Pressure-temperature evaluation of a contact metamorphic mineral assemblage from the Larderello geothermal field, Italy

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ABSTRACT. — The emplacement of post-Miocene granitic intrusions below the Larderello-Travale geothermal area, generally at depths $\geq$3000 m below the present ground-level (b.g.l.) led to contact metamorphic phenomena in the surrounding rocks. In a gneiss cored at 3450 m b.g.l. from geothermal well badia 1B (south-west of the town of Larderello), contact metamorphism is shown by the crystallization of post-tectonic biotite and the development of a high-temperature mineral assemblage (andalusite, cordierite, muscovite, tourmaline, apatite, titanite). Fluid inclusion and mineral chemistry data, together with computed mineral equilibria, allowed evaluation of pressure - temperature conditions and fluid characteristics during contact metamorphism. Electron microprobe analyses showed that cordierite is Mg-rich (Mg-cordierite ca. 66%), whereas the annite and phlogopite end-members are present in biotite in similar proportions. Tourmaline compositions are dominated by the schorl-dravite solid solution. Tourmalines are often zoned, with cores enriched in Na and Fe and depleted in Al in comparison with the rims. Microthermometric and Raman analyses on the fluid inclusions in quartz and tourmaline crystals revealed that the fluid trapped during contact metamorphism was low-density (0.30-0.35 g/cm^3) and water-rich (65.9-70.7 mol%), containing significant amounts of CO_2 (9.4-15.7 mol%) and CH_4 (14.9-19.4 mol%). The carbonic phases probably originated from interactions between fluid and graphite present in the Larderello-Travale basement rocks. Fluid inclusion isochores were constructed and an equilibrium curve was developed (calculated using thermodynamic data in the KFMASH system) for a mineral reaction involving quartz and contact phases (andalusite, muscovite and mineral solid solutions: biotite and cordierite). The intersections of the fluid inclusion isochores and this equilibrium curve provide the ranges of temperature (520-545°C) and pressure (940-1140 bar) of the contact metamorphism. Lastly, geothermometric measurements based on the Mg/Fe ratio in biotite and tourmaline indicated a temperature range (525-550°C) consistent with that evaluated for contact metamorphism.

RIASSUNTO. — Nel sottosuolo dell'area geotermica di Larderello-Travale, in seguito alla messa in posto di plutoni granitici di età post-Miocenica, a profondità in genere $\geq$3000 m sotto il piano di campagna, le rocce incassanti sono state soggette a fenomeni di metamorfismo di contatto. In uno gneiss perforato nel pozzo geotermico Badia 1B (a sud-ovest di Larderello) alla profondità di 3450 m sotto il piano di campagna, l'effetto del metamorfismo di contatto è evidenziato dalla

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cristallizzazione di biotite statica e dallo sviluppo di una associazione mineralogica di alta temperatura (andalusite, cordierite, muscovite, tormalina, apatite e titanite). Le analisi delle inclusioni fluide e lo studio della composizione di alcuni minerali, insieme a dati sugli equilibri mineralogici, hanno consentito di determinare le condizioni di temperatura e pressione e la composizione del fluido presente durante l'evento di metamorfismo di contatto. Le analisi ottenute con la microsonda hanno mostrato che nella cordierite prevale significativamente il termine magnesiaco (Mg-cordierite ca. 65%), mentre nella biotite annite e flogopite sono in proporzioni simili. La tormalina analizzata è prevalentemente costitutita da una soluzione solida sciorlo-dravite, ed è spesso zonata con una zona interna arricchita di Na e Fe ed impoverita in Al rispetto ai bordi. Le analisi microtermometriche e Raman sulle inclusioni fluide presenti all'interno di cristalli di quarzo e tormalina hanno evidenziato che il fluido intrappolato durante il metamorfismo di contatto è un fluido con densità tra 0,30 e 0,35 g/cm^3, costituito in gran parte da acqua (65,9-70,7 mol%), e contenente significative quantità di CO_2 (9,4-15,7 mol%) e CH_4 (14,9-19,4 mol%). L'origine delle fasi carboniche può essere ricercata nell'interazione tra il fluido e la grafite delle rocce del basamento dell'area di Larderello-Travale. Alcuni programmi di calcolo hanno consentito di determinare le isocore delle inclusioni fluide ed una curva di equilibrio (sulla base dei dati termodinamici nel sistema KFMASH) per una reazione mineralogica comprendente quarzo e le fasi di metamorfismo di contatto (andalusite, muscovite e le soluzioni solide: biotite e cordierite). L'intersezione delle isocore con questa curva di equilibrio suggerisce che il metamorfismo di contatto si è sviluppato a temperature comprese tra 520 e 545°C ed a pressioni tra 940 e 1140 bar. Infine, l'applicazione del geotermometro basato sul rapporto Mg/Fe nella biotite e tormalina ha fornito un intervallo di temperatura (525-550°C), coerente con quello stimato per il metamorfismo di contatto.

Introduction

In the Larderello-Travale geothermal area, several wells have been drilled by ERGA S.p.A. (Energie Rinnovabili Geotermiche e Alternative) of the ENEL group (Italian Electricity Board) to 3.5-4.5 km below ground-level (b.g.l.), with the aim of finding deep productive horizons of hot steam. These wells cross polymetamorphic units of Paleozoic age, which rarely outcrop in the Northern Apennines (Bagnoli *et al.*, 1979). Some wells (e.g. Monteverdi 7, VC11, Radicondoli 26, Carboli Cbis) also found aplite and leucogranite dykes, and two-mica granites at depths >2.5 km b.g.l., with radiometric ages between 3.8 and 2.5 Ma (Villa and Puxeddu, 1994; Villa *et al.*, 1997) or around 1Ma (Ruggieri *et al.*, 1999b). These igneous rocks are probably more or less evolved products of post-Miocene intrusions which were emplaced at different times beneath the Larderello-Travale geothermal region. Geophysical data also suggest that a partially molten intrusive body exists at a depth >7 km b.g.l. in the Larderello area (Foley *et al.*, 1992; Batini *et al.*, 1995).

