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# The crystalline units of the middle-upper crust of the Larderello geothermal region (southern Tuscany, Italy): new data for their classification and tectono-metamorphic evolution

ENRICO PANDELI (\*), GIOVANNI GIANELLI (\*\*) & MARCO MORELLI (\*\*\*)

## ABSTRACT

New structural and mineralogical-petrographical studies were conducted on the crystalline units (Micaschist Complex and the underlying Gneiss Complex) present at depth in the Larderello geothermal region. These data, which have been compared with others derived from similar outcropping (Cerreto Pass) and drilled (Pontremoli 1 well) metamorphic units in the Tuscan-Emilian sector of the Northern Apennines, allow the refinement of the structural-metamorphic evolution of the upper-middle crust in southern Tuscany. A low-medium to high grade regional metamorphism (e.g. zoned garnets, oligoclase-andesine blasts) was recognized in both complexes, overprinted by a 285 Ma thermometamorphic event, during which andalusite+ muscovite crystallised. Only the rocks of the Micaschist Complex were then affected by traspositive polyphase tectono-metamorphism in the greenschist facies. Finally, both complexes underwent a low- to high-grade contact metamorphism (crystallisation of poikilitic andalusite, cordierite, biotite, muscovite and, in places, corundum with sanidine rims) due to the emplacement of Pliocene-Quaternary granitoids and hydrothermalism, which locally obliterated the previous textures and mineral assemblages. In spite of the lack of radiometric dates for the foliations, comparison of the structural and mineralogical framework of the Larderello micaschists and gneisses with those of other dated metamorphic, Alpine and pre-Alpine successions of the Northern Apennines (e.g. Cerreto Pass) and northern Sardinia, allow us to hypothesize that the older, up to high-grade Barrovian framework (well-preserved in the Gneiss Complex) can be related to the Variscan Orogeny. In the Micaschist Complex, the following pervasive greenschist facies tectono-metamorphism was due to the Alpine events. The Micaschist Complex and the Gneiss Complex, now tectonically superposed in the Northern Apennines nappe pile, probably represent contiguous sectors of the original Variscan middle crust of the Adriatic Plate. Notwithstanding the evident local strong Pliocene-Quaternary contact metamorphic imprint, these rocks can mostly be classified as regional metamorphic rocks rather than hornfels. This classification allows a better reconstruction of the structural framework of the middle-upper crust in the Larderello geothermal area along the CROP 18 seismic profile.

**KEY WORDS:** Northern Apennines, Larderello geothermal field, metamorphic rocks, Variscan Orogeny, Alpine Orogeny.

## RIASSUNTO

**Le unità cristalline della crosta media e superiore della regione geotermica di Larderello (Toscana meridionale, Italia): nuovi dati per la loro classificazione e sulla loro evoluzione tectonica-metamorfica.**

Sono stati ottenuti nuovi dati strutturali e petrografico-mineralogici sulle unità cristalline (Complesso dei Micascisti ed il sottostan-

te Complesso degli Gneiss) presenti nel sottosuolo della regione geotermica di Larderello. Questi dati, comparati con altri derivati dallo studio di rocce simili affioranti (Passo del Cerreto) e del sottosuolo (Sondaggio Pontremoli 1) del settore Tosco-Emiliano dell'Appennino settentrionale, hanno permesso di rifinire il quadro strutturale-metamorfico della crosta superiore e media nella Toscana meridionale. Entrambi i complessi furono interessati da metamorfismo regionale polifasico di basso-medio fino ad alto grado (testimoniato ad esempio da granati zonati e da blasti di plagioclasio oligoclasico-andesino), seguito da un evento termometamorfico durante il quale cristallizzò andalusite e muscovite (quest'ultima datata circa 285 Ma). Soltanto le rocce del Complesso dei Micascisti furono poi interessate da più eventi tettone-metamorfici in Facies di Scisti Verdi. Infine, entrambi i complessi presentano blastesi termometamorfica da basso ad alto grado (cristallizzazione di peciloblasti di andalusite, cordierite, biotite, muscovite e, talora, anche di corindone con orli di sanidino), legata alla messa in posto dei granitoidi pliocenico-quaternari, e successiva cristallizzazione di minerali idrotermali che localmente hanno obliterato le precedenti tessiture e associazioni mineralogiche. Nonostante la mancanza di età radiometriche delle diverse foliazioni, la comparazione tra i caratteri strutturali mineralogico-petrografici dei micascisti e degli gneiss di Larderello con quella di altre successioni metamorfiche regionali di età Alpina e pre-Alpina dell'Appennino settentrionale (es. quella del Passo del Cerreto) e della Sardegna settentrionale, permette di ipotizzare che l'evento Barroviano di medio-alto grado (ben preservato nel Complesso degli Gneiss) possa essere attribuito all'Orogenesi Varisica. Nel Complesso dei Micascisti, i successivi eventi tettone-metamorfici traspositivi di basso grado sarebbero da attribuirsi, invece, alla tectonica alpina. Il Complesso dei Micascisti e il Complesso degli Gneiss, attualmente tectonicamente sovrapposti, rappresentano probabilmente settori contigui della originaria crosta intermedia varisica della Placca Adriatica. Nonostante che la cristallizzazione termometamorfica plio-quaternaria abbia localmente prodotto l'obliterazione delle precedenti strutturazioni tettone-metamorfiche, noi ritieniamo che le rocce del Complesso dei Micascisti e del Complesso degli Gneiss di Larderello possono ancora essere classificate in gran parte come metamorfiti regionali invece di cornubianiti. Infine, la correlazione nel sottosuolo delle unità come sopra definite permette di migliorare le ricostruzioni strutturali della crosta intermedia-superiore dell'area geotermica di Larderello lungo il profilo sismico del CROP18.

**TERMINI CHIAVE:** Appennino settentrionale, Campo geotermico di Larderello, Rocce metamorfiche, Orogenesi varisica, Orogenesi alpina.

## INTRODUCTION

The Micaschist Complex and the Gneiss Complex, drilled in the Larderello geothermal field (BAGNOLI *et alii*, 1979; BATINI *et alii*, 1983; ELTER & PANDELI, 1990; PANDELI *et alii*, 1994 with references therein), are the deepest metamorphic units (more than 3.5 km deep) of the Northern Apennines tectonic pile. In the Larderello geothermal field, these complexes underlie a ?Lower Paleozoic Phyllitic-Quartzitic Complex which is tectonically overlain by a complex of tectonic slices, including Triassic (Verru-

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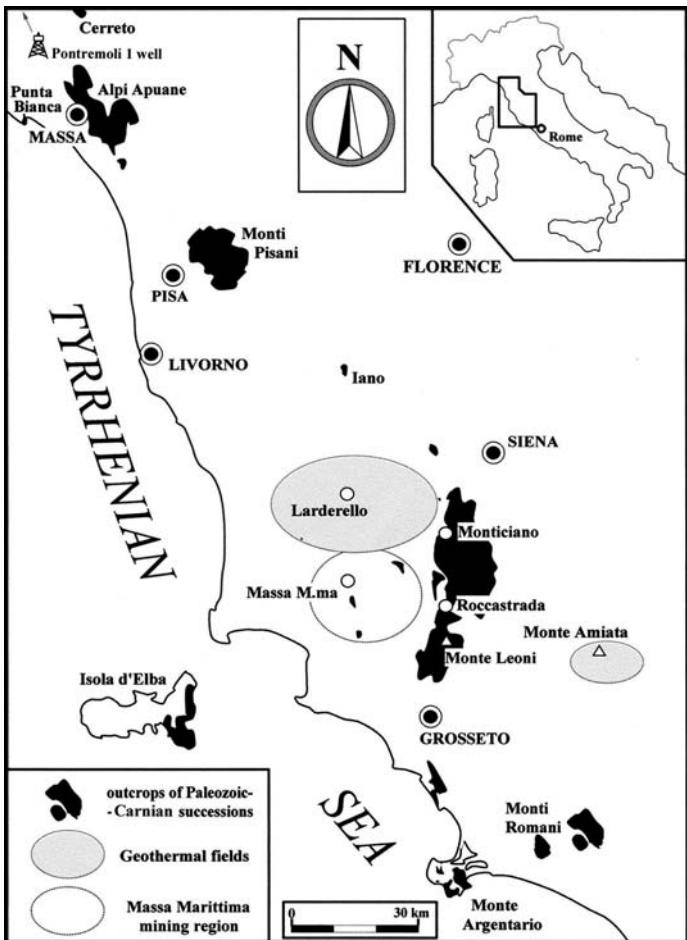


Fig. 1 - Regional distribution of the outcrops of the Paleozoic-Triassic metamorphic successions (in black) and locations of the studied areas.

- Distribuzione regionale degli affioramenti delle successioni paleozoico-triassiche (in nero) e ubicazione delle aree studiate.

cano and Tocchi Fm.) and Upper Paleozoic metasediments and Upper Triassic evaporites (ELTER & PANDELI, 1990; PANDELI *et alii*, 1991 and references therein). The Micaschist Complex, consisting of two-mica, garnet-bearing albite micaschist with amphibolite intercalations, is also present in northern Tuscany: the deepest part of the Pontremoli 1 oil well (unpublished data of the authors) and the outcrops of the Cerreto Pass, NW and N/NE of the Apuan Alps respectively (RICCI, 1968; DI SABATINO *et alii*, 1979; MOLLI *et alii*, 2002) and in Elba Island (PUXEDDU *et alii*, 1984; GARFAGNOLI *et alii*, 2005 this volume) (fig. 1). In the Pontremoli 1 well, the Micaschist Complex underlies a tectonic slices complex (ANELLI *et alii*, 1994 and unpublished data of the authors) similarly to the Larderello subsurface, whereas the micaschists and amphibolites are tectonically included within the Triassic Burano anhydrites in the Cerreto outcrops (DI SABATINO *et alii*, 1979; PLESI *et alii*, 2000 and references therein). A radiometric age of  $285 \pm 11$  Ma was obtained for a micaschist cored at Larderello (Rb/Sr method on muscovite: DEL MORO *et alii*, 1982), whereas dates of about 330 Ma and 240 Ma ( $^{40}\text{Ar}/^{39}\text{Ar}$  method on hornblende) were defined for the amphibolites of Cerreto Pass by MOLLI *et alii* (2002). The Gneiss Complex consists of muscovite-

biotite gneiss with layers of orthogneiss and amphibolite, and minor calc-silicate rocks (ELTER & PANDELI, 1990; PANDELI *et alii*, 1994; FRANCESCHINI, 1995). The Micaschist Complex overlies the Gneiss Complex through an Alpine quartz-mylonite horizon (ELTER & PANDELI, 1990). According to the same authors, both complexes show textures and minerals linked to the Variscan medium-grade regional metamorphism and to the Late Variscan thermometamorphism. Only the Micaschist Complex was affected by the Alpine tectono-metamorphic events. Finally, during Plio-Quaternary times, both complexes suffered Late Alpine contact metamorphism due to the granitoid intrusions of southern Tuscany (BATINI *et alii*, 1983; VILLA & PUXEDDU, 1994; FRANCESCHINI, 1998; GIANELLI & RUGGIERI, 2002; MUSUMECI *et alii*, 2002 and references therein). CARELLA *et alii* (2000) and MUSUMECI *et alii* (2002) ruled out the possibility of Variscan metamorphism in the crystalline complexes in the Larderello subsurface. In particular, these authors and FRANCESCHINI (1998) attributed all the high-temperature/low-pressure (HT-LP) minerals (e.g. Late Variscan andalusite porphyroblasts: PANDELI *et alii*, 1994; BERTINI *et alii*, 1994) to the Neogene contact metamorphism, suggesting a thickness for the Late Alpine metamorphic aureole of more than 1.5 km. The Micaschist Complex and Gneiss Complex are mostly described by these authors as Late Alpine prograde thermometamorphic units (e.g. Spotted Schist Complex and Honfels Complex in MUSUMECI *et alii*, 2002).

