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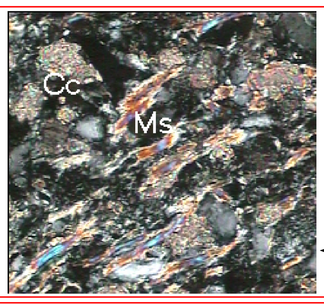
Fluid evolution and water-rock interaction in the Larderello geothermal field: evidence from mineralogical, petrographic and fluid inclusions studies

The study of core-samples and cuttings from geothermal wells provide important information either on the underground geology of the geothermal systems and on the hydrothermal and contact metamorphic minerals, filling veins or replacing previous phases. Such minerals result from fluid-rock interaction processes. The past fluid circulation in geothermal systems are also recorded by fluid inclusions trapped in minerals. Mineralogical, petrographic and fluid inclusions studies, therefore, can provide useful data on the characteristics of the reservoir rocks and on the physical-chemical evolution of the fluid migrating in geothermal systems. A good example of the information which can be obtained using these studies is represented by the reconstruction of the fluid history in the Larderello geothermal field. The Larderello geothermal field is a long-living systems characterized by different phases of evolution and a complex hydrothermal activity. On seismic reflection profiles, a high-amplitude reflector exhibiting local "bright spot" features, known as the "K-horizon" is located at about 3-6 km depth below the ground level and coincides with temperature of 400-450°C. This horizon was never reached during deep drilling, except in the San Pompeo 2 well which blew out on reaching this zone of pressurized fluids. Regardless of the interpretation of the K-horizon, the only phenomenon that is able to account for the seismic characteristics of this horizon is the presence of micro-cracks and micro-fractures filled locally with fluids, this feature would produce seismic "bright spots".

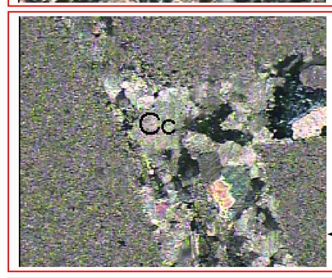
Another seismic horizon (H-horizon) with seismic features similar to the K-horizon, but occurs above the latter, at depth of 2-4 km below the ground level, in correspondence of the contact metamorphic rocks. Important productive layers of superheated steam with temperatures of 300-350°C occurs within the H-horizon.

Geological units



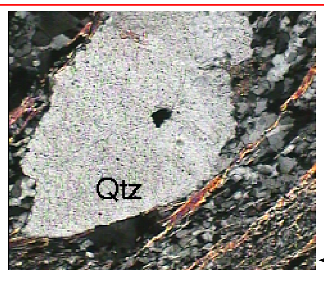
Ligurian and sub-ligurian units: Jurassic to Eocene ophiolite and flysch sequences

Sasso 22-130



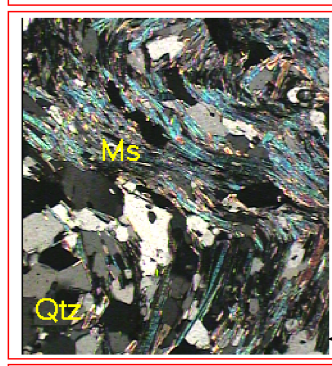
Tuscan nappe: Upper Triassic to Oligo-Miocene siliciclastic, carbonate and evaporitic sequences

San Pompeo 2-469, Mesozoic carbonates



Tectonic wedges complex: mainly made up of Triassic metasiliciclastics and carbonates, Palaeozoic quartzite and phyllite and Upper Triassic evaporites.

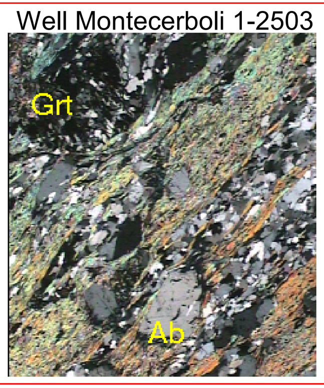
Sasso 22-1365



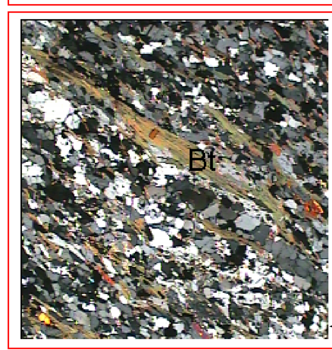
Phyllitic and quartzitic complex: metagreywacke with minor metabasite levels of probably Late Cambrian–Ordovician age and locally Silurian/Devonian carbonate–siliciclastic metasediments.