Core samples and cuttings collected from several deep wells contain high- to medium-temperature mineral assemblages characterized by biotite, plagioclase and variable amounts of cordierite, andalusite, K-feldspar, muscovite, tourmaline and, more rarely, corundum. Franceschini (1994) related the development of these assemblages to the contact metamorphism which arose during the emplacement of the post-Miocene intrusions. However, on the basis of petrographic and microstructural studies, Puxeddu (1984), Elter and Pandeli (1990), Bertini *et al.* (1994), Gianelli (1994) and Pandeli *et al.* (1994) distinguished several different metamorphic assemblages containing all or some of the above-mentioned minerals: one or two related to pre-Triassic (Hercynian) metamorphic event(s), and a post-tectonic assemblage which developed during the contact metamorphic Pliocene imprint.

On the basis of metamorphic reactions, Franceschini (1994) suggested that the post-Miocene contact metamorphism developed at a pressure <3000 bar and a maximum temperature around 700°C. Previous fluid inclusion studies also provided some information on high-temperature fluid circulation related to granite emplacement.
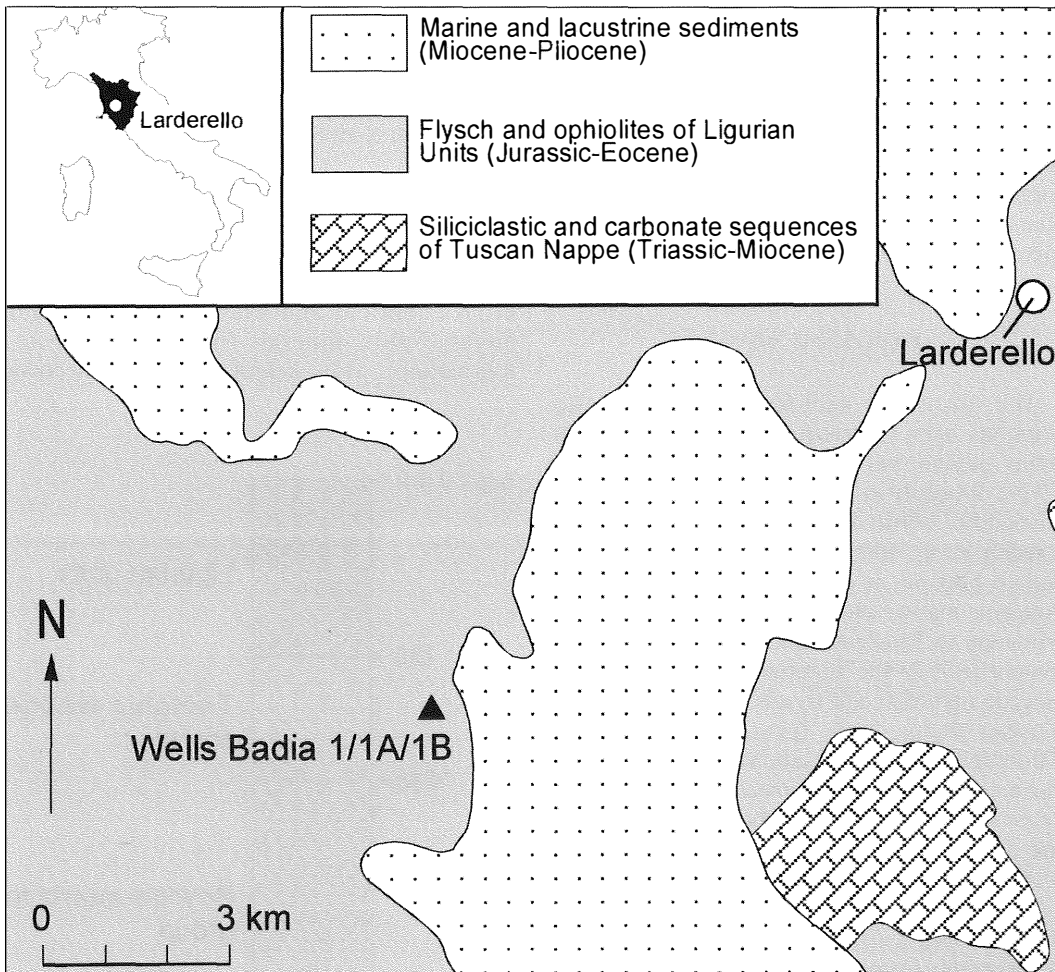
Fig. 1 – Geological sketch-map of the area around drilling site of wells Badia 1, 1A and 1B, modified after Gianelli and Bertini (1993).

During this stage, two main types of fluids were present within and around the intrusions: high-salinity Na-Li-rich liquids of magmatic origin, and aqueous-carbonic fluids resulting from heating of the Paleozoic rocks (locally C-rich) during the contact metamorphism (Valori *et al.*, 1992; Cathelineau *et al.*, 1994). These fluids circulated under lithostatic pressure and at elevated temperatures (425-690°C), whereas the subsequent stage of hydrothermal activity was characterized by the presence of fluids of mainly meteoric origin, with temperatures usually ≤400°C, under hydrostatic pressure (Cathelineau *et al.*, 1989; Valori *et al.*, 1992; Ruggieri *et al.*, 1999a). Further decompression of the system produced the present-day vapor-dominated condition.

A more precise estimate of the pressure-temperature conditions and the composition of the fluid present during contact metamorphism may be obtained by combining mineral equilibria with fluid inclusion data. We therefore

carried out a detailed study on a post-tectonic high-temperature mineral assemblage found in a core-sample drilled in well Badia 1B (fig. 1). In particular, we carried out petrographic observations and electron microprobe analyses on the minerals which developed during contact metamorphism, and microthermometric and Raman analyses on fluid inclusions found in the quartz of the core-sample.