To improve our knowledge of the middle-upper part of the Tuscan crust, crossed by the CROP-18 seismic profile in the Larderello geothermal region, we performed petrographical-microstructural and EMPA analyses of 25 new core samples from the Larderello geothermal field, from the amphibolites cropping out at Cerreto Pass and from the bottom core sample (garnet-bearing micaschists) of the Pontremoli 1 oil well (locations in fig. 1). We also revised approximately 300 thin-sections from cores of previous deep geothermal wells in the Larderello field.

## ANALYTICAL DATA

### STRUCTURAL DATA

#### *Micaschist Complex*

In the Larderello and Pontremoli subsurface, the micaschists display the same structural features. In particular, they show granolepidoblastic to porphyroblastic textures mostly defined by two foliations: a main schistosity Sp followed by a Sp+1 foliation (fig. 2a, 2b and 2c). The main, fine-grained, continuous schistosity Sp is defined by alignment of quartz + sericite/muscovite + chlorite + albite + opaque minerals and is locally associated with isoclinal folds. Plagioclase porphyroblasts (fig. 2a and 2b) can also be recognized and can be defined as syn-Dp and inter-tectonic (between Dp and Dp+1), following the description and classification of PASSCHIER & TROUW (1996) and pre-Dp (see later). The above mineral association is typical of the greenschist facies. Sp is deformed by millimetre-spaced, zonal to discrete crenulation cleavage (Sp+1 in figs. 2a and 2b) which is the axial planar foliation of close to isoclinal folds. At depth, Sp+1 evolves into a penetrative, millimetre-spaced foliation (fig. 2c) with syn-kinematic growth of sericite

+opaque minerals  $\pm$  quartz  $\pm$  chlorite and Sp is preserved in the microlithons. Later zonal crenulation cleavage or kinks (Sp+2) (fig. 2c) and fracture systems (often filled by hydrothermal minerals) can also be observed.

In addition, pre-Sp textures and minerals are also recognisable. In particular, local pre-Sp, coarse-grained relict schistosity (Sp-1 = chloritized biotite + muscovite + quartz) is present as intrafolial mica fishes (fig. 2c) (see also fig. 4a in ELTER & PANDELI, 1990). Pre-Sp porphyroclasts are represented by:

- garnets (figs. 2a and 2c), locally with helicitic inclusion trails (Si) consisting of opaque minerals  $\pm$  quartz  $\pm$  muscovite and discordant with respect to Sp, are generally fractured and partially substituted by chlorite; this mineral, together with quartz, muscovite and albite, also forms syn-Dp pressure shadows around the porphyroblasts;

- plagioclase (figs. 2a and 2b), generally with graphite + opaque Ti-minerals  $\pm$  muscovite inclusion trails (Si in fig. 2a) sometimes discordant with respect to Sp, locally show a zoning consisting of a syn-Sp clear rim or pressure shadows (see fig. 5b in ELTER & PANDELI, 1990);

- rare andalusite, including quartz  $\pm$  muscovite trails (Si in fig. 2d) at a high angle with respect to Sp, is co-genetic with muscovite dated to about 285 Ma by DEL MORO *et alii* (1982).

The amphibolites sampled within the Micaschist Complex in the Larderello (fig. 2e) and Cerreto area show a grano-nematoblastic, coarse-grained foliation defined by the alignment of green hornblende+intermediate plagioclase+titanite which is typical of amphibolitic facies metamorphic conditions. In the studied samples, the amphibolitic foliation is variously transposed by millimetre-spaced foliations made up of chlorite, tremolite-actinolite, albite, epidote and titanite which points to a re-equilibration under greenschist facies conditions. Chlorite and tremolite-actinolite crystallisation also occurred during the post-tectonic hydrothermal alteration. MOLLI *et alii* (2002) also found garnet porphyroclasts within the main foliation of the Cerreto amphibolites which was locally affected by mylonitic to ultramylonitic deformation linked to a retrograde metamorphic evolution (from epidote-amphibolite facies to greenschist facies)

#### Gneiss Complex

The gneisses are characterized by a medium to coarse-grained differentiated or gneissic layering which defines the main foliation (Sp in fig. 2f) made up of an amphibolite facies mineral association (quartz + biotite + muscovite + andesine  $\pm$  K-feldspar and, locally, green hornblende in the amphibolite levels e.g. in fig. 2g). In the upper part of this unit the syn-Dp biotite is often decoloured and chloritized and partially replaced by static thermometamorphic fresh biotite (see later). The discovery of prismatic sillimanite, plagioclase (with helicitic inclusions) and almandine in the andesine poikyloblasts (fig. 2h), and almandine and staurolite relicts within andalusite (see also BERTINI *et alii*, 1994) allow comparisons with pre-Dp textures and minerals of the Micaschists Complex (see also ELTER & PANDELI, 1996). A later weak crenulation event of Sp is also locally recognizable.

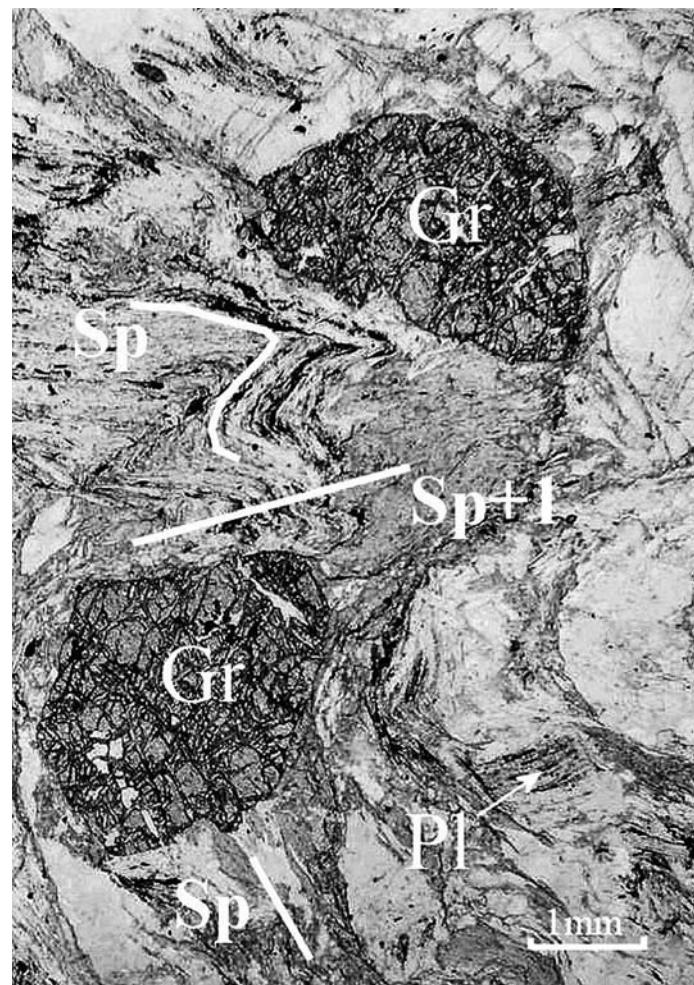


Fig. 2 - a) Syn-tectonic garnet (Gr) and plagioclase (Pl) including Si at high angle respect to Sp) porphyroclasts enveloped within the Sp and Sp+1 foliations, single polars, micaschist, well Secolo 2, 2496 m, Larderello field.

- a) *Porfiroclasti di granato (Gr) e di plagioclasio (Pl) includente Si posta ad alto angolo rispetto a Sp) sin-tettonici avvolti dalle foliazioni Sp e Sp+1, nicols paralleli, micaschisti, Pozzo Secolo 2, m2496, Campo di Larderello; Larderello field.*

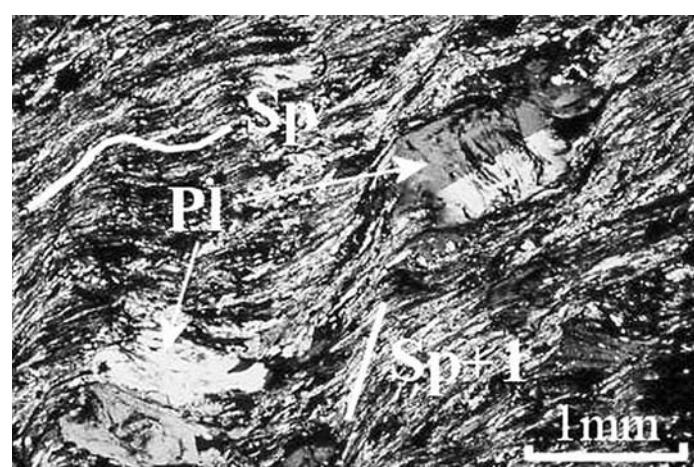


Fig. 2 - b) Plagioclase porphyroblasts (Pl) enveloped by Sp, crossed polars, micaschist, well Selvaccia 3, 2620 m, Larderello field.  
- b) *Porfiroblasti di plagioclasio (Pl) avvolti dalla foliazione Sp, micaschisti, Pozzo Selvaccia 3, m 2620, Campo di Larderello.*

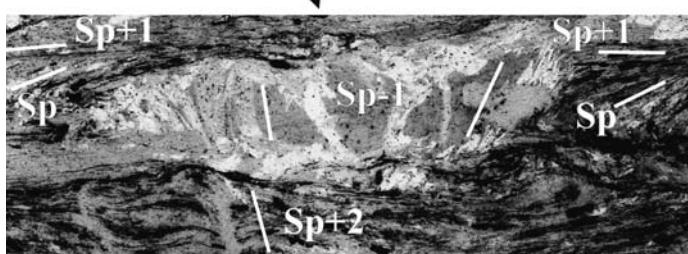
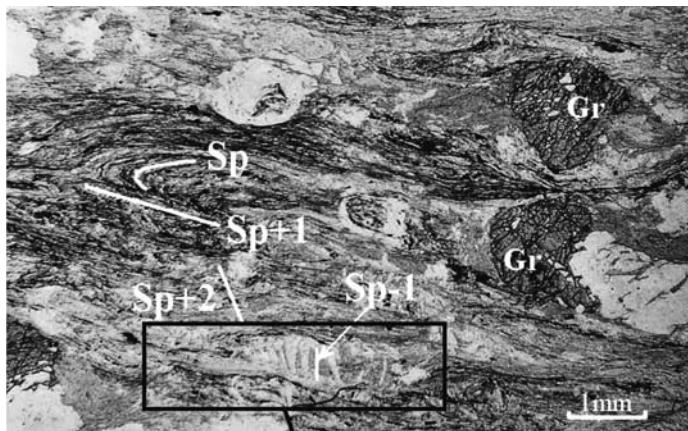


Fig. 2 - c) Fine-grained Sp and Sp+1 foliations, Sp+2 crenulations and coarse-grained Sp-1 foliation; Gr = pre-Sp garnet porphyroblasts. The magnification shows in more detail the relationships of the mica fish Sp-1 with Sp and Sp+1 foliations, single polars, micaschist, well Montecerboli 1, 2806 m, Larderello field.

- c) Foliazioni Sp, Sp+1, Sp+2 e Sp-1 e porfiroclasti di granato pre-Sp (Gr); nell'ingrandimento sono evidenziati i rapporti tra Sp-1 del mica fish e le foliazioni Sp e Sp+1, nicols paralleli, micaschisti, Pozzo Montecerboli 1, m 2806, Campo di Larderello.

