# Capítol 4

# FORMACIÓ DEL KARST I PRECIPITACIÓ DE SULFURS I SULFATS A ROCABRUNA, PIRINEUS ORIENTALS, PER MESCLES DE FLUIDS HIDROTERMALS

## RESUM

Les cavitats en roques carbonàtiques poden ser generades per l'efecte de mescla de solucions calentes, és a dir, per fluids de composició química diferent malgrat que tots dos estiguin saturats en minerals carbonàtics. També hi poden precipitar sulfurs metàl·lics com a conseqüència de la barreja si les solucions transporten sofre i metalls. La precipitació de sulfurs també causa dissolució de l'encaixant carbonàtic, però en un volum molt inferior al de l'efecte mescla. Això ha estat observat a Rocabruna, als Pirineus Orientals, on una fina banda de sulfurs no superior als 10 cm de gruix revesteix parcialment la paret de cavitats decamètriques desenvolupades en dolomies, que són reblertes posteriorment per cristalls de barita d'ordre mètric. Dipòsits similars apareixen en tot el domini hercinià europeu. La seva gènesi ha estat explicada a partir de dades geoquímiques (isòtops, inclusions fluides) per barreges de fluids que envaeixen cavitats prèviament formades. Anant una mica més enllà, aquí proposem que a Rocabruna la mescla de fluids no tan sols va ser la desencadenant del rebliment, sinó també de la generació de les cavitats. Simulem el procés de barreja química als dipòsits de Rocabruna utilitzant mètodes numèrics. Els resultats ens mostren que la barreja entre una aigua subterrània relativament diluïda però rica en sofre i una salmorra calenta rica en metalls i bari, totes dues en equilibri amb dolomita, produeix una forta dissolució de dolomita. A la vegada precipiten sulfurs quan la salmorra és molt reduïda, o bé precipiten sulfats quan la salmorra és més oxidant.

# Chapter 4

# KARST FORMATION AND SULFIDE AND SULFATE DEPOSITION IN ROCABRUNA, EASTERN PYRENEES, DUE TO HYDROTHERMAL FLUID MIXING

## ABSTRACT

Cavities in carbonate rocks may be generated by mixing two warm solutions of different chemistry, even though they are in equilibrium with respect to carbonate minerals. Sulfides may also precipitate in the cavity as a consequence of mixing if the fluids bring in sulfur and metals. Sulfide precipitation also causes dissolution of the host rock, but much less than that caused by the mixing effect. This has been observed in Rocabruna, Eastern Pyrenees, where a thin rim of sulfides and metric crystals of barite fill decametric cavities developed in dolostones. Similar ore deposits occur in most of the European Hercynian domain; they have been explained by mixing of fluids invading previously formed cavities. Based on the mixing model, we propose that the mixing not only caused the filling of the cavity but also generated the cavity in the carbonate host.

The chemical fluid mixing process for the deposits of Rocabruna is simulated with the aid of numerical methods. Our results show that when a dilute groundwater rich in sulfur mixes with a hot brine rich in metals and barium, both in equilibrium with respect to dolomite, strong dissolution of dolomite occurs. Simultaneously to the dissolution, some sulfides precipitate if the brine is very reduced, or sulfate deposits if the brine is not as reduced.

## INTRODUCTION

A mixture of warm and chemically disimilar fluids that are both saturated with respect to calcite is known to be subsaturated or supersaturated with respect to this mineral, or

both, at different proportions of the end-member solutions (chapter 2).  Whenever the initial fluids bring in sulfides and metals, the mixture may also become supersaturated with respect to metal sulfides and, given sufficient time, form an ore deposit (chapter 3). If the mixing process is the sole responsible for the formation of the cavities that contain metal sulfides, the amount of carbonate dissolved may be much higher than the amount of sulfides precipitated according to the models of chapter 1.  Rocabruna deposits keep such a proportion between volume of cavities and sulfides, so they are a good site to simulate the mixing model relative to other models.

Many deposits of metal sulfides and carbonates, fluorite and/or barite are found in the Hercynian domain of Western Europe (von Gehlen, 1987;  Behr et al. 1987;  Dill and Nielsen, 1987) and North Africa (Jebrak, 1984).  In the Iberian Peninsula they are common in the Pyrenees (Subias and Fernandez-Nieto, 1995;  Johnson et al. 1996), the Central System (Tornos et al. 1991;  Lillo et al. 1992;  Galindo et al.,1994) and the Catalan Coastal Ranges (Ayora et al. 1990;  Canals et al. 1992;  Canals and Cardellach, 1993).  Most of them are hosted in rocks of Paleozoic age, either as veins crosscutting metapelites and granites or in carbonate cavities.  The origin of these mineralizations has typically been explained by a mixing of fluids, one that is rich in sulfate with another that has evolved into a metal-rich and warm brine, in open spaces at or below the water table.  Rocabruna is a good representative deposit of the carbonate-hosted type, with cavities that are filled up by barite after a thin rim of Cu-Fe sulfides.  The available field (Soler, 1983;  Soler and Ayora, 1985) and geochemical data (Canals et al. 1999) point to mixing of solutions as the cause of sulfate precipitation.