GEOLOGICAL SETTING

The subsurface geology of the Larderello area has been reconstructed using data from many geothermal deep wells (Gianelli *et al.*, 1978; Bagnoli *et al.*, 1979; Cavarretta and Puxeddu, 1990; Elter and Pandeli, 1990; Pandeli *et al.*, 1994; Baldi *et al.*, 1995). From top to bottom, it consists of: 1) a cover of Neogene marine and lacustrine sediments (Late Miocene to Pliocene sands, clays, marls and evaporites); 2) the Ligurian units (Jurassic to Eocene ophiolite and flysch sequences); 3) the Tuscan Nappe (Late Triassic to Oligocene-Miocene siliciclastic, carbonate and evaporitic formations); the uppermost formations of the sequence, and locally the whole Tuscan Nappe, are usually completely missing; 4) the tectonic wedge complex, incorporating thrusted stacks of: *a)* carbonate and evaporite formations of the Tuscan Nappe, *b)* the Middle-Upper Triassic «Verrucano formation», and *c)* the Paleozoic formations; 5) three metamorphic groups, including a «phyllite-quartzite group» of Paleozoic age, a «micaschist group» and a «gneiss group», thought to be of Paleozoic to Precambrian age. Post-Miocene granites and aplites usually intrude the «micaschist» and «gneiss groups», while the post-tectonic contact metamorphism may also affect the «phyllite-quartzite group». The thickness of the contact aureole has been estimated up to 600 m by Cavarretta and Puxeddu (1990) or up to 1500 m by Franceschini (1994).

The three wells Badia 1, 1A, and 1B are directional, and start from the same drilling site. The surface geology of the area around

them and the stratigraphy of well Badia 1B are illustrated in figs. 1 and 2. The studied sample was cored within the «gneiss group» at a depth of about 3450 m b.g.l., where the present-day temperature is around 350°C.

STUDY METHODS

Optical study was followed by microchemical analyses of some contact metamorphic minerals (biotite, cordierite, tourmaline), using a Jeol JXA 8600 electron
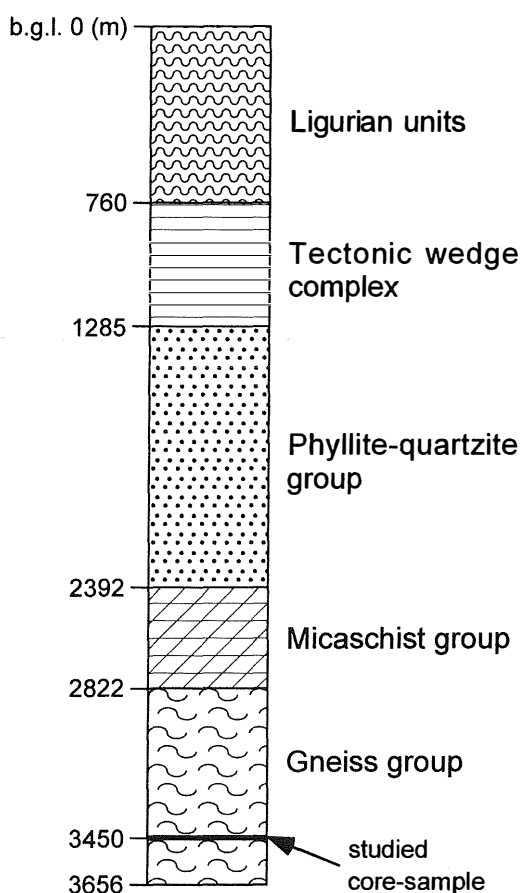

Fig. 2 – Stratigraphy of well Badia 1B and location of studied core-sample.

microprobe, at the CNR - Centro di Studio per la Minerogenesi e la Geochimica Applicata in Florence. Operating conditions were: 15kV accelerating voltage, 10 nA excitation current, beam width <5 μm.

Pressure-temperature mineral equilibria in the KFMASH (K_2O, FeO, MgO, Al_2O_3, SiO_2, H_2O) system were computed using the PeRpLeX code of Connoly (1990, 1995) and thermodynamic values from Holland and Powell's thermodynamic data set (1990, updated to 1998). SiO_2 and H_2O were considered in excess.

Microthermometric studies of fluid inclusions were performed on doubly polished wafers (100-200 μm thick) of the core-sample, using a LINKAM THMSG 600 heating-freezing stage. Stage calibration was carried out using pure CO_2 natural inclusions, pure H_2O synthetic fluid inclusions at T ≤ 0°C, and synthetic organic and inorganic melting point standards for T > 0°C. The accuracy of the measurements is estimated at ± 0.2°C for temperatures < 20°C and ± 2.0°C for high temperatures (100-350°C). Volumetric proportions between volatile and aqueous phases in the inclusions were estimated optically at room temperature. Molar fractions of CH_4, CO_2 and N_2 in the gas phase and the Cl^- molality in the liquid phase were determined by micro-Raman analyses in single inclusions using a (Labram, Dilor) Raman micro-spectrometer equipped with a CCD detector, at UMR G2R-7655 and CREGU (Vandoeuvre les Nancy, France). Measurements were performed with 514.5-nm radiation emitted from an Ar^+ (Spectraphysics) laser. Laser power was 500 mW and spectral resolution 2 cm^{-1}. Five accumulations of 5- or 10-second counts allowed acquisition of high-quality Raman spectra for each gas component.

Bulk composition and density of fluid inclusions were calculated using Bakker's (1997) computer programs. Isochores of fluid inclusions were calculated using Bakker's (1999) method, based on the adaptation of Bowers and Helgeson's (1983) equation of state to the H_2O-CO_2-CH_4-N_2-NaCl system.

CONTACT METAMORPHIC ASSEMBLAGE

Optical observations

The core sample drilled at 3450 m b.g.l. shows the typical features of rocks of the «gneiss group» as found in the deep wells of the Larderello area, i.e., only one well-defined penetrative schistosity which developed during a pre-Triassic (Hercynian) deformation event (Elter and Pandeli, 1990). In this sample, pre-Triassic minerals are mainly represented by synkinematic quartz, plagioclase and biotite, with minor muscovite and oxides. In particular, the Hercynian schistosity is displayed by biotite layers with lepidoblastic texture alternating with granoblastic bands of fine-to medium-grained quartz and plagioclase a few mm thick; more rarely, centimetric lenses of coarse quartz crystals also occur.

