

At the root of the geothermal field of Larderello: boron isotope constraints

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The geothermal field of Larderello (Tuscany) is one of the most important economic realities worldwide in the renewable energy sector. At this site, the B-rich geothermal fluids were exploited for boric acid production since 1818. Two main types of super-heated steam reservoirs have been exploited during time[1]: a shallow one (200-1200 m; 120-260°C) hosted by pelite-carbonate formations, and a deeper one (1200-5000 m; 260-400°C) hosted by Palaeozoic metamorphic basement and Pliocene-Pleistocene granite intrusions. A dominantly meteoric origin of the fluids is recognized in the system. In the deeper part of the geothermal system (1900-5000 m), exploratory wells intersected peraluminous, tourmaline-bearing granite intrusions ranging in age from 4.3 to 1.6 Ma [2]. The recent deepening of the Venelle well during the H2020 DESCramBLE Project evidenced local occurrence of extremely hot, supercritical conditions ($T > 500^{\circ}\text{C}$, $P \approx 400$ bar at 2900 m) suggesting that a granite intrusion is currently crystallizing at depth [3]. $\delta^{11}\text{B}$ analyses of sublimates, fluids, sedimentary/metamorphic rocks, tourmaline bearing granites/veins and mafic volcanic-subvolcanic rocks have been performed by TIMS and Neptune Plus MC-ICP-MS at IGG-CNR Pisa. The aim is unravelling the boron geochemical cycle of the Larderello geothermal field from magmas/host rocks to issued fluids.

$\delta^{11}\text{B}$ of steam condensates (+19.5 to +2.2 ‰), inversely correlates with B content (from 8 to 190 ppm). Two main boron-rich reservoirs can potentially provide boron to the fluids: 1) pelites of the upper sedimentary sequence (B up to 500 ppm; $\delta^{11}\text{B} = -10/-16$); 2) B-rich fluids from granite intrusions (magmatic and hydrothermal tourmalines with $\delta^{11}\text{B} = -6/-9$). Most of the fluids plot at intermediate values (B=50-100 ppm; $\delta^{11}\text{B} \approx +10\text{‰}$) compatibly with medium T exchange with sedimentary rocks. Minor input from magmatic fluids is recorded by samples with B>100 ppm and $\delta^{11}\text{B} < +6\text{‰}$. A complex, temperature/coordination-controlled, isotope fractionation is invoked to explain the recorded boron pattern. This research received funding from the European Union's Horizon2020 Research and Innovation Program under grant agreement No 640573 (Project DESCramBLE).

[1] Minissale (1991) *Earth Sci. Rev.* **31**, 133-151. [2] Dini *et al.* (2005) *Lithos* **81**, 1-31. [3] Manzella *et al.* (2018) Proceedings of WGRE-Stanford, SGP-TR-213.