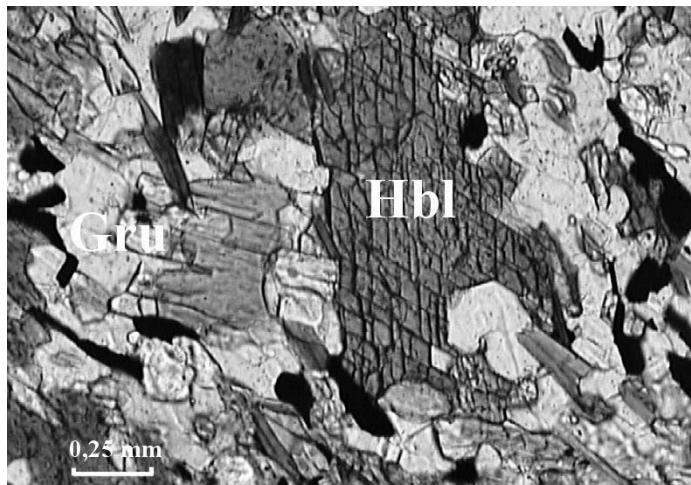


Fig. 2 - e) Green hornblende (Hbl) surrounded by a metamorphic colourless grunerite (Gru), single polars, amphibolite intercalation in micaschist, well Lumiera 1b, 3110 m, Larderello field.  
- e) Orneblenda verde (Hbl) circondato da anfiboli incolori termomorfici (grunerite = Gru), nicols paralleli, intercalazione anfibolitica nei micaschisti, Pozzo Lumiera 1b, m 3110, Campo di Larderello.

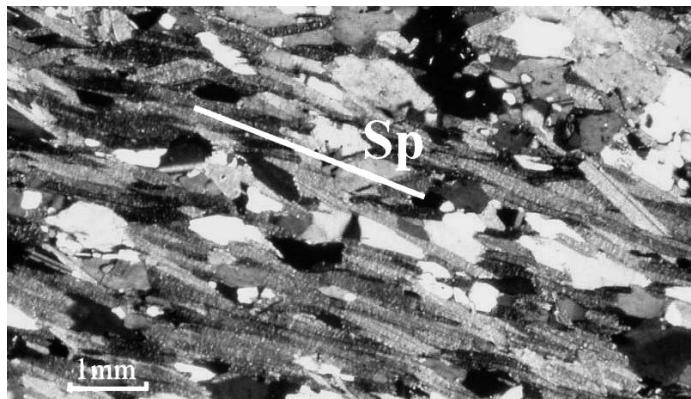


Fig. 2 - f) Sp gneissic foliation, crossed polars, gneiss, well VC11, 2949 m, Larderello field.  
- f) foliazione gneissica (Sp), nicols incrociati, gneiss, Pozzo VC11, m 2949, Campo di Larderello.

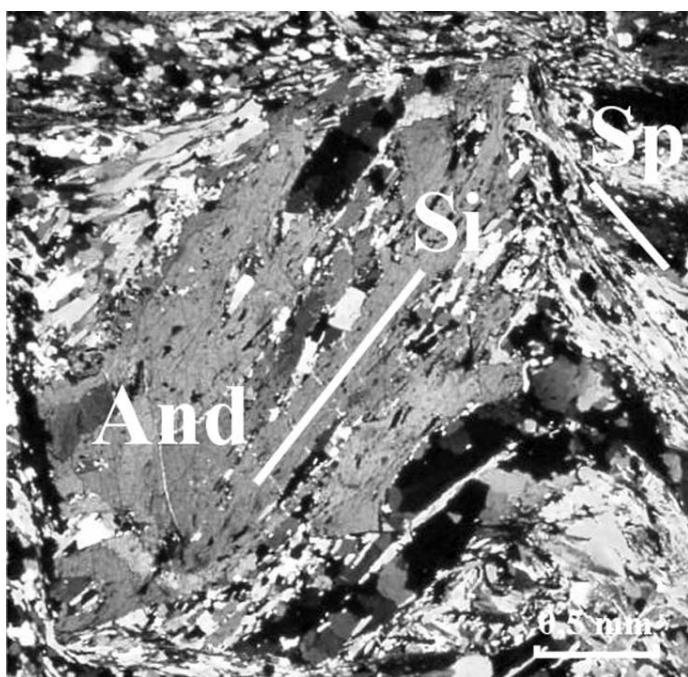


Fig. 2 - d) Pre-Sp andalusite porphyroblast, crossed polars, micaschist, well Lumiera 1bis, 2236 m, Larderello field.

- d) Porfiroclasto pre-Sp di andalusite, nicols incrociati, micaschisti, Pozzo Lumiera 1bis, m 2236, Campo di Larderello.

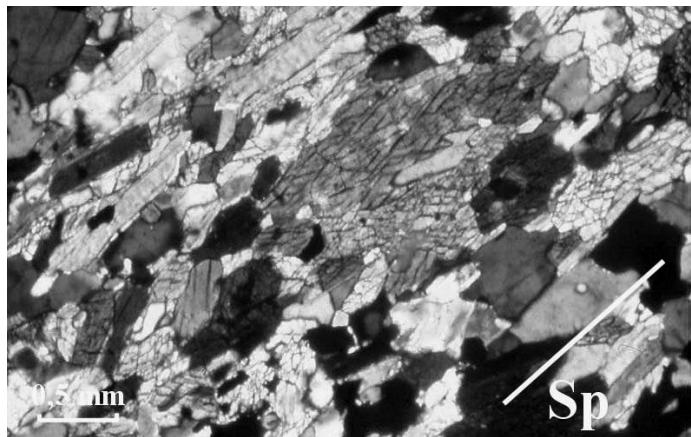


Fig. 2 - g) Amphibolite intercalation in the gneisses, crossed polars, gneiss, well Sasso 22, 3204 m, Larderello field.

- g) Intercalazione di anfiboliti negli gneiss, nicols incrociati, Pozzo Sasso 22, m 3204, Campo di Larderello.

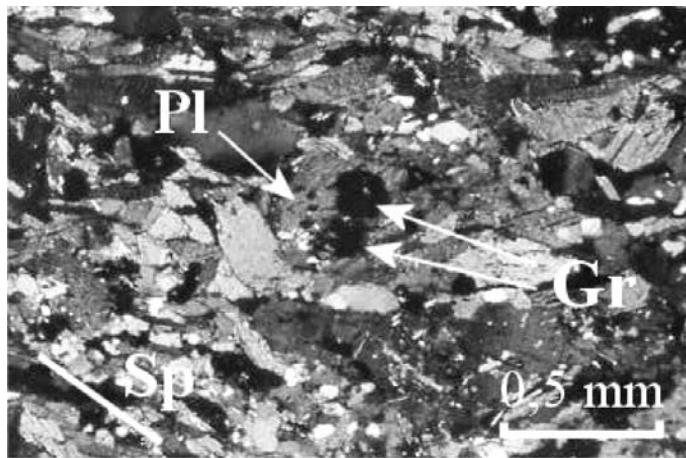


Fig. 2 - h) Garnet inclusions (Grt) in a syn-tectonic plagioclase (Pl) of the Sp gneissic foliation, crossed polars, gneiss, well Sasso 22, 2636 m, Larderello field.

- h) Granato (Grt) inclusi in plagioclasio (Pl) della foliazione gneissica Sp, nicols incrociati, gneiss, Pozzo Sasso 22, m 2636, Campo di Larderello.

Post-tectonic porphyroblasts of corundum ± sanidine, andalusite (fig. 2 i), cordierite (often pinnitized) and garnet (fig. 2 l), poikiloblastic cordierite, and decussate micas and quartz+An-rich plagioclase aggregates with triple-point junctions are present in both complexes, with an evident downward thermometamorphic prograde zoning and replacement of previous textures (see also FRANCESCHINI, 1998; MUSUMECI *et alii*, 2002). The association of post-tectonic K-feldspar + corundum (indicating muscovite break-down at approximately 600-620°C) and the presence of B-minerals are distinctive features of the thermometamorphic aureole linked with all the Miocene to Quaternary magmatic intrusions in southern Tuscany and the Tuscan Archipelago (GIANELLI & RUGGIERI, 2002; DINI *et alii*, 2004).

Finally, micaschists and gneisses were affected by pneumatolitic (e.g. tourmaline+biotite veins in fig. 11 of PANDELI *et alii*, 1994) and hydrothermal alterations due to the circulation of hot fluids through fracture networks (CAVARRETTA *et alii*, 1980; BERTINI *et alii*, 1985; PANDELI *et alii*, 1994 and references therein).

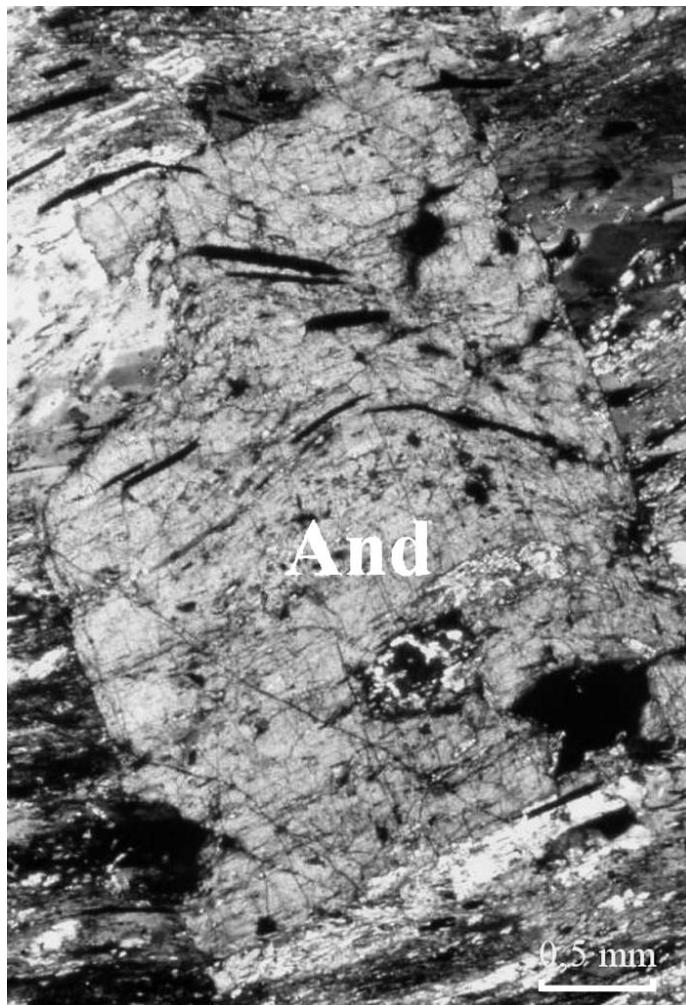


Fig. 2 - i) Post-tectonic idiomorphic andalusite which overprints the foliations, crossed polars, micaschist, well S. Pompeo 2, 2718 m, Larderello field.

- i) Porfiroblasti post-tettonico di andalusite che si sovrappone alle foliazioni, nicols incrociati, micaschisti, Pozzo S. Pompeo 2, m 2718, Campo di Larderello.



Fig. 2 - l) Sub-idiomorphic blasts of garnet which overprint the Sp, Sp+1 and Sp+2 foliations, crossed polars micaschist, well Anqua, 2135 m, Larderello-Travale geothermal area.

- l) Blasti sub-idiomorfi post-tettonici di granato che si sovrappongono alle foliazioni Sp, Sp+1, Sp+2 e, nicols incrociati, micaschisti, Pozzo Anqua, m2135, Area geotermica di Larderello-Travale.

