

**BORON ISOTOPE SYSTEMATICS FROM THE LARDERELLO  
GEOTHERMAL FIELD (ITALY) AND ASSOCIATED  
BORON ISOTOPE FRACTIONATION FACTORS**

by

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**Abstract**

The boron isotopic systematics and concentrations of geothermal fluids, vapours and minerals from the geothermal field of Larderello (Tuscany, Italy) are presented. Boron provenance is clearly reflected in the boron isotopic composition: boron from bore hole vapours originates in the evaporitic "Anidriti di Burano" series; it shows marine  $\delta^{11}\text{B}$ -values between +25.5‰ and +35.9‰. Fresh water boron is derived from the desorbable boron of the flysch sequence of the Ligurids; its composition varies between +11.4‰ and +22.5‰. Sassolites are depleted in  $^{11}\text{B}$  by 5‰ with respect to the fluids. Empirical mineral/fluid fractionation factors are 0.9953 for sassolite and 0.9963 for sborgite. Negative thermal ionisation mass spectrometry is used to analyse the boron isotopic composition in combination with isotope dilution for concentration analysis. Many of the analytical problems encountered with the traditional positive thermal ionisation method can be overcome using this new technique.

**Introduction**

The high mobility of boron together with the large relative mass difference between the two stable isotopes  $^{10}\text{B}$  and  $^{11}\text{B}$  can produce large natural isotopic variations. Two major boron reservoirs can be distinguished ( $\delta^{11}\text{B}$ -values are reported relative to NBS 951 boric acid with  $^{11}\text{B}/^{10}\text{B} = 4.04362$ ):

- 1) seawater with  $\delta^{11}\text{B} = +40\text{‰}$  to +50‰
- 2) a "crustal" reservoir with  $\delta^{11}\text{B} = -20\text{‰}$  to +10‰

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This large spread in isotopic composition of boron can be used to investigate the origin and circulation paths of fluids in volcanics and hydrothermal systems, the origin of boron in minerals (in particular tourmalines and borates), subduction and recycling of crustal material, seafloor metamorphism, weathering, etc.

The geothermal field of Larderello is situated in the northern part of the central Apennine Belt south-west of Florence (Tuscany, Italy). It is well known for its boric acid fluids and for the production of electricity from geothermal fluids. There has been some debate concerning the origin of these geothermal fluids. Are the fluids of purely magmatic origin or do they represent meteoric water penetrating through the sediments overlying the supposed heat source? Taking the large fractionation of boron isotopes between "marine" and "crustal" environments into account, boron isotope geochemistry should allow a characterisation of the geothermal fluids.

Until recently however, analytical difficulties associated with boron geochemistry have partly prohibited approaching such problems and questions. Using negative thermal ionisation mass spectrometry (NTI-MS) instead of the commonly used positive thermal ionisation mass spectrometry (PTI-MS) many of the analytical problems can be overcome. The aim of the investigations in Larderello are thus twofold:

- 1) To prove whether or not NTI-MS is a useful and applicable tool for isotope geochemical investigations;
- 2) To examine the origin of the geothermal fluids in Larderello.

The present work gives the first results of the investigations of fluids and minerals from the geothermal system in Larderello.

### **Analytical techniques**

The NTI-MS is described in detail in DU CHATEAU & DE BIEVRE (1983), ZEININGER & HEUMANN (1983), ZEININGER (1984), HEUMANN & ZEININGER (1985), DU CHATEAU et al. (1986), VENGOSH et al. (1989) and KLÖTZLI (1991a, 1991b).  $\text{BO}_2^-$  ions are formed in a single Re-filament ion source and measured at masses 42 and 43. With the addition of  $\text{La}(\text{NO}_3)_3$  as an activator, a 100 to 1000 fold increase in ion beam intensities as compared to the classical sodium or caesium metaborate PTI-MS is achieved. With this high sensitivity, as little as 0.1 ng of boron is needed for analysis. Data acquisition follows a normal peak jumping routine. The measured intensities are corrected for machine and load dependent fractionation and for  $^{17}\text{O}$  interferences.