We undertake geochemical modeling of Rocabruna deposits in order to, not only replicate in the computer the precipitation of barite, but also the previous dissolution of the carbonate host and the deposition of sulfides, processes that have not been addressed until now.  We invoke the mixing of fluids as the principal cause of carbonate dissolution, due to the intrinsic mixing effects, and suggest it is also responsible for sulfide and sulfate deposition.

## GEOLOGY OF ROCABRUNA

Several Ba-bearing deposits are known to occur in the Eastern Pyrenees;  among them, Rocabruna is the most important in size (20 000 tones of barite).  It consists of a set of irregular cavities developed in dolostones of Paleozoic age, filled with sulfides and barite.  They are situated 150 km to the N of Barcelona.

In the study area the Paleozoic series consists of Cambrian rithmites with alternating beds of sandstones, lutites and shales of millimetric to centimetric scale.  Sporadically in the series a few dolostone strata appear, hosting the Ba-Cu deposits (figure 1).  The Paleozoic rocks were deformed during the Hercynian orogeny, and its effects are observable in the form of slight chloritization of the rocks, and in the appearance of cleavage associated with folds.
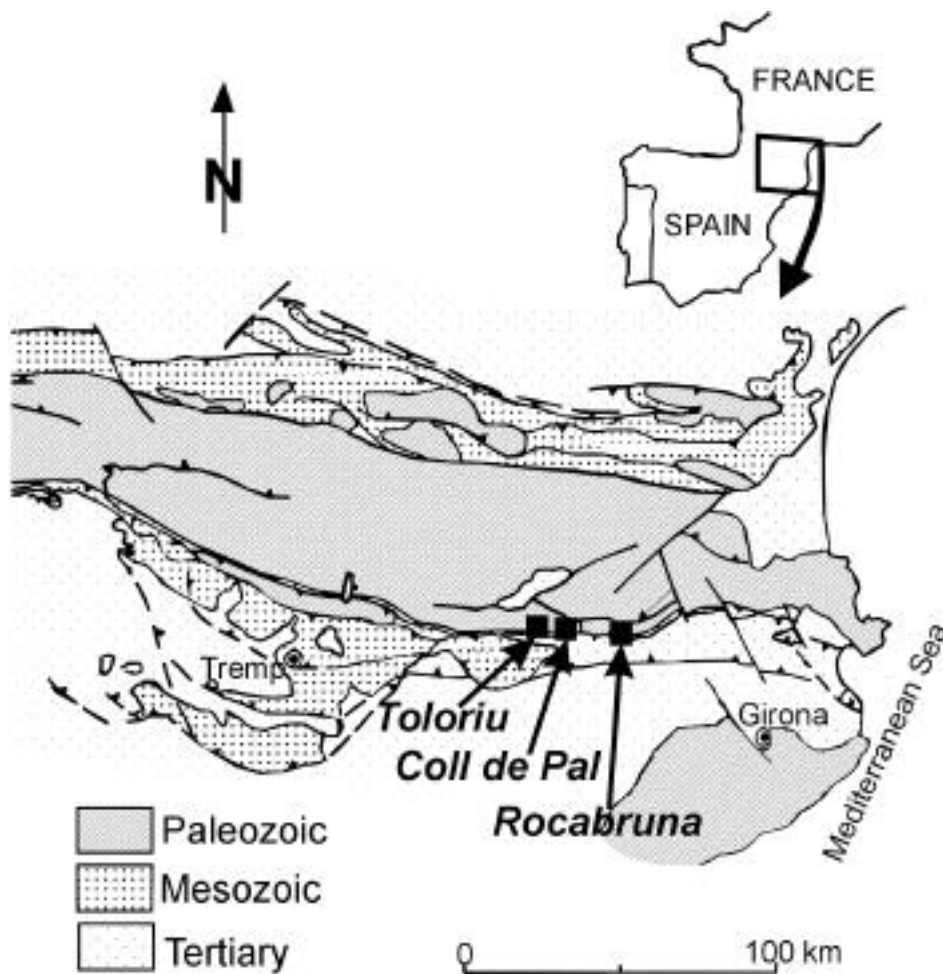


*Figure 1.  Location map of Rocabruna in the Eastern Pyrenees.*

The Triassic series of this study zone, which unconformably overlay the Paleozoic basement, has been eroded away.  Nevertheless, its materials are fairly homogeneous throughout the Iberian Peninsula, consisting of detritic red bed facies that alternate with marine carbonates, and topped by a strata with evaporites.

The sedimentary rocks of Cretaceous-Paleocene age, known as Garumnian facies, are the autochthonous material of this area.  They are made of detritic (conglomerate, sandstones and lutites of red color) and carbonate rocks.  No evaporites have been recognized in the Garumnian facies of the Pyrenees.  The Alpine orogeny affected the whole area during Tertiary times, developing a set of thrusts of a WSW-ENE direction.