In the studied sample, the minerals which crystallised during contact metamorphism are biotite, andalusite, tourmaline and cordierite, with minor amounts of muscovite, titanite and apatite. Particularly evident is static neo-crystallization of abundant, widespread biotite and lesser amounts of muscovite. Small tourmaline crystals are also scattered throughout the sample, and are often associated with static biotite. In places, a contact metamorphic assemblage develops subparallel to the schistosity, and consists of variable proportions of post-tectonic biotite, muscovite, cordierite, andalusite and tourmaline (figs. 3A, 3B, 3C). Contact metamorphic minerals appear in textural equilibrium. Cordierite, andalusite, biotite and muscovite are partially replaced by a secondary fine-grained clay mineral (possibly illite) (fig. 3A). Sporadically, biotite is also altered to late chlorite.

Mineral chemistry

Chemical analyses and calculated atoms per formula unit (*apfu*) of cordierite, biotite and tourmaline are shown in Table 1.

Cordierite is characterized by relatively constant compositions, with Mg/(Mg+Fe)

TABLE 1

Representative microprobe analyses of cordierite, biotite and tourmaline in contact metamorphic assemblage of sample cored at 3450 m b.g.l. in well Badia 1B.

|	Cordierite				Biotite					Tourmaline			
Oxides	Crd/1	Crd/4	Crd/5	Oxides	Bt/1	Bt/7	Bt/3	Bt/2	Oxides	Tm/4 core	Tm/2 rim	Tm/6 rim	Tm/5 rim
SiO_2	49.20	49.85	48.81	SiO_2	36.98	35.99	36.08	36.26	SiO_2	36.97	35.77	36.87	38.35
TiO_2	0.00	0.00	0.00	TiO_2	3.72	3.76	3.36	3.73	TiO_2	0.44	0.97	0.86	0.12
Al_2O_3	34.00	33.84	33.81	Al_2O_3	19.82	20.02	20.32	19.85	Al_2O_3	31.88	35.34	36.09	36.60
Cr_2O_3	0.00	0.02	0.00	Cr_2O_3	0.07	0.09	0.04	0.07	Cr_2O_3	0.04	0.10	0.08	0.00
FeO	7.95	7.52	8.35	FeO	17.64	17.61	18.43	17.98	FeO	8.85	5.93	5.41	5.79
MnO	0.32	0.41	0.39	MnO	0.31	0.31	0.25	0.28	MnO	0.00	0.03	0.01	0.02
MgO	8.12	8.29	8.04	MgO	10.29	9.14	8.90	9.61	MgO	6.46	6.03	6.35	5.57
CaO	0.03	0.00	0.03	CaO	0.08	0.02	0.03	0.12	CaO	0.19	0.76	0.86	0.13
Na_2O	0.14	0.29	0.32	Na_2O	0.09	0.13	0.09	0.10	Na_2O	2.10	1.40	1.49	1.12
K_2O	0.02	0.02	0.02	K_2O	9.88	9.81	9.04	9.27	K_2O	0.03	0.08	0.05	0.03
Total	99.78	100.24	99.77	Total	98.88	96.88	96.54	97.27	Total	86.96	86.41	88.07	87.73
pfu based on 18 oxygens				*apfu based on 22 oxygens*					*apfu based on 24.5 oxygens*				
Si	4.98	5.02	4.96	Si	5.37	5.34	5.36	5.35	Si	6.03	5.77	5.81	6.02
Al	4.06	4.02	4.05	Al^{IV}	2.63	2.66	2.64	2.65	Al^T	0.00	0.23	0.19	0.00
Cr	0.00	0.00	0.00	Al^{VI}	0.76	0.85	0.93	0.81	Al^Z	6.00	5.99	5.99	6.00
Ti	0.00	0.00	0.00	Cr	0.01	0.01	0.00	0.01	Cr	0.00	0.01	0.01	0.00
Fe^{2+}	0.67	0.63	0.71	Fe^{2+}	2.14	2.19	2.29	2.22	Fe^{3+}	0.00	0.00	0.00	0.00
Mn	0.03	0.03	0.03	Mn	0.04	0.04	0.03	0.04	Al^Y	0.13	0.51	0.53	0.78
Mg	1.23	1.24	1.22	Mg	2.23	2.02	1.97	2.11	Fe^{2+}	1.21	0.80	0.71	0.76
Ca	0.00	0.00	0.00	Ti	0.41	0.42	0.38	0.41	Mn	0.00	0.00	0.00	0.00
Na	0.03	0.06	0.06	Ca	0.01	0.00	0.00	0.02	Mg	1.57	1.45	1.49	1.30
K	0.00	0.00	0.00	Na	0.03	0.04	0.03	0.03	Ti	0.05	0.12	0.10	0.01
				K	1.83	1.86	1.71	1.75	Ca	0.03	0.13	0.15	0.02
									Na	0.66	0.44	0.46	0.34
									K	0.01	0.02	0.01	0.01

