

# USE OF FLUID INCLUSIONS FOR THE DISCRIMINATION OF MULTI-SOURCE COMPONENTS AND P-T-X RECONSTRUCTION IN GEOTHERMAL SYSTEMS : APPLICATION TO LARDERELLO

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## ABSTRACT

Although geothermal systems would provide excellent materials for the description of major processes such as mixing, boiling, cooling, ..., the studies have rarely been conducted in a similar way than for ancient systems, e.g. using a detailed petrography of fluid inclusions as a function of the mineral sequences and assemblages for a correct description of the evolution with time of trapped fluids. The application of fluid inclusion systematics to the Larderello field has shown that distinct fluid sources and fluid production mechanisms characterize the reservoir since a few million years. Several fluid components may be used to discriminate the different processes such as Li chloride (considered in that case as a magmatic fluid component), CO<sub>2</sub> and CH<sub>4</sub> issued from the contact metamorphism of C-rich sediments in the early stages of the magmatic/hydrothermal activity, Ca and Mg chlorides attesting water-rock interactions in specific geologic formations of the reservoir. Fluid inclusions give local information on well-defined zones within the reservoir. Furthermore, they are the only direct information on paleofluids which have circulated through the rocks, and may yield very useful data on the P-T evolution with time of a given part of the field during pre-exploitation stages.

Key words : Fluid inclusions, thermometry, paleofluid chemistry, Larderello reservoir, fluid sources.

## 1. INTRODUCTION

Quantitative estimation of P-V-T-X properties of fluids in an active geothermal field throughout the course of the hydrothermal activity is of considerable interest for the understanding and appropriate exploitation of geothermal resources. Present-day features of the fluids and physical properties of the reservoir are relatively well documented from data obtained by direct measurements in the wells, but several difficulties are inherent to these methods. Although composition of produced fluids may yield important information, especially an estimation of temperature using available chemical geothermometers it is difficult to use in the case of high enthalpy systems such as Larderello where only vapours are produced by the wells.

As fluids may originate from heterogeneous sources, P-T-X estimates may be obtained from fluid inclusions (FI) which give local information on well-defined zones within the reservoir (Cathelineau and Marignac, 1994). Furthermore, fluid inclusions give the only direct information on paleofluids which have circulated through the rocks. Although active geothermal systems would provide excellent materials for the description of major processes such as mixing, boiling, cooling, ..., the studies have rarely been conducted using a detailed petrography of fluid inclusions as a function of the mineral sequences and assemblages for a correct description of the evolution with time of trapped fluids. Reasons are to be found in two specific aspects of geothermal fields : i) an appropriate description of fluid chronology, and mineral sequences is problematic when only cuttings are available, ii) mostly the search for a temperature estimate at depth is the applied objective in such studies. Therefore, the time-space evolution of the geothermal fluid (P-T-X) is still poorly described from fluid inclusion (FI) data. Especially, few data are available on the fluid migration and production during the early stages of geothermal activity linked to magmatic intrusions (Roedder, 1984) at the exception of works on the Larderello (Cathelineau et al., 1986; 1994) and Geysers (Moore et al., 1992) geothermal fields.

This paper shows the power of fluid inclusion studies applied to the reconstruction of P-T-X properties of fluids since the initiation of

the geothermal activity, with an application to the Larderello system where new microthermometric, Raman, and stable isotope data have been obtained on fluid inclusions and their host hydrothermal quartz.

## 2. TRAPPING OF FLUIDS IN HYDROTHERMAL/GEOTHERMAL FIELDS

In an active geothermal field, fluid circulation is essentially a continuous process. However, fluid sampling by trapping in FI is basically a discontinuous process. At separate intervals (not necessarily the same in the whole volume involved), elementary batches of fluids are trapped, either in primary or in secondary sets of FI, during the growth of favourable minerals or the healing of cracks inside them. Elementary batches are theoretically characterized by a unique set of values of P, T and X, i.e., the corresponding FI should yield constant values of measurable parameters such as temperatures of the phase transitions (see below, the section on P-T estimation). It is from that series of batches that the FI workers have to reconstruct the whole P-T-X-t path from the sequence of trapping of these separate batches through a careful petrographic examination of the FI.