TABLE 1a

Selected analyses of plagioclases and K-feldspars in metamorphic rocks of the Larderello geothermal wells.  
*- Analisi selezionate di plagioclasio e K-feldspati in rocce metamorfiche di sondaggi geotermici di Larderello.*

Well name depth in m	Capannoli 2b 2494 micaschist	Canneto 4a 2419 micaschist	Dolmi 4 3521 micaschist	Colline 2c 2480 gneiss	Bruciano 1 2443 gneiss	Capannoli 2b 3170 hornfels	Canneto 4a 3523 hornfels
SiO <sub>2</sub>	67,73	64,07	68,57	64,51	45,43	47,18	58,18
Al <sub>2</sub> O <sub>3</sub>	21,49	23,77	20,32	18,54	35,97	34,74	28,92
FeO	0,03	0,08	0,1	0,22	0	0,44	0,05
CaO	1,14	4,01	0,15	0,03	18,8	17,22	8,23
Na <sub>2</sub> O	10,62	9,26	11,89	0,58	0,78	1,67	7,09
K <sub>2</sub> O	0,04	0,21	0,08	15,99	0	0,03	0,11
Total	101,05	101,4	101,11	99,87	100,98	101,28	102,58
Structural formula on the basis of 8 oxygen equivalents							
Si	2,93	2,79	2,97	2,99	2,07	2,14	2,54
Al	1,10	1,22	1,04	1,01	1,93	1,86	1,49
Fe+3	0,01	0,00	0,00	0,01	0,00	0,02	0,00
Ca	0,05	0,19	0,01	0,00	0,92	0,84	0,38
Na	0,89	0,78	1,00	0,05	0,07	0,15	0,60
K	0,00	0,01	0,00	0,94	0,00	0,00	0,01
total	4,98	5,00	5,01	5,00	5,00	5,00	5,02
	albite	oligoclase	albite	K-feldspar	anorthite	bytownite	andesine

## MINERAL CHEMISTRY

Analyses were carried out using a WDS microprobe (Jeol-FXA-8600), operating under the following conditions: acceleration voltage 15kV, counting time 15s, excitation current 10nA, correction program by BENCE & ALBEE (1968). Chemical analyses of minerals are reported in tables 1a-f.

*Plagioclase.* The plagioclases of the Gneiss Complex have an anorthite content ranging from 12% to 39% (fig. 3a). The inter-tectonic plagioclase porphyroblasts of the Micaschist Complex are frequently zoned, with an oligoclase core (An = 10-29%) and albite rim (fig. 3b). The latter mineral also characterises the surrounding syn-D<sub>p</sub> pressure shadows and foliations).

TABLE 1b

Selected analyses of garnet from micaschists of Larderello wells and of Pontremoli 1 well.  
*- Analisi selezionate di granati nei micaschisti dei sondaggi di Larderello e del sondaggio Pontremoli 1.*

Well name depth in m	Radicondoli 30 3055	Montecerboli 1 2916 core	Montecerboli 1 2916 rim	San Martino 1 2722	Sesta 6B 3835	SP Serrazzano 2078	Pontremoli 1 3514	Anqua 3585	Anqua 1939
SiO <sub>2</sub>	36,44	37,37	37,34	37,34	38,55	35,95	37,8	39,01	37,35
TiO <sub>2</sub>	0,08	0,14	0,05	0,13	0,2	0,12	0	0,09	0
Al <sub>2</sub> O <sub>3</sub>	21,66	20,9	21,3	21,01	20,59	23,95	21,39	21,81	21,16
Cr <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0,09
FeOt <sub>tot</sub>	28,53	32,67	37,83	29,99	30,75	32,6	38,68	31,98	28,35
MnO	0,37	1,92	0,78	4,75	0,49	2,29	0,34	0,22	4,98
MgO	1,13	1,35	1,8	1,22	2,06	1,56	1,9	1,42	0,71
CaO	11,78	5,64	2,68	5,76	9,51	4,53	2,61	8,62	8,2
Total	99,99	99,99	101,78	100,2	102,15	101	102,72	103,15	100,84
Structural formula on the basis of 24 oxygens									
Si	5,835	6,022	5,96	6,011	6,04	5,72	5,981	6,04	5,973
AlIV	0,165	0	0,04	0	0	0,28	0,019	0	0,027
total IV	6	6,022	6	6,011	6,04	6	0	6,04	6
AlVI	3,924	3,969	3,967	3,985	3,802	4,212	3,97	3,98	3,96
Fe+3	0,076	0,031	0,033	0,015	0,178	0	0,03	0,02	0,028
Cr+3	0	0	0	0	0	0	0	0	0,012
totalVI	4	4	4	4	3,98	4,212	4	4	4
Fe+2	3,749	4,372	5,016	4,022	3,85	4,339	5,078	4,12	3,763
Mg	0,27	0,325	0,428	0,294	0,482	0,37	0,448	0,328	0,169
Mn	0,05	0,263	0,106	0,643	0,064	0,309	0,046	0,028	0,674
Ca	2,02	0,974	0,459	0,994	1,596	0,772	0,442	1,43	1,404
total	6,089	5,934	6,009	5,953	5,992	5,79	6,014	5,906	6,01
Mole fraction of end-members (calculated as per Deer et al., 1966)									
Almandine	0,62	0,75	0,84	0,67	0,64	0,749	0,85	0,698	0,626
Pyrope	0,04	0,05	0,07	0,05	0,08	0,064	0,07	0,056	0,028
Spessartine	0,01	0,04	0,02	0,11	0,01	0,064	0,01	0,004	0,112
Grossular	0,31	0,15	0,07	0,17	0,216	0,133	0,06	0,237	0,224
Andradite	0,02	0,01	tr	0	0,05	0	0,01	0,005	0,007
Uvarovite	0	0	tr	0	0	0	0	0	0,003

TABLE 1c

Selected analyses of biotites from metamorphic rocks of the Larderello geothermal wells.  
*- Analisi selezionate di biotiti di rocce metamorfiche dei sondaggi geotermici di Larderello.*

Well name depth in m	Bruciano 1 2443	Lumiera 1b 3110	Canneto 4a 2419	Sesta 6b 3835	Monteverdi 3 2636	Monteverdi 3 2636	Monteverdi 2c 3940	Badia 1b 3654
	gneiss	micaschist	micaschist	micaschist	porphyroclastic hornfels	neoblastic hornfels	hornfels	hornfels
SiO <sub>2</sub>	36,76	36,05	34,84	35,92	35,52	34,91	35,19	34,67
TiO <sub>2</sub>	1,98	3,27	1,28	1,65	3,57	2,99	3,48	2,6
Al <sub>2</sub> O <sub>3</sub>	16,35	15,62	21,82	18,73	19,91	20,55	19,67	20
FeO	19,05	23,4	19,05	23,73	19,43	19,22	20,89	18,24
MnO	0,53	0,08	0,1	0,31	0,17	0,18	0,26	0,21
MgO	12,61	9,08	9,12	7,67	8,5	8,77	7,56	9,9
CaO	0,02	0,05	0,05	0,02	0	0	0	0,06
Na <sub>2</sub> O	0,1	0,18	0,26	0,04	0,22	0,15	0	0,13
K <sub>2</sub> O	9,69	9,31	9,1	9,28	9,3	9,11	9,52	9,25
BaO	0,14	0,45	0,32	nd	nd	nd	nd	0,24
Cl	0,17	0,09	0,02	0,07	0	0	0,25	0,03
F	0,62	nd	0,28	0,16	0,29	0,39	0,16	0,27
H <sub>2</sub> O	nd	nd	nd	nd	nd	nd	nd	nd
Total	98,02	97,58	96,24	97,58	96,79	96,27	96,98	95,6
Structural formula, oxygen equivalent per formula unit = 22								
Si	5,504	5,501	5,249	5,452	5,322	5,264	5,324	5,261
AlIV	2,496	2,499	2,751	2,548	2,677	2,736	2,676	2,739
total IV	8	8	8	8	8	8	8	8
AlVI	0,389	0,31	1,123	0,802	0,838	0,916	0,831	0,838
Fe	2,385	2,986	2,4	3,011	2,435	2,424	2,643	2,315
Mn	0,067	0,01	0,013	0,04	0,022	0,023	0,033	0,027
Mg	2,815	2,066	2,048	1,735	1,899	1,971	1,705	2,24
Ti	0,223	0,375	0,145	0,188	0,402	0,339	0,396	0,297
totalVI	5,879	5,747	5,729	5,776	5,596	5,673	5,608	5,717
Ca	0,003	0,008	0,008	0,004	0	0	0	0,01
Na	0,029	0,053	0,076	0,012	0,064	0,044	0	0,038
K	1,851	1,812	1,749	1,797	1,778	1,752	1,837	1,791
Ba	0,008	0,027	0,019	0	0	0	0	0,014
total	1,891	1,9	1,852	1,813	1,842	1,796	1,837	1,853
Cl	0,043	0,023	0,005	0,018	0	0	0,064	0,008
F	0,294	nd	0,133	0,077	0,137	0,186	0,07	0,13
Cl+F	0,337		0,138	0,095	0,137	0,186	0,134	0,138
OH	3,663	3,977	3,862	3,905	3,863	3,814	3,866	3,862

*K-Feldspar.* It is present in the gneisses, rare in the micaschist, and shows almost stoichiometric composition.

*Garnet.* The pre-Sp garnet porphyroclasts of the Micaschist Complex are rich in the almandine end-member ( $X_{\text{alm}} > 0.67$ ) (fig. 4a) and are often zoned, with a spesartine-rich core (fig. 4b). The inter-tectonic garnets present in the Gneiss Complex show similar compositions (BERTINI *et alii*, 1994). Instead, the post-tectonic garnets show a minor almandine contents end-member and a higher grossular component (see the samples from wells Anqua and Radicondoli 30 in fig. 4a).

*Biotite.* Biotites of both gneisses and micaschists show Mg/(Mg+Fe) ratios ranging from 0.3 to 0.6. Both post-tectonic and pre-tectonic biotites show a similar chemical composition at least on the basis of the major elements. Selected samples are plotted in AFM phase diagrams (figs. 5a, 5b and 5c), see Discussion.

*Dioctahedral potassic white mica (KWM).* These are more or less phengitic muscovites with variable Si a.p.f.u. (3.04-3.45). The chemical composition of KWM does not show relationship with their pre- (Variscan), syn- (Alpine) or post-tectonic (Miocene-Quaternary contact metamorphism) crystallisation inferred by microstructural analyses or with the rock type.

*Amphibole.* The composition of the green amphiboles (fig. 6 a and 6b) ranges between Mg-hornblendes and parg-

asites. Syn- to post-tectonic colourless or faintly pleochroic amphiboles are Na and K-poor (grunerite or actinolite-tremolite) (fig. 2e).

*Cordierite.* It has Mg/(Mg+Fe) ratios around 0.6-0.5, they are always post-tectonic, poikiloblastic and often altered in an aggregate of secondary phyllosilicates, which show to be chlorite and phengitic mica on the basis of EDS analyses.

*Chlorite.* Two populations of chlorites can be distinguished on the basis of textural evidence: (1) syn-tectonic chlorites crystallised during the Dp and Dp+1 events; (2) chlorites after biotite, cordierite and other femics (e.g. amphiboles) due to late magmatic/hydrothermal alteration. No significant chemical differences have been found between the two populations: the Mg/(Mg + Fe) ratios are in the range 0.4 to 0.5 and, assuming the thermodynamic model of VIDAL *et alii* (2001) is valid, the octahedral vacancies are low (0.03-0.045) and the amesite mole fractions are around 0.3-0.4.