apfu=atoms per formula unit.
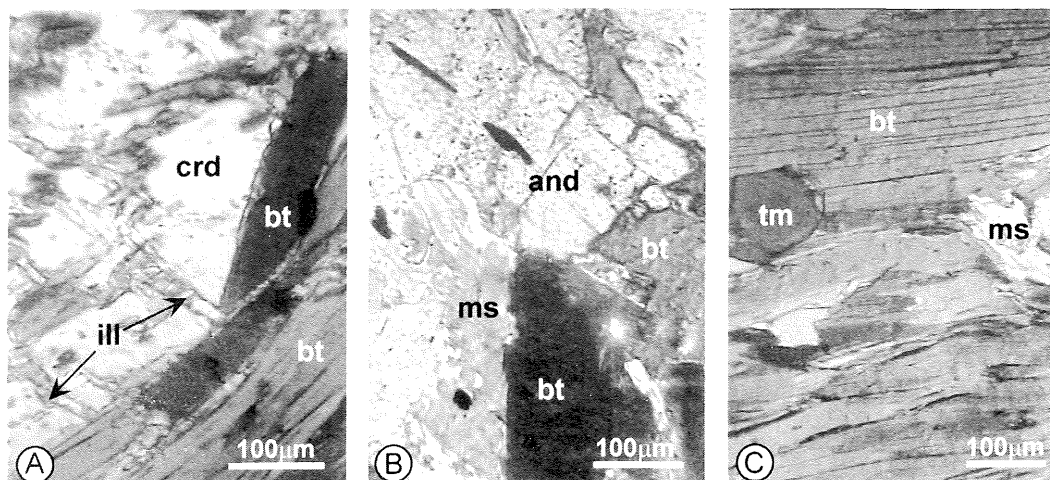
Fig. 3 – Photographs of contact metamorphic assemblage showing: A) cordierite (crd) and biotite (bt) association; a late clay mineral, possibly illite (ill), replaces and fills fractures present in cordierite; B) andalusite (and), muscovite (ms) and biotite (bt); C) biotite (bt), muscovite (ms) and a tourmaline (tm) crystals enclosed in biotite. All photomicrographs taken in trasmitted light with crossed polars.

atomic ratios between 0.63 and 0.66. Hence, in the studied sample, this mineral is a solid solution between about 2/3 Mg-cordierite and 1/3 Fe-cordierite. The sum of the oxides, about 100 wt% (Table 1), suggests that H_2O was scarce or absent.

Biotite compositional variations may be ascribed to Fe-Mg substitution and replacement of Al^{VI} by (Fe,Mg), balanced by replacement of Al^{IV} by Si (Tschermak substitution). The Mg/Fe ratio varies between 0.88 and 1.04, indicating approximately similar proportions of phlogopite and annite end-members.

Tourmaline is usually chemically zoned. Crystal cores are enriched in Na and Fe and depleted in Al in comparison with rims (Table 1). This chemical variation may be related to substitution of Fe by Al in the Y site and the coupled loss of Na from the X site for charge balance reasons (i.e., alkali-deficient substitution); Fe-Mg and Tschermak substitutions explain the Fe, Mg, Al and Si variations within the crystal rims. In general, these tourmalines consist of schorl-dravite solid solutions similar to those previously reported for magmatic tourmalines found in the Larderello geothermal field (Cavarretta and Puxeddu, 1990). However, the significant vacancy in the X site suggests that a foitite component may be present.

FLUID INCLUSIONS

Description of fluid inclusions

Microthermometric studies were carried out on fluid inclusions trapped in the crystals of the quartz lenses of the gneiss. One fluid inclusion, suitable for microthermometric analysis, was also found in a tourmaline crystal of the contact metamorphic assemblage. All observed fluid inclusions are vapor-rich; at room temperature, they appear to be two-phase or single-phase, but in the latter case some amounts of liquid water, not visible under the optical microscope, may be present. Vapor-rich inclusions in quartz usually occur along secondary fluid inclusion trails (fig. 4). The single fluid inclusion studied in tourmaline and the few in quartz are isolated (fig. 4). Their size is usually between 10 and 70
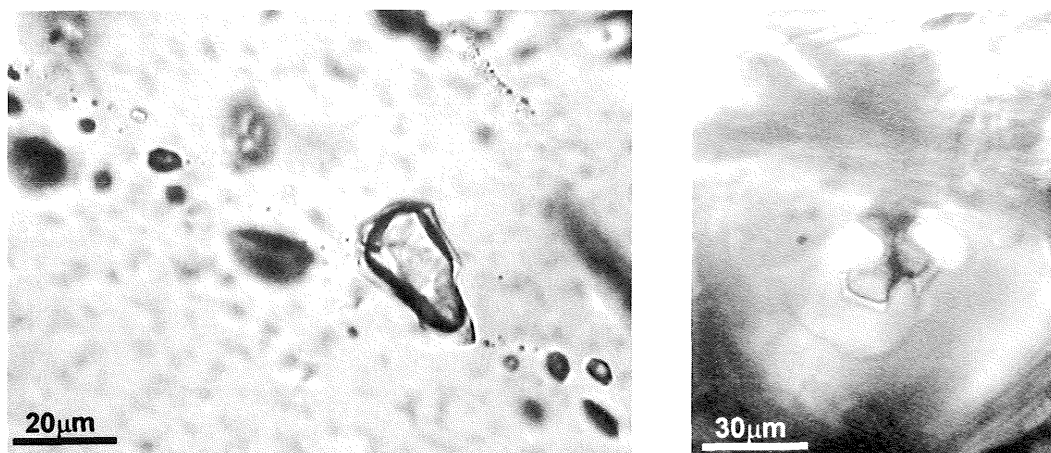
Fig. 4 – Photomicrographs of fluid inclusions. Left: a vapor-rich fluid inclusion along a secondary inclusion trail; right: an isolated (primary) inclusion in tourmaline.

mm. Vapor-rich inclusions were also observed in andalusite crystals. However, because of their small size (usually <5 µm) and the poor optical quality of andalusite, microthermometric analyses on fluid inclusions trapped in this mineral could not be performed.

Microthermometric results

All observed inclusions (two-phase and single-phase) show the formation of clathrate and solid CO_2 on cooling (to about –120°C). Clathrate nucleation in apparently single-phase inclusions also indicates that these inclusions contain an aqueous liquid, in addition to the carbonic phase.