## 3. FLUID COMPOSITION

The characterization of fluid compositions is necessary to understand the evolution of fluids in the reservoirs from the early stages of the geothermal activity up to now. Most often, different fluid sources contribute to the reservoir fluid : magmatic (Hedenquist, 1992), waters equilibrated with metamorphic rocks (Cathelineau et al., 1994), and more generally meteoric. The nature, composition and amount of the different fluids is likely to have changed with time. The compositions of the different fluids trapped as inclusions may give rather good indications on their sources (magmatic/ metamorphic/ meteoric) and on their production mechanism.

The indispensable microthermometric data obtained during classic FI studies may yield rather significant informations on the fluid compositions

### 3.1 Ions

The dominant salt(s) of an aqueous inclusions may be roughly estimated by considering the eutectic temperatures (Te), by referring to the existing data base. Eutectic temperatures can greatly help to discriminate different populations of volatile poor (or free) inclusions, which display rather similar homogenization temperatures (Th) or melting temperatures of ice (Tm ice). Te may also reveal a rather unusual fluid composition, such as the presence of LiCl (Valori et al., 1992, Cathelineau et al., 1994).

In multicomponent systems, melting temperatures of solid compounds in FI like salt-hydrates and pure ice (review in Roedder, 1984) at low temperature are useful and may be determined by microthermometry. A good identification and chronology of the melting solids ensures the correct determination of the dominant salts and gases. It is not always easy to achieve this requirement by microscopic observation. As demonstrated at Larderello, Raman microspectroscopy coupled with a freezing-heating stage is able to follow the sequence of formation or melting of a series of hydrates (Dubessy et al., 1992).

The features of vapour rich FI are poorly documented in most published works on geothermal systems. Their study is frequently dismissed without any good reasons, except to rule out any possibility to study fluid inclusions issued from heterogeneous

trapping. The study of vapours is the necessary complement to the study of liquids, especially to demonstrate boiling conditions. In addition, the consideration of Te in vapour rich FI may help to study mixing processes occurring in the reservoir (remixing of vapours with parent fluids, mixing with other liquids, ...)

Finally, crush/ leach techniques to determine bulk ion contents are already well calibrated and give significant constraints on the chemistry of the inclusion fluids (Banks and Yardley, 1992). This technique is the most promising way to compare the present day and ancient compositions of the geothermal fluids, and is currently tested on Larderello samples.

### 3.2. Gases

Gases are frequently present at low concentrations in the geothermal fluids (0.05-0.2 moles %), and most published works addressed the geochemistry of geothermal gases using isotopic characterization and noble gases geochemistry (Hedenquist, 1992 for epithermal systems). Thus, studies focused mostly on the gas from the discharge fluids and only in exceptional cases from FI. At a CO<sub>2</sub> content down to 3.5 mole%, clathrate may form on cooling in FI which otherwise exhibit no feature indicative of their volatile content. The coupling of microthermometry and Raman microspectroscopy yield quantitative estimation of the gas content in individual FI. By this way, at Larderello, Valori et al. (1992) and Cathelineau et al. (1994) show that the volatile rich (CO<sub>2</sub>-CH<sub>4</sub>) vapours formed during the thermal metamorphism associated with the intrusion of the inferred granite body at depth, diluted progressively with shallow liquids, finally evolving towards fluids with a gas fraction rather similar to the one in modern fluids. It must be emphasized that in that case, melting temperature of clathrate (T<sub>m</sub> cl) measurement was possible in most CO<sub>2</sub>-bearing inclusions.

## 4. INTERPRETATION OF MICROTHERMOMETRIC MEASUREMENTS : IDENTIFICATION OF MAJOR PROCESSES

At any scale, several processes are likely to be (or have been) operative in geothermal fields, which are potentially of consequence for the durability of these fields or their ability to yield recoverable enthalpy. These processes are basically the transient temperature changes, the mixing of fluids (with or without correlative temperature changes) and the boiling of fluids with steam separation. All these processes may be identified through FI studies, basically by the use of correlation diagrams involving Th : Th-T<sub>m</sub> ice, Th-T<sub>m</sub> cl, Th-T<sub>m</sub>s (melting temperature of daughter minerals).