Similar barite-sulfide mineralizations have been described in other areas of the Pyrenees (Canals et al. 1999).  Some of them, as Coll de Pal and Toloriu (figure 1), fill karst cavities apparently similar to Rocabruna, but most are veins hosted by Paleozoic metasediments and granites, usually close to the pre-Triassic paleosurface.

**THE MINERALIZATION**

The mineralization of Rocabruna is located in one of the occurrences of massive dolostone, that is more than 200 m thick, and slightly tilted at present.  The deposits consist of irregular bodies, of several meters in diameter, preferentially developed along strata and joints, that are usually interconnected.  Corrosion of the host dolostone is observed in the mineralized bodies.  Metal sulfides and quartz are distributed as a thin rim up to a few centimetres thick, placed between the dolostone host rock and the barite, which fills most of the cavity (figure 2).  In many ore bodies quartz and sulfides are more abundant at the bottom than in the rest of the cavity.

The main mineral present in Rocabruna is barite, that forms radial aggregates of metric-sized crystals.  The most abundant ore mineral found is tetrahedrite-tennantite, with minor chalcopyrite and sphalerite.  Galena, which appears in small amounts, replaces

previous sulfides.  Some pyrite crystals included in other sulfides have also been described (Soler and Ayora, 1985).  A few dolomite crystals, coexisting with sulfides, have been found as well.  Quartz is not abundant, and may replace the host carbonate in contact with sulfides.  The order of deposition, according to Soler and Ayora (1985) is as follows:  quartz, pyrite, tetrahedrite, sphalerite, chalcopyrite, galena and barite.



*Figure 2.  Photograph of one of the ore bodies of Rocabruna with the metric barite crystals filling up the cavities.  Dolostone clasts (dark gray) have accumulated at the base.*

Iron showings also appear in the area; they consist of irregular bodies of centimetric to metric dimensions located in the dolostone. They contain fine grained hematite and sometimes minor barite (Soler and Ayora, 1985).

The mineralization must be post-Hercynian in age, as it would have been difficult to be preserved during the Hercynian orogeny. And it must be pre-Alpine, because it is affected by a reverse fault, attributed to the Alpine thrust system. This conclusion is reinforced by the even distribution of dolostone fragments at the bottom of the cavities, that suggests they accumulated before the strata were tilted. An alpine thrust restitution indicates that the dolostones must have been very close to the red bed facies before thrusting (Soler and Ayora, 1985).

Primary fluid inclusions in sphalerite, quartz, dolomite or barite are small and scarce, so it has not been possible to perform microthermometric studies in these minerals. Nevertheless, microthermometric data of the nearby Coll de Pal deposit, situated 40 km to the west of Rocabruna, yield a temperature of formation between 125 and 150ºC as measured from quartz and dolomite fluid inclusions. CRYO-SEM data indicate that these fluids are Cl and Ca rich, and unusually low in Na (Canals et al. 1999).

The host dolomite carbon isotope values in Rocabruna are lower than those of the Cambrian dolostones of the area (Canals et al. 1999). This indicates that the host dolomite has interacted with an isotopically $^{12}$C-enriched fluid, probably rich in organic carbon from the surrounding metapelites.

The values of sulfur isotopes of barite increase from bottom to center of cavities, implying there was enrichment in $^{34}$S through time, from values of 14 to 19 ‰. Sulfur isotopes of tetrahedrite and chalcopyrite are 1 and 8 ‰ respectively (Canals et al. 1999).

$^{87}$Sr/$^{86}$Sr ratios in carbonates are higher than those of the Cambrian marine carbonates, indicating that the rock must have interacted with a radiogenic fluid at some point, and higher than later barites. Besides, the Sr isotopic ratio varies through time as suggested by the measured barites of sampled cavities (Canals et al. 1999).

## ORE DEPOSIT FORMATION: CONCEPTUAL MODEL

The model most often invoked to explain these paleosurface-related mineralizations is the mixing between two fluids. In essence, deep convective fluids mobilize and carry Ba and metals along deep faults and mix at some point with $SO_4$-rich waters, causing the deposition of sulfides, sulfates and other gangue minerals.

From the geochemical data of Rocabruna and similar deposits along the Pyrenees and Catalan Coastal Ranges it is inferred that two fluids mixed at the site of the ore bodies. In this manner, the genetic model proposed for the formation of Coll de Pal deposit required a karst system saturated with $SO_4$-rich water and an invading hot fluid that was rich in Ba and metals (Canals et al. 1999). The mixing of the two caused the precipitation of barite and carbonates, that formed at temperatures of 125-150ºC.

The genesis of the Rocabruna mineralization was assumed to be somewhat similar to that of Coll de Pal, that is, a mixing of two fluids in previously formed karstic cavities. According to Canals et al. (1999) one fluid had high $^{87}Sr/^{86}Sr$ ratio, was hot and had low $^{34}S$-sulfate, the other had a lower $^{87}Sr/^{86}Sr$ ratio, was $^{34}S$-enriched and sulfate rich-fluid. Ba and metals must have been leached out of the Cambrian series and granites by the first fluid. This classic model is only applicable to the formation of the barite mineralization, once the cavity is formed and some sulfides have precipitated.