Well Anqua-1805

Well Montecerboli 1-2503



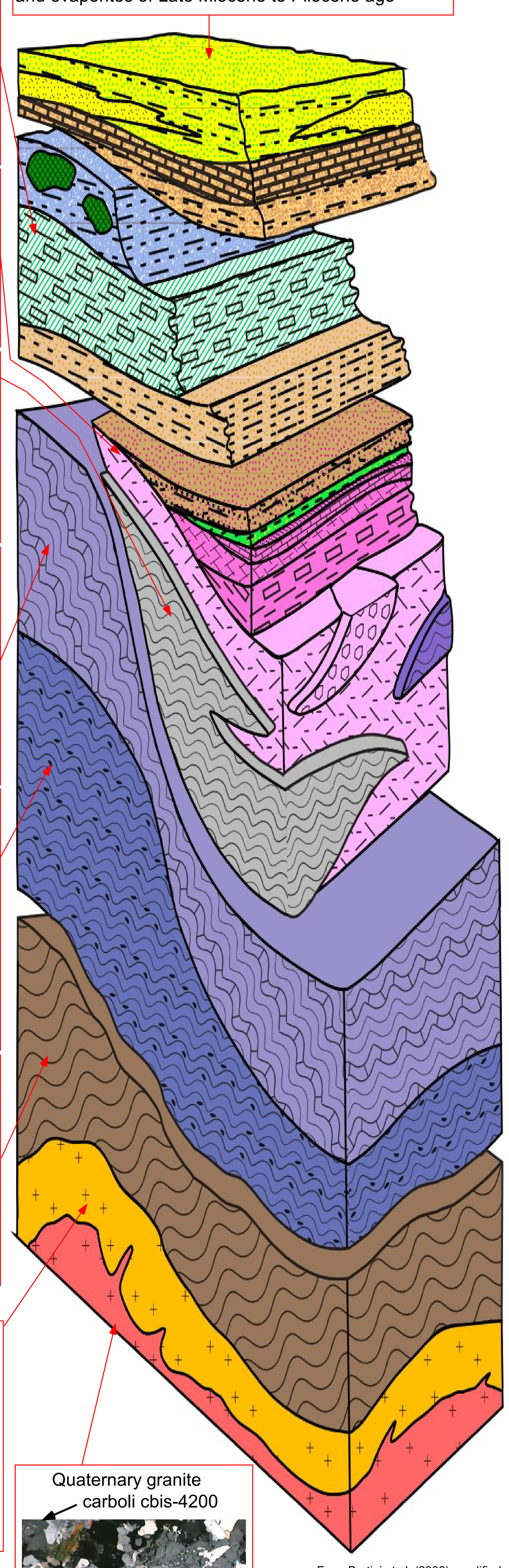
Micaschist complex: almandine-bearing albite micaschist with minor amphibolite (?Precambrian–?Early Palaeozoic). A single Rb–Sr age (285 ± 11 Ma) has been related to the Late Variscan high temperature–low pressure (HT–LP) event.



Gneiss complex: gneiss, consisting of quartz, plagioclase, biotite and garnet as major components, minor amphibolite layers and rare calc-silicate rocks (?Precambrian–?Early Palaeozoic).

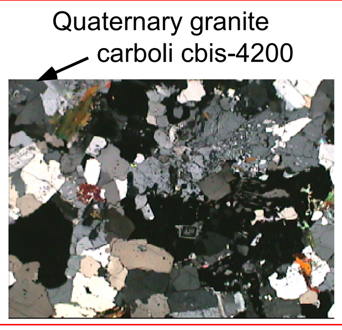
Well Sasso 22-3530

Marine and lacustrine sediments: sands, clays, marls and evaporites of Late Miocene to Pliocene age



Pliocene granite

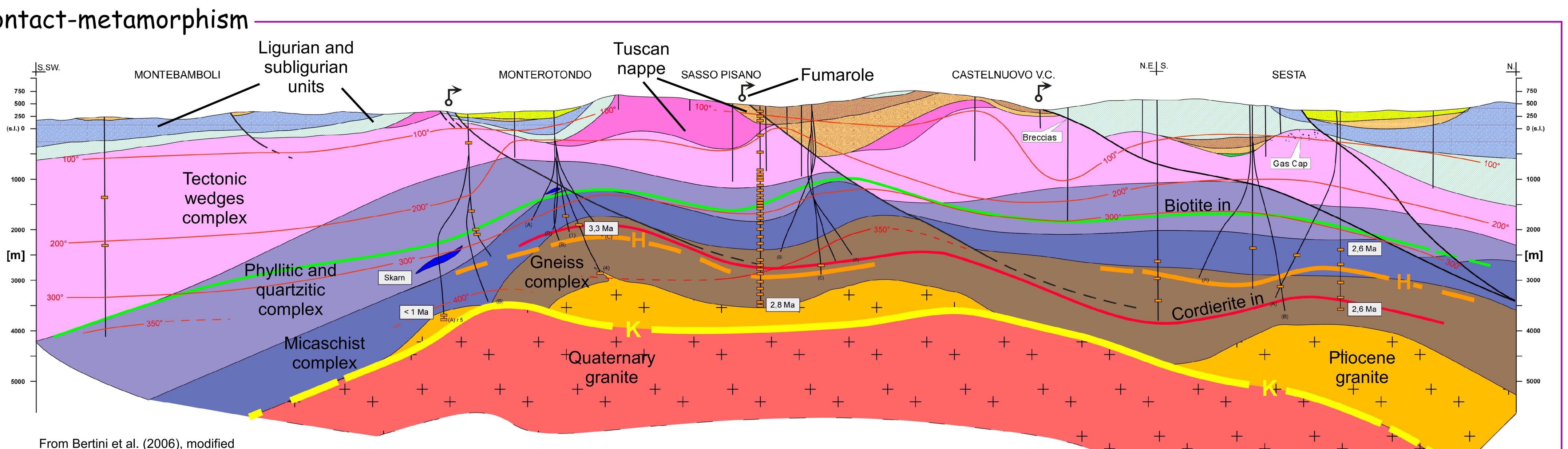
Quaternary granite carboli cbis-4200



From Bertini et al. (2006), modified

The Rb-Sr, 40Ar-39Ar and K-Ar ages of both granite and contact metamorphic minerals range from 1.0 to 3.8 Ma.