Internal  $1\sigma$ -reproducibilities of the method are in the range of 0.04% to 0.2%. External  $1\sigma$ -reproducibilities lie between 0.7% and 3.8%, respectively. The reproducibilities of impure, natural samples are about twice as good as of standard materials (VENGOSH et al., 1989; KLÖTZLI, 1991a). All reported errors are  $1\sigma$ -reproducibilities.

Boron concentrations are determined with isotope dilution using a  $^{10}\text{B}$  enriched spike. Depending on the sample boron concentration, the  $1\sigma$ -reproducibilities for the isotope dilution analyses vary between 0.01% (> 100 ppm) and 4% (< 0.1 ppm).

### **Geological outline**

In the vicinity of Larderello five main tectonic elements may be distinguished (BENCINI & DUCHI, 1988; CAVARETTA et al., 1980; GIANELLI et al., 1978; PUXEDDU et al., 1977):

- 1) "Basement" complex: A nappe complex of pre-Hercynian gneisses, amphibolites, marbles, metagraywackes, anhydrite, quartzitic and phyllitic rocks of the Paleozoic.
- 2) Triassic Verrucano.
- 3) Tuscan nappe complex: Triassic to Oligocene formations, the lowermost being the "Anidriti di Burano" series.
- 4) "Ligurids": nappes of flysch sequences with ophiolites (Upper Jurassic to Eocene)
- 5) Autochthon: lacustrine, lagoonal (Upper Miocene) and marine Neogene sediments (Upper Miocene to Pliocene).

The complete nappe complex is of Alpine age. Today, the region forms a horst and graben structure due to extensional tectonics during the Upper Pliocene and Pleistocene. The autochthonous Neogene sediments are mainly found in the graben structures.

The whole of Tuscany and parts of Latium were affected by an intensive Pliocene and Quaternary magmatism and volcanism (BORSI et al., 1967; DELMORO et al., 1982). Figures 1 and 2 show a geological sketchmap and a cross section of the region investigated.

### **The geothermal system of Larderello**

Larderello is one of the biggest and longest exploited geothermal systems of the world. To our knowledge, the system was formed by the relative shallow intrusion of a magmatic body around 4 Ma ago. This intrusion must be attributed to the Pliocene and Quaternary magmatism in Tuscany mentioned above. Larderello is situated on a fault system between Roccastrada and Montecatini along which many other very young intrusives and extrusives may be found. The occurrence of leucogranitic dikes in the deepest bore holes with K-Ar white mica ages between 3.8 Ma and 2.9 Ma supports this assumption (CAVARETTA & PUXEDDU, 1990). Newly formed corundum and sanidine in the bore hole San Pompeo 2 also favours the existence of a shallow seated intrusive body. Maximum temperatures attained were between 350° C and 560° C.