Even though Rocabruna and Coll de Pal share many similarities and are close by, the two differ in some interesting points. Rocabruna deposits display corrosion of the carbonate host, while Coll de Pal ore bodies do not. The carbonate horizon that hosts Rocabruna is much thinner and is interbedded within metapelites, whereas Coll de Pal is located in a thick carbonate sequence of Devonian age. Rocabruna is hosted in a dolostone but the cavities only contain a small amount of dolomite, whereas Coll de Pal is hosted by a dolomitized limestone and has abundant dolomite. The sulfur isotopic signature of barites from Rocabruna is variable while that of Coll the Pal is homogeneous and is in accordance with Triassic evaporites or seawater values.

Our model is not restricted to the more evident phenomenon of barite precipitation, but includes the formation of the cavity and the deposition of sulfides. All these processes are explained in terms of mixing two chemically distinct solutions. In a first stage, the intrinsic effects of mixing cause dolomite dissolution, that is, the generation of the cavity; this may be contemporaneous with some sulfide precipitation whenever one fluid carries sulfur and the other is reduced and brings about metals and barium. When the reducing potential of the brine diminishes, because of the exhaustion of organic matter, the mixing of the fluids causes barite precipitation instead of sulfide precipitation. These two stages are well recorded in Rocabruna, and seem continuous in time.

## NUMERICAL SIMULATIONS

The quantification of the mixing process is done through numerical modeling with the Fortran code RETRASO (Saaltink et al. 1998; Ayora et al. 1998). It is a geochemical simulator that includes steady transport of fluids as well as speciation and adsorption of chemical components, and precipitation and dissolution of minerals by means of either kinetics or thermodynamics. It uses the databases of EQ3NR (Wolery, 1992), and other kinetic data gathered from the literature, so that calculations are allowed from 0 to 300ºC.

The system, host rock and fluids at the scale of the ore bodies, has supposedly equilibrated to the temperature of the brine after some years. Therefore, a constant temperature of 150ºC is used throughout the simulation time. This is the temperature recorded in fluid inclusions of the nearby deposit of Coll de Pal (Canals et al. 1999) and agrees well with that of other deposits in the Catalan Coastal Ranges as well (Canals and Cardellach, 1993).

The geology of Rocabruna is not as simple as to easily infer which were the principal fluid conduits at the time of formation of the ore. Therefore, the big picture of heat and

fluid flow circulation of the area is not tried.  Besides, the large cavities of Rocabruna are shaped irregularly, with some dissolution also occurring along joints and bedding planes;  then, there is no loss of information if such cavities are considered as spherical or to have a radial symmetry, so that the geochemical simulations are carried along one of these radii in the carbonate host.   We therefore perform one-dimensional geochemical mixing with two different fluids continuously entering the system from the two ends.

BOUNDARY FLUIDS

The composition of the fluids is described in table 1.  One of the fluids involved brings most of the sulfur, either as $H_2S$ or $SO_4^{2-}$.  It is supposedly slightly oxidizing, as may have not traveled at great depths and must have leached red beds and evaporites of probably Triassic age.  The salinity of the fluid is assumed to be low, so a value of 1 mol/L of chlorine is used, although it is increased in later runs.  According to Hanor's data (2001) the low salinity fluids of basins are usually basic, thus a tentative pH of 6.5 is chosen.  It is further equilibrated with dolomite, as all series, Paleozoic, Triassic or Tertiary, contain dolomitic beds and the deposits are located in dolostones, and with quartz, a ubiquitous mineral.

The other fluid brings in metals and barium.  This solution, independent of its primary origin, has circulated through a diversity of basement rocks mostly through deep fractures.  Such fluids in basins are usually described as brines and have their pHs buffered in the acidic side (Hanor, 2001), thus we choose a chlorinity and a pH of 5.0 for them.  This pH agrees with the fluid being equilibrated with quartz-muscovite-K-feldspar, common minerals in granites and pelites.   The fluid is assumed to be equilibrated with dolomite, the host rock, and this constrains the amount of carbonate in solution.  The redox potential is chosen to be in the hydrocarbons field (see figure 2 of chapter 2).  Ca and Mg are chosen in accordance with Hanor's proportions (table 1); various values of Zn (representative of metals) are tried, and a high concentration of Ba is applied.