During freezing runs, ice crystals could not be clearly distinguished from clathrate, so that final ice melting could not be recorded. The final melting temperature of the carbonic phase (T_{mCO_2}), final clathrate melting temperature (T_{mcl}) and total homogenization (T_h) of the two-phase inclusions are shown in fig. 5. The T_{mCO_2}, T_{mcl} and T_h of the isolated inclusions in quartz and tourmaline fall within the range of values recorded for inclusions found in secondary trails in quartz (fig. 5). In particular, T_{mCO2} is in the range –64.9 to –59.7°C, most of

the values being from –62 to –60°C (fig. 5A). These values are significantly lower than the melting temperature of pure CO_2 (–56.6°C), indicating the presence of volatile compounds other than CO_2, presumably CH_4 and N_2, in these inclusions. During cooling down to <-60°C, the formation in a few inclusions of a liquid carbonic phase could also be observed, which homogenized to the vapor phase in the presence of clathrate between –52 and –43°C. The T_{mcl} values are between 10.1 and 15.2°C, most ranging from 12 to 14°C (fig. 5B). Total homogenization always occurs in the vapor phase and ranges between 305 and 345°C, with many values falling between 310 and 330°C (fig. 5C). However, the T_h data must be regarded with some caution, as T_h measurements on vapor-rich inclusions may suffer from significant errors (Roedder, 1984; Sterner, 1992).

Raman analyses, bulk fluid composition and density

Table 2 shows the Cl⁻ concentrations in the liquid phase of selected fluid inclusions in quartz, calculated from Raman spectroscopy
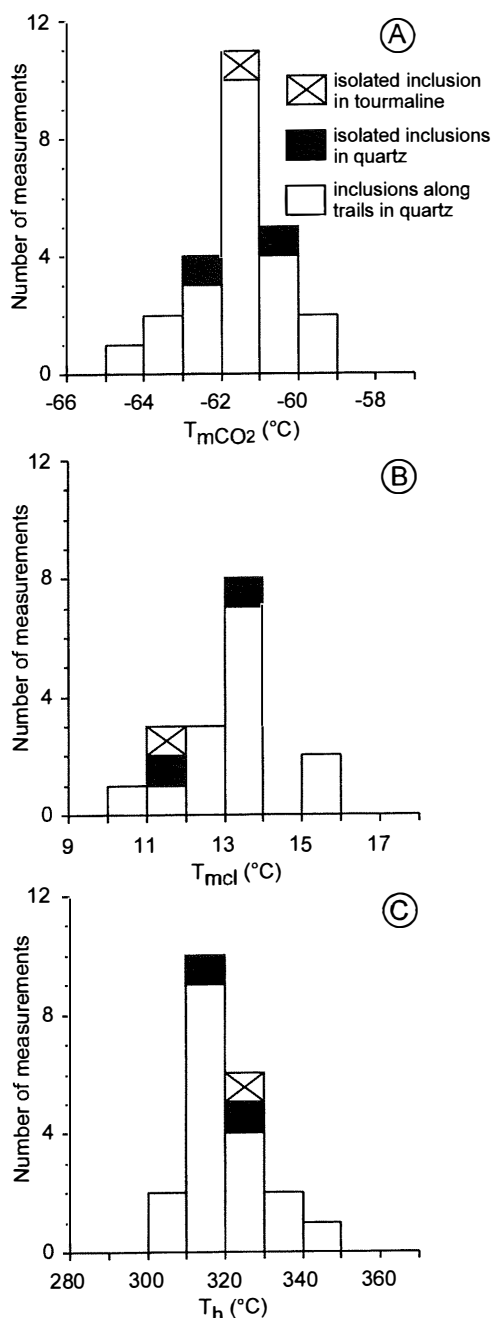
Fig. 5 – Histograms of: A) final melting temperature of carbonic phase (T_{mCO_2}), B) final clathrate melting temperature (T_{mcl}) and C) total homogenization (T_h) of studied inclusions in quartz and tourmaline.

analyses using the method described by Lhomme *et al.* (1999). The method is based on the measurement of some parameters related to the change in shape of the Raman peak of water due to the presence of Cl^- in the aqueous solution. Table 2 also lists Raman data on the volatile phase of the selected inclusions and the calculated densities and bulk compositions. Total dissolved salt contents, expresed as mol% of NaCl, were calculated from the Cl^- concentration. Bulk compositions and total fluid densities were computed according to the compositions of the volatile and aqueous phases, the volumetric proportions between volatile and aqueous phases (about 20% liquid and 80% gas), and T_{mcl} values (Bakker, 1997). Raman analyses confirmed that the volatile phase of the vapor-rich inclusions contains CH_4 and N_2 in addition to CO_2. In most cases, CH_4 (45.4-65.0 mol%) was higher than CO_2 (28.8-48.8 mol%), whereas N_2 was present in lower concentrations (5.7-10 mol%). Bulk composition is dominated by water, which represents more than 65 mol% of the total fluid, whereas the NaCl concentration in the total fluid is relatively modest: between 0.9 and 1.0 mol% (corresponding to 2.5-2.8 wt% of NaCl). Calculated fluid density ranges from 0.30 to 0.35 g/cm³.

DISCUSSION

The microthermometric and volumetric characteristics of the fluid inclusions in quartz lenses and tourmaline are relatively similar, suggesting that both minerals trapped the same type of fluid. According to the criteria of Roedder (1984), the isolated fluid inclusion found in tourmaline is of primary origin. As tourmaline formed during contact metamorphism, the fluid trapped in the primary inclusion represents the fluid present during crystallisation of contact metamorphic minerals. The secondary fluid inclusions in quartz lenses probably trapped the contact metamorphic fluid, which entered fractures in the pre-Triassic metamorphic quartz. The isolated inclusions in this mineral may be pre-

TABLE 2

Microthermometric and Raman analyses, and calculated bulk composition and density of selected fluid inclusions.

				Raman data								
				Gas composition (mol %)			Bulk fluid composition (mol %)					d
Inclusion	T_{mCO_2} (°C)	T_{mcl} (°C)	Cl (moles/kg)	CO_2	CH_4	N_2	H_2O	CO_2	CH_4	N_2	NaCl	(g/cm³)
BD-2	−61.7	13.9	0.8	48.8	45.4	5.7	65.9	15.7	15.7	1.9	0.9	0.35
BD-3	−61.4	12.9	0.8	32.4	57.5	10.0	70.7	9.8	15.8	2.7	1.0	0.30
BD-4	−61.8	13.7	0.8	40.8	50.5	8.7	67.1	13.7	15.5	2.7	1.0	0.33
BD-6	−62.6	13.7	0.8	28.8	65.0	6.2	68.3	9.4	19.4	1.8	1.0	0.31
BD-7	−62.2	13.1	0.8	34.8	56.8	8.3	70.0	10.7	16.0	2.3	1.0	0.31
BD-10	−61.9	13.0	0.8	38.6	53.7	7.7	70.2	11.8	14.9	2.1	1.0	0.31

T_{mCO_2}=final melting temperature of carbonic phase; T_{mcl}=final clathrate melting temperature; d=bulk density.

existing ones which leaked their original fluid and were refilled during contact metamorphism.

