

## Noble gases and carbon isotopic composition of fluid inclusions from the Larderello geothermal field (Italy), preliminary data

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The intracontinental geothermal field of Larderello (Tuscany, Italy) is a vapour-dominated system, which has been exploited for electricity production throughout this century.

At Larderello, studies on hydrothermal mineral assemblages and related fluid inclusions evidenced the presence of several fluid types of different sources and a complex evolution of the geothermal system, from early stage circulation, related to granite emplacement, to present-day condition (Valori *et al.*, 1992; Cathelineau *et al.*, 1994). In this study we measured N<sub>2</sub>/Ar ratio and the isotopic compositions of noble gases and carbon of CO<sub>2</sub> extracted by undervacuum crushing of fluid inclusions in order to: 1) define the origin of the palaeo-geothermal fluids, 2) compare noble gas and CO<sub>2</sub> isotopic compositions of the fluid trapped in the inclusions with present-day discharged fluid and evaluate if the source of these fluids has been changed with time.

The stratigraphy of the deep geothermal wells (up to 4.5 km below the ground level, b.g.l.) schematically consists of (from top to bottom): 1) a cover of siliciclastic sediments, carbonatic rocks, evaporite and ophiolite rocks (Late Triassic to Pliocene), 2) a complex of tectonic slices which include the lower formation of the sedimentary rocks and the uppermost part of the metamorphic basement, 3) a metamorphic basement (Palaeozoic), consisting of phyllitic-quartzitic rocks, micaschists and gneisses. The deepest wells at Larderello have also encountered contact metamorphic rocks and granite dykes and intrusion with ages between 1.3 and 3.8 Ma. Geophysical data suggest that a large intrusion is present below the Larderello area; the geothermal activity can be related to the presence of this

intrusion. The productive horizons were found in Triassic carbonate and anhydrite formations (shallow reservoir) of the upper units and in some permeable levels of the Palaeozoic metamorphic basement (deep reservoir).

### Present-day and palaeo-geothermal fluids

Present-day discharged fluids are dominated by H<sub>2</sub>O vapour. Superheated steam of Larderello is mainly of meteoritic origin as indicated by oxygen and hydrogen isotope analyses. The gas phase associated is dominated by CO<sub>2</sub> (88-95%), with minor amount of N<sub>2</sub> (1-2%), H<sub>2</sub>S (1-3%), H<sub>2</sub> (1-5%) and CH<sub>4</sub> (1-4%). The origin of the fluids at Larderello are object of large debate. For example the CO<sub>2</sub> isotopic data ( $\delta^{13}C$  ranging from -1 to -7‰) were interpreted either as an evidence of magmatic source, or the product of thermometamorphic reactions or deriving from hydrolysis of the Triassic carbonatic rocks (Minissale *et al.*, 1997 and reference therein). In addition, mantle contribution to fluids at Larderello are evidenced by He isotopic composition of the present-day discharged fluid (R/Ra ranging from 1.5 to 3.5) (Hooker *et al.*, 1985).

On the basis of fluid inclusions, two stages of past hydrothermal activity were also recognised: 1) an early stage recorded only by inclusions in deep (2.9-4.0 km b.g.l.) core samples, and 2) a late stage hydrothermal activity testified by inclusions either in some deep core samples and in intermediate to shallow depth (2.5-0.4 km b.g.l.) core samples (Valori *et al.*, 1992; Cathelineau *et al.*, 1994; Gianelli *et al.*, 1997). Early stage circulation related to granite emplacement was characterised by the presence of: 1) magmatic derived fluids, represented by H<sub>2</sub>O-

NaCl-LiCl brines, aqueous vapours, and complex highly saline liquids; 2) CO<sub>2</sub>-H<sub>2</sub>O-(CH<sub>4</sub>-N<sub>2</sub>) fluids resulting from graphite-water interaction in the metamorphic basement (often C-rich) or by decarbonation reactions during contact metamorphism. Late stage activity was characterised by boiling and mixing processes and it was recorded by: H<sub>2</sub>O-NaCl-(CO<sub>2</sub>) and H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> liquid-rich fluid inclusions with variable salinity and by H<sub>2</sub>O-(CO<sub>2</sub>) vapour-rich inclusions derived from the boiling of the liquids. Late stage fluids were interpreted to be meteoric waters, in some case interacting with evaporite layers (Valori *et al.*, 1992).