*Tourmaline and F-apatite.* They are common in contact-metamorphic rocks, indicating that B and F metasomatism characterised this metamorphic event (GIANELLI & RUGGIERI, 2002). A B-mineral of the warwickite-yuafulite group (fig. 7) was found for the first time in calc-silicate rocks in the Gneiss Complex during this research work. This relatively rare boron mineral has been

TABLE 1d  
Selected analyses of muscovites from metamorphic rocks of the Larderello geothermal wells.  
*Analisi selezionate di rocce metamorfiche dei sondaggi geotermici di Larderello.*

TABLE 1e

Selected analyses of amphiboles in the Micaschist Complex from Larderello geothermal wells and Cerreto Pass.  
*- Analisi selezionate di anfiboli nel Complesso dei Micaschisti dei sondaggi geotermici di Larderello e del Passo del Cerreto.*

Well name depth in m	Capannoli 2b 3170	Lumiera 1b 3110	Lum1b hornblende 3110	Sesta 6B grunerite 3710	Monteverdi 2c 3567	Cerreto Pass
SiO <sub>2</sub>	38,37	42,98	52,34	42,53	42,61	44,16
TiO <sub>2</sub>	0,22	0,99	0,17	0,48	0,62	0,5
Al <sub>2</sub> O <sub>3</sub>	11,57	13,12	0,71	15,2	12,38	13,3
Fe <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0
FeO	2 7,58	21,8	31,28	19,55	2,32	17,63
MnO	0,23	0,25	0,56	0,38	0	0,3
MgO	4,3	7,51	12,88	7,67	19,78	9,74
CaO	1 1,53	11,29	0,89	11,43	12,54	11,56
Na <sub>2</sub> O	0,85	1,31	0,06	1,16	3,34	1,59
K <sub>2</sub> O	3,29	0,74	0,04	0,51	0,68	0,31
Cl	3,68	nd	nd	nd	0	0
F	0	nd	nd	nd	0	0
H <sub>2</sub> O	nd	nd	nd	nd	0	nd
Total	101,62	99,99	98,93	98,91	94,27	99,09
Structural formula on the basis of 23 oxygen equivalents						
Si	6,109	6,395	7,865	6,306	6,252	6,487
AlIV	1,891	1,605	0,126	1,694	1,748	1,513
total IV	8	8	7,991	8	8	8
AlVI	0,281	0,696	0	0,974	0,329	0,789
Fe+3	0,627	0,135	0	0,202	0	0,103
Fe+2	3,045	2,577	3,93	2,222	0,284	2,063
Mn	0,031	0,03	0,07	0,048	0	0,037
Mg	0,99	1,464	1,023	1,5	4,328	1,953
Ti	0,026	0,11	0,02	0,054	0,069	0,055
totalVI(C)	5	5,012	5,043	5	5,01	5
Ca	1,967	1,799	0,143	1,816	1,972	1,819
Mg	0,033	0,201	1,857	0,196	0	0,181
Na	0	0	0	0	0,028	0
totalVI(B)	2	2	2	2,012	2	2
Na	0,263	0,378	0,017	0,334	0,921	0,453
F	0,669	0,14	0,008	0,097	0,127	0,058
total (A)	0,932	0,518	0,025	0,431	1,048	0,511
Cl	0,995	nd	nd	nd	0	0
F	0	nd	nd	nd	0	0
Cl+F	0,995	nd	nd	nd	0	0
OH	1,005	2	2	2	2	2

TABLE 1f

Selected analyses of chlorites from metamorphic rocks of the Larderello geothermal wells.

*- Analisi selezionate di cloriti di rocce metamorfiche dei sondaggi geotermici di Larderello.*

Well depth	Capannoli 2b 2494 micaschist	Dolmi 4 3521 micaschist	Miniera 4 3011 micaschist	Sughere 3 hornfels	Canneto 4a 3523 hornfels
SiO <sub>2</sub>	25,94	24,9	24,17	24,98	25,07
TiO <sub>2</sub>	0,08	0,05	0,07	0,21	0,11
Al <sub>2</sub> O <sub>3</sub>	21,23	20,5	22,53	20,47	22,42
FeO	31,12	38,07	32,54	33,59	29,82
MnO	0,29	0,36	0,19	0,39	0,43
MgO	11,52	6,54	9,53	8,89	11,87
Total	90,18	90,42	89,03	88,53	89,72
Structural formula on the basis of 14 oxygen equivalent and atom site partition (method of Vidal <i>et alii</i> , 2001).					
Si(T1,T2)	2,729	2,724	2,606	2,727	2,64
Al <sup>IV</sup> (T2)	1,271	1,276	1,394	1,273	1,36
Ti	0,007	0,004	0,06	0,017	0,09
Al <sup>VI</sup> (M4)	1	1	1	1	1
Mg(M2,3)	1,555	0,917	1,346	1,254	1,634
Fe(M2,3)	2,356	2,993	2,579	2,658	2,294
Al <sup>VI</sup> (M2,3)	0,089	0,09	0,075	0,088	0,072
Mg(M1)	0,252	0,15	0,186	0,193	0,229
Fe(M1)	0,382	0,489	0,355	0,409	0,332
Al <sup>VI</sup> (M1)	0,322	0,316	0,421	0,394	0,408
(M1)	0,045	0,045	0,038	0,044	0,031

reported from contact-metamorphic dolostones very near to the contact of shallow granite intrusions in Japan. Fluid inclusion and petrographic studies reveal a fluid as hot as 530°C at a pressure of 70-100 MPa. Boron exsolved from the granite (ISHIYAMA *et alii*, 1998).

## DISCUSSION

The study of the rocks of the crystalline Tuscan basement is fundamental to understanding the tectonic and metamorphic evolution of the continental crust of the Northern Apennines chain. Given the scarcity of outcrops at the regional scale (PANDELI *et alii*, 1994 and references therein), the crystalline rocks cored in the Larderello-Travale field are particularly important because they represent the deepest units of the Apenninic tectonic pile. All the authors cited in the introduction acknowledge a complex polyphased tectono-metamorphic evolution for the studied rocks, and a final static recrystallisation and metasomatism due to the emplacement of Pliocene-Quaternary granitoids in southern Tuscany. On the other hand, the attribution of the structural framework of the Micaschist Complex and of the Gneiss Complex to the Variscan and/or to the Alpine Orogeny is still a matter of debate (e.g. ELTER & PANDELI, 1990 vs. MUSUMECI *et alii*,

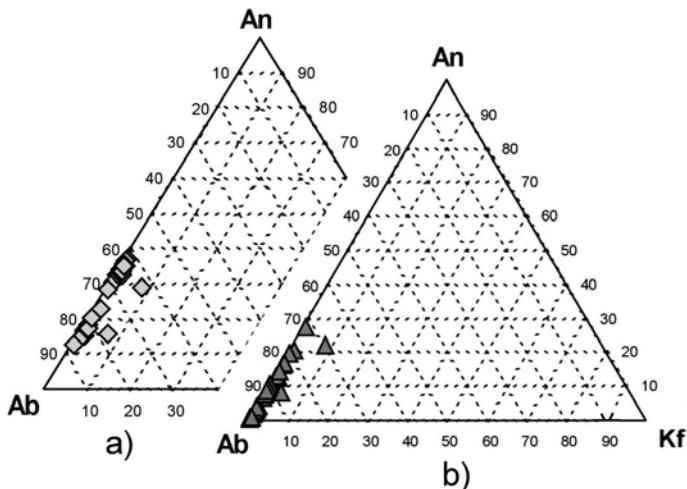


Fig. 3 - Composition of the feldspar blasts: a) in the gneiss; b) in the micaschists.

- Composizione dei blasti feldspatici: a) negli gneiss, b) nei micaschisti.

2002). In addition, FRANCESCHINI (1994, 1998) suggested that the foliation of the deepest gneisses could be due to the stress field induced by the uprising Plio-Quaternary plutons.

The precise chronological attribution of the foliations recognized in the Micaschist Complex and the Gneiss Complex is complicated by:

1) The lack of radiometric ages of the minerals lying along the foliations.  $^{40}\text{Ar}/^{39}\text{Ar}$ , K/Ar and Rb/Sr radiometric ages of about 10 Ma to 1.6 Ma were obtained from muscovite, hornblende and biotite samples collected in the micaschists and gneisses (DEL MORO *et alii*, 1982; BATINI *et alii*, 1983, 1985; VILLA & PUXEDDU, 1994; DALLMEYER & LIOTTA, 1998), but these data are clearly related to cooling ages of thermometamorphic and partially recrystallised minerals linked to the Late Miocene-Quaternary magmatism. Only a single pre-Late Miocene age was obtained by DEL MORO *et alii* (1982), who defined a  $285 \pm 11$  Ma Rb/Sr age for a muscovite associ-

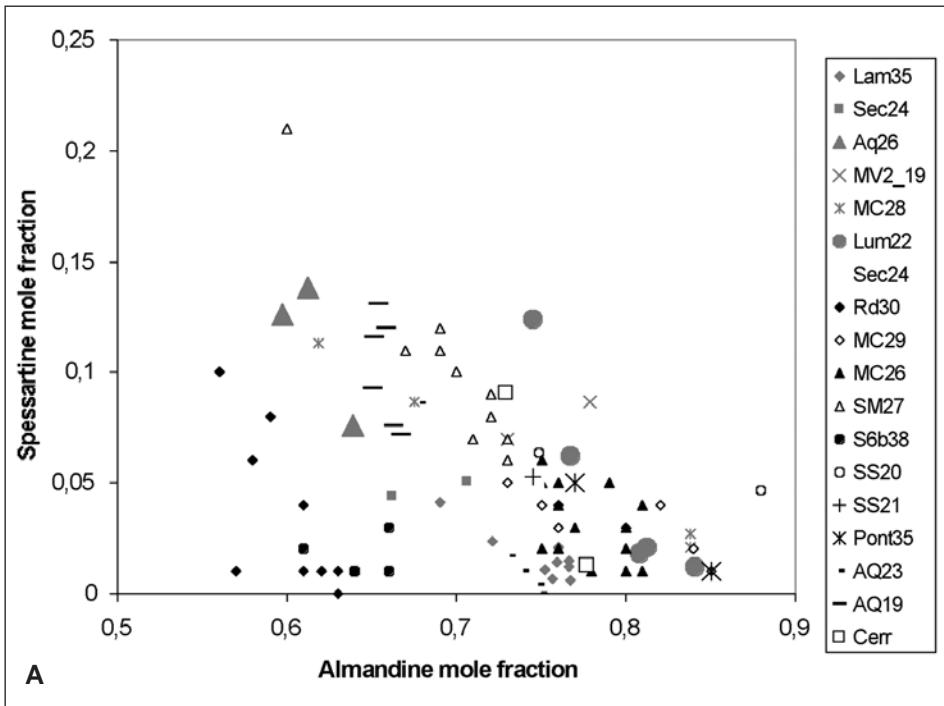
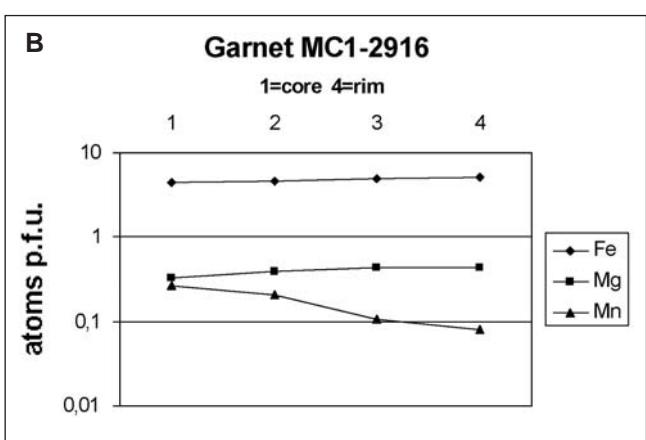


Fig. 4 - a) Spessartine vs. almandine mole fraction of the garnets in the micaschists. Each point refers to a single garnet (at least two per sample). For each sample the Mn-rich compositions refer to the central part and the  $\text{Fe}^{2+}$ -rich compositions to the peripheral parts of the garnets, respectively. LEGEND (well name/core sample depth): Lam35 = Lamarello 1/3501m; Sec24 = Secolo 1/2496m; Aq26 = Anqua/2635m; MV2\_19 = Monteverdi 2/1934m; MC28 = Montecerboli 1/2806m; Lum22 = Lumiera 1b/2236m; Sec24 = Secolo 1/2496m; Rd30 = Radicondoli 30b/3055m; MC29 = Montecerboli 1/2916m; MC26 = Montecerboli 1/2610m; SM27 = San Martino/2722m; S6b\_38 = Sesta 6b/3835m; SS20 = SP Serrazzano/2078m; SS21 = SP Serrazzano/2159m; Pont35 = Pontremoli 1/3514m; AQ23 = Anqua/2385m; AQ19 = Anqua/1939; Cerr = outcrop of the Cerreto Pass (datum from MOLLI *et alii*, 2002).

b) Traverse across a single garnet crystal (2.5 mm size), from the core to the rim, sample Montecerboli 1/2916, showing the variations in almandine (Fe), pyrope (Mg) and spessartine (Mn) composition.