The chemical characteristics of the fluid inclusions trapped in the Badia 1B sample differ totally from those found in the upper part (depths of < 2500 m b.l.g.) of the Larderello-Travale geothermal field, and sporadically at greater depths. These are meteoric-derived fluids which entered the hydrothermal system after the early, high-temperature, contact-metamorphic and magmatic stage of fluid circulation (Valori *et al.*, 1992; Cathelineau *et al.*, 1994; Ruggieri *et al.*, 1999a), whereas the studied inclusions show compositions relatively similar to the low-density aqueous-carbonic fluids trapped in the inclusions in a core-sample of well Sasso 22 at 4027 m b.g.l., also interpreted by Cathelineau *et al.* (1994) as examples of early high-temperature fluids which formed during post-Miocene contact metamorphism.

The compositions of the fluid inclusions analysed by Raman spectroscopy indicate that the trapped contact metamorphic fluid is water-rich and aqueous-carbonic, with significant amounts of CH_4 (Table 2). The aqueous component may have resulted from devolatilisation reactions during the heating of the Larderello Paleozoic rocks. In agreement with Cathelineau *et al.* (1994), the CH_4-rich composition of the contact metamorphic aqueous-carbonic fluid may have derived from interactions, at temperatures of more than 400°C, between water and graphite, which is locally abundant in the Larderello Paleozoic rocks. As graphite was not observed in the studied sample, the contact metamorphic fluid may have been introduced into the area of well Badia 1B at 3450 m b.g.l. after water-graphite interactions had occurred in the surrounding rocks.

Graphite-saturated fluids trapped at relatively high-temperatures (>350°C) may precipitate graphite within fluid inclusions during cooling, resulting in significant modifications of fluid composition and density (Cesare, 1995). However, graphite was not detected in our fluid

inclusions, either by optical observation or by Raman analysis, indicating that the trapped fluid was undersaturated in this phase at the time of inclusion formation (and did not became saturated on cooling to room temperature), or fluid metastability conditions if graphite saturation was reached.

Pressure-temperature conditions during contact metamorphism were evaluated using fluid inclusion isochores and mineral reaction equilibria of contact metamorphic phases. The equilibria of the latter phases (andalusite, cordierite, biotite, muscovite) and pre-contact metamorphic quartz, which coexisted with contact metamorphic minerals during the thermal event, were calculated in the KFMASH systems for temperature and pressure ranges of 300-600°C and 0-2000 bar respectively. Computations were made considering variable compositions for the mineral solid solutions (biotite, cordierite), assuming that each solid solution was a component. Carbon was excluded because of the lack of solid phases containing it in the studied sample. However, fluid inclusion data indicate significant carbonic phases in the contact metamorphic fluid (average XCO_2 and XCH_4 are 12 mol% and 16 mol% respectively). These phases, although they do not take part in contact metamorphic reactions, can greatly modify H_2O activity. Jacobs and Kerrick (1981) showed that, compared with the binary H_2O-CO_2 system, a relatively small amount of CH_4 ($XCH_4 \leq 0.2$) in the H_2O-CO_2-CH_4 system causes only a slight modification of H_2O activity. Thus, for the calculation of phase equilibria, the activity of H_2O was computed for a H_2O-CO_2 fluid mixture (with non-ideal mixing conditions) with XCO_2 contents equal to the average XCO_2+XCH_4 (around 0.29 for a fluid constituted only of H_2O, CO_2 and CH_4).

The calculations generated more than 600 possible reactions. However, only one was characterized by the contemporaneous presence of the examined pure phases and mineral solid-solutions with compositions relatively similar to those of the analysed minerals. This reaction was: 15quartz + 12andalusite + 16biotite(phl:
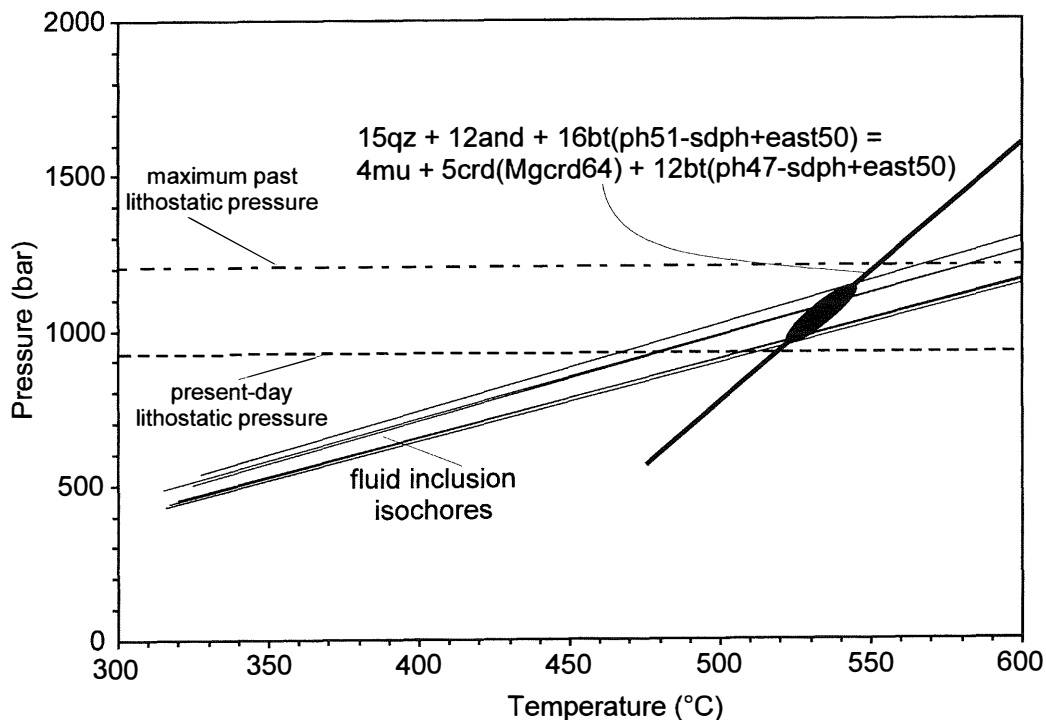
Fig. 6 – Pressure *vs* temperature diagram showing evaluated pressure-temperature conditions (black field) of contact metamorphism, as determined by fluid inclusion isochores and equilibrium curve (calculated in KFMASH system) for a mineral reaction involving quartz, andalusite, muscovite, and solid solutions of biotite and cordierite with compositions similar to those displayed by contact metamorphic biotite and cordierite. Present-day and maximum past lithostatic pressures are also shown. Mineral assemblage stable at high temperature is to right of the = sign of reaction. qz = quartz; and = andalusite; mu = muscovite; Mgcrd64 = cordierite containing 64 mol% of Mg-cordierite; bt(ph51-sdph+east50) = biotite containing 51 mol% of phlogopite (in phlogopite/annite solid solution) and 50 mol% of siderophyllite+eastonite (in siderophyllite+eastonite/phlogopite+annite solid solution); bt(ph47-sdph+east50) = biotite containing 47 mol% of phlogopite (in phlogopite/annite solid solution) and 50 mol% of siderophyllite+eastonite (in siderophyllite+eastonite/phlogopite+annite solid solution); see text for details.