*Table 1. Chemical composition of end-member solutions.*

| Stages | 1. Cavity formation and sulfide precipitation | | | | | | 2. Cavity filling by barite precipitation | |
|---|---|---|---|---|---|---|---|---|
| Cases | Mixing | | Sulfide addition | | Sulfide addition | | Sulfate addition | |
| | gw | gw | gw | br | gw | br | gw | br |
| Cl | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 | 1.0 | 5.0 |
| Na | 0.80 | 1.5 | 0.80 | 1.5 | 0.80 | 1.5 | 0.80 | 1.5 |
| Ca | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 | 0.01 | 0.1 |
| Mg | $5\ 10^{-3}$ | 0.01 | $5\ 10^{-3}$ | 0.01 | $5\ 10^{-3}$ | 0.01 | $5\ 10^{-3}$ | 0.01 |
| $C_{inorganic}$ | $\underline{2\ 10^{-4}}$ | $\underline{0.05}$ | $\underline{2\ 10^{-4}}$ | $\underline{0.05}$ | $\underline{2\ 10^{-4}}$ | $\underline{0.05}$ | $\underline{2\ 10^{-4}}$ | $\underline{0.04}$ |
| $C_{organic}$ | $6\ 10^{-4}$ | 0.05 | $6\ 10^{-4}$ | 0.05 | $6\ 10^{-22}$ | 0.08 | $6\ 10^{-22}$ | $1\ 10^{-11}$ |
| S | $10^{-10}$ | $10^{-7}$ | $10^{-4}$ | $10^{-7}$ | $10^{-4}$ | $10^{-7}$ | $10^{-4}$ | $10^{-7}$ |
| Zn | $10^{-10}$ | $10^{-10}$ | $10^{-10}$ | $10^{-4}$ | $10^{-10}$ | $10^{-4}$ | $10^{-10}$ | $10^{-4}$ |
| K | 0.01 | 0.3 | 0.01 | 0.3 | 0.01 | 0.3 | 0.01 | 0.3 |
| Ba | $10^{-10}$ | $10^{-1}$ | $10^{-10}$ | $10^{-1}$ | $10^{-10}$ | $10^{-1}$ | $10^{-10}$ | $10^{-1}$ |
| pH | 6.5 | 5.0 | 6.5 | 5.0 | 6.5 | 5.0 | 6.5 | 5.0 |
| $fO_2$ (bar) | $10^{-51}$ | $10^{-51}$ | $10^{-51}$ | $10^{-51}$ | $10^{-42}$ | $10^{-51}$ | $10^{-42}$ | $10^{-46}$ |

*Concentration units are mol/kg. The underlined numbers have been calculated to fulfill the condition of dolomite ($C_{inorg}$) equilibrium. gw: groundwater, br: brine.*

A second stage of ore deposit formation is considered, when the brine has shifted its redox stage to a more oxidized one, probably because of the exhaustion of organic matter in its source. The pH and solute content of this brine is exactly the same as before (table 1) except for the oxygen fugacity, which is supposedly controlled by the iron system.. The groundwater that mixes with the modified brine remains chemically the same as well.

**RESULTS AND DISCUSSION**

CAVITY FORMATION AND SULFIDE PRECIPITATION

The mixing in a dolomitic host of two warm fluids equilibrated with dolomite but with different solute content causes a strong dissolution of the mineral (figure 3). It also produces very minor precipitation at the dilute end of the mixture, unobservable at the scale of figure 3. This is due to the intrinsic effects of mixing, as explained in chapter 2, that is, the salinity, the algebraic and pH-pCO2 effects. At high proportions of the dilute and more basic fluid, the algebraic effect slightly predominates causing the precipitation of dolomite. At other proportions, the salinity and pH-pCO$_2$ effects contribute more so that dissolution of dolomite is produced. As they are non-linear, the combination and compensation of these effects is not easily predictable, and may turn up one being more important than another in different parts of the system (at different proportions of the two initial fluids), as occurs in this case.
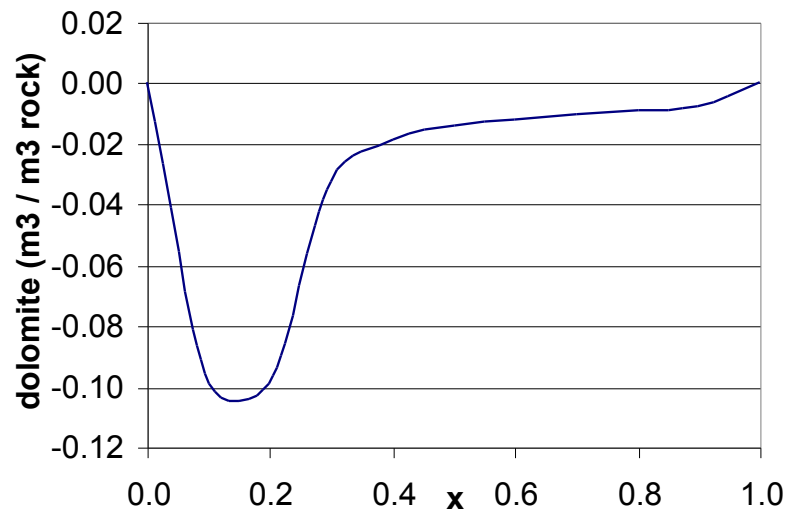


*Figure 3. Dissolution of dolomite caused by the mixing of two solutions saturated in dolomite but of different salinity and pH (their composition is described in table 1), after 0.5 Ma of simulation time.*

