

Título: Insights into the geochemistry of F, Ba and Zn-(Pb) hydrothermal systems: examples from northern Iberian Peninsula
Profundización en la geoquímica de sistemas hidrotermales de F, Ba y Zn-(Pb): ejemplos del norte de la Península Ibérica

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Fecha de lectura: 22 de Diciembre de 2008

Tribunal: Esteve Cardellach López (Presidente), Fernando Tornos Arroyo (Secretario), Lluís Fontboté

Calificación: Sobresaliente "Cum laude"

Insights into the Geochemistry of F, Ba and Zn-(Pb) Hydrothermal Systems: Examples from Northern Iberian Peninsula

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SUMMARY

This PhD thesis deals with the fluid geochemistry of several hydrothermal systems, including F-Ba veins, a Zn-Pb MVT occurrence and a current low enthalpy geothermal field, all of them located in the northern part of the Iberian peninsula. The objectives of this thesis were to constrain the pathways of base-metal rich brines, their links to tectonic events and their possible implications in the formation of base metal mineralizations.

Inclusion brines were analyzed by LA-ICP-MS in F-Ba veins from the Catalan Coastal Ranges (CCR). High amounts of base metals (up to hundreds of ppm) were found in the brines, which were also sulfate-rich, however, no significant sulfide precipitation took place in the veins. The role of organic matter in the reduction of sulfate to sulfide and in Zn-Pb ore formation, was studied in a MVT occurrence from the Basque-Cantabrian basin. Also, in order to go deeply into the knowledge of the fossil hydrothermal mineralizations, a current geothermal system from the CCR was studied. This system is also of interest as a natural analogue of CO₂ leakage, of high interest in the deep sequestration of this greenhouse gas. Finally, both thermal and non-thermal groundwaters in the geothermal field were known to have high amounts of arsenic, up to 20 times the drinking water threshold. The geochemistry of these waters was also studied in order to reveal which are the arsenic-releasing processes. The results and conclusions of each of these topics are briefly summarized in the following sections.

Two papers derived from this thesis have been already published: (1) *Piqué, À., et al., (2008)*; (2) *Piqué, À., et al., (2009)*. Other three have been submitted for publication to international journals.

BASE METAL-RICH BRINE CIRCULATION DURING EXTENSIONAL EVENTS

Basinal brines are commonly involved in the formation of hydrothermal base metal ore deposits in sedimentary basins, although in many instances, the source of metals is often thought to be the underlying basement rocks. The evidence of brine infiltration through the basement is sometimes directly found in vein systems in fracture zones cross-cutting the basement. That is the case of the fluorite-barite-base metal veins found throughout the Hercynian basement of Europe, North Africa and the Appalachians. A geochemical study of brines trapped in these veins can reveal their origin and evolution, but also their mineralizing potential, and coupled with the timing of fluid circulation, can give clues to elucidate the role of these, or similar brines in the genesis of base metal mineralizations, together with their possible links to tectonic events. The Sm-Nd dating of fluorite samples from one of these veins in NE Spain, the Rigròs fluorite vein, yielded an age of 137 ± 25 Ma (2σ) (MSWD=0.40). The vein formation took place during the Late Jurassic-Early Cretaceous rifting event in the western European basins, which is related to the opening of the Atlantic Ocean. Inclusion fluids in fluorite from Rigròs (fluorite I generation) and from another vein system in the same

region, the Berta vein, were studied by microthermometry, crush-leach and LA-ICP-MS. The brines trapped in the two vein systems are Na-Ca-Cl-(K-Mg), with homogenization temperatures ~120°C and salinities up to 25 equiv. mass % NaCl. The source of this salinity is related to evaporated seawater, at least in the halite precipitation field, and to the leaching of Mesozoic halite and gypsum sequences by seawater and/or meteoric water. The basinal brines later evolved through water-rock interaction with the crystalline basement, resulting in some sodium loss and potassium, calcium, strontium (the latter inferred from isotope data) and barium enrichment. The analyzed brines have concentrations of Zn between 3 and 790 ppm and of Pb between 3 and 995 ppm, which are similar to those reported in comparable hydrothermal veins and Mississippi Valley-type deposits, but higher than in most present-day sedimentary brines. Despite the fact they were able to transport large amounts of metals, no significant precipitation of sulfides occurred in the veins and, consequently, the mineralizing potential of these brines was still preserved after fluorite vein formation.

ALTERNATIVE INTERPRETATION OF MICROTHERMOMETRIC DATA

Two finely intergrown fluorite generations were recognized in some samples from the Rigròs vein system during cathodoluminescence studies. Fluorite I is the most abundant and fluorite II selectively grew in some fluorite I growth bands. Fluid inclusions considered primary in fluorite II have elongate angular shapes, and are found in 3D

palabras clave: : Sistemas Hidrotermales, Baja Entalpía, Geoquímica.

key words: : Hydrothermal Systems, Low Enthalpy, Geochemistry.

clusters generally oriented along the same direction. The fluid inclusion study revealed large differences in ice melting temperatures among inclusions from a single cluster, which are not expected to be caused by the mixing of coetaneous fluids during fluorite II precipitation. Instead, the similarity with fluid inclusion data from fluorite I and the textural relationships, point to another hypothesis. It is postulated that the fingerprint of fluorite I fluid inclusions was preserved in fluorite II fluid inclusions, which could be possible if dissolution and precipitation happened simultaneously in a submicrometric solution film. This new hypothesis could be applicable to those cases where replacement, or dissolution-precipitation could take place, such as hydrothermal veins, MVT and Irish-type deposits, and entails a mixing between different fluid generations during the migration of the precipitation front, in particular, between the solution film and fluid inclusions in the host phase. As a result, the microthermometric signature of the primary fluid inclusions in the newly formed phase can be undistinguishable from the signature proposed elsewhere for coeval fluid mixing.

