasca Unit" (modified from Compagnoni and Rolfo, 2003) emphasizing the pre-Alpine structural and mineralogical relics within the Polymetamorphic Complex. Undifferentiated units: graphite-rich schists and metaclastics of the epidote-blueschist 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 triangle shows location of the studied sample 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); Dent Blanche nappe (DB) and Sesia-Lanzo Zone (SZ) of the Austroalpine Domain. SA: Southern Alps. TO: Town of Torino.

Compagnoni *et al.* (1995), Compagnoni and Rolfo (2003) and Castelli *et al.* (2007) describe pre-Alpine relics in the largest marble lens exposed at Costa Monforte (Fig. 1), that may be ascribed either to the regional amphibolite-facies Variscan event or to the late-Variscan contact metamorphism. This occurrence is likely similar to that reported by Chopin *et al.* (1991), who describe mm-sized Crn-Mag-bearing pockets in a dolomitic marble from the same area.

PETROGRAPHY

The BIU marbles usually occur within the paraschists as lenses from a few metres to tens of metres long and from a few dm to several metres thick. The largest lens, about 800 m long and 70 m thick, is exposed at Costa Monforte (Fig. 1) and consists of both calcite- and dolomite-rich layers locally with thin discontinuous interlayers of micaschist and boudins of eclogite. The grain-size is usually coarse, but very fine-grained mylonitic types locally occur, reflecting different stages of the polyphase, Alpine tectono-metamorphic evolution. The most common types include pure marbles and phengite marbles, locally characterized by silicate-rich domains stretched parallel to the regional foliation. These silicate-rich layers contain different additional minerals, including garnet, clinopyroxene, phengite, epidote and rutile (Compagnoni and Rolfo, 2003; Castelli *et al.*, 2007).

A unique sample of a dolomite-rich marble (DM1171), collected in the southwestern portion of the Costa Monforte quarry, differs from the common marble types occurring in the Costa Monforte lens because it preserves relics of a pre-Alpine paragenesis, overprinted by the Alpine metamorphic assemblages. This marble consists of chlorite, corundum, dolomite, bluish-green spinel, calcite, minor margarite and rutile. Its fabric is characterized by irregular to lens-shaped spinel + dolomite + corundum + chlorite ± calcite domains that are set in a matrix of fine- to medium-grained chlorite + calcite ± dolomite (Fig. 3). These composite domains are aligned to define a poor foliation running parallel to the main regional foliation. The Alpine P-T-$X(CO_2)$ evolution of the Costa Monforte marble lens is characterized by peak conditions in the diamond stability field [$P = 4.0$ GPa at $T = 730°C$ and $X(CO_2) \leq 0.10$] followed by a significant decompression coupled with a moderate and continuous cooling to $T = 650°C$ at $P = 2.5$ GPa (Castelli *et al.*, 2007).

On the basis of microstructural observations and mineral relationships, three different mineral assemblages have been recognized (Castelli *et al.*, 2007): (i) a pre-Alpine relict assemblage; (ii) an UHP peak assemblage, and (iii) a retrograde assemblage (Table 1).
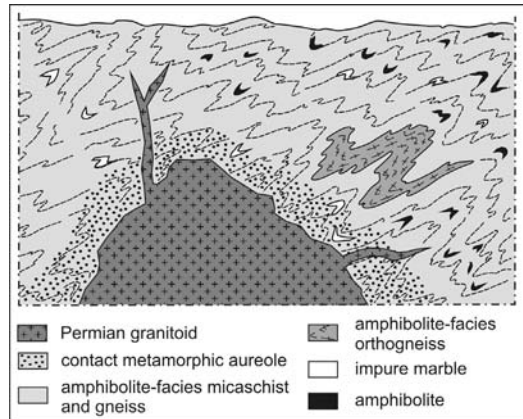

Fig. 2 – Inferred pre-Alpine geologic setting for the UHP Brossasco-Isasca Unit, Dora-Maira Massif, prior to the Alpine metamorphic event (modified from Compagnoni and Rolfo, 2003). Variscan micaschist, gneiss, marble and amphibolite are the protoliths of the Polymetamorphic Complex; the Permian granitoids are the protoliths of the Monometamorphic Complex.

The partially preserved pre-Alpine, most likely Variscan, mineral assemblage (i) consists of bluish-green spinel, ilmenite (Ilm I), dolomite and calcite (Figs 3a, b, c), pre-kinematic with respect to the main foliation that in most marble types is defined by UHP minerals. The relict bluish-green spinel occurs as medium- to coarse-grained, fractured and corroded, porphyroclasts which locally include roundish crystals of Ilm I. Porphyroclastic dolomite does not display any calcite exsolution, being only partially replaced by calcite at the rim and along fractures (Fig. 3c). The original occurrence of a silicate, most likely plagioclase, is inferred (Table 1) from the presence of chlorite among the Alpine minerals and the significant Na component of margarite (see below).