## Results and discussion

The samples selected for the extraction of the gas phases from fluid inclusions come from four geothermal wells: San Pompeo 2 (from 2.7 km b.g.l.), Monteverdi 7 (from 3.5 km b.g.l.), Monteverdi 2A (from 1.9 km b.g.l.) and Carboli 11A (from 1.5 km b.g.l.). The sample San Pompeo 2 is constituted by a high temperature early hydrothermal mineral assemblage (tourmaline-biotite-quartz) whereas the sample Monteverdi 7 is a granitic dyke. Monteverdi 2A and Carboli 11A samples contain late hydrothermal assemblage veins: in the first is present a quartz and chlorite vein, the other is characterised by hydrothermal calcite. Preliminary <sup>230</sup>Th/<sup>234</sup>U dating on late stage hydrothermal veins indicates ages from 7,000 to 100,000 years (Gianelli *et al.*, 1997). In San Pompeo 2 sample only early stage inclusions are present in quartz (Cathelineau *et al.*, 1994), in Monteverdi 2A quartz and Carboli 11A calcite only late stage fluids were trapped, whereas both early and late fluids are contained in secondary inclusions of Monteverdi 7 magmatic quartz (Valori *et al.*, 1992).

The gas entrapped into fluid inclusions was extracted by means of under-vacuum crushing of 2 or 3 g. of quartz or calcite chips separated from selected samples. The <sup>3</sup>He/<sup>4</sup>He ratio was measured by a rare gas mass spectrometer (MAP 215-50); the <sup>40</sup>Ar/<sup>36</sup>Ar and the N<sub>2</sub>/Ar ratios were measured by a quadrupole mass spectrometer (Spectralab-200 VG-Micromass), the 28/29 ratio was monitored to correct mass 28 from contribution of species different from N<sub>2</sub>. The CO<sub>2</sub> isotopic composition was measured on the gas extracted from quartz chips whereas the isotopic composition of the CO<sub>2</sub> in equilibrium with calcite was taken from Gianelli *et al.*, (1997). The Monteverdi 7 sample shows a positive δC value of 0.47‰, whereas the δC values of the other three samples are from -3.2 to -4.1‰. These values are in the range of the isotopic compositions of the

present-day geothermal CO<sub>2</sub> (from -1 to -7‰). Except sample Carboli 11A, the fluid in inclusions (in particular San Pompeo 2 sample) are enriched in <sup>3</sup>He, suggesting that a fraction of the fluid is mantle derived, similarly to present-day fluids.

The R/R<sub>a</sub> and the N<sub>2</sub>/Ar ratios in fluid inclusions, present-day geothermal fluids and natural gas manifestation are reported in Fig. 1. The gas composition of the late stage fluid inclusions falls in the field of the present-day fluid composition (Monteverdi 2A sample) or it is close to this field (Carboli 11A sample). This data and the CO<sub>2</sub> inclusion isotopic composition indicates that the origins of the gases trapped in Monteverdi 2A and possibly in Carboli 11A samples can be the same of present-day discharged fluids, suggesting long lived and similar gas sources at least for the last 7,000 years.

The samples containing early stage inclusions (San Pompeo and Monteverdi 7) highly diverged from the present-day gas pattern, in particular they show a very high N<sub>2</sub>/Ar ratio. Moreover, the positive value of δC and the excess of radiogenic Ar (<sup>40</sup>Ar/<sup>36</sup>Ar = 450) are distinctive characteristics of the gas extracted from Monteverdi 7 sample.

Microthermometric and Raman analyses reveal that in the inclusions which trapped magmatic derived fluids, the volatile (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>) content is very low or absent (Cathelineau *et al.*, 1994). This suggests that in San Pompeo 2 sample the δC of the extracted CO<sub>2</sub> is representative of the carbonic fluids produced during the heating of the basement rocks related to granite emplacement. In particular, the δC value (-3.2‰) is consistent with the production of carbonic fluids from graphite-water reaction in the C-rich basement. The positive δC value value of the CO<sub>2</sub> of Monteverdi 7 sample suggests that the CO<sub>2</sub> may come from thermometamorphic decarbonation and/or carbonate rocks hydrolysis. However it is difficult to determine if this δC value is related to thermometamorphic or to meteoric fluids which interacted with carbonate rocks as both early and late carbonic-bearing inclusions are present in this sample

The N<sub>2</sub>/Ar ratio of an Pompeo 2 and Monteverdi 7 samples can be explained by an excess of N<sub>2</sub> related to the degassing of magmatic body and/or the release of N<sub>2</sub> by heating of sedimentary rocks containing nitrogen and ammonium in feldspar and micas. The second hypothesis seems to be more reliable for early stage fluids at Larderello, as in both samples, N<sub>2</sub> is present in significant amounts in the carbonic inclusions which trapped the thermometamorphic fluids (Cathelineau *et al.*, 1994).