Contact-metamorphism



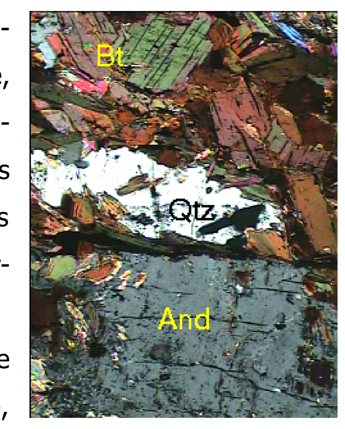
From Bertini et al. (2006), modified

Contact-metamorphism on phyllites produced the re-crystallization of muscovite and the crystallization of a post-tectonic biotite (after chlorite), mimetic on previous folds and crenulations, andalusite, tourmaline. The schistose fabric of the rocks gives way to a granoblastic texture, sometimes with triple-point grain boundaries, although not pervasively diffuse. Thermally metamorphosed micaschists show a similar post-tectonic mineral assemblage. In these rocks a relict almandine-rich garnet is often present, and is clearly distinguished by less common post-tectonic spessartine- and grossular-rich garnet. In the pelitic hornfelses, K-feldspar, plagioclase and minor corundum can be present.

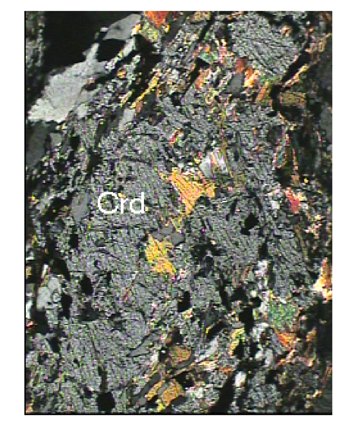
The thermometamorphic mineral assemblage in the gneissic rocks consists of post-tectonic biotite with decussate texture, poikiloblastic cordierite and andalusite, frequent crystallization of tourmaline, and re-crystallization of plagioclase and feldspar.

Thermally metamorphosed amphibolites are characterized by a granoblastic texture. These rocks consist of a post-tectonic grunerite crystallised after a green pargasitic hornblende, plagioclase, biotite, quartz and Fe-Ti-oxide.

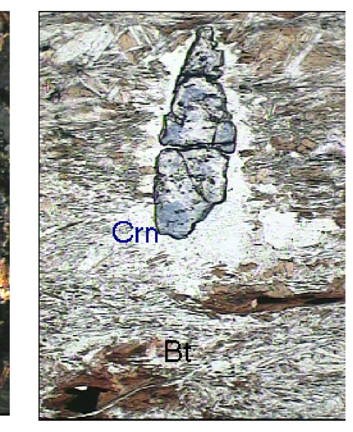
Rare marbles and calc-silicate contact metamorphic rocks have been found in a few geothermal wells. In particular, in the Selva 4 well (3370 m depth), the mineral assemblages consist of: i) calcite, dolomite, diopside, forsterite, tremolite and phlogopite, and ii) calcite, dolomite, anhydrite, phlogopite, plagioclase (oligoclase-andesine) and diopside.



Well Serrazzano Sperimentale 1-2243. Contact-metamorphic biotite (Bt), quartz (Qtz) and andalusite (And)

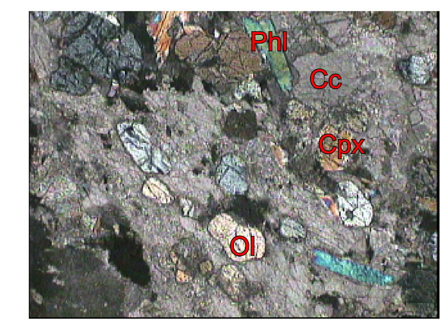


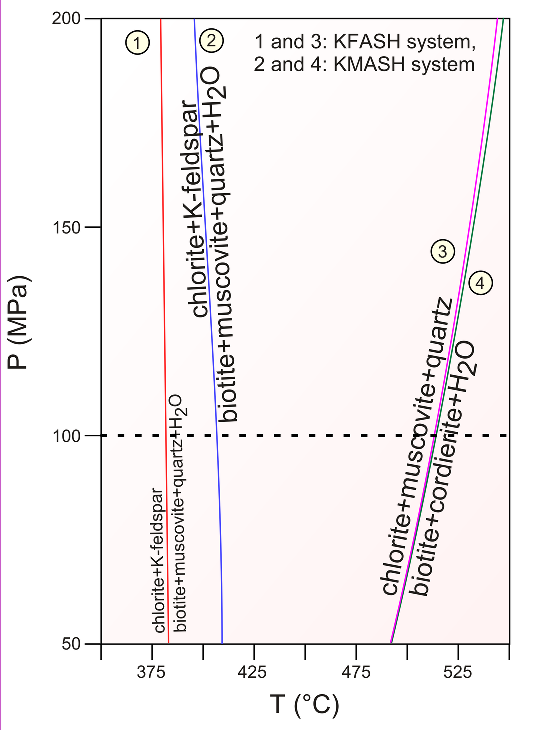
Well Sasso 22-2507. Contact-metamorphic cordierite (Crd) partially replaced by sericite



Well San Pompeo 2-2900 (fragments ejected well blow out). Contact-metamorphic minerals: corundum (Crn) and biotite (Bt) in gneiss.