- a) Diagramma spessartina vs. almandina dei granati nei Micaschisti. Ciascun punto si riferisce a un singolo granato (almeno due per campione). Per ciascun campione, le composizioni ricche in Mn si riferiscono rispettivamente al nucleo e quelle ricche in  $\text{Fe}^{2+}$  alle parti periferiche dei granati. LEGENDA (nome del Pozzo/profondità della carota): Lam35 = Lamarello 1/3501m; Sec24 = Secolo 1/2496m; Aq26 = Anqua/2635m; MV2\_19 = Monteverdi 2/1934m; MC28 = Montecerboli 1/2806m; Lum22 = Lumiera 1b/2236m; Sec24 = Secolo 1/2496m; Rd30 = Radicondoli 30b/3055m; MC29 = Montecerboli 1/2916m; MC26 = Montecerboli 1/2610m; SM27 = San Martino/2722m; S6b\_38 = Sesta 6b/3835m; SS20 = SP Serrazzano/2078m; SS21 = SP Serrazzano/2159m; Pont35 = Pontremoli 1/3514m; AQ23 = Anqua/2385m; AQ19 = Anqua/1939; Cerr = affioramento Passo del Cerreto (dati da MOLLI *et alii*, 2002). b) Traversa compositonale all'interno di un singolo cristallo di granato (dimensione 2.5 mm), dal nucleo al bordo, campione Montecerboli 1/2916, mostra le variazioni compostionali in almandina (Fe), piropo (Mg) e spessartina (Mn).



ated with a deformed pre-Sp andalusite (e.g. fig. 2c) in the micaschists which suggests a likely pre-Permian age for such rocks.

2) The lack of stratigraphic contacts between the metamorphic Mesozoic cover formations (imprinted only by the Alpine tectono-metamorphic events) and the micaschists and gneisses. In fact, the Triassic metasediments (e.g. Verrucano) are present only in a tectonic slices complex above the shallower Paleozoic Phyllitic-Quartzitic Complex (ELTER & PANDELI, 1990; PANDELI *et alii*, 1991). In contrast, in many outcropping metamorphic inliers of the Northern Apennines (e.g. Apuan Alps), the Alpine structural framework of the Triassic-Tertiary crystalline succession has also been easily recognized in the underlying pre-Triassic successions. In the latter, relicts of a coarse-grained, pre-Alpine schistosity were also locally identified at the meso- and microscale and related to the Sudetian Event of the Variscan Orogeny (CONTI *et alii*, 1991; PANDELI *et alii*, 1994 and references therein). This attribution is also supported by the lack of relict pre-Alpine schistosity in the fossiliferous Upper Visean to Permian units of Tuscany (e.g. the Carboniferous Farma Group: CONTI *et alii*, 1991; PANDELI *et alii*, 1994 and references therein).

3) The difficulties in performing a continuous structural analysis and correlating the different structural elements along the well profiles.

4) The post-tectonic, thermometamorphic imprint (from low-grade hornfels in the micaschists to high-grade hornfels in the deepest gneisses: see FRANCESCHINI, 1993, 1994, 1998; GIANELLI, 1998; RUGGIERI & GIANELLI, 2001; GIANELLI & RUGGIERI, 2002; CARELLA *et alii*, 2000; MUSUMECI *et alii*, 2002). In fact, it locally completely obliterated the previous mineralogical assemblages and textures. In particular, an overall massive hornfels texture is locally present in the deepest parts of the Gneiss Complex (Hornfels Complex in MUSUMECI *et alii*, 2002).

In spite of these difficulties, our re-examination of core samples and studies performed on cores of recent wells improves our knowledge of the complex geological framework of the Larderello subsurface and, more generally, of the tectonic-metamorphic evolution of the middle-upper crust of southern Tuscany. In particular, the following points can be outlined and discussed:

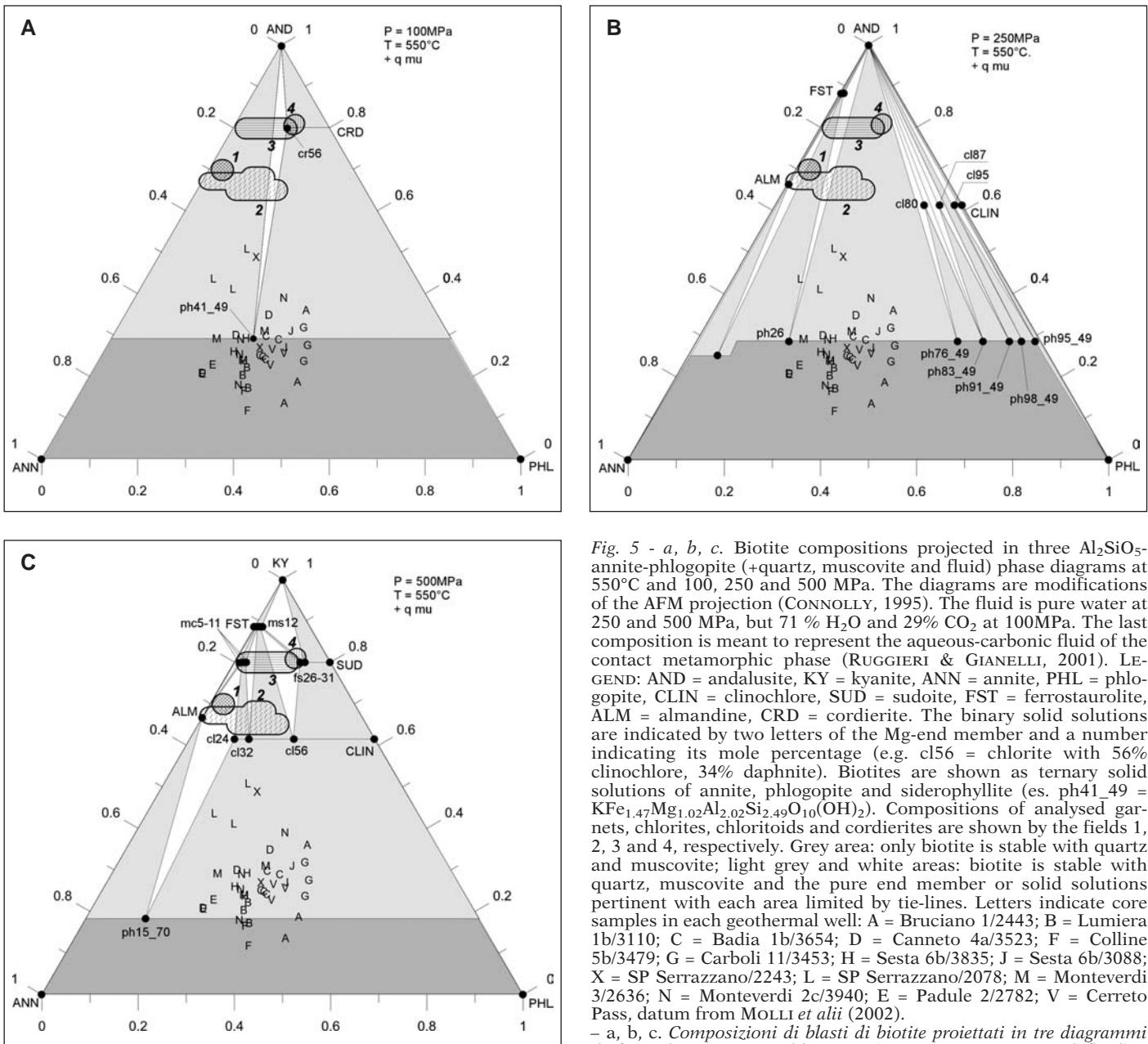
*a)* The structural framework of the Micaschist Complex rocks in the Larderello and Pontremoli subsurface is mostly due to two tectono-metamorphic events in the greenschist facies (D<sub>p</sub> and D<sub>p+1</sub>) and to a final folding (D<sub>p+2</sub>). This metamorphic assemblage is quite similar to that described for the Cerreto micaschists by MOLLI *et alii* (2002), who related these recrystallisation events to the retrograde mylonitic deformation occurred during «the Variscan post-orogenic collapse or Tethyan rift-related crustal attenuation» (i.e. the 240 Ma radiometric age obtained from the amphibolites). We do not have any additional data to support it, but the main tectono-metamorphic framework of the micaschists shows the same features as that recognized for the Alpine deformation, Oligocene-Miocene in age, of the Tuscan Metamorphic Units at the regional scale (CARMIGNANI & KLIGFIELD, 1990; FRANCESCHELLI *et alii*, 1984, 2004; ELTER & PANDELI, 1993, 1996, 2001; CAROSI *et alii*, 1995, 2002; CORSI *et alii*, 2001 and references therein). We also note that similar foliations are also present in the shallower metamor-

phic, Upper Paleozoic-Mesozoic rocks of the Larderello subsurface (FRANCESCHELLI *et alii*, 1984; ELTER & PANDELI, 1990). This attribution is strengthened by the presence at Mt. Calamita Promontory (south-eastern part of Elba Island: GARFAGNOLI *et alii*, 2004 this volume), of Sp and Sp+1 foliations in the corresponding garnet-bearing micaschists and in the overlying Verrucano metasediments together affected by Alpine folding. In this view, Molli's radiometric age of 240 Ma could be attributed to a partial resetting of the radiometric clock in the Variscan minerals.

The presence of (*a*) coarse-grained, Sp-1 foliation within pre-Sp deformed andalusite (+muscovite dated to about 285 Ma) and in mica fishes and (*b*) pre-Sp porphyroclasts (e.g. almandine garnet, characterized by a spessartine-rich core and with relicts of a previous Si foliation) suggest an older, possibly regional metamorphic evolution for the micaschists. In any case, we found no evidence of Alpine syn- or inter-kinematic garnet porphyroblasts as described by FRANCESCHINI (1998) and MUSUMECI *et alii* (2002).

Post-tectonic grossularitic garnets were found only in the eastern part of the Larderello geothermal region (Travale field). This peculiar high Ca content of the thermometamorphic garnets could be related to metasomatic fluids interacting with the numerous carbonate and carbonate-evaporitic intercalations present in the buried metamorphic successions (GIANELLI & PUXEDDU, 1978; BAGNOLI *et alii*, 1979; CASTELLUCCI *et alii*, 1983; ELTER & PANDELI, 1994 and references therein).