During the UHP metamorphism, spinel was converted into fine-grained aggregates of bluish corundum + clinochlore (Chl I) (Fig. 3d). Coarse-grained corundum locally develops at the rim of Crn + Chl I pseudomorphs after spinel and close to rutile it shows a deeper blue colour. Pre-Alpine Ilm I was replaced by aggregates of rutile (Fig. 3f and 4a). The inferred UHP peak mineral assemblage (ii) thus consisted of Crn + Chl I + Rt + Dol + Arg. Pre-Alpine plagioclase would have been replaced by UHP zoisite, but

no evidence of this phase has been observed in the marble, possibly because it was consumed by later reactions.

The later re-equilibration developed, at the expense of both assemblages (i) and (ii), a third retrograde assemblage (iii) that includes calcite inverted from aragonite, högbomite and ilmenite (Ilm II) after the spinel + corundum + rutile domains, a new chlorite (Chl II) overgrowing Chl I (Fig. 3c), and the late growth of margarite. Högbomite occurs as small deep orange-brownish grains associated to spinel, bluish corundum, rutile and Alpine ilmenite (Ilm II) (Fig. 3f). Microstructural relationships suggest that högbomite formed at the expense of spinel (as observed elsewhere: e.g. Gieré, 1986; Rammlmair *et al.*, 1988; Petersen *et al.*, 1989; Sengupta *et al.*, 2004) with the involvement of rutile (Fig. 4a). Following Petersen *et al.* (1989) who discussed the pressure-independent reactions Spl + Rt + Crn + H_2O → Hög, and Spl + Rt + H_2O → Hög + Ilm, with högbomite stable on the low temperature side, we consider that högbomite formed as a retrograde phase (Table 1). Margarite flakes, up to 5-7 vol%, depending on different microstructural domains, radially grow around the fine-grained aggregates of corundum + Chl I after spinel (Fig. 3e).

MINERAL CHEMISTRY AND MICRO-RAMAN IDENTIFICATION

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 Table 2. Micro-Raman spectroscopy has been used to further characterize högbomite crystals, since it is rarely reported from marbles. Micro-Raman spectra were acquired using an integrated micro/macro Raman system Horiba Jobin Yvon HR800; a polarised solid state Nd 80 mW laser operating at 532.11 nm was used as the excitation source. Correct calibration of the instrument was verified by checking the position of the Si band at ± 520.7 cm^{-1}. The spectra was acquired using a 50X objective, resulting in a laser beam size at the sample of the order of 10 µm. To optimize the signal to noise ratio, spectra were acquired using 10 scans of 10 seconds for each spectral region.

Mg-Fe-Ti oxides are present both in the pre-Alpine and in the Alpine assemblages and their compositions are reported in Table 2 and Fig. 4a. The relict pre-Alpine bluish-green spinel is moderately zoned from $Spl_{88}Hc_{12}$ in the core to