Fluid mixing is easily demonstrated in Th-T<sub>m</sub> ice diagrams by the existence of linear trends (quasi-linear in reality, as cogently pointed out by Hedenquist and Henley, 1985). Mixing processes are overwhelmingly important in many modern and fossil geothermal fields. A variety of situations has been encountered :

- isothermal mixing, which is easily demonstrated when fluids display contrasted salinities (input of saline fluids for instance, equilibrated with evaporites)
- anisothermal mixing (infiltration of cool meteoric waters, a case extremely frequent in most systems ; advection of warmer fluids in discharge zones; Valori et al., 1992).

In such low pressure environments as those of many geothermal systems, boiling is potentially a frequent process and indeed has been advocated in many studies referring to modern or ancient geothermal systems. Basically, unmixing of a given fluid yields two phases, a dense "liquid" of higher salinity (often a brine) and a "vapour" of lower density and low salinity. In that case, the Th for both types of fluids should be the same, and conversely, the fact that Th of "brines" and "vapours" are the same is a convincing proof of the boiling phenomenon. It must be emphasized that in many FI studies in geothermal fields, boiling is assumed on the basis of the coexistence of "brines" and "vapours", with the Th only measured in "brines" FI, i.e., boiling is not really demonstrated in those cases.

The reservoirs are generally characterized by a combination of elementary processes, especially boiling and fluid mixing. The common mixing processes likely to occur is the mixing of the boiling products (vapours, and its related liquid) with other fluids including the parent fluid.

### 5. P-T-t DEPTH RELATIONSHIPS IN GEOTHERMAL FIELDS FROM FI DATA

The recognition of the temperature distribution in a geothermal field

is of critical importance and may help to evaluate the temperature evolution with time in the field, in order to get some constraints on the rate of cooling, and on the past physical state of the fluids in the reservoir prior to exploitation. As mentioned above, it is sometimes difficult to establish the full chronological relationships of FI in small size cuttings. However, it is always possible to get much informations from a careful treatment of the data. The P-T reconstruction is conducted as in any other FI study. For each stage of fluid trapping as revealed by the petrographic study (see above) P and T are estimated :

- directly, in the case of boiling (unmixing) fluids, since Th is thus the trapping T and pressure is given by considering the L/L+V curve at Th. This ideal situation is not always encountered, and may be difficult to recognize.
- indirectly by the use of isochores ; but then, another independent estimate of the trapping T or P is needed. Such an independent estimate for T may be obtained by different ways (see below). It is also customary, in studies of modern geothermal activities to use a P-depth relationships in order to get the desired value of T at a given depth.

### 5.1 Shallow modern geothermal reservoirs

In modern geothermal fields, at relatively shallow depth, the porespace is generally connected to surface, and therefore, the pressure is at most hydrostatic under such conditions, the pressure correction is generally low, and for instance, it does not exceed 10°C at 200°C, for low salinity fluids. Precise pressure correction requires a correct pressure estimation according to the physical features of the fluid column (see above), and the calculation of the isochores (Cathelineau et al., 1989). In most published works, however, Th data are used without any pressure correction. Although basically uncorrect, this practice leads to minimal underestimations as far as the above mentioned conditions are fulfilled.

### 5.2 Deep modern or ancient geothermal reservoirs

Several examples have shown that the Th-depth curve may differ from the present day T depth curve. Two cases may be distinguished :

- a) significant T changes occurred in the field such as cooling or heating, but under similar pressure conditions; in such case, trapping temperature is not significantly different from Th (see above) and in any case may easily be derived from the Th.
- b) Th cannot be interpreted easily as trapping temperatures, due to significant pressure correction (cases of non hydrostatic conditions which appear in relatively deep, and therefore high temperature conditions). This is the case at Larderello.

To discriminate these two hypotheses, several tests can be made as well as significant constraints may be derived from the consideration of the fluid densities, mineral assemblages, or mineral geothermometry.

