

## The Dramatic Fractionation of REEs in Hydrothermal Calcites from the Xikuangshan Antimony Deposit, Hunan, China

JIANTANG PENG, RUIZHONG HU, JUNHONG ZHAO AND LIANG QI

Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China (jtpeng@chinese.com)

The Xikuangshan antimony deposit located at Central Hunan, China, is the largest Sb deposit in the world. Despite the previous detailed investigation, few attempts have been made on the REE geochemical signatures of hydrothermal calcites.

Based on the field textural features and microscopic observation, calcite coevally stibnite can be divided into two types: the early syn-sulphide and the late syn-sulphide calcites. REE concentrations in the samples were determined by the ICP-MS method. Abundances of Sm and Nd were determined by isotope dilution.  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were measured from unspiked dissolutions of pre-concentrated sample spilt.

The REE contents of the early syn-sulphide calcites vary in the range of 29.61~78.40ppm. The chondrite-normalized REE patterns for the calcites are characterized by MREE- and HREE-enriched and LREE-depleted. The Sm/Nd ratios vary between 1.56 and 13.9; obviously, the dramatic fractionations between Sm and Nd in the early syn-sulphide calcites took place. It is the great fractionation that leads to the higher  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios for the early syn-sulphide calcites. The  $^{147}\text{Sm}/^{144}\text{Nd}$  values greatly varies, falls in the range of 0.941~8.420, mostly more than 1.

The dramatic fractionation of REEs in the early syn-sulphide calcites is probably associated with the process of mineral precipitation. If some LREE-enriched mineral, analogous to monazite, preceded to precipitate, or some mineral such as apatite was involved in the dissolution in the hydrothermal solution, the dramatic decrease of LREE in the hydrothermal fluid should happen, and cause the corresponding decrease in LREE of the consequent calcites.

### Reference

Halliday A. N., Shepherd T. J., Dickin A.P., et al., (1990). *Nature*. 344, 54-56

## Boron-rich groundwaters in alluvial aquifers of Tuscany: memory effect of past geothermal activity?

M.PENNISI<sup>1</sup>, G. BIANCHINI<sup>1</sup>, N. CERBAI<sup>3</sup>, R. CIONI<sup>1</sup>, R. GONFIANTINI<sup>1</sup>, A. MUTI<sup>2</sup>

<sup>1</sup>Istituto di Geoscienze e Georisorse, CNR, Pisa, Italia  
(m.pennisi@igg.cnr.it; g.bianchini@igg.cnr.it;  
r.cioni@igg.cnr.it; r.gonfiantini@igg.cnr.it)

<sup>2</sup>CIGRI SpA, Venturina, Livorno, Italia (Muti@cigri.it)

<sup>3</sup>TECHNE TEAM, Cecina, Livorno, Italia  
(Nicola.cerbai@techneteam.it)

The boron content of groundwater in the Cornia River alluvial plain, central-western Tuscany, is often above the European limit for potable water (1 mg/L), and may reach values as high as 8 mg/L. This boron contamination origin and distribution is now being investigated within the frame of the BOREMED project co-financed by the European Union, using chemical and isotopic ( $\delta^{11}\text{B}$ ,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) data as tracers.

The groundwater boron content, as shown by detailed GIS maps, increases as water moves southwards (towards the Tyrrhenian coast) within the aquifer, and this is accompanied by a geochemical facies change from bicarbonate to chloride-type water. In coastal aquifers, the  $\delta^{18}\text{O}$  signature and Br/Cl ratio indicate a sea water encroachment up to 30-40 %. However, sea water intrusion alone would not explain the boron increase and the parallel  $\delta^{11}\text{B}$  variation from 10 ‰ in inland wells to -7 ‰ close to the coast, i.e. with a reversed trend with respect to that produced by mixing with sea water (which has  $\delta^{11}\text{B} = 39$  ‰).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of dissolved strontium is rather uniform ( $0.7088 \pm 0.0001$ ) indicating a quite homogeneous aquifer lithology.  $^{87}\text{Sr}/^{86}\text{Sr}$  composition is shifted towards the value typical of the Mesozoic carbonate reservoir (0.7080) only in a localised sector of the plain, where mixing with uprising sulphate-rich hydrothermal fluids do not increase the boron content.

The increase of boron, potassium and lithium concentration indicates that the groundwater composition is controlled by an ion-exchange process with the fine fraction of the alluvial sediments. This is in agreement with the hydrogeological evidence that towards the coast the clay fraction increases and the aquifer becomes less permeable. In particular, the boron content enrichment and the parallel  $^{11}\text{B}$  depletion in groundwater suggest that the source of contamination is the boron adsorbed by clay minerals, which is now being released. It is hypothesised that the boron adsorbed in these sediments reflects an ancient involvement of boron-rich fluids from the nearby Larderello geothermal field.