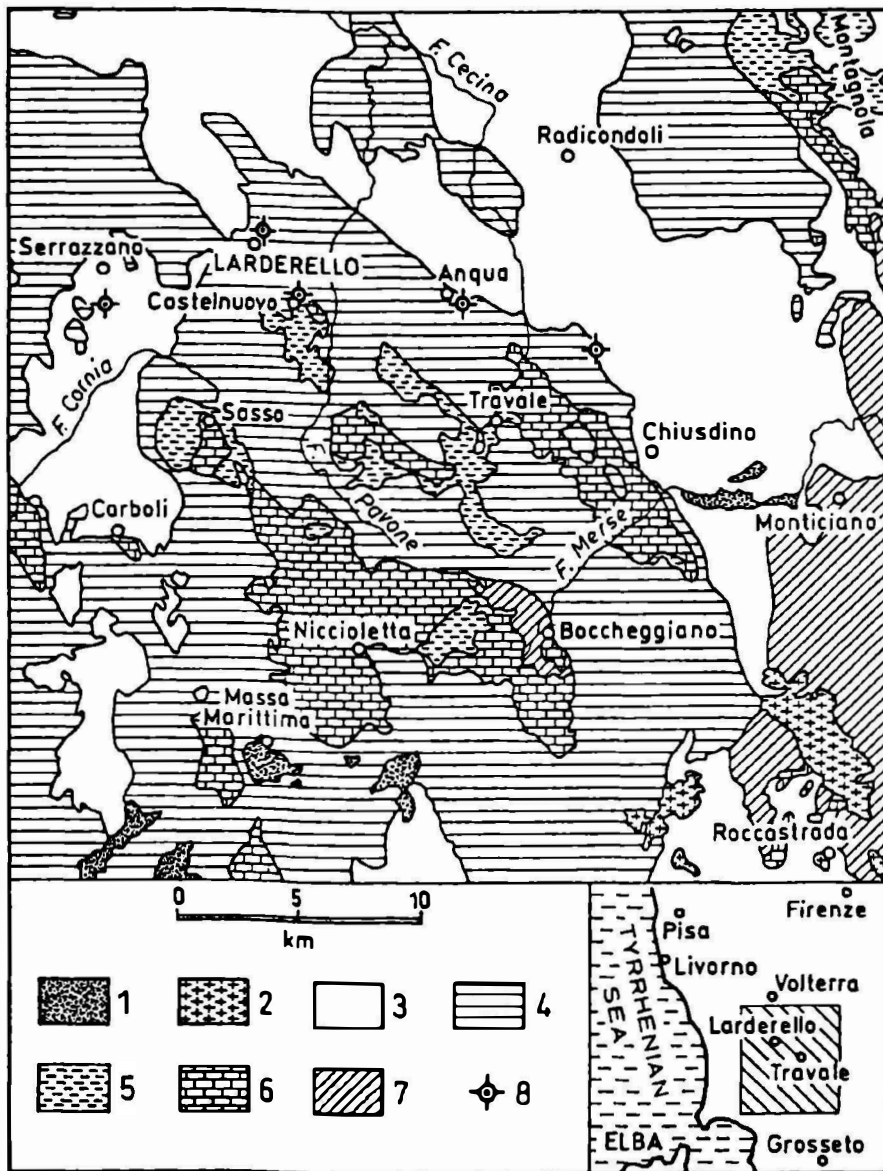


Fig. 1: Geological sketch map of the geothermal area of Larderello (Tuscany, Italy) (Modified after CAVARETTA et al., 1980).

Legend: 1) Quaternary travertine; 2) Roccastrada rhyolites (2.3 Ma); 3) Upper Miocene - Pliocene sediments; 4) Ligurids; 5) Tuscan nappe: "Macigno" and "Scaglia"; 6) Tuscan nappe: Triassic and Jurassic carbonate formations; 7) Verrucano and Paleozoic phyllitic complex; 8) location of deepest boreholes.