TABLE 1
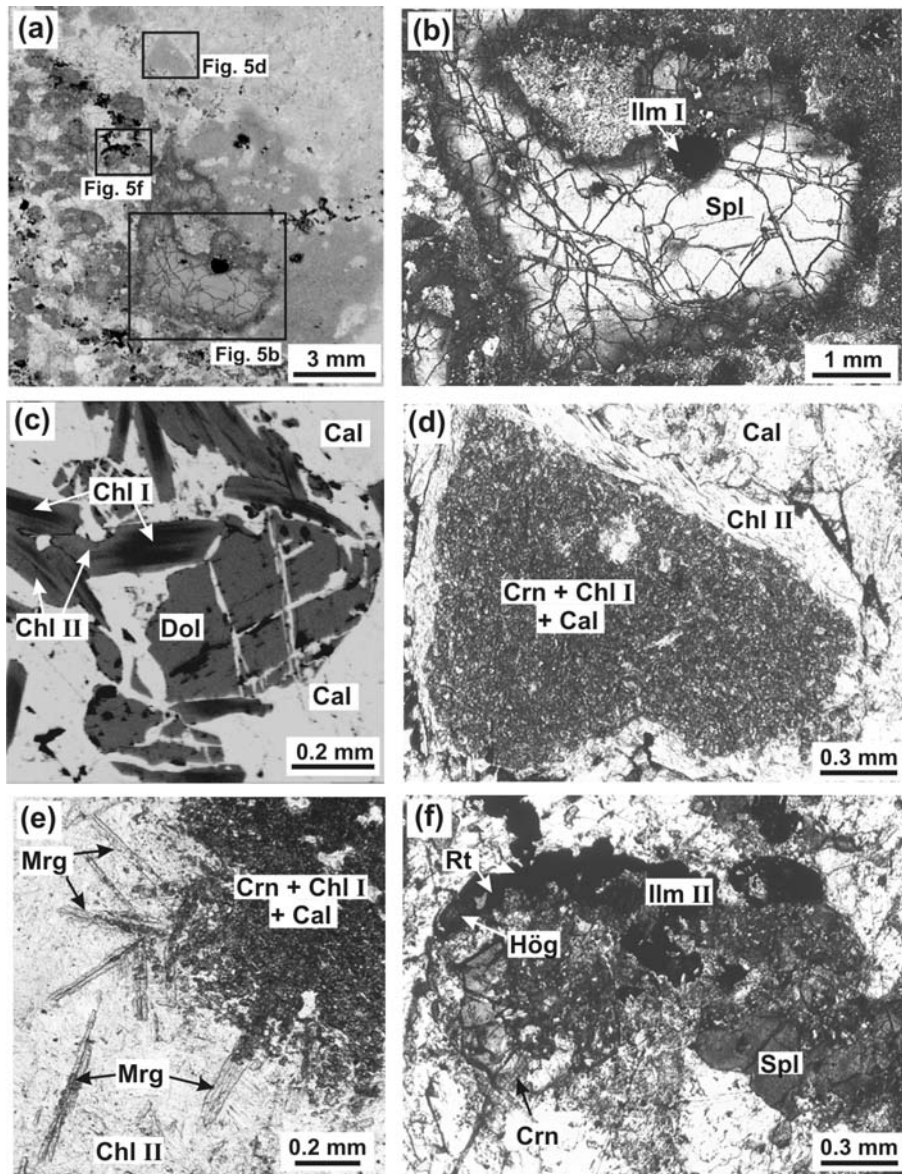*Pre-Alpine and Alpine parageneses*

Fig. 3 – Representative microstructures of dolomite marble DM1171 as seen under optical and scanning electron microscope. (a) Overview of a marble portion consisting of dolomite, Mg-chlorite, calcite, and rutile. Relict pre-Alpine and Alpine domains are underlined by insets and shown enlarged in the other figures. PPL (plane polarized light). (b) Detail of pre-Alpine greenish spinel (Spl) and ilmenite (Ilm I). Spinel is partially replaced by fine-grained corundum aggregates. PPL. (c) Back-scattered electron 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-richer chlorite (Chl II). (d) Fine-grained corundum (Crn) + Mg-chlorite (Chl I) + calcite (Cal) aggregates pseudomorphous after pre-Alpine spinel. PPL. (e) Margarite (Mrg) flakes radially grown around fine-grained aggregates of corundum (Crn) + Mg-chlorite (Chl I) + calcite (Cal) after spinel. (f) Pre-Alpine spinel (Spl) + Alpine rutile (Rt) and corundum (Crn) partially converted to lath-shaped högbomite (Hög) + ilmenite (Ilm II). PPL. (a), (b), (c), (d) and (f) modified from Castelli *et al.* (2007).