The mineral assemblages found in the calc-silicate rock of Selva 4 well at 3177 m depth, with calcite and dolomite coexisting with diopside, forsterite and phlogopite (with sporadic tremolite), indicate intermediate-to-high XCO_2 (near the pseudo-invariant: point A in figure below, corresponding to an XCO_2 around 0.50 and a temperature of 545 °C at a pressure of 100 MPa).

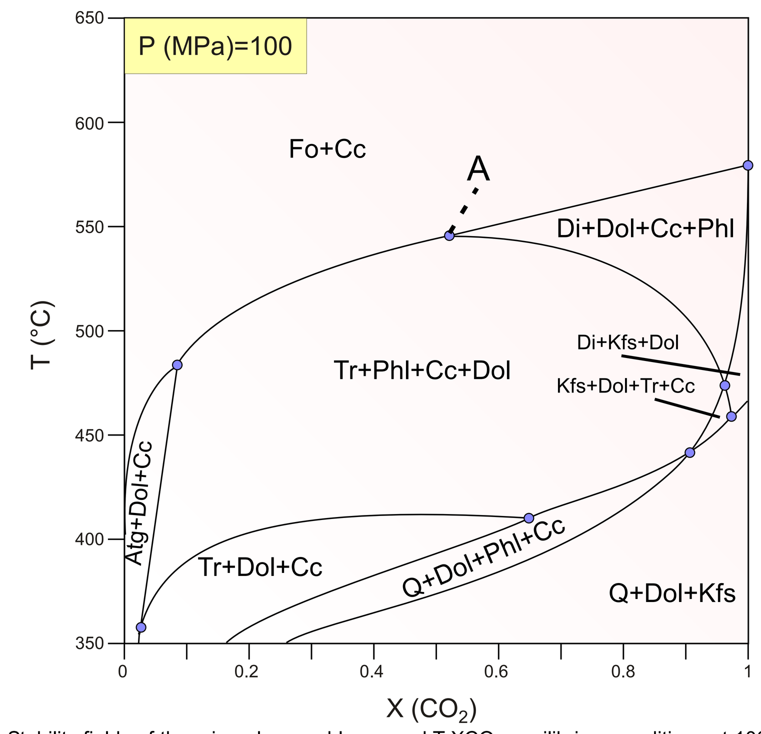




Mineral equilibria of typical contact metamorphic reaction found in the Larderello geothermal field computed for the KMASH and KFASH systems using the PeRpLeX code (from Gianelli and Ruggieri, 2002; modified).

In addition, high-temperature mineral assemblages (quartz, tourmaline, biotite and plagioclase) were also found along hydrothermal veins cross-cutting micaschist and gneiss. Tourmaline, in particular, is a widespread mineral in deep samples and testify a B-metasomatism related to contact-metamorphism. An example, of HT minerals along veins is given by this core-sample from the well Carboli 11-3455 were tourmaline, quartz, biotite are the most common minerals

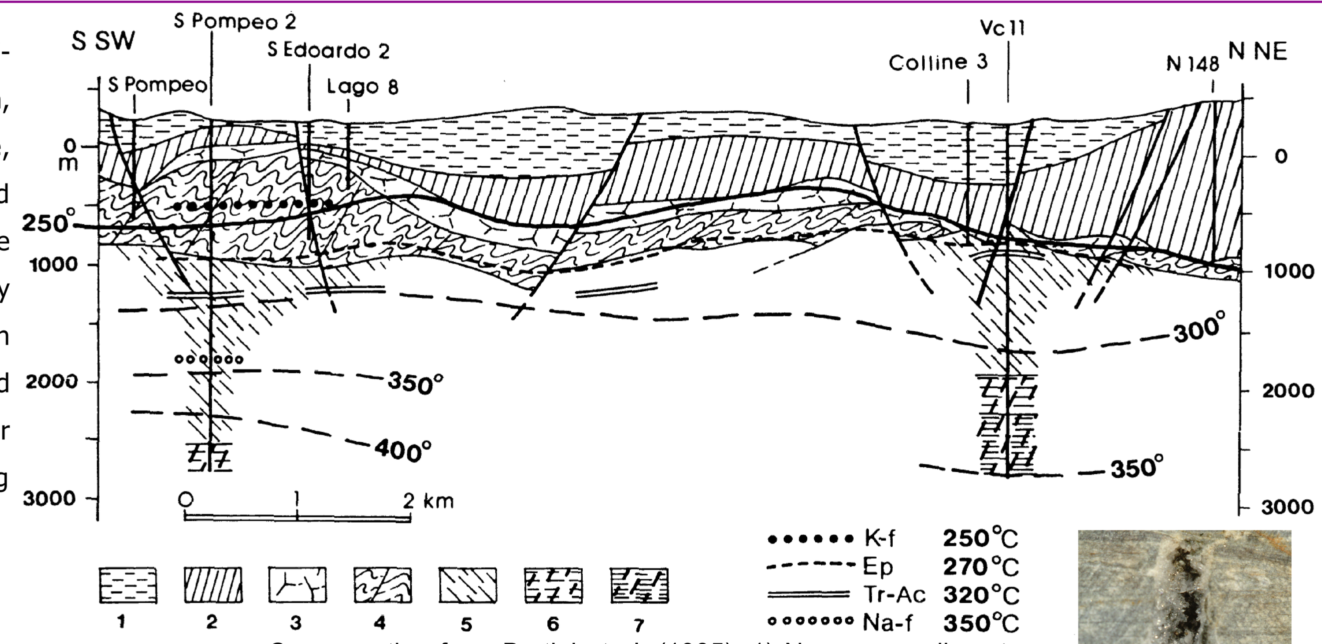
A minimum temperature of 400°C can be assumed for a contact metamorphic event, on the basis of the first appearance of biotite in the presence of quartz, K-feldspar, chlorite and muscovite. The attainment of the cordierite isograde, with the disappearance of chlorite and muscovite and the crystallization of biotite in metapelites, can occur at temperatures of about 500°C. These temperatures are in agreement with the temperatures estimated at 100 MPa from the P-T equilibrium lines. The occurrence of grunerite in the amphibolite, together with the labradoritic composition of plagioclase, indicates the attainment of the amphibolite zone and temperatures possibly over 600°C. Whereas the occurrence of corundum in equilibrium texture with K-feldspar, observed in some core-samples, indicates temperature of about 620°C