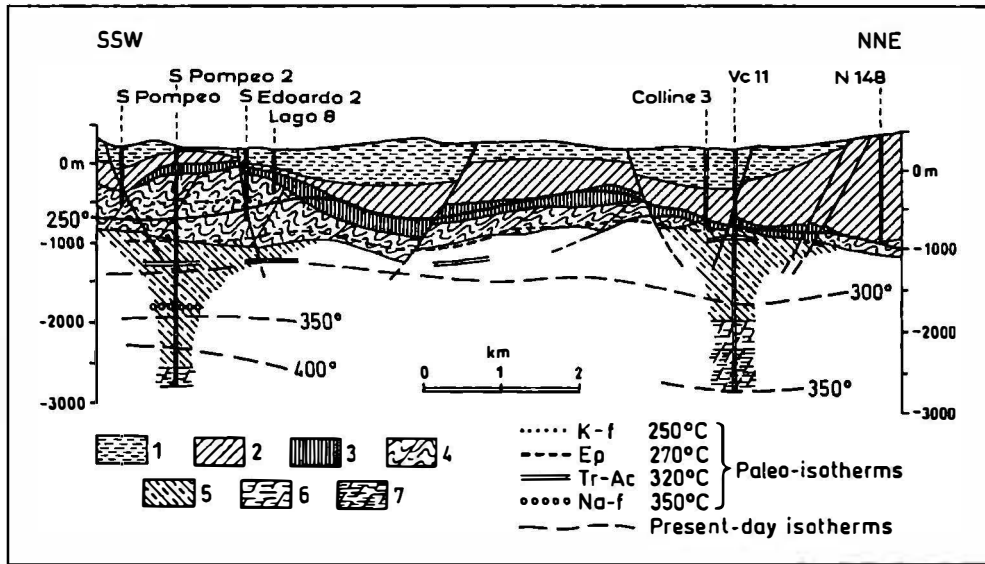


Fig. 2: Schematic geologic cross section of the Larderello geothermal system (modified after CAVARETTA and PUXEDDU, 1990).

Legend: 1) Neogene sediments; 2) flysch units (Cretaceous-Eocene); 3) anhydrite and dolostone (Upper Triassic); 4) tectonic slices; 5) phyllite and quartzite (Silurian-Ordovician); 6) mica schist (lower Paleozoic to Precambrian); 7) gneiss (lower Paleozoic to Precambrian).

The whole geothermal system was primarily liquid dominated. In contrast, today the system is predominantly vapour dominated with 1 to 20 weight-% of vapour in the geothermal fluid phase. Fluid temperatures vary between 150° C and 260 °C. Most other geothermal systems in the region (Monte Amiata, Torre Alfina, Latera) are still liquid dominated (BENCINI & DUCHI, 1988). The therapeutic use of the boron rich fluids of Larderello has been widely discussed, but very few authors have investigated the hydro-geochemical aspects of the thermal system. BENCINI et al. (1977) distinguish three different water types. The source of boron is thought to be the evaporitic "Anidriti di Burano"-series. In an investigation of geothermal springs from Tuscany and Latium, BENCINI & DUCHI (1988) define 3 different water types:

- A) Meteoric waters percolating through the "Anidriti di Burano"-series. These waters reach the surface with no interaction with the Neogene sediments. The water samples investigated in this study belong to this group.
- B) Meteoric water percolating through the "Anidriti di Burano"-series but interacting with the Neogene sediments.

- C) Meteoric water not reaching the "Anidriti di Burano"-series. These waters circulate through the Tuscan and Ligurian nappe series and the Neogene sediments.

Sample	$^{11}\text{B}/^{10}\text{B}$	$\pm 1\sigma$	$\pm 1\sigma$ (%)	$\delta^{11}\text{B}$	$\pm 1\sigma$	ppm B	$\pm 1\sigma$	$\pm 1\sigma$ (%)
Castelnuovo fresh water	4.0919	0.0151	0.37	+11.9	8	0.195	0.001	0.51
Larderello Centrale 2 geothermal water, 50° C	4.1844	0.0008	0.02	+34.8	4	139.3	0.33	0.24
Larderello Centrale 2 geothermal water, 25° C	4.1886	0.0159	0.38	+35.9	8	147.3	0.45	0.32
Monterotondo fresh water	4.1348	0.0012	0.03	+22.5	6	12.60	0.02	0.16
Monterotondo fumarole vapour	4.0173	0.0124	0.31	-6.5	6	0.243	0.003	1.24
N75 bore hole vapour	4.1467	0.0068	0.16	+22.5	3	3.80	0.07	1.84
Sasso Pisano fumarole vapour	3.9179	0.0139	0.35	-30.9	7	0.702	0.002	0.29
Secolo 2 bore hole vapour	4.1492	0.0089	0.22	+26.1	4	88.8	0.01	0.01
Terme la Perla fresh water	4.1006	0.0086	0.21	+14.1	4	0.201	0.003	1.49

Table 1: Analytical data of fluids from Larderello (Tuscany, Italy). Values cited are from at least 3 replicate analyses.