When the same fluids also carry sulfur and metals respectively, the dissolution of dolomite is enhanced (figure 4). This is due to two separate processes. On one hand, the addition of sulfur and metals to the geochemical model changes slightly the balance of mixing effects as the speciation of reduced S induces changes in the pH (1):

$$H_2S_{(aq)} = H^+ + HS^- . \tag{1}$$

This mainly causes less dissolution and a bit more precipitation of dolomite near the dilute terms of the mixture, still in very small amounts so it is unappreciable in the plot. On the other hand, the sulfide precipitation reaction liberates protons that are used to dissolve the country rock (2) (Anderson, 1975):

$$2\ H_2S_{(aq)} + 2\ Zn^{2+} + CaMg(CO_3)_{2\ (s)} =$$
$$= 2\ CO_{2\ (aq)} + 2\ ZnS_{(s)} + 2\ H_2O + Ca^{2+} + Mg^{2+} . \tag{2}$$
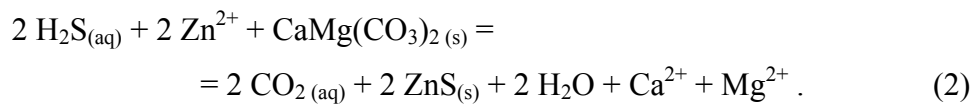
This explains the second dissolution minimum of dolomite in figure 4. The dissolution observed as corrosion of the host in the contact between the sulfide rim and the dolostone would respond to such effect.

The cavity forms in the dilute side of the mixture (figure 4) for the compositions of the initial solutions chosen (table 1). Sulfide precipitates where the proportion of sulfide equals that of metal, that is at x=0.5 if the concentrations of sulfur and metal are equal in groundwater and brine respectively (figure 4 A). Nevertheless, if the total concentration of metal is higher in the brine than the total concentration of sulfur in groundwater, sulfide precipitation coincides with the dissolution of dolomite in the dilute terms of the mixture (figure 4 B). On the other hand, if the concentration of sulfide in groundwater is larger than that of metals in the brine sulfide deposition happens at the saline side of the mixture (figure 4 C), away from the main cavity.

The process of sulfide precipitation is able to maintain open cavities, as the molar volume of dolomite is much larger than that of sphalerite (64.365 versus 2x 23.830 cm$^3$ mol$^{-1}$ respectively), but more than 80% of that porosity would be occupied by sphalerite. This is obviously not the case of Rocabruna nor of Coll de Pal, where sulfides are either absent or deposited only as a thin rim around some walls of the decametric cavities. The precipitation effect of other sulfides is comparable to that of sphalerite (figure 5)
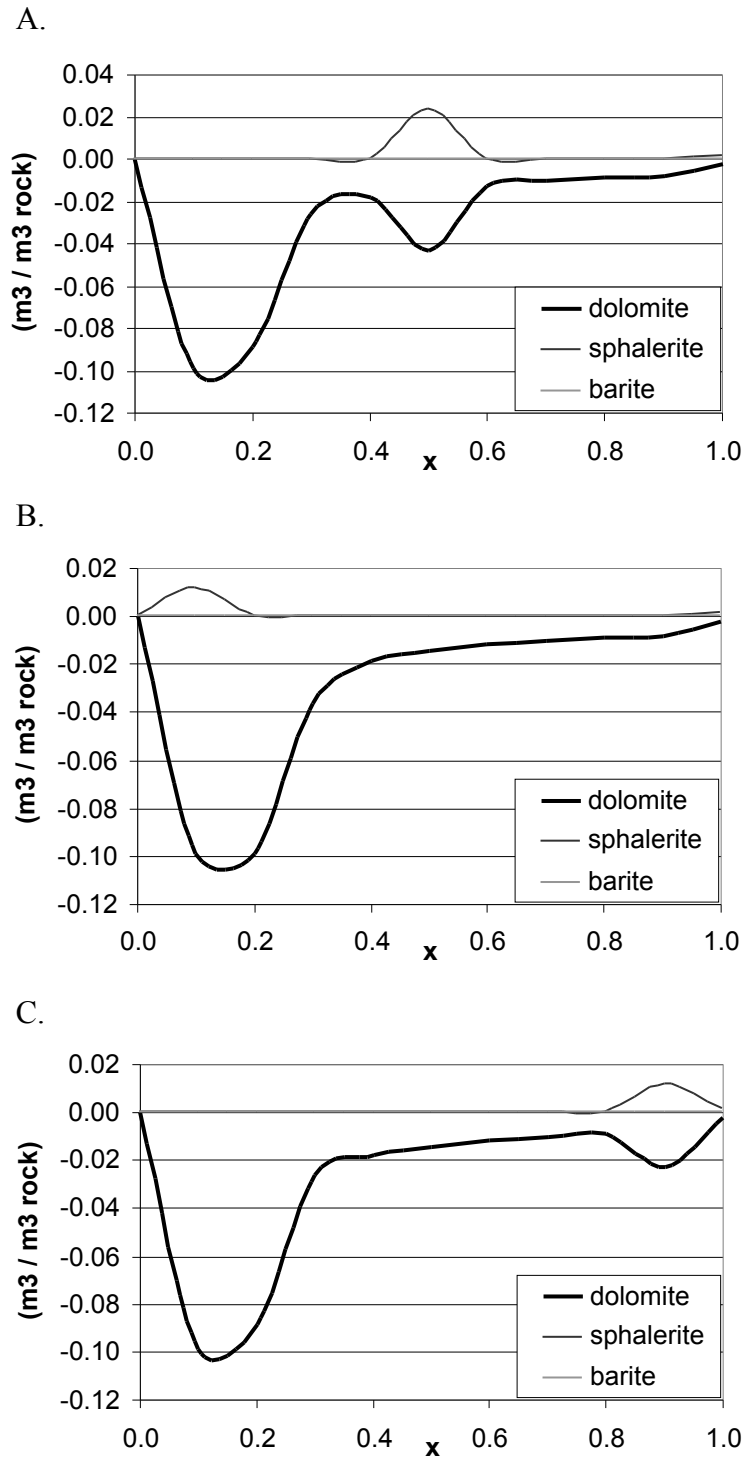
A.