Stability fields of the mineral assemblages and T-XCO_2 equilibrium conditions at 100 MPa for calc-silicate rocks at Larderello. A: pseudo-invariant point describing the condition of Selva 4 well (3177 m depth), with calcite and dolomite coexisting with diopside, forsterite, phlogopite and sporadic tremolite. The diagram assumes saturation with calcite, dolomite and H2O. Abbreviations: Atg = antigorite, Cc = calcite, Di = diopside, Dol = dolomite, Fo = forsterite, Kfs = potassium feldspar, Phl = phlogopite, Q = quartz, Tc = talc, Tr = tremolite. From Gianelli and Ruggieri (2002)

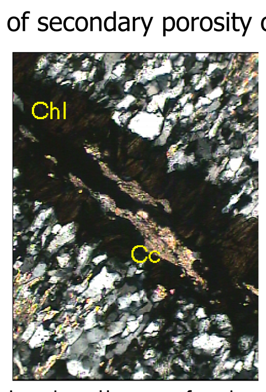
Hydrothermal alteration

The hydrothermal stage at Larderello produced in the reservoir rocks basically two types of late hydrothermal alteration: a propylitic-type alteration, characterized by epidote, chlorite, quartz, calcite, K-feldspar, titanite, tremolite-actinolite, anhydrite, albite and pyrite in variable proportions; and sericitic-type, with K-mica, chlorite and quartz in different proportions. The propylitic-type alteration is probably related to the circulation of nearly neutral-pH solution, whereas the sericitic-type alteration, which has been found in cordierite-bearing contact metamorphic rocks and granite, formed from a solution with a pH below neutrality. The hydrothermal phases occur as fracture filling, hydraulic breccias cement and, more commonly, as filling of secondary porosity originated by the dissolution of previous minerals.

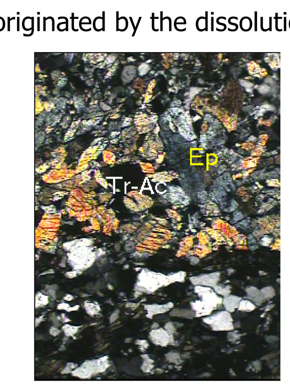


Cross section from Bertini et al. (1985). 1) Neogene sediments, 2) Ligurian units, 3) Tuscan Nappe, 4) tectonic wedge complex, 5) phyllitic and quartzitic complex, 6) micaschist complex, 7) gneiss complex

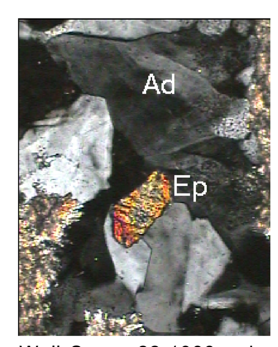
The distribution of hydrothermal minerals with temperature allowed the identification of the following four "key minerals" whose first appearance indicates the attainment of well defined temperature ranges in the deep reservoir: K-feldspar (K-f); epidote (ep); tremolite-actinolite (tr-ac) albite or plagioclas (Na-f).



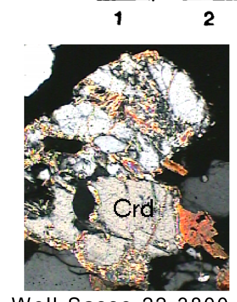
Larderello profondo-1407,hydrothermal veins filled by chlorite (chl) and calcite (cc).



Well Sasso 22-2895, hydrothermal minerals (epidote: ep,tremolite-actinolite:tr-ac).



Well Sasso 22-1988, adularia (Ad), and epidoto (ep).