## **Results**

Figure 3 presents a very schematic view of the geothermal field of Larderello with the established boron systematics. All sampled localities with their respective boron isotopic composition and boron concentration are shown. Tables 1 and 2 give the analysis data.

The geothermal fluid and water samples (N75, Secolo 2, Centrale 2) exhibit  $\delta^{11}\text{B}$ -values between +25.5‰ and +35.9‰.  $\delta^{11}\text{B}$  increases from N75 to the reinjection point at Centrale 2, but the  $\delta^{11}\text{B}$ -values for the two bore holes cannot be

statistically distinguished. The same is true for the samples from Centrale 2. The measured boron concentrations show the same behaviour with values between 3.8 ppm (N75) and 147.3 ppm (Centrale 2).

The boron concentration of the fresh water samples from Castelnuovo, Terme la Perla, and Monterotondo range from 0.125 ppm to 12.6 ppm. The respective  $\delta^{11}\text{B}$ -values lie between +11.4‰ and +22.5‰. The sampled fumaroles from Sasso Pisano and Monterotondo show  $\delta^{11}\text{B}$ -values between -30.9‰ and -6.5‰.

Sassolites from Secolo 2 and N75 have  $\delta^{11}\text{B}$ -values between +18.9‰ and +22.2‰, sborgite from Centrale 2 +31.6‰. The boron concentrations of these boron minerals were not determined. Gypsum from N75 gives -1.1‰ and a boron concentration of 13.3 ppm.

Sample	$^{11}\text{B}/^{10}\text{B}$	$\pm 1\sigma$	$\pm 1\sigma$ (%)	$\delta^{11}\text{B}$
Larderello Centrale 2 sassolite	4.1314	0.0249	0.60	+21.7
Larderello Centrale 2 sborgite	4.1714	0.0133	0.32	+31.6
N75 gypsum	4.0394	0.0345	0.85	-1.1
Secolo 2 sassolite	4.1200	0.0198	0.48	+18.9
Secolo 2 sassolite	4.1333	0.0015	0.04	+22.2

Table 2: Analytical data of minerals from Larderello (Tuscany, Italy). Values cited are from at least 3 replicate analyses.

## Discussion

### Fluid systematics

The  $\delta^{11}\text{B}$ -values from the bore holes (N75 and Secolo 2) indicate that the boron source is either formed by marine, evaporitic sediments (SWIHART & MOORE, 1986; VENGOSH et al., 1989) or by marine carbonates (HEMMING, 1990). A non-marine boron source is rather improbable (KLÖTZLI, 1991a). In the nappe sequence of Larderello two appropriate boron sources are found: the evaporitic "Anidriti di

Burano"-series and the Mesozoic carbonates. As the boron concentration, the permeability, and the solubility of the evaporites is far more suitable, it is concluded, that the "Anidriti di Burano" forms the boron reservoir. This conclusion is in excellent agreement with geological data proposing that the main aquifer of the geothermal system of Larderello is formed by the "Anidriti di Burano"-series (BENCINI et al., 1977; GIANELLI et al., 1978; PUXEDDU et al., 1977).

At the moment it is not known of which degree the boron isotope fractionation between the evaporites and the circulating fluid or between the fluid and the sampled steam is. Marine evaporites have  $\delta^{11}\text{B}$ -values ranging from +25.5‰ to +40‰, thus only a total boron isotope fractionation between +0‰ and -15‰ can be postulated.

The secondary boron and  $^{11}\text{B}$  enrichment between the bore holes and the Larderello Centrale 2 power plant can be explained in two ways:

- a) Fluids from other productive wells being fed into the Larderello Centrale 2 power plant are higher enriched in boron and  $^{11}\text{B}$  than those sampled from the two bore holes. The measured  $\delta^{11}\text{B}$ -values and boron concentrations from Larderello Centrale 2 water samples may thus just represent a mixture between different boron sources.
- b) The boron and  $^{11}\text{B}$  enrichment is due to fractionation during evaporation and condensation processes within the cooling tower. There, water is preferentially evaporated and thus boron slightly enriched as compared to water (139.3 ppm and 147.3 ppm, respectively).  $^{10}\text{B}$  evaporates easier than  $^{11}\text{B}$  leading to the observed  $^{11}\text{B}$  enrichment (+34.8‰ to +35.9‰, respectively). Recycling of the cooled and fractionated water may lead to the observed enrichments.