51%, sdph+east: 50%) = 4muscovite + 5cordierite(Mg-crd: 64%) + 12biotite (phl: 47%, sdph+east: 50%), figures in brackets show contents in mol% of the Mg end-member of cordierite (Mg-crd); for biotite: the mol% of phlogopite (phl) and siderophyllite+eastonite (sdph+east) in the phlogopite/annite and siderophyllite+eastonite/phlogopite+annite solid solutions, respectively. These minerals can coexist from about 475°C and 550 bar to >600°C and >1550 bar (fig. 6). Equilibrium conditions during contact metamorphism were, therefore, within the pressure-temperature

ranges (940-1140 bar and 520-545°C, respectively) defined by the intersections of this mineral reaction curve and the fluid inclusion isochores (fig. 6).

Independent information on the temperature during contact metamorphism was obtained from the Mg/Fe ratios of coexisting tourmaline and biotite, using Colopietro and Frieberg's (1987) geothermometer: $T(°C)=3150/(4.52-\ln K_D)-273.15$, where $\ln K_D=\ln[(Mg/Fe)_{Tourmaline}/(Mg/Fe)_{Biotite}]$, calibrated for K_D between 1.49 and 2.11. Application of this geothermometer to the

high-temperature assemblages of the Larderello geothermal field showed that the temperatures obtained are roughly comparable with the those indicated by fluid inclusions (Cathelineau *et al.*, 1994; Ruggieri and Gianelli, 1995). The K_D of the analysed biotite-tourmaline pairs of the Badia 1B sample is between 1.75 and 1.97, and the calculated temperature range (525-550°C) is in good agreement with the temperature evaluated from fluid inclusions.

The estimated pressure range for contact metamorphism, 940-1140 bar, does not greatly differ from the present-day lithostatic pressure (920 bar, calculated on the basis of a mean density of 2.7 g/cm³) at the depth of sampling. The maximum value of the past lithostatic pressure (1200 bar), calculated considering an average denudation rate of 0.35 mm·a^{-1} for the Larderello area (Cathelineau *et al.*, 1994) and a maximum age of about 3.8 Ma for contact metamorphism, corresponding to the age of the oldest intrusion at Larderello (Villa and Puxeddu, 1994), is close to the estimated pressure range for contact metamorphism. This, and the fact that hydrostatic pressures of 940-1140 bar are unrealistic, suggest that the contact metamorphism occurred under lithostatic pressure, as also indicated in other parts of the Larderello geothermal field by Cathelineau *et al.* (1994).

On the basis of the estimated pressure-temperature trapping conditions and the compositional features of the fluid inclusions examined here, the theoretical CO fugacity during contact metamorphism was also estimated from the equation: $3CO_2 + CH_4 = 4CO + 2H_2O$. Calculations were performed using the temperature-pressure-dependent equations for equilibrium constants of formation of H_2O, CO_2, CO and CH_4 of Lobotka (1991) and the fugacity coefficients of Duan *et al.* (1992), assuming ideal mixing conditions. This calculation indicates that, for a temperature of 530°C and a pressure of 1000 bar, the maximum CO fugacity compatible with fluid inclusion compositions was relatively low: around 0.6 bar.

CONCLUSIONS

Fluid inclusion data and thermodynamic calculations of mineral reaction equilibria in the KFMASH system indicate that the contact metamorphic assemblage found in well Badia 1B at 3450 m b.g.l. formed in temperature and pressure ranges of 520-545°C and 940-1140 bar. Quartz, andalusite, muscovite and mineral solid-solutions (such as biotite and cordierite) with compositions similar to those of the contact metamorphic assemblage, can coexist at equilibrium within these ranges. The temperature range (525-550°C) computed from the tourmaline/biotite geothermometer is also consistent with the evaluated range of temperature.

Fluid inclusion compositions indicate that a low-density, aqueous-carbonic (water-rich, low-salinity) fluid was present during contact metamorphism. The significant amounts of CH_4 (up to 19.4 mol%) and CO_2 (up to 15.7 mol%) in this fluid may have derived from high-temperature graphite-water interactions in the Larderello Paleozoic rocks. The fluid probably circulated in lithostatic conditions.

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