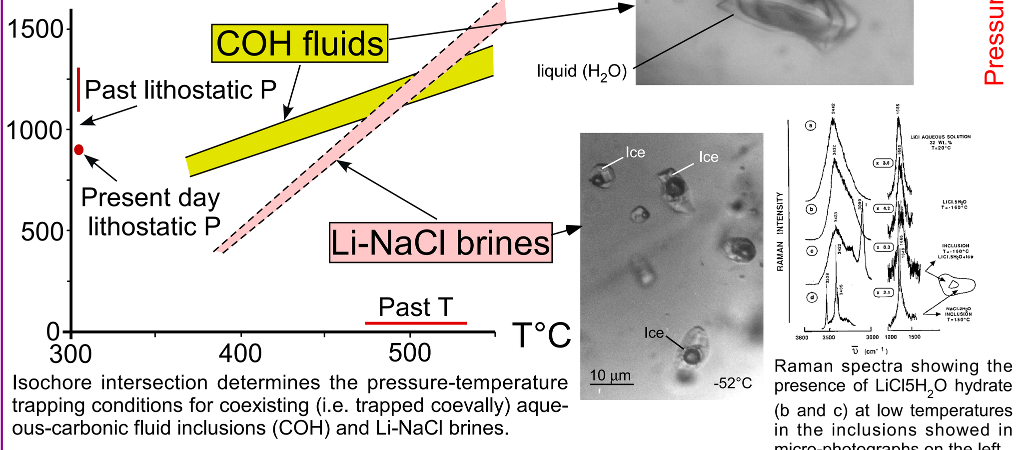


Well Sasso 22-3800, contact-metamorphic cordierite (Crd) partially replaced by sericte.

Well MV2A-1871. Hydrothermal vein cross-cutting phyllites. Main hydrothermal minerals: quartz and chlorite.

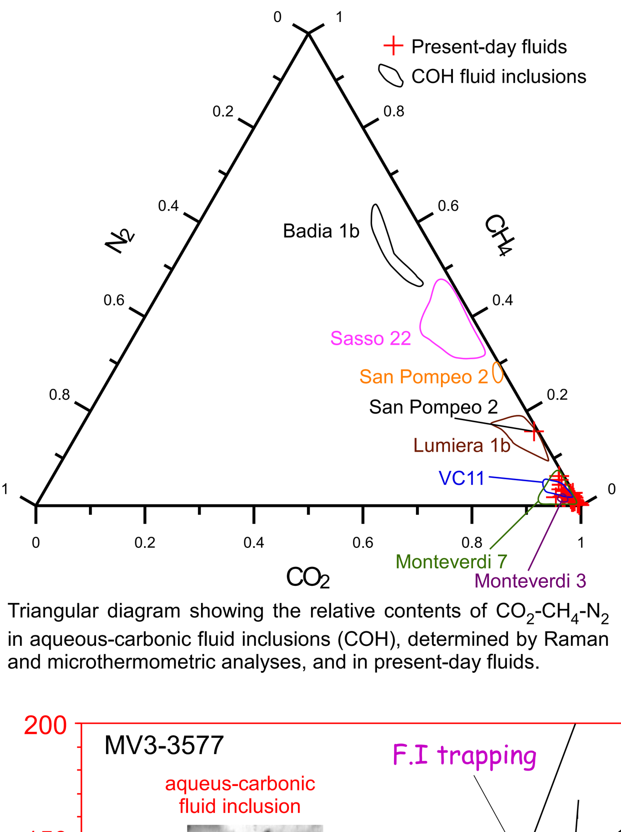
Fluid inclusions

Fluid inclusions are the most direct evidence of the fluid migration that occurred in the past within the crust. The study of fluid inclusions, therefore, provides information on the types of fluids that circulated in geothermal fields, on their physical-chemical nature, and on the fluid evolution and origin. At Larderello, two main stages of fluid migration were determined from fluid inclusion studies. The fluids present during the early stage were: 1) Li-Na-rich high-salinity liquids and vapours, 2) brines of complex compositions, and 3) aqueous-carbonic (COH) fluids with varying proportions of H_2O, CO_2, CH_4 and N_2. All these fluids were trapped in fluid inclusions of deep samples (at depths > 2500 m) synchronously, at temperature of 425-690 °C, under lithostatic pressure (90-135 MPa) or between lithostatic and hydrostatic conditions. These pressures are in agreement with the present-day depths of the contact metamorphic minerals assuming an uplift rate of 0.2 mm/years in the last 4 Ma. The Na-Li-rich fluids and the complex brines were probably exsolved from granites, whereas aqueous-carbonic fluids are interpreted as metamorphic fluids produced by heating (de-hydration reactions) of Paleozoic rocks during contact metamorphism. The carbonic phase of aqueous-carbonic fluids probably originated from high-temperature graphite–water interaction in the metamorphic basement (often C-rich), and/or from decarbonation reactions. Fluid inclusion temperatures agree with the temperature estimated by contact metamorphic minerals.