At the moment it is impossible to quantify either of the proposed effects, but both may play a certain role.

The fresh water samples Castelnuovo (0.125 ppm) and Terme la Perla (0.20 ppm) show slightly elevated boron concentrations as compared to normal fresh water (0.01 ppm to 0.1 ppm). The  $\delta^{11}\text{B}$ -values (+11.9‰ and +14.1‰, respectively) are distinctly lower than the values of the above mentioned hydrothermal samples. The boron of these samples seems to be derived from a completely different source, unless a presently unknown fractionation process is postulated.

$\delta^{11}\text{B}$ -values between +13.9‰ and +15.8‰ are characteristic for the desorbable boron of fine grained, clastic, marine sediments of the Mississippi delta (SPIVACK et al., 1987), although the total range of boron fractionation in such sediments may be quite bigger. It seems possible, that boron from the two fresh water samples originates from such sediments. Different horizons of suitable lithologies are found within the geothermal system of Larderello: the Cretaceous "Scaglia"-marls and the Oligocene turbiditic "Macigno"-sandstone of the Toscanids and the flysch complex of the Ligurids. Boron of the fresh water samples is extracted from one of these clastic series. Any evident influence of hydrothermal boron from the "Burano"-



series can be ruled out. The very high, near surface thermogradient of 150° C/km suggests, that the relatively cool waters originate from not too deep regions. Taking this into account, it seems most probable, that the aquifer for these waters is sited in the flysch sequence of the Ligurids. BENCINI et al. (1977) designate the water from Terme la Perla to their group C (low sulfate hot waters), which is related to the emergence of water from the flysch formation. In the division given by BENCINI & DUCHI (1988) the investigated waters fall into group C but without circulating through the Neogene sediments. Thus it may be concluded, that the fresh water from Castelnuovo and Terme la Perla is derived from the flysch formations of the Ligurids.

The fresh water sample from Monterotondo (Monterotondo 7) is clearly a mixture of fresh water from the flysch formation (Castelnuovo or Terme la Perla type) and the hydrothermal water derived from the "Burano"-series. The  $\delta^{11}\text{B}$ -value of +22.5‰ and boron concentration of 12.6 ppm are intermediate to the above described waters when these are considered as endmembers of a mixing line. This is not astonishing taking into account, that the spring of Monterotondo is situated about 150 m away from active fumaroles. Another probable explanation could be, that the water is derived from hydrothermal waters diluted with the relative light boron from the fumaroles (-6.5‰).

The sampled fumaroles Sasso Pisano and Monterotondo show negative  $\delta^{11}\text{B}$ -values (-30.9‰ and -6.5‰, respectively). For the waters discussed above it seems evident, that the boron originates from marine boron reservoirs. From a geological point of view it is rather improbable, that boron from the fumaroles comes from another reservoir than boron from the investigated waters. Therefore, an isotope fractionation process must be found, which leads from the heavy marine boron (+25‰ to +40‰) to the lighter boron of the fumaroles. A multiple stage evaporation and condensation process could lead to the observed isotope fractionation: Boron evaporating from an aqueous fluid will be enriched in  $^{10}\text{B}$  in respect to the fluid. If this vapour is condensated and evaporated step wise, the boron composition can be fractionated to the fumarole values. At the moment, no experimental or on natural systems determined isotope fractionation factors exist, that would allow to quantify such fractionation processes. Using the data of this study it is possible to semi-quantify the process: As discussed for the data from the two bore holes N75 and Secolo 2, a maximum isotope fractionation of -15‰ between marine boron reservoir and vapour phase can be postulated. In a first approach, the whole evaporation process can be thought of as one single step. The vapour is led directly from the aquifer into the bore hole and does not condensate before sampling. Thus, a maximum isotope fractionation of -15‰ can be postulated for a one step evaporation - condensation process. So a two- to five-step process could lead to the observed fractionation of the boron isotopes of the fumarole vapour. But several problems arise: Is the fractionation process controlled by equilibrium processes or by kinetic processes? How large is the fraction of water sampled with the vapour and the isotope fractionation associated with it? How significant is the effect of temperature changes?