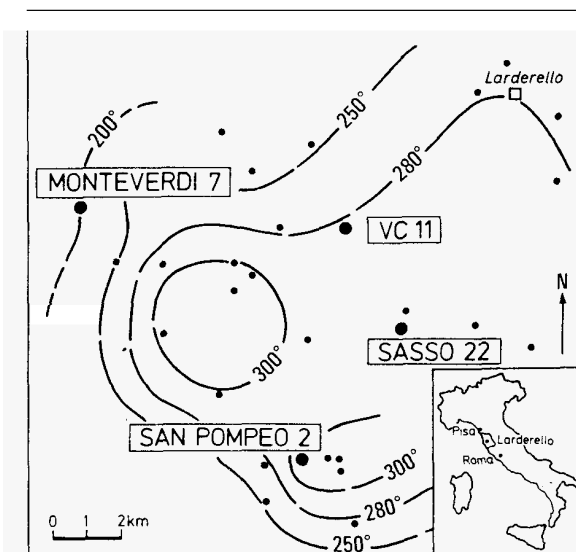


Figure. 1. Location of the sampled wells in the Larderello field. The isotherms at 2000 m depth are shown (from Bertini et al., 1985).

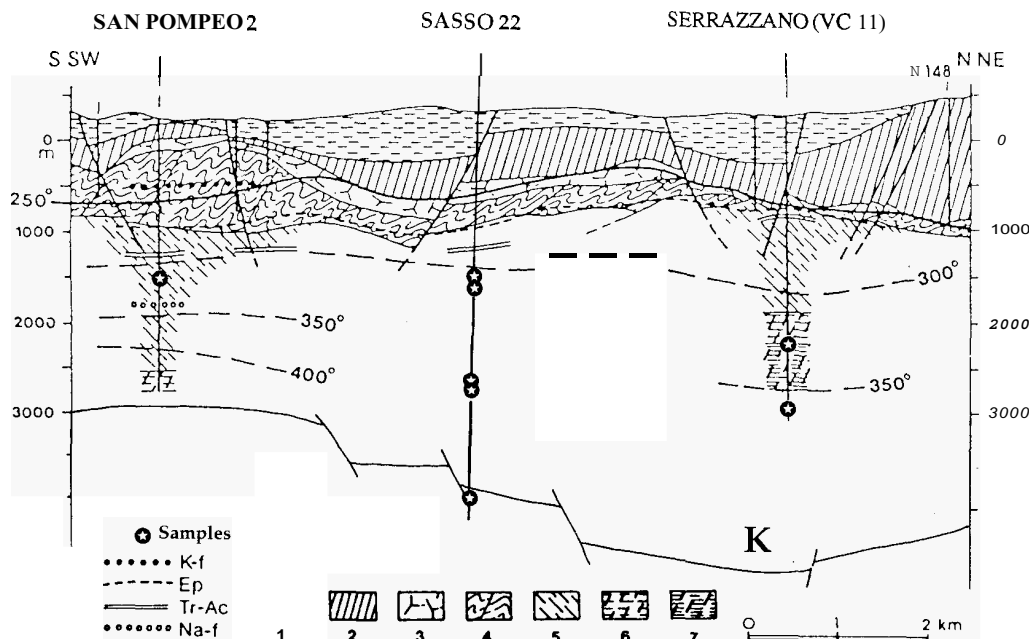


Figure 2 : Cross-section of the Larderello field, showing the major geological units, the location of the K horizon (noted K) and the position of some mineral hydrothermal isograds (from Bertini et al., 1985) together with present day isotherms. 1 : Neogene sediments ; 2 : Ligurian flysch complex (Cretaceous-Eocene); 3 : Tuscan Nappe ; 4 : tectonic slices ; 5 : phyllite and quartzite ; 6 : micaschist ; 7 : gneiss ; K-f : K-feldspar ; Ep : epidote ; Tr-Ac : tremolite-actinolite ; Na-f : Na plagioclase. The Sasso 22 well has been projected on the San Pompeo 2-Serrazzano cross section. Elevations relative to sea level are shown in m. Samples studied for stable isotopes, fluid inclusions and crush-leach analyses of inclusion fluids are shown by a star.