B.

C.

*Figure 4. Precipitation and dissolution of dolomite, sphalerite and barite due to the mixing of a sulfide-rich solution and a zinc and barium-rich brine after 0.5 Ma, at different proportions of Zn and S in brine and groundwater.  A.  $S_{gw}=Zn_{br}=10^{-4}$ mol/L.  B.  $S_{gw}=10^{-5}$ mol/L, $Zn_{br}=10^{-4}$ mol/L.  C.  $S_{gw}=10^{-4}$ mol/L, $Zn_{br}=10^{-5}$ mol/L.*

except for pyrite, that has a much smaller molar volume and only one mol of it is needed to dissolve one mol of dolomite.

A.

B.

C.

D.
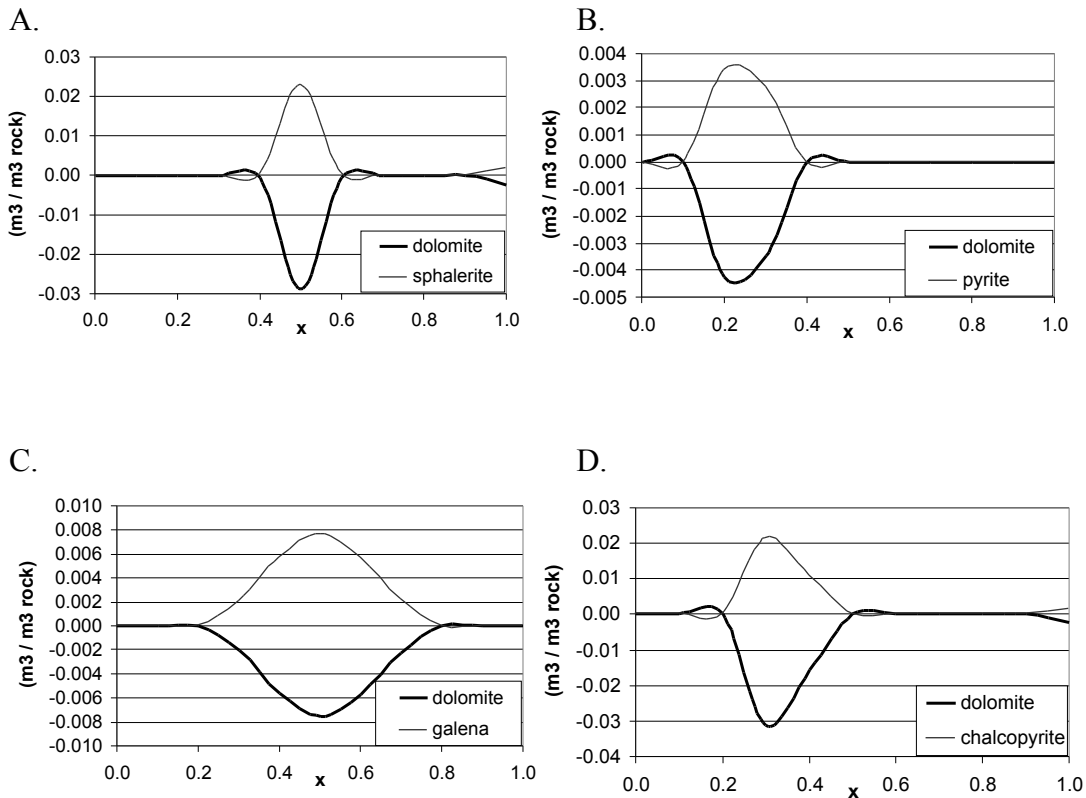


*Figure 5.  Dissolution of dolomite due to different metal sulfide precipitation from two brines of identical composition except for the sulfur and metal content, after 0.5 Ma of simulation time. A.  ZnS preciptation when $S_{br1}=Zn_{br2}=10^{-4}$ mol/L.   B.  $S_{br1}=10^{-4}$ mol/L, $Fe_{br2}=10^{-2}$ mol/L.   C. $S_{br1}=10^{-4}$ mol/L, $Pb_{br2}=10^{-4}$ mol/L.   D.  $S_{br1}=10^{-4}$ mol/L, $Cu_{br2}=10^{-4}$ mol/L, $Fe_{br2}=10^{-4}$ mol/L.*