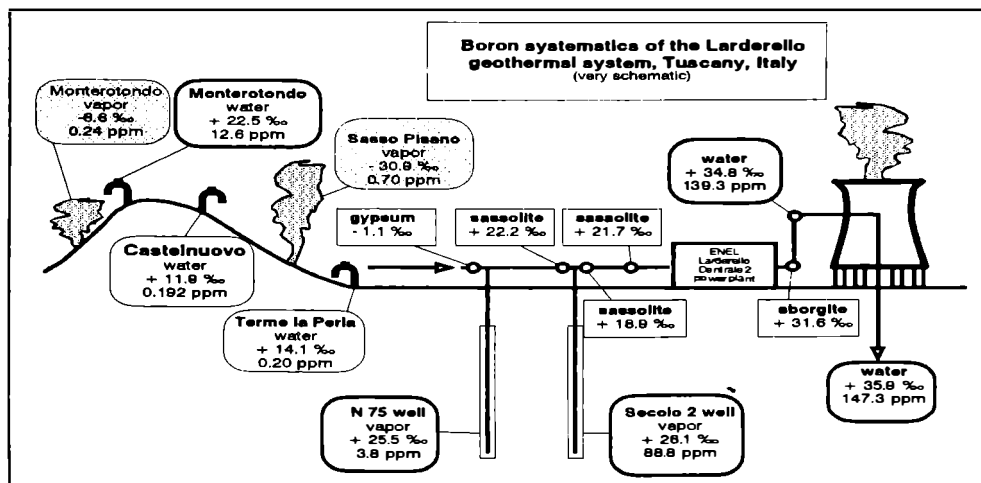


Fig. 3: Boron systematics of the Larderello geothermal system.

### Mineral systematics

The sassolites ( $\text{B}(\text{OH})_3$ ) investigated from the bore holes Secolo 2 and N75 are depleted in  $^{11}\text{B}$  by approximately 5‰ (+ 18.9‰ and + 22.2‰, respectively) in respect to the sampled bore hole vapour. They most probably formed directly from the boron rich fluid. This means that the sassolites should be in isotopic equilibrium with the fluid. The  $^{11}\text{B}$  depletion of 5‰ thus may be characteristic for the equilibrium isotope fractionation between sassolites and the vapour in the fluid.

In waters with  $\text{pH} < 7.5$  boron is co-ordinated predominantly in the planar  $\text{B}(\text{OH})_3$ -form (KAKIHANA et al., 1977; OI et al., 1989; PALMER et al., 1987; SPIVACK and EDMOND, 1987). The sampled fluids from the bore holes show pH-values between 6.5 and 7.7. This leads to the assumption that the investigated sassolites formed solely from  $\text{B}(\text{OH})_3$ . In aqueous solutions planar co-ordinated  $\text{B}(\text{OH})_3$  is enriched in  $^{11}\text{B}$ , tetragonal co-ordinated  $\text{B}(\text{OH})_4^-$  accordingly depleted in  $^{11}\text{B}$  (KAKIHANA et al., 1977; OI et al., 1989; KLÖTZLI, 1991). This seems to be contradictory to the  $^{11}\text{B}$ -depletion found in the sassolites. But if all boron in the solution is planar co-ordinated, as may be assumed for the investigated vapour phases, this relative  $^{11}\text{B}$ -enrichment between  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  becomes inexistent. It thus can be concluded that the sassolites formed from boron with  $\delta^{11}\text{B} = +25.8\text{‰}$  (mean value from Secolo 2 and N75). Assuming isotopic equilibrium between sassolite and vapour phase an empirical mineral/fluid fractionation factor  $\alpha = 0.9953$  for the isotope fractionation between sassolite and fluid phase can be calculated (KLÖTZLI, 1991a). Using the data from OI et al. (1989) fractionation factors (for 25° C) between  $\alpha = 0.9904$  (Na-borates) and  $\alpha = 0.9874$  (Ca-borates) are obtained. These values are higher than the values for the sassolites. Two reasons may be given: Different precipitation temperatures (> 100° C in Larderello, 25° C for the