Table 2

Representative analyses of selected minerals from the BIU dolomite marble

| | Spinel | | | | Ilmenite | | | Corundum | | Chlorite I | Chlorite II | Högbomite | | Margarite |
| | core | core | rim | rim | Ilm I | Ilm I | Ilm II | core | rim | | | | | |
	1Spl56*	1Spl61	1Spl57r*	1Spl64	1Ilm45*	1Ilm62	6Ilm20	6Cor10c	6Cor1r	11Chl77	11Chl78r	6Hog42c	6Hog13c	Marg81
SiO$_2$	0.48	0.89	0.24	0.67	0.34	0.12	0.15	0.00	0.00	31.27	28.37	0.00	0.00	33.64
TiO$_2$	0.00	0.00	0.00	0.08	56.18	56.31	52.54	0.20	0.98	0.00	0.00	10.44	10.52	0.12
Cr$_2$O$_3$	-	-	-	-	-	-	-	0.05	-	-	-	0.03	0.05	-
Al$_2$O$_3$	67.88	68.97	67.59	67.52	0.01	0.08	0.03	99.45	97.82	21.83	23.87	65.54	64.52	49.24
Fe$_2$O$_3$	1.33	0.00	0.00	0.00	0.00	0.00	3.19	0.06	0.52	0.00	0.00	0.00	0.00	0.00
FeO	6.23	6.78	12.57	12.37	38.04	39.16	40.99	0.00	0.00	1.81	9.41	9.41	13.63	0.23
MnO	0.00	0.15	0.13	0.00	0.22	0.58	0.38	0.16	0.02	0.00	0.00	0.17	0.00	0.04
MgO	24.23	23.61	19.72	19.80	5.32	3.81	1.96	0.20	0.21	31.90	25.75	14.01	10.75	0.00
CaO	0.13	0.00	0.06	0.02	0.00	0.08	0.18	0.05	0.02	0.09	0.13	0.00	0.08	10.22
Na$_2$O	-	-	-	-	0.63	0.39	0.50	0.08	0.14	0.00	0.09	0.29	0.73	2.16
K$_2$O	-	-	-	-	0.00	0.00	0.00	0.01	0.00	0.00	0.09	0.00	0.01	0.19
SUM	100.28		100.29	100.49	100.73	100.52	99.93	100.26	99.71	86.90	87.71	99.89	100.29	95.84
Si	0.012	0.022	0.006	0.017	0.008	0.003	0.004	0.000	0.000	5.891	5.499	0.000	0.000	4.387
Ti	0.000	0.000	0.000	0.001	1.009	1.029	0.977	0.003	0.013	0.000	0.000	0.206	0.210	0.012
Cr	-	-	-	-	-	-	-	0.001	-	-	-	0.001	0.001	-
Al	1.952	1.980	1.992	1.986	0.000	0.002	0.001	1.985	1.970	4.848	5.453	2.022	2.020	7.568
Fe^{3+}	0.024	0.000	0.000	0.000	0.000	0.000	0.060	0.001	0.007	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	0.127	0.138	0.263	0.258	0.760	0.795	0.849	0.000	0.000	0.285	1.526	0.206	0.303	0.025
Mn	0.000	0.003	0.003	0.000	0.005	0.012	0.008	0.002	0.000	0.000	0.000	0.004	0.000	0.004
Mg	0.881	0.857	0.735	0.737	0.189	0.138	0.072	0.005	0.005	8.958	7.440	0.546	0.426	0.000
Ca	0.003	0.000	0.002	0.001	0.000	0.002	0.005	0.001	0.000	0.018	0.028	0.000	0.002	1.428
Na	-	-	-	-	0.029	0.019	0.024	0.002	0.005	0.000	0.033	0.015	0.038	0.545
K	-	-	-	-	0.000	0.000	0.000	0.000	0.000	0.000	0.021	0.000	0.000	0.031
SUM	3.000	3.000	3.000	3.000	2.000	2.000	2.000	2.000	2.000	20.000	20.000	3.000	3.000	14.000

* Analyses from Castelli *et al.* (2007). Structural formulae are calculated on the basis of 3 cations and 4 oxygens for Fe-Ti-Mg oxides, 2 cations and 3 oxygens for corundum and ilmenite, 20 cations and 28 oxygens and 16 OH for chlorite, 14 cations and 22 oxygens and 4 OH for margarite.
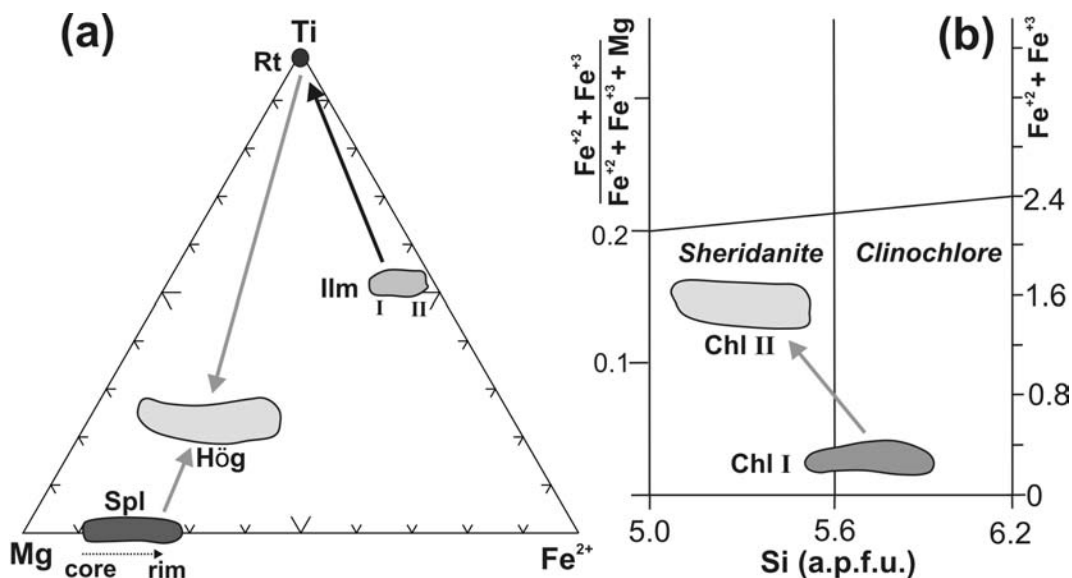
Fig. 4 – Compositional fields for ilmenite, högbomite, spinel and rutile (a) and chlorites (b) from the studied dolomite marble, plotted in the Mg-Ti-Fe^{2+} diagram and the Si *vs* X(Fe$_{tot}$) and Fe$_{tot}$ diagram (Hey, 1954), respectively. Pre-Alpine ilmenite (Ilm I) was replaced by rutile during the UHP Alpine stage (black arrow); högbomite formed after Rt + Spl, and Chl II grew around Chl I during the Alpine retrograde stages (grey arrows). Modified from Castelli *et al.* (2007).