Whenever groundwater is very rich in sulfide (more than $10^{-3}$ mol/L) dolomite precipitates from the mixture (figure 6).  The extent of dolomite dissolution is much smaller than that of precipitation, so that no cavity would form in this situation.
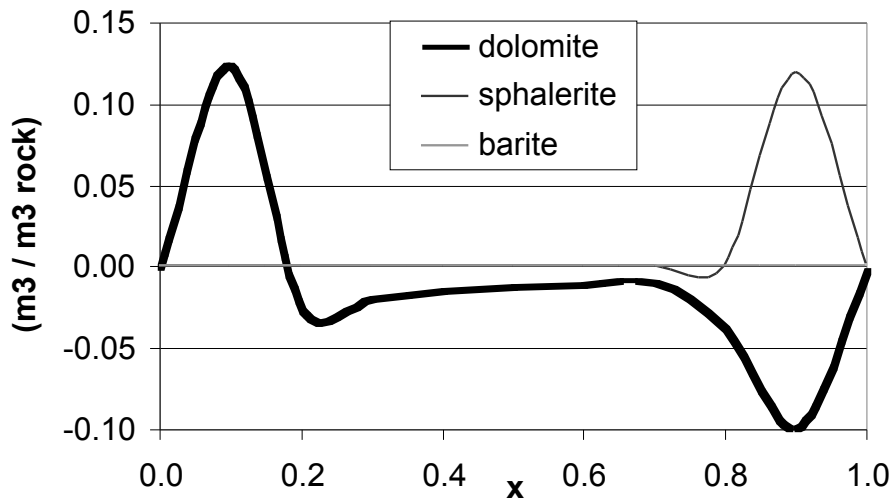
*Figure 6. Precipitation and dissolution of dolomite, sphalerite and barite due to the mixing of a sulfide-rich ($S_{gw}=10^{-3}$ mol/L) solution and a zinc and barium-rich brine after 0.5 Ma of simulation time.*

The mixture of a sulfate-rich groundwater with the same reduced brine yields dissolution of the dolomite host and precipitation of sphalerite (figure 7) similar to the sulfide-addition mixture. This implies that, in our equilibrium model, when the dilute solution is slightly oxidized and carries $SO_4^{2-}$ instead of $H_2S_{(aq)}$, the organic matter of the brine partly reduces the sulfate molecules, allowing the precipitation of sulfides, and still no barite precipitates from the mixture. The contribution of sulfide precipitation to the dissolution of dolomite is the same as before, but the change in the oxidation state of the mixture from the dilute and basic terms (x=0) to the saline and acidic terms (x=1) triggers further variations in the speciation of such components as S and C from one end to the other, that traduces in slight changes in the pH as explained in chapter 2, and therefore in a final decrease of dolomite dissolution.

Both possibilities, the sulfide-rich groundwater (figure 4) and the sulfate-rich groundwater (figure 7) that mix with a brine, yield large cavities that are only partially rimmed by sulfides. The sulfate model is preferred here because the most abundant mineral filling the cavity is barite; in this way, just with a variation of the oxidation state of the brine, we can explain the precipitation of all minerals found in Rocabruna's

cavities.  Although according to Ohmoto and Lasaga, (1982) the kinetics of the sulfate reduction process is very slow at low temperatures, there are studies that report the occurrence of the sulfate reduction process, triggered by organic matter, in deep carbonates (e.g.  in the oil fields of W Canada,  Krouse et al., 1988).

SULFATE FILLING

Once the cavity is formed and some sulfide deposited, the redox potential of the system must increase in order to allow the precipitation of barite.  The mixing of a the sulfate-rich groundwater with the metal and barium-rich brine of the previous stage, which now must have an oxygen fugacity of $10^{-48}$ bar or less, results again in dissolution of some dolomite, as well as in deposition of large amounts of barite (figure 8).  With the concentrations used in this example (table 1) the precipitation of barite occurs from the dilute terms of the mixture;  nevertheless, mixtures with groundwaters richer in sulfate or with brines poorer in barium, would yield deposition of barite in different proportions of the end member fluids.

The volume of barite precipitated at the concentrations of the example is much larger than the volume of dolomite that dissolves simultaneously with barite precipitation. This agrees with the observed textures of barite that completely fill some of the cavities. If the first stage of cavity and sulfide formation is maintained for a long time, the cavity will become large, and barite will take a long time to fill it up.  However, if the first stage is short, that is, there is not abundant organic matter along the pathway of the brine, the cavity will be small and the second stage of barite filling will rapidly end.

The change in the brine from the reduced state to a more oxidizing one must have been gradual.  This is observed as a transition zone, that is less than 5 cm thick, where sulfide minerals coexist with barite crystals (Soler, 1983) that is located between the sulfide and the sulfate mineral zones.  Simulations of a mixture between a sulfate rich-groundwater and a brine with an oxygen fugacity that changes from $10^{-50}$ bar to $10^{48}$ bar replicate this observations  (figure 9).  Only  sulfides precipitate when the brine is more