## 6. APPLICATION TO LARDERELLO

The intracontinental geothermal field of Larderello (Tuscany, Italy) is characterized by productive horizons in the permeable levels of Triassic dolostone and anhydrite in the depth range 300-1500 m below ground level (b. g. l.) (Figure 1). A gradual decrease in productivity observed during the last tens of years emphasized the need for finding new productive horizons at greater depth. For this purpose a deep exploration program, based on deep drilling (Bertini et al., 1980 ; Batini et al., 1983a) and multidisciplinary studies have been carried out in the last fifteen years. The geological, petrological, geochemical and geophysical data so far obtained yield a reliable model of the geothermal field and in particular a reconstruction of its deep structural setting (Batini et al., 1983b ; Batini et al., 1985). The presence at great depth of a deep composite batholith surrounded by a swarm of dykes and differentiates was demonstrated (Batini et al., 1985 ; Foley et al., 1992).

Studies on hydrothermal mineral assemblages (Cavarretta et al., 1980 ; 1982 ; Cavarretta and Puxeddu, 1990, Bertini et al., 1985) and related fluid inclusions (Belkin et al., 1985 ; Cathelineau et al., 1986, 1989, 1994 ; Marignac et al., 1987 ; Valori et al., 1992) found in the deepest levels of the Larderello wells (1500-4000m b. g. l.) have pointed to the complex evolution of the geothermal fluids from an early stage of the hydrothermal metamorphism, soon after the climax of the thermal event related to the origin of the field, up to the present day.

The deepest wells at Larderello have provided exceptional materials, including contact metamorphic rocks and intrusive bodies. Detailed studies of solids (alteration assemblages, whole rock geochemistry) and fluids (fluid inclusions) from such deep levels have been especially carried out to understand the early water-rock interaction processes which occurred during and immediately after the emplacement of the granite body .

### 6.1 New analytical data on fluid inclusions

Fluid inclusions from recrystallized quartz lenses and quartz veins in samples displaying HT parageneses and magmatic quartz in leucogranite were studied. They are mainly of the secondary type, being located in fluid inclusion planes (FIP). FIP are healed microcracks and are therefore related to hydrothermal circulation in the Larderello field. Several generations of high temperature fluids trapped in specific networks of FIP record the early hydrothermal circulation and include : (i) aqueous-carbonic vapours (Vc) and

liquids (Lc) ; (ii) aqueous vapours (Vaq) containing LiCl, with variable salinity ; (iii) aqueous brines, often oversaturated with respect to halite ; these are LiCl (L'), LiCl-NaCl (Lh) or NaCl (Lh) dominated brines ; (iv) complex brines always oversaturated at room temperature with respect to 2 (Ls2, with halite and sylvite) or n salts (Lsn). Raman determination of the vapour content of Vc fluids showed variable but significant contents in CH<sub>4</sub> (in the range 0.6-7.0 mole % CH<sub>4</sub>) (Cathelineau et al., 1994).

Detailed studies of the geometrical and chronological relationships between FIP revealed close relationships and mutual contamination between aqueous-carbonic and LiCl fluids. These fluids are sub-contemporaneous. They were generated and trapped under high temperatures (450°-600°C, depending on the depth and location in the field) under lithostatic pressures of 1 to 1.2 kb (4-4.2 km depth). These results are interpreted as recording the interaction between magmatic and contact metamorphic fluids in the early Larderello aquifer. The aqueous-carbonic fluids are thought to result from the reheating of the basement metamorphic series (often C-rich) under relatively high temperatures during contact metamorphism. Other fluids, such as Vaq, other Li-brines and possibly Lsn are interpreted as the result of a boiling of the primitive Li-magmatic fluid.

New analytical data have been obtained on samples from shallower levels in the reservoir (Sasso 22) and on fluids trapped in between the early contact metamorphism stages and present conditions (Figure 2). Series of fluids belong to three main types, especially :

- Ca-Mg fluids, showing boiling by places, which could be due to water-rock interactions in specific parts of the field (sedimentary layers, evaporites), characterized by eutectic temperatures in the range of -30 to -40°C, and variable salinities (Tm ice from -20°C to -5°C) attesting of dilution processes,
- nearly pure aqueous liquids (Tm ice around 0.0°C), issued from the condensation of aqueous vapours issued from boiling at greater depth,
- shallow meteoric waters in the more surficial horizons reacting with the host rocks to give a chlorite-quartz-epidote-adularia zone. These fluids are characterized by Tm ice mostly in the range of -4 to -0.5°C with modes around -0.5°C, -1.5°C.