Spl$_{74}$Hc$_{26}$ in the rim (Fig. 4a; Table 2). The relict pre-Alpine ilmenite (Ilm I) is Mg-rich with 15 to 20 mol.% geikielite, whereas the Alpine ilmenite (Ilm II) is characterized by lower Mg-content (7–10 mol% of geikielite) than pre-Alpine Ilm I.

Högbomite crystals [general formula (Mg,Fe,Ti)$_2$O$_4$], associated with spinel, corundum, rutile and Alpine ilmenite (Ilm II), are almost unzoned, though their Mg/(Mg+Fe^{+2}) ratio ranges from 0.57 to 0.87 in crystals pertaining to different microdomains (Fig. 4a and Table 2). The Ti contents (0.38 < Ti < 0.50 a.p.f.u. on the basis of 8 oxygens) are among the highest ever reported in the literature (e.g. Sengupta *et al.*, 2004, with ref.). Micro-Raman spectra acquired from two högbomite crystals characterized by a Mg/(Mg+Fe^{+2}) ratio of 0.58 and 0.73 respectively, are very similar (Fig. 5). Tsunogae and Santosh (2005) reported micro-Raman spectra of two högbomite crystals with an Mg/(Mg+Fe^{+2}) ratio similar to that of högbomite from marble DM1171, but with a lower TiO$_2$ content (< 0.1 wt% for Manavadi högbomite and 5.7 wt% for Rajapalaiyam högbomite). The three main peaks for Dora-Maira högbomite occur at 868-870, 708-710 and 507-508 cm^{-1}, respectively.

The same three peaks at 846, 723 and 529 cm^{-1} occur in the Rajapalaiyam högbomite, whereas in the Manavadi sample only the 855 and 556 cm^{-1} peaks are observed. As the Manavadi högbomite is Ti-free, it may be inferred that the 708-723 cm^{-1} peak, absent in its spectrum, is related to the Ti-O vibrations. On the whole, the spectra for the Dora-Maira högbomite are comparable with those reported by Tsunogae and Santosh (2005), being the shifts in the peak positions probably due to the differences in chemical compositions.

Corundum in the pseudomorphs after spinel is almost pure, and its deeper blue colour at the contact with rutile is due to the presence of Ti (Ti > 0.01 a.p.f.u. on the basis of 3 oxygens) (Table 2).

Two generations of chlorite have been observed, belonging to the Alpine UHP (Chl I) and retrograde (Chl II) assemblages, respectively. They differ in both grain size and composition. The finer grained Chl I mostly plots in the clinochlore field of Hey (1954) and has X_{Mg} = 0.97; the coarser grained Chl II is a sheridanite, with 0.83 < X_{Mg} < 0.85 (Fig. 4b). Margarite flakes, mainly developed at expense of corundum (+ Chl I), display significant but variable amounts of Na, with up to Na/(Na+Ca) = 0.28.
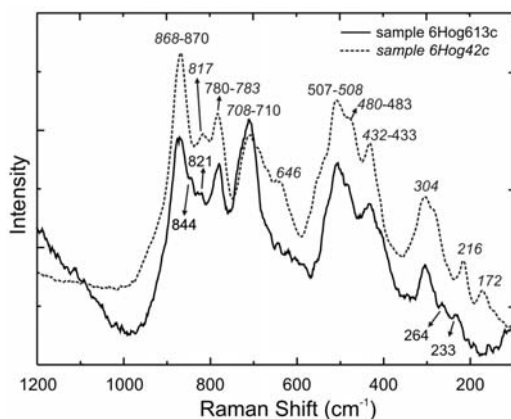
Fig. 5 – Micro-Raman spectra of two högbomite crystals with a X_{Mg} of 0.58 (6Hog13c) and 0.73 (6Hog42c), respectively (complete chemical data are given in Table 2).

Two carbonates are present in the studied marble: the relict pre-Alpine dolomite is homogeneous in composition [X_{Dol} = 0.98, Mg/(Mg+Fe^{2+}) = 0.98]; calcite partially replacing dolomite at the rim and along fractures is almost pure calcite [X_{Cal} = 0.98, Mg/(Mg+Fe^{2+}) = 0.80 on average].