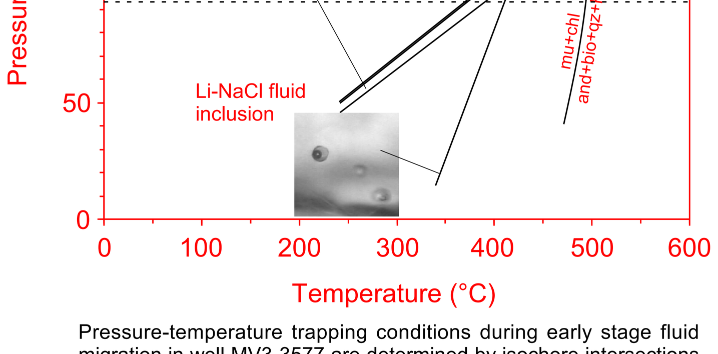


Isochore intersection determines the pressure-temperature trapping conditions for coexisting (i.e. trapped coevally) aqueous-carbonic fluid inclusions (COH) and Li-NaCl brines.

Raman spectra showing the presence of $LiCl5H_2O$ hydrate (b and c) at low temperatures in the inclusions showed in micro-photographs on the left.

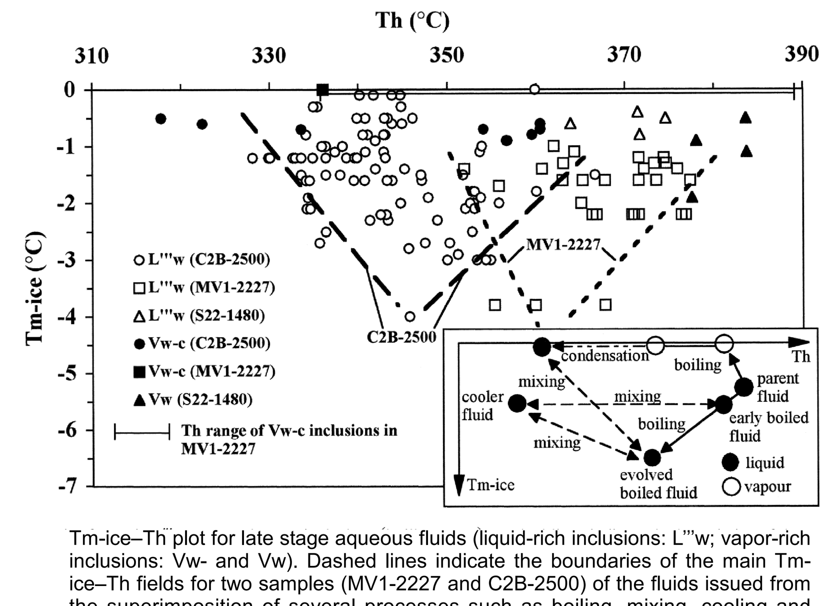


Triangular diagram showing the relative contents of CO_2-CH_4-N_2 in aqueous-carbonic fluid inclusions (COH), determined by Raman and microthermometric analyses, and in present-day fluids.

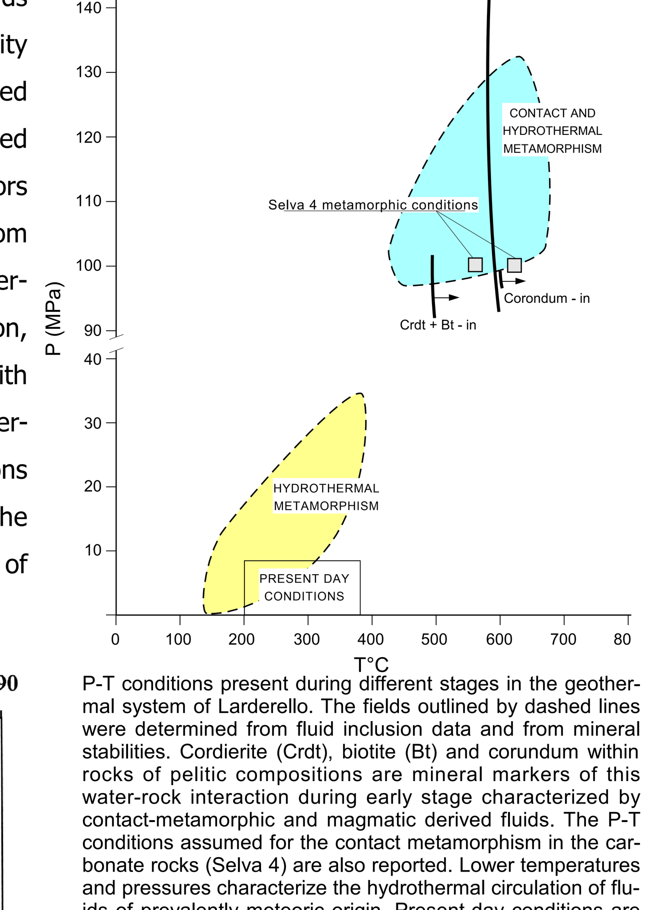


Pressure-temperature trapping conditions during early stage fluid migration in well MV3-3577 are determined by isochore intersections of coexisting aqueous-carbonic and Li-NaCl fluid inclusions and by the intersection between aqueous-carbonic fluid inclusions isochores with contact-metamorphic mineral assemblage (muscovite + chlorite = andalusite + biotite + quartz + H_2O) equilibrium curve.