*b)* The coarse-grained differentiated layering of the Gneiss Complex is made up of amphibolite facies minerals which locally include relicts of typical medium-to high-grade Barrovian minerals (e.g. garnet, staurolite, prismatic sillimanite) and of a previous foliation (see ELTER & PANDELI, 1990 and BERTINI *et alii*, 1994). The sharp contact with the overlying micaschists, characterized by a different structural framework, suggests a tectonic boundary. In any case, this boundary is clearly overprinted by the post-tectonic thermometamorphic mineralogical assemblages. Besides the absence of HT-LP blastesis during the development of gneissic Sp foliation, the hypothesis of its syn-intrusive nature (i.e. FRANCESCHINI, 1994, 1998) can be ruled out by the P-T conditions of the contact metamorphism in the Larderello subsurface. They are based on fluid inclusions and mineralogical data (CATHELINÉAU *et alii*, 1994), and by assuming on the pressure conditions close to the actual depth of the contact metamorphic rocks (2.5-4.0 km), plus an extra cover of approximately 800 m, eroded in the last 4 my, with an uplift rate of approximately 0.2 mm/y (DEL MORO *et alii*, 1982; DALLMEYER & LIOTTA, 1998). In particular, the contact metamorphism in the Larderello subsurface occurred in a pressure range of approximately 85-120 MPa, assuming an average rock density of 2.6 g/cm<sup>3</sup> and lithostatic conditions (GIANELLI & RUGGIERI, 2002). According to CARELLA *et alii* (2000) and MUSUMECI *et alii* (2002), the upper pressure limit is higher (150-200 MPa). The chemical compositions of micas of both micaschists and gneisses reveal that the X<sub>Mg</sub> of the biotites is higher than 0.3, also in contact metamorphic rocks where cordierite, andalusite, quartz and muscovite are present. This indicates minimum pressures of 150-250 MPa, depending on the thermodynamic data-set and the presence or absence of graphite in the system (PATTISON *et alii*, 1997). These values are higher than the lithostatic



*Fig. 5 - a, b, c.* Biotite compositions projected in three  $\text{Al}_2\text{SiO}_5$ -annite-phlogopite (+quartz, muscovite and fluid) phase diagrams at  $550^\circ\text{C}$  and 100, 250 and 500 MPa. The diagrams are modifications of the AFM projection (CONNOLY, 1995). The fluid is pure water at 250 and 500 MPa, but 71 %  $\text{H}_2\text{O}$  and 29%  $\text{CO}_2$  at 100MPa. The last composition is meant to represent the aqueous-carbonic fluid of the contact metamorphic phase (RUGGIERI & GIANELLI, 2001). LEGEND: AND = andalusite, KY = kyanite, ANN = annite, PHL = phlogopite, CLIN = clinochlore, SUD = sudoite, FST = ferrostaurolite, ALM = almandine, CRD = cordierite. The binary solid solutions are indicated by two letters of the Mg-end member and a number indicating its mole percentage (e.g. cl56 = chlorite with 56% clinochlore, 34% daphnite). Biotites are shown as ternary solid solutions of annite, phlogopite and siderophyllite (es. ph41\_49 =  $\text{KFe}_{1.47}\text{Mg}_{1.02}\text{Al}_{2.02}\text{Si}_{2.49}\text{O}_{10}(\text{OH})_2$ ). Compositions of analysed garnets, chlorites, chloritoids and cordierites are shown by the fields 1, 2, 3 and 4, respectively. Grey area: only biotite is stable with quartz and muscovite; light grey and white areas: biotite is stable with quartz, muscovite and the pure end member or solid solutions pertinent with each area limited by tie-lines. Letters indicate core samples in each geothermal well: A = Bruciano 1/2443; B = Lumiera 1b/3110; C = Badia 1b/3654; D = Canneto 4a/3523; F = Colline 5b/3479; G = Carboli 11/3453; H = Sesta 6b/3835; J = Sesta 6b/3088; X = SP Serrazzano/2243; L = SP Serrazzano/2078; M = Monteverdi 3/2636; N = Monteverdi 2c/3940; E = Padule 2/2782; V = Cerreto Pass, datum from MOLLI et alii (2002).

- a, b, c. Composizioni di blasti di biotite proiettati in tre diagrammi di fase  $\text{Al}_2\text{SiO}_5$ -annite-phlogopite (+quartz, muscovite and fluid) a  $550^\circ\text{C}$  e 100, 250 e 500 MPa. I diagrammi sono modificazioni

della proiezione AFM (CONNOLY, 1995). Il fluido è acqua pura a 250 e 500 MPa, ma 71 %  $\text{H}_2\text{O}$  e 29%  $\text{CO}_2$  a 100MPa. L'ultima composizione vuole rappresentare il fluido acquoso-carbonico della fase metamorfica di contatto (RUGGIERI & GIANELLI, 2001). LEGENDA: AND = andalusite, KY = cianite, ANN = annite, PHL = flogopite, CLIN = clinocloro, SUD = sudoite, FST = ferrostaurolite, ALM = almandino, CRD = cordierite. Le soluzioni solide binarie sono indicate da due lettere del termine ricco in Mg e da un numero che rappresenta la mole % (es. cl56 = clorite con 56% clinocloro, 34% dafnito). Le biotiti sono rappresentate come soluzioni ternarie solide di annite, flogopite e siderofillite (es. ph41\_49 =  $\text{KFe}_{1.47}\text{Mg}_{1.02}\text{Al}_{2.02}\text{Si}_{2.49}\text{O}_{10}(\text{OH})_2$ ). Le composizioni dei granati, cloriti, cloritoidi e cordieriti analizzate sono rappresentate rispettivamente dai campi 1, 2, 3 e 4. Area grigia: soltanto la biotite è stabile con il quarzo e la muscovite; Aree grigio chiare e bianche: la biotite è stabile con quarzo, muscovite e il termine puro o soluzioni solide pertinenti con ciascuna area limitata da linee. Le lettere indicano la composizione del nucleo dei campioni in ciascun pozzo geotermico: A = Bruciano 1/2443; B = Lumiera 1b/3110; C = Badia 1b/3654; D = Canneto 4a/3523; F = Colline 5b/3479; G = Carboli 11/3453; H = Sesta 6b/3835; J = Sesta 6b/3088; X = SP Serrazzano/2243; L = SP Serrazzano/2078; M = Monteverdi 3/2636; N = Monteverdi 2c/3940; E = Padule 2/2782; V = Passo del Cerreto (dati da MOLLI et alii, 2002).

pressure of the thermal aureole (85-120 MPa, see above), and this may suggest that the system was not under-equilibrium conditions for the reaction  $2\text{muscovite} + 3\text{cordierite} = 2\text{biotite} + 8\text{Al}_2\text{SiO}_5 + 7\text{quartz} + 3\text{nH}_2\text{O}$ , possibly because one or more minerals are relicts, or keep a chemical composition inherited from previous regional metamorphic phases. The high Si a.p.f.u. value of mus-

covites in metapelites, where cordierite and andalusite are present, indicate that this mineral did not, or only partially, re-equilibrated during the contact metamorphic phase. For example, values of 3.45 are found in gneisses with clear evidence of contact metamorphism, and the corresponding minimum pressure value, estimated using the geobarometer of MASSONNE & SZPURKA (1997) is

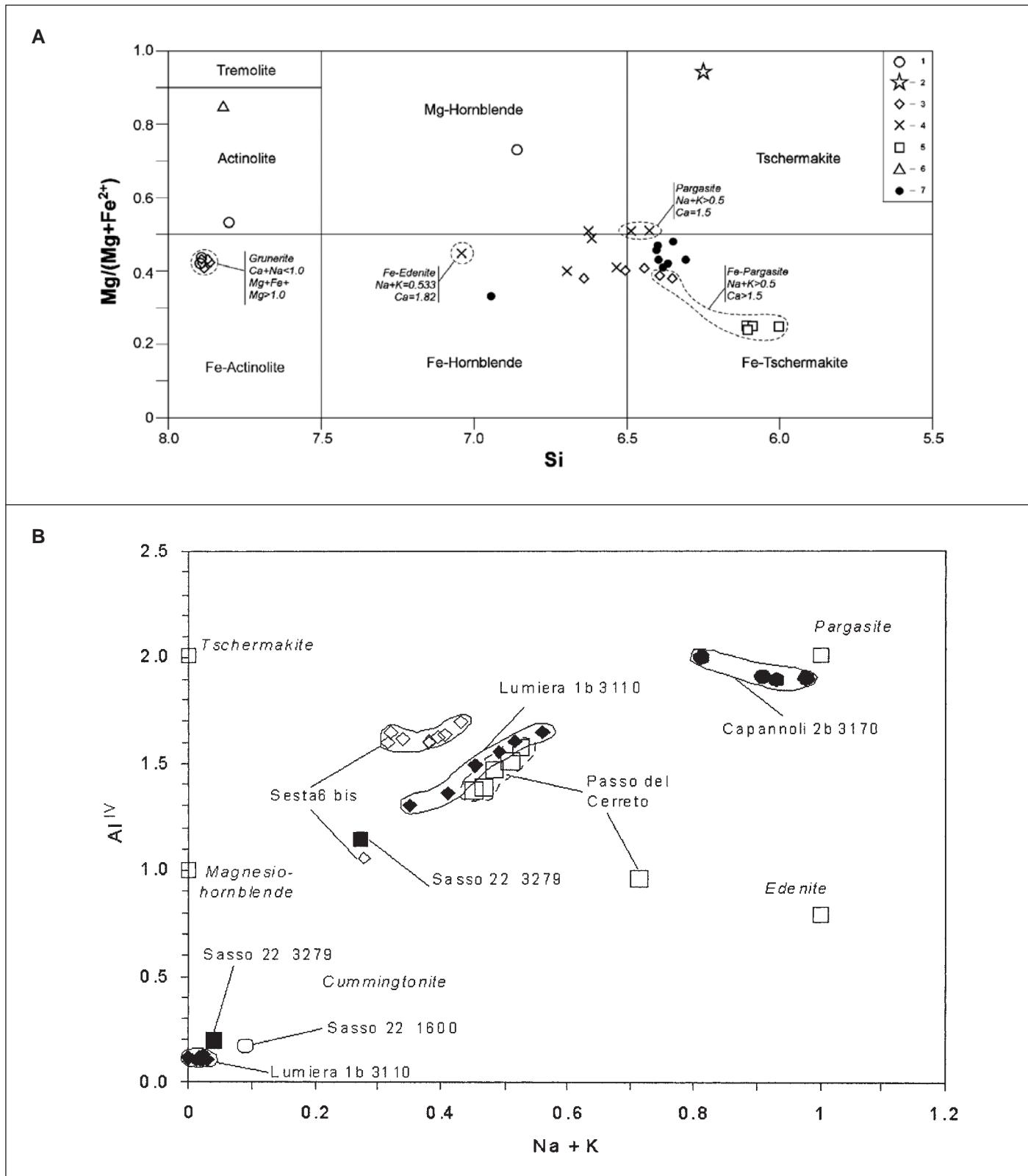


Fig. 6 - Amphibole compositions from the amphibolites in the micaschist: a) Mg/(Mg+Fe<sup>2+</sup>) vs. Si (a.p.f.u.) diagram, according to the classification of LEAKE *et alii* (1997). The Mg-Fe hornblendes and Fe-tschermakites along the main foliation are distinguished from post-tectonic actinolites, grunerites and Mg-rich tschermakites formed by contact or hydrothermal metamorphism. LEGEND (well name/core sample depth): 1) Sasso 22/3279 (CAVARRETTA *et alii*, 1982); 2) Monteverdi 2c/3567; 3) Lumiera 1b/3110; 4) Cerreto Pass; 5) Capannoli 2b/3170; 6) Sasso 22/1600; 7) Sesta 6b/3710; b) Al<sup>IV</sup> vs. Na+K (a.p.f.u.) diagram.

- Composizioni di anfibi nei Micaschisti: a) Diagramma Mg/(Mg+Fe<sup>2+</sup>) vs. Si (a.p.f.u.) secondo la classificazione di LEAKE et alii (1997). Le Mg-Fe orneblende e le Fe-tschermakiti della filiazione principale sono distinte da actinoliti, gruneriti e dalle tschermakiti ricche in Mg post-tettoniche formate dal metamorfismo di contatto o idrotermale. LEGENDA (nome del pozzo/profondità della carota): 1) Sasso 22/3279 (CAVARRETTA et alii, 1982); 2) Monteverdi 2c/3567; 3) Lumiera 1b/3110; 4) Cerreto Pass; 5) Capannoli 2b/3170; 6) Sasso 22/1600; 7) Sesta 6b/3710; b) Diagramma Al<sup>IV</sup> vs. Na+K (a.p.f.u.).