ESTIMATE OF THE PRE-ALPINE P-T-X(CO$_2$) CONDITIONS

Based on microstructural relationships and mineral chemistries, the mineral assemblages occurring in the studied marble indicate different re-equilibration stages that occurred during both pre-Alpine and Alpine metamorphisms (Table 1). We will focus here on its pre-Alpine P-T-X(CO$_2$) evolution, as the Alpine evolution has been described in detail by Castelli *et al.* (2007).

The pre-Alpine, spinel-bearing assemblage could be referred either to the regional amphibolite-facies event of Variscan age (recorded in the BIU paraschists), or to the thermal metamorphic event linked to the intrusion of late-Variscan granitoids, as suggested by Compagnoni *et al.* (1995). The late-Variscan contact metamorphic event in the paraschists has been roughly estimated to have occurred at temperatures that are similar to those of the Variscan amphibolite-facies regional event, but at lower pressures for the widespread occurrence

of contact metamorphic andalusite and cordierite in the paraschists (e.g. Compagnoni *et al.*, 1995; Compagnoni and Rolfo, 2003). The pre-Alpine P-T path reconstructed for the Variscan, amphibolite-facies metamorphism of the BIU (Compagnoni *et al.*, 1995; Compagnoni and Rolfo, 2003; and Fig. 6a) will be used in the following as a reference P-T frame.

To model mineral assemblages and fluid compositions in the studied marble during its pre-Alpine metamorphic evolution, the approach of Connolly and Trommsdorff (1991) has been adopted. This approach consists of projecting univariant phase equilibria as a function of pressure and temperature and fluid composition onto a P-T coordinate frame (cf. Baker *et al.*, 1991; Carmichael, 1991). Details on the calculation of phase equilibria in the CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O-CO$_2$ (CMAS*HC*) system and the resulting petrogenetic grid are reported in Castelli *et al.* (2007, Fig. 9). Focusing on both fluid-absent and fluid-present univariant reactions modelled by Castelli *et al.* (2007) at amphibolite- to granulite-facies conditions, a new petrogenetic grid for the same model system has been calculated, assuming end-member composition of all phases but spinel (Fig. 6b). Thermodynamic properties of spinel (Holland and Powell, 1998, revised version 2002) have been modified to match its real composition in order to ideally model the changes in its P-T-X(CO$_2$) 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 I); 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 phases (such as for anorthite and zoisite).