IN SITU TSR DURING ORE FORMATION AT A Zn-(Pb) MVT OCCURRENCE

Organic matter is known to play a significant role in the genesis of many Mississippi Valley-type (MVT) deposits, acting as a reducing agent during thermochemical sulfate reduction (TSR). Although TSR is an extremely slow reaction at low temperatures (<100 °C), under favorable conditions it may possibly supply the necessary reduced sulfur during ore formation. To test this hypothesis, the Itxaspe Zn-(Pb) MVT occurrence in the Basque-Cantabrian basin (N Spain), was studied. Sphalerite, the main ore phase, is generally found disseminated in Urgonian (Lower Cretaceous) carbonates, and in close relationship with solid bitumen. The bitumen source rock was very likely deposited in a marine marginal setting. Differences in composition of the bitumen samples are attributed to a fractionation during hydrocarbon expulsion and/or migration. The fluids involved in ore deposition were low temperature (Th ~130 °C), Na-Ca-Cl-(K-Mg)-type brines (salinities ~12.5 equiv. mass % NaCl). The origin of brine solutes (including sulfate) is related to the dissolution of Mesozoic evaporite units, although the contribution of evaporated seawater brines cannot be ruled out. The temperatures of ore deposition, the

close relationship between the bitumen and ore phases, the presence of aromatic sulfur-bearing compounds and the $\delta^{34}\text{S}$ of sulfides and sulfates are consistent with an in situ TSR during ore formation in the Itxaspe Zn-(Pb) occurrence. Therefore, at least for small mineralizations like Itxaspe, the necessary reduced sulfur could be supplied by TSR during ore genesis at the site of metal deposition.

MINERALOGY AND GEOCHEMISTRY OF A LOW ENTHALPY GEOTHERMAL FIELD

The Caldes de Malavella low enthalpy geothermal field was selected to study the effect of low temperature (≤ 150 °C) interactions between CO_2 -rich fluids and granitic rocks over a relatively long period of time (>10,000 years). Located at the southern margin of La Selva basin (NE Spain), it comprises present-day and fossil travertine, barite and silica precipitates and active CO_2 -rich thermal springs. The current thermal fluids are of meteoric origin and acquired their solute content through CO_2 -enhanced water-rock interaction processes with the late Hercynian granitoids from the basement. $^{87}\text{Sr}/^{86}\text{Sr}$ and REE data point to a differential leaching of the granitoids, dominated by plagioclase, and to a lesser extent by K-feldspar and biotite. Opal ageing suggests that hydrothermal fluid circulation has been active for several thousands of years. Furthermore, extensive travertine deposits record a long history of CO_2 migration and leakage to the atmosphere, of at least 20,000 years, as revealed by U/Th travertine dating. According to geothermometry, the flowpath of the current fluids reaches depths of 3 km into the basement. The source of sulfate is considered to be magmatic (either sulfides or H_2S) and its isotopic composition modified by bacterial reduction processes (BSR). The positive correlation defined by the sulfur and oxygen isotopic compositions of barite and dissolved sulfate are the result of a mixing between residual sulfate after BSR and new sulfate produced during reoxidation and/or disproportionation processes in a nearly closed system.

ARSENIC RELEASE TO GROUNDWATER IN THE GEOTHERMAL FIELD

Arsenic concentrations exceeding up to 20 times the WHO drinking water limit (10 $\mu\text{g}/\text{l}$) were measured in thermal and non-thermal groundwaters from the Caldes de Malavella geothermal area. A geochemical monitoring of 13 wells and

three thermal springs was carried out monthly during ten months. CO_2 -rich NaHCO_3 thermal (up to 60 °C at the spring) waters have $[\text{As}_\text{T}]$ from 50 to 80 $\mu\text{g}/\text{L}$ and cool groundwaters are of $\text{Ca-Na-HCO}_3\text{-Cl}$ type and have $[\text{As}_\text{T}]$ between <1 and 200 $\mu\text{g}/\text{L}$. Arsenate is clearly predominant in most groundwaters, in agreement with measured E_H (72-464 mV, SHE), although in some high-As groundwaters, arsenite reaches up to 100%. The possible mechanisms that could explain the high arsenic contents in the cool groundwaters are: (1) Arsenic desorption from ferric oxyhydroxides due to ion competition; (2) reductive dissolution of ferric oxyhydroxides; and (3) thermal water inputs. Groundwaters from the area of study are saturated or oversaturated with ferrihydrite and dissolution is unlikely in most of the sampled wells and springs, however, it can account for high arsenic contents in groundwaters with the lowest Eh values and highest amounts of arsenite. Arsenic release due to competition for adsorption sites with carbonate and silica species is another plausible mechanism to account for the high arsenic concentration in the studied wells, as evidenced the calculations using a surface complexation model. Geothermal indicators such as Li and F do not correlate with arsenic and geothermal inputs are not considered to be the main arsenic contributor to cool groundwaters.

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