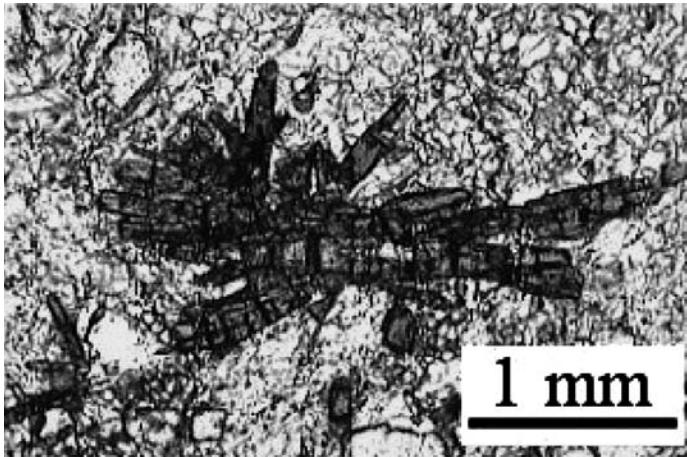


Fig. 7 - A mineral of the warwickite-yuanfuliite group found in a calc-silicate rock in the Larderello subsurface (well Monteverdi 2c/3567).

– Un minerale del gruppo della warwickite-yuanfuliite trovato in una roccia calc-silicatica del sottosuolo di Larderello (pozzo Monteverdi 2c/3567).

unrealistically close to 500 MPa, if we assume that muscovite re-equilibrated during the contact metamorphic event. The chlorite compositions are consistent with a poorly defined pressure and temperature range ( $200 < P < 700$  MPa;  $250 < T < 375^\circ\text{C}$ , see VIDAL *et alii*, 2001), and cannot be used for precise geothermobarometric estimates.

These data suggest that the muscovite and biotite of the gneissic layering cannot belong to a primary thermometamorphic foliation, but originated during a regional metamorphic evolution and were then only partially recrystallised by the Late Alpine contact metamorphism. In this framework it is significant that BERTINI *et alii* (1994) designate, through micro-chemical analyses, an amphibolite facies for the micas aligned along the gneissic layering.

Other minerals in the gneisses are incompatible with the P-T conditions estimated for the contact metamorphic aureole. For example, the incompatibility of the almandine-rich garnet included in the gneissic Dp is shown by the AFM projections (fig. 5). In these projections the garnet is stable at pressures higher than 100 MPa, at  $550^\circ\text{C}$ , and probably crystallised in equilibrium with staurolite (or carpholite) or chlorite, or staurolite and biotite which locally represent (as well the garnet) pre-Dp mineral relicts in the gneiss (see also ELTER & PANDELI, 1990; BERTINI *et alii*, 1994). Also the finding of relict prismatic sillimanite is not in contrast with this Barrovian zone. In fact, temperatures over  $600^\circ\text{C}$  were estimated by MOLLI *et alii* (2002) for the pre-Alpine Barrovian metamorphism of the amphibolites at Cerreto Pass.

c) The attribution of Sp in the gneisses to the Variscan (ELTER & PANDELI, 1990) or to the highly pervasive Alpine Sp+1 foliation (FRANCESCHINI, 1994; 1998; MUSUMECI *et alii*, 2002) needs further discussion.

Rocks similar to Larderello micaschists, amphibolites and gneisses crop out in central and NE Sardinia. In particular, paragneiss and garnet- and staurolite-bearing micaschists characterised the deepest unit of the Nappe Zone (M. Grighini Unit) (CAROSI *et alii*, 1992), of the

Low- to Medium- grade Complex of the Axial Zone (FRANCESCHELLI *et alii*, 1982; OGGIANO & DI PISA, 1992) and of the Posada-Asinara Shear Zone (ELTER *et alii*, 1990; CARMIGNANI *et alii*, 1982, 2001). The syn-collisional Barrovian metamorphic evolution of the Low- to Medium- grade Complex (dated 336-350 Ma: Rb/Sr and Ar/Ar radiometric ages in DEL MORO *et alii*, 1991) shows evident analogies with respect to the Larderello gneisses. For example, plagioclase and garnet porphyroblasts, including relict schistosity and surrounded by the later main foliation, are a typical feature of the rocks of the Garnet+albite+oligoclase and Staurolite+biotite Zones, within the Sardinian Low- to Medium- grade Complex of the Axial Zone (CARMIGNANI *et alii*, 1982, 2001; FRANCESCHELLI *et alii*, 1982; OGGIANO & DI PISA, 1988; ELTER *et alii*, 1989; DI VINCENZO *et alii*, 2004). Further analogies can be found with the sillimanite+muscovite gneiss of the High- Grade Complex of the Axial Zone (cfr. FRANCESCHELLI *et alii*, 1982; OGGIANO & DI PISA, 1992). In addition, the garnet porphyroclasts show a prograde zoning (decrease of spessartine from core to rim: FRANCESCHELLI *et alii*, 1982; DI VINCENZO *et alii*, 2004) which is also present in the pre-Dp garnets of the Larderello subsurface (this paper) and of Cerreto Pass (MOLLI *et alii*, 2002) (see fig. 4a). Finally, the main foliation of the considered Sardinian rocks is overprinted by the thermometamorphic mineral assemblage related to the Uppermost Carboniferous-Lower Permian, peraluminous magmatism (Granitoid Complex in OGGIANO & DI PISA, 1992; RICCI, 1992; CARMIGNANI *et alii*, 2001) of Northern Sardinia. This magmatic event is also indicated by the crystallisation of andalusite+muscovite at 285 Ma in the Larderello micaschists.

The amphibolite facies fabric of the gneisses is recognizable as pre-Dp mineralogical relicts in the micaschists (e.g. garnet, coarse-grained mica-fish). These similarities are also strengthened by our data and, in particular, by the similar composition of the garnets in both complexes, and of the oligoclase core of the albite porphyroblasts in the micaschists and the plagioclase blasts of the gneissic Dp. Moreover, the analytical data obtained from amphiboles show that the 330 Ma main foliation of the Cerreto Pass amphibolites (MOLLI *et alii*, 2002) is made up of the same minerals as the amphibolites occurring in the Larderello micaschists and gneisses. A further analogy is provided by their ocean floor basalts (OFB) affinities (PUXEDDU *et alii*, 1984; MOLLI *et alii*, 2002), which recall the Variscan OFB orthoamphibolite intercalations within the Posada-Asinara Shear Zone in Sardinia (cfr. ELTER *et alii*, 1990; CAPPELLI *et alii*, 1992), whereas the other Paleozoic and Triassic metabasites of Tuscany are within plate (WP) or calc-alkaline metavolcanites (CONTI *et alii*, 1988; PUXEDDU *et alii*, 1984; PANDELI *et alii*, 1994; PANDELI, 2002 and references therein).

In conclusion, we think that the gneissic layering can be related to a pre-Alpine foliation and that the rocks of the Micaschist and Gneiss Complexes were affected by the same medium grade, probably Variscan, tectono-metamorphic events. In particular, the reconstructed metamorphic evolution of both complexes (BERTINI *et alii*, 1994; MOLLI *et alii*, 2002; FRANCESCHELLI *et alii*, 2004), besides higher peak P-T values for the gneisses, passed through an earlier Barrovian-type intermediate P event ( $P \approx 6-7$  kb and  $T = 550^\circ\text{-}650^\circ$  according to BERTINI *et alii*, 1994) to a subsequent lower P syn-tectonic event

( $P \approx 2-3.5$  kb and  $T = 550^\circ-600^\circ$  according to BERTINI *et alii*, 1994). These P-T paths are comparable to those of other well-known Variscan units of southwestern Europe and northern Africa (e.g. Massif Central, NE-Sardinia, Calabrian-Peloritan arc, Betic-Rifean belt: see fig. 5 in ELTER & PANDELI, 1996).

In this model, we believe that only the rocks of the Micaschist Complex were affected by the pervasive Alpine tectono-metamorphic evolution which obliterated most of the Variscan framework. This Alpine overprint is in the P-T range estimated by different authors for the outcropping Paleozoic-Tertiary Tuscan metamorphic units (200-600 MPa and 300-450 °C for DESCHAMPS, 1980; DECHOMETS, 1983; PUXEDDU *et alii*, 1984; FRANCESCHELLI *et alii*, 1986; or with pressures up to 1500 MPa according to JOLIVET *et alii*, 1998; see also FRANCESCHELLI *et alii*, 2004 for a general review).

## CONCLUSIONS

The textural and mineralogical data discussed in the previous paragraphs point to a complicated tectonic and metamorphic evolution for the Micaschist Complex and Gneiss Complex, and more generally of the middle-upper crust of the inner part of the Northern Apennines. Notwithstanding the difficulties in performing a classical continuous structural analyses of the micaschists and gneisses cut by the wells, and the lack of radiometric dates for their foliations, comparison of their structural and mineralogical features with those of other dated metamorphic, Alpine and pre-Alpine successions of the Northern Apennines and Sardinia allows the following conclusions:

1) The occurrence, in the deepest part of the Larderello field, of two regional metamorphic complexes: the Micaschist Complex and the Gneiss Complex. These rocks, as well as the overlying phyllitic-quartzitic units (e.g. the «Phyllitic-Quartzitic Complex» of ELTER & PANDELI, 1990), have been affected by contact metamorphism under P-T conditions of 85-100 MPa and 500-600°C which locally obliterated previous textures (see also MUSUMECI *et alii*, 2002). The contact metamorphic aureole thickness of more than 1500m (CARELLA *et alii*, 2000 and MUSUMECI *et alii*, 2002) can be related to the co-existence of Late Alpine and pre-Alpine HT-LP minerals and/or to the interference of different contact aureoles linked to multiple granitoid intrusions within the middle-upper crust of the Larderello geothermal region.

2) The hypothesized pre-Alpine medium-high grade Barrovian to HT-LP metamorphic evolution recognized in the Micaschist Complex and in the Gneiss Complex is comparable to that defined for the Paleozoic units of northern Sardinia during the Variscan orogeny. The presence, in both units of similar orthoamphibolite layers with OFB affinity could also suggest that, notwithstanding their actual tectonic contact, the two complexes had an original relationship of continuity in the middle part of the Variscan crust. Therefore, we disagree with FRANCESCHINI (1998) and MUSUMECI *et alii* (2002) on their conclusions that a pre-Alpine tectonic fabric is absent in all the units at Larderello and that the gneissic layering can be related to the locally very pervasive Sp+1 Alpine foliation observed in the deepest micaschists.

3) According to ELTER & PANDELI (1990) and this paper, only the Micaschist Complex was affected by pervasive Alpine foliations and recrystallisation. Therefore, this Complex has been grouped with other Paleozoic to Tertiary Tuscan successions which were deformed by the Alpine tectono-metamorphic events (e.g. Monticiano-Roccastrada Unit in BERTINI *et alii*, 1991). If the main foliation of the Larderello gneisses represents the Variscan foliation (which was only weakly affected by Alpine crenulations), the Gneiss Complex can be interpreted as the substantially undeformed basement of the Apennines foreland (BERTINI *et alii*, 1991) or as a more rigid thick slice within the Apenninic tectonic pile of nappes (ELTER & PANDELI, 1996). In any case, the discovery of well-preserved Variscan rocks within the units of the Northern Apennines chain is not surprising. In fact, the Cerreto amphibolites, which preserve most of their 330 Ma main foliation (cfr. MOLLI *et alii*, 2002), and the associated micaschists are part of an Alpine tectonic slice complex together with Mesozoic-Tertiary units (e.g. the Triassic Verrucano and Burano anhydrite Fm.: DI SABATINO *et alii*, 1979; ANDREOZZI *et alii*, 1987; CALZOLARI *et alii*, 1987; PLESI *et alii*, 2000).

4) The classification of the studied rocks as hornfels (FRANCESCHINI, 1998; CARELLA *et alii*, 2000; MUSUMECI *et alii*, 2002) is undoubtedly important for defining the shape and areal extent of the buried granitoids in the Larderello geothermal region. On the other hand, notwithstanding the locally pervasive Pliocene-Quaternary thermometamorphic imprint, we think that is more useful to classify the studied rocks as regional metamorphic rocks, in order to reconstruct the structural relationships between the crystalline units of the middle-upper crust of southern Tuscany and in particular of the subsurface of the Larderello geothermal region along the CROP-18 seismic profile.

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