The P-T projection of Fig. 6b differs from the complete grid of Castelli *et al.* (2007, Fig. 9) in that it displays a moderate shift towards lower temperatures ($\Delta T \leq 15$°C, at constant pressure) of the invariant, Spl$_{ss}$-bearing assemblages. The fluid-saturated stability field of the Cal + Spl + Dol assemblage (including either zoisite or anorthite, see also Table 1 and the petrography section) overlaps the estimated P-T path, confirming the relict, pre-Alpine nature of the above mineral assemblage. The lack of relict pre-Alpine reactants and products
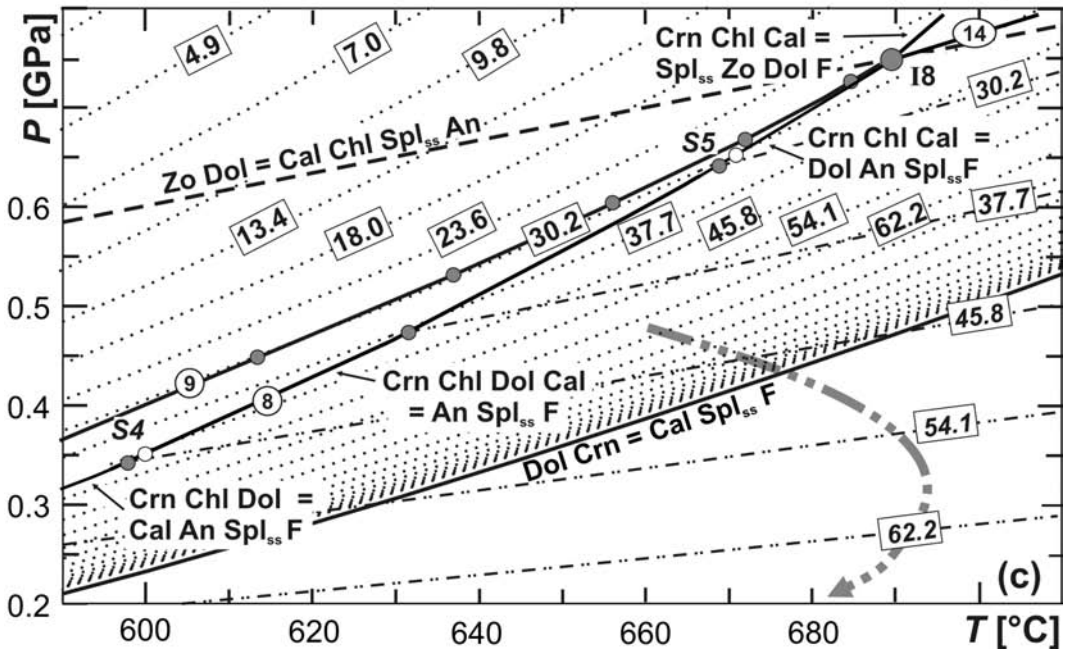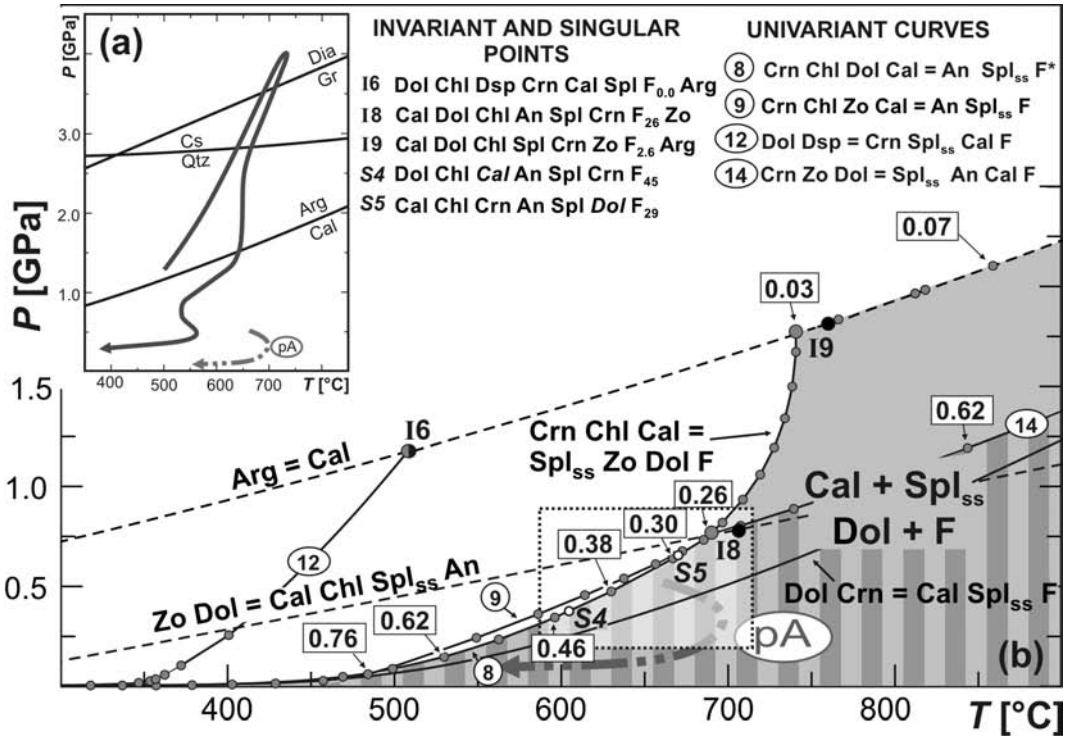
(spinel and dolomite excepted with reference to the model CMAS*HC* system) prevents recognition of the actual spinel-producing reaction(s). However, two possible prograde reactions can be envisaged. The first, anorthite-producing reaction is suggested by the *P-T* path crossing the degenerate univariant equilibrium assemblage Cal + Dol + Chl + Crn + An + Spl$_{ss}$ + F (curve 8 in Fig. 6b) in the *P-T-X*(CO$_2$) region between S4 and S5 singular points. This would imply Crn + Chl + Dol + Cal as reactants to produce An + Spl$_{ss}$ + F (with a modelled equilibrium fluid composition of about 35 mol% CO$_2$). A more probable option is the Dol + Crn = Cal + Spl$_{ss}$ + F reaction as modelled in Fig. 6c for both pure CO$_2$ and variable H$_2$O-CO$_2$ fluid compositions. In the *P-T* region of pre-Alpine path the modelled equilibrium fluid composition for this reaction has CO$_2$ > 60 mol%.