data from OI et al. (1989)) can be responsible for the observed spread, or the formation of the more complex borates investigated by OI et al. (1989) leads to a more extent isotope fractionation between the different minerals. Also, sassolite was not included in the investigations of OI et al. (1989). To our knowledge, no experimentally determined fractionation factors between sassolite and fluid phase exist. Comparable fractionation factors for sassolite - fumarole isotope fractionation from Japan vary between  $\alpha = 1.008$  and  $\alpha = 0.9906$  ( $60^\circ \text{C} < T < 176^\circ \text{C}$ ; calculated from KANZAKI et al., 1979).

Sborgite ( $\text{Na}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ ) shows a  $^{11}\text{B}$ -depletion of approximately 4‰ ( $50^\circ \text{C} < T < 100^\circ \text{C}$ ) in respect to geothermal water. With the same assumptions as stated for sassolite, a fractionation factor of  $\alpha = 0.9963$  can be calculated. Using the data from OI et al. (1989), the fractionation factor for sborgite at  $25^\circ \text{C}$  should be  $\alpha > 0.9886$  (ulexite-group with  $\text{B}(\text{OH})_3:\text{B}(\text{OH})_4^- = 2:3$ , see OI et al., 1989). Theoretically, the fractionation factor must increase with decreasing temperatures. Whether or not the relative great difference observed between empirical and theoretical fractionation factor for sborgite is only due to differences in precipitation temperature is not certain.

Gypsum from N75 shows a slightly negative  $\delta^{11}\text{B}$ -value of -1.1‰, again assuming isotope equilibrium between mineral and fluid phase. The relative low value can be explained by the preferential incorporation of tetragonal co-ordinated  $\text{B}(\text{OH})_4^-$  into the gypsum. With the data from KAKIHANA et al. (1977) isotope fractionation factors for the  $\text{B}(\text{OH})_3 - \text{B}(\text{OH})_4^-$  fractionation can be calculated to be between  $\alpha = 1.0206$  at  $0^\circ \text{C}$  and  $\alpha = 1.0177$  at  $50^\circ \text{C}$ , respectively. For a fluid with  $6 < \text{pH} < 7.5$  (that means with max. 10% tetragonal co-ordinated boron) and with  $\delta^{11}\text{B} = +25.8\text{‰}$   $\delta^{11}\text{B}$ -values for the tetragonal  $\text{B}(\text{OH})_4^-$  are between +8‰ and +5.1‰, respectively. Taking into account (KLÖTZLI, 1991a, 1992) the big relative error on  $\delta$ -values in the range of the reference value ( $\delta = 0$ ), the measured  $\delta^{11}\text{B}$ -value of -1.1‰ may still be in the theoretically determined range. But as long as the mechanism of boron adsorption or incorporation into gypsum and the associated isotope fractionation effects are not known and understood, no better quantification is possible.

## Conclusions

The present work demonstrates the applicability and usefulness of NTI-MS in investigating geothermal systems.

The isotopic composition of boron clearly reflects the different lithologies of reservoir formations in the geothermal field of Larderello. Thus, geothermal systems, which by convection transfer anomalous quantities of heat to the surface, seem to mobilise boron more in relation to the geological, lithological, and mineralogical environments, than in relation to temperature and chemical type of fluids in the system. This is additionally supported by the main geochemistry of the involved fluids.

In future, boron isotopes should provide a reliable tool for the investigation of geothermal fluids, their origin, thermal history and flow path.

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