The figure 3 shows, on the example of well Sasso 22, that shallow levels in the range of 1400 to 1700 m depth are mostly characterized by fluids of moderate to low salinities, with minimal trapping temperature (Th in the range of 280 to 350°C) contrasting with those of the deepest levels which have recorded a more complex temperature and fluid history.

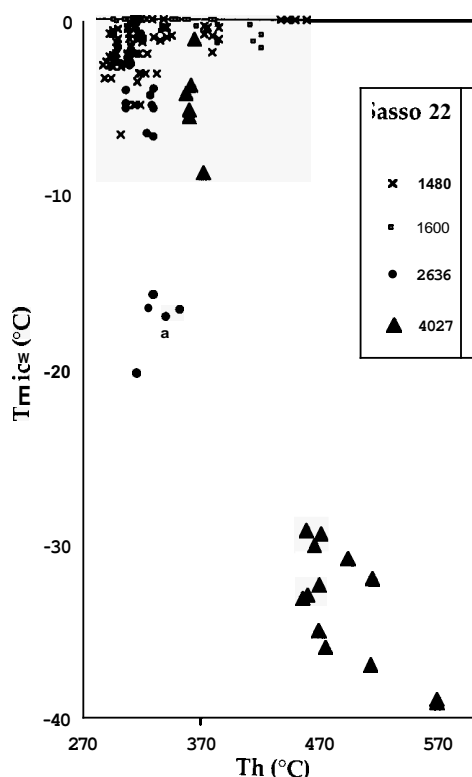


Figure 3.: Tmi-Th plot for aqueous inclusions from four samples from the well Sasso 22.

## 6.2 New isotopic data on FI bearing quartz

Vein quartz from a series of depths in the Sasso 22 well, and also examples from a number of other wells (San Pompeo, Serrazzano 1, Ceretta 3, Bruciano 1) has been analysed for its oxygen isotopic composition using on-line laser fluorination at the Department of geology and Geophysics, University of Wisconsin at Madison. Sample sizes were typically around 1 mg, and in most cases the same material had been previously investigated by microthermometry, and currently studied by crush-leach methods for ion content determinations.

The results show a variation in  $\delta^{18}\text{O}$  SMOW from c. + 11.0 to 14.5 per mil, with no significant trends within the Sasso 22 well as a function of depth or temperature, or between other deep wells (13 samples). These data confirm previous  $\delta^{18}\text{O}$  determination obtained on quartz samples from Monteverdi 2 and San Giovanni 1b (depths from 888m to 2400m) reported by Petrucci et al. (1993) who mention values in between 13.4 and 14.2 per mil.

This pattern indicates that the oxygen composition of the vein fluids was locally buffered by wall rock interactions, suggesting relatively low flow rates. However, a single epidote analysed from 1600 m depth at Sasso 22 was very light however (-1.2 per mil), and indicate that the same fractures were sometimes occupied by lighter, surface-derived fluids at different times from those at which the quartz precipitated.

## 7. CONCLUSIONS

The study of fluid inclusions in an active geothermal system gives a new example of the validity and accuracy of the FI studies for geothermobarometric purposes, and for the discrimination of fluid sources during past geothermal activities. Fluid inclusion data give useful information on the P-T-X evolution on each stage of fluid movement identified by the crystallization or the healing of minerals. The information on the natural state of the system in the pre-exploitation stage is valuable in any attempt to monitor the changes occurring in the reservoir (initial point before exploitation).

Such a study during drilling may give a relatively quick information compared to other methods (direct measurement, fluid analysis) which are time consuming. However, it requires that a number of inclusions are analysed in order to be certain that the variation range is not too large. In spite of the higher uncertainty of temperature estimation in some samples, results are in general consistent with the general thermal gradient of the field.

At Larderello, fluid inclusions give valuable information on the fluid chemistry throughout the evolution of the geothermal system. Hottest and earliest fluids are issued from the active contact metamorphism at depth, and from a magmatic source. Data demonstrate that a quasi-monotonous cooling of the field occurs in the following stages. The progressive dilution of early circulation of fluids by shallow waters is characterized by a significant decrease of the volatile and salt contents towards present day fluid compositions. However, if fluids have significantly migrated through the field and underwent mutual mixing, relatively low flow rates seem to characterize the reservoir as shown by the oxygen composition of the vein fluids.

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