Discussion

The *P-T* conditions suggested by Compagnoni *et al.* (1995) and Compagnoni and Rolfo (2003) for the pre-Alpine evolution of the BIU polymetamorphic complex (Fig. 6a) are compatible with the high-*T*, relic assemblage spinel + dolomite + calcite (± Ilm I) recognized in the dolomite marble. In spite of the lack of some pre-Alpine reactants and products, the *P-T-X*(CO$_2$) modelling suggests that the Dol + Crn = Cal + Spl + F decarbonation reaction is the most probable spinel-producing reaction during the pre-Alpine prograde path. The growth of spinel after corundum + dolomite has already been described by Jansen *et al.* (1978), that observed Mg-calcite II (low in Mg) + spinel as a reaction rim between Mg-calcite I (high in Mg) and relict corundum, in an aluminous dolomitic marble from Naxos (Greece). The fact that corundum + dolomite assemblages persist up to high temperatures of metamorphism (up to 700°C) was interpreted by Jansen *et al.* (1978) as an indication for the presence of CO$_2$-rich fluids. A similar spinel reaction rim between corundum and dolomite has been reported by Liati (1988) in a Crn-Zo-bearing marble from the Rhodopes (Greece).

A comparison of these pre-Alpine *P-T-X*(CO$_2$) estimates with the Alpine evolution inferred by Castelli *et al.* (2007) for the same dolomite marble shows that fluids produced by the modelled pre-Alpine reactions are significantly different from those released during the Alpine subduction. Not surprisingly, the pre-Alpine fluids are relatively enriched in CO$_2$, being produced by decarbonation reactions during a low-*P*, prograde evolution. Conversely, the UHP fluids are mainly aqueous

Fig. 6 – (previous page) (a) Pre-Alpine (pA) and Alpine *P-T* paths (dashed and continuous lines, respectively) estimated for the BIU polymetamorphic complex by Compagnoni *et al.* (1995) and Castelli *et al.* (2007). The Cal-Arg, Qtz-Cs and Gr-Dia equilibria are shown as reference.
(b) Fluid-present (solid curves) and fluid-absent (dashed curves) selected equilibria in the CMAS*HC* model system, including the phases An, Arg, Cal, Chl, Crn, Dol, Dsp, Mrg, Spl$_{ss}$, Zo, and a H$_2$O-CO$_2$ fluid phase (F) of variable composition (cf. Castelli *et al.*, 2007, Fig. 9), and limiting the stability field of the pre-Alpine assemblage Cal + Spl$_{ss}$ + Dol + F in the dolomite marble. Large and small grey circles are true invariant and pseudo-invariant (cf. Connolly, 1990) assemblages, respectively. End-member, spinel-bearing invariant points I6, I8 and I9 (large black circles) from Castelli *et al.* (2007, Fig. 9) are shown for comparison. Small empty circles are the singular points S4 and S5 occurring along the univariant equilibrium (8) that is marked by an asterisk. All reaction equations are written such that the high-*T* assemblage is on the right side. Approximate compositions (mol% CO$_2$) of the equilibrium fluid phase at the invariant and singular assemblages are given (phases whose coefficient vanishes at singular points are given in italics). Numbers in boxes are the *X*(CO$_2$) values of coexisting H$_2$O-CO$_2$ fluid at pseudo-invariant and at true invariant points, respectively. The Crn + Chl + Dol + Cal = An + Spl$_{ss}$ + F* (curve 8) and the Crn + Chl + Cal = Spl$_{ss}$ + Zo + Dol + F equilibria limit the Cal + Spl$_{ss}$ + Dol + F (+ An) stability field (pale-grey field with dark-grey pattern) that also overlaps the low-pressure portion of the Cal + Spl$_{ss}$ + Dol + F (+ Zo) stability field (pale-grey field). The pre-Alpine (pA: dotted-dash, arrowed curve) *P-T* path is from Fig. 6a.
(c) Enlargement of the inset in Fig. 6b, showing details of univariant (solid curves) and pseudo-univariant (dotted and dashed-dotted curves) assemblages at pre-Alpine *P-T-X*(CO$_2$) conditions. Each pseudo-univariant assemblage includes two fluid pseudocompounds and represent fluid isopleths of the univariant assemblage for which the approximated fluid composition (number in boxes) is given as mol% CO$_2$ averaging those of the two pseudocompounds (Connolly and Trommsdorff, 1991). Dotted pseudo-univariant curves show the shift, at higher *T*, of the Dol + Crn + Cal + Spl$_{ss}$ + F assemblage with increasing *X*(CO$_2$). Dashed-dotted curves locate the pseudo-univariant Dol + An + Cal + Chl + Spl$_{ss}$ + F assemblage and emanate at different *X*(CO$_2$) compositions from the pseudo-invariant points occurring along the Crn + Chl + Dol + Cal = An + Spl$_{ss}$ + F equilibrium (curve 8). Other elements as in (b).

fluids with very low $X(CO_2)$ in agreement with other occurrences in metacarbonates (e.g. Franz and Spear, 1983; Castelli, 1991; Wang and Liou, 1993; Kato *et al.*, 1997; Ogasawara *et al.*, 1998; Omori *et al.*, 1998; Manning, 2004) and in agreement with Kerrick and Connolly (2001) who modelled very little devolatilization of carbonate rocks upon subduction.

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