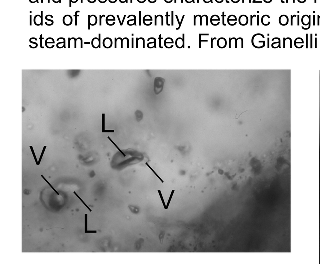
During the second stage (late-stage) of hydrothermal activity fluids with different compositions were trapped in samples at variable depths: 1) liquids ($H_2O+NaCl\pm CO_2$) with low-to-moderate salinity, 2) relatively high-salinity waters ($H_2O+NaCl+CaCl_2$), 3) high-salinity solutions ($H_2O+NaCl$) produced by local boiling with steam loss, 4) low-density vapours ($H_2O\pm CO_2$) derived from boiling, and 5) nearly pure H_2O resulting from condensation of vapors issued from boiling. These fluids were trapped at temperatures varying from 150 to 400°C, under hydrostatic pressures (<35 MPa) and they are interpreted as being meteoric-derived fluids, and to have changed composition, salinity and temperature through water-rock interactions (in particular with evaporite layers), fluid boiling, mixing and cooling. In many cases, the average fluid inclusion homogenization temperatures of types 1 or 2 inclusions approximate present-day well temperatures with an error of ±30°C. The final evolution of the hydrothermal system resulted in the development of the present-day vapor-dominated conditions.



Tm-ice–Th plot for late stage aqueous fluids (liquid-rich inclusions: L'''w; vapor-rich inclusions: Vw- and Vw). Dashed lines indicate the boundaries of the main Tm-ice–Th fields for two samples (MV1-2227 and C2B-2500) of the fluids issued from the superimposition of several processes such as boiling, mixing, cooling and steam condensation. The main trends are schematically summarized in the lower right part of the figure. From Ruggieri et al. (1999).

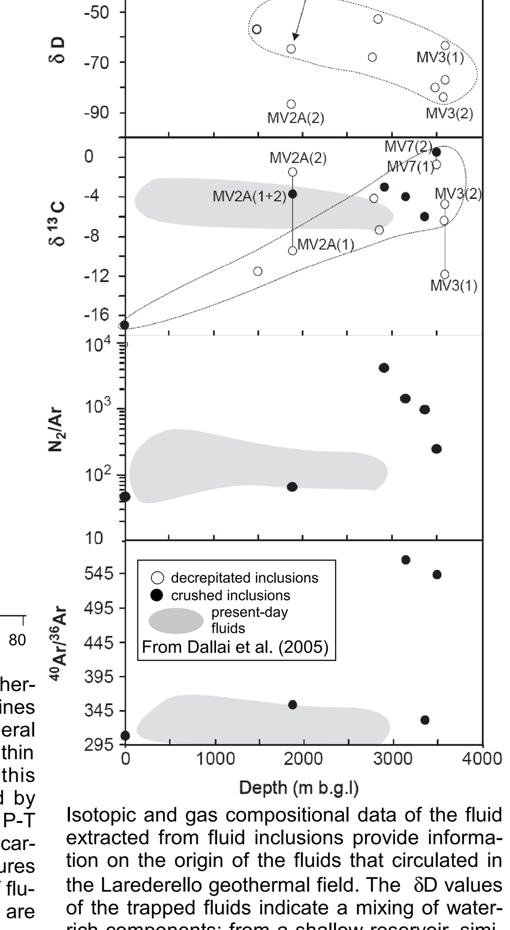


P-T conditions present during different stages in the geothermal system of Larderello. The fields outlined by dashed lines were determined from fluid inclusion data and from mineral stabilities. Cordierite (Crdt), biotite (Bt) and corundum within rocks of pelitic compositions are mineral markers of this water-rock interaction during early stage characterized by contact-metamorphic and magmatic derived fluids. The P-T conditions assumed for the contact metamorphism in the carbonate rocks (Selva 4) are also reported. Lower temperatures and pressures characterize the hydrothermal circulation of fluids of prevalently meteoric origin. Present-day conditions are steam-dominated. From Gianelli and Ruggieri (2002)



Coexisting liquid-rich and vapor-rich fluid inclusions trapped during boiling processes in the C2B-2500 sample. L=aqueous-liquid phase, V=aqueous-carbonic vapor phase.

Primary liquid-rich fluid inclusions in hydrothermal quartz of MV1-2227 sample.



Isotopic and gas compositional data of the fluid extracted from fluid inclusions provide information on the origin of the fluids that circulated in the Larederello geothermal field. The δD values of the trapped fluids indicate a mixing of water-rich components: from a shallow reservoir, similar in composition to present-day meteoric waters, and from a deeper reservoir (magmatic and/or contact-metamorphic fluids). Relatively high $\delta^{13}C$ values for CO_2 from deep samples, were produced by carbonate country rock devolatilisation; whereas low $\delta^{13}C$ values were likely produced by oxidation of organic matter at shallow depths.

Relatively high $^{40}Ar/^{36}Ar$ and N_2/Ar ratios of fluid inclusions from some deep samples indicate the presence of radiogenic ^{40}Ar and excess N_2 when compared to air/asw (air saturated water), and can be related to an early-stage hydrothermal circulation. On the other hand, low N_2/Ar and $^{40}Ar/^{36}Ar$ ratios, similar to present-day geothermal fluids, were found in shallow samples, and reflect the late-stage hydrothermal activity.

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