

Stable isotope and noble gas isotope compositions of inclusion fluids from Larderello geothermal field, Italy

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In the steam-dominated field of Larderello two distinct geothermal reservoirs have been identified: a mostly sedimentary (limestones, shales, slightly metamorphosed sandstones) shallow reservoir, and a metamorphic (phyllite, micaschist, gneiss, granite) deep-reservoir. Both produced superheated steam, consisting of different proportions of meteoric, metamorphic and magmatic water components. Fluid inclusion studies on quartz from hydrothermal veins, contact-metamorphic assemblages and granites documented the circulation of several fluid types during the geothermal activity. The first hydrothermal stage was dominated by aqueous-carbonic fluids, formed during contact-metamorphism, and Li-Na-rich brines of magmatic derivation. The late stage hydrothermal activity was characterized by the circulation of meteoric-derived aqueous and aqueous-carbonic liquids, vapour produced during boiling processes, and saline fluids related to evaporite/fluids interaction. In addition, inherited quartz veins in metamorphic formations may also contain fluids trapped during regional metamorphism and, therefore, not related to the geothermal activity.

Stable isotope investigation of minerals and fluid extracted from inclusions, formed during different periods of time, has been used to constrain the nature of fluid-rock interaction processes at Larderello. In situ laser-fluorination of quartz-dominated veins revealed marked difference in the $\delta^{18}\text{O}$ values of primary (metamorphic) and/or secondary (recrystallized lenses in the metamorphic assemblage) quartz, varying from 13.4 to 14.0 ‰, and from 6.0 to 8.4 ‰, respectively. Fluids extracted from thermally decrepitated inclusions have δD values of from -52.9 to -85 ‰ and indicate that the fluids were derived from mixing of water-rich components, likely a surface reservoir similar in composition to

present day meteoric waters, and a deep reservoir. A deep source of He contribution at Larderello is suggested by R/Ra ratios (up to 3.2) of paleofluids and present-day fluids.

The fluids trapped in texturally late fluid inclusions show N_2/Ar and $^{40}Ar/^{36}Ar$ ratios as low as those of air saturated water, similar to present-day geothermal fluids, whereas early stage fluids are characterized by excess radiogenic Ar and high N_2/Ar ratios, likely resulting from the circulation of fluids during contact metamorphism subsequent to the emplacement of granitoid rocks, and from devolatilisation of basement rocks. The $\delta^{13}C$ values for CO_2 from the early stage fluid inclusions were produced by carbonate country rock devolatilization; $\delta^{13}C$ values as low as -17 ‰ were measured in late stage fluid inclusions, likely produced by oxidation of organic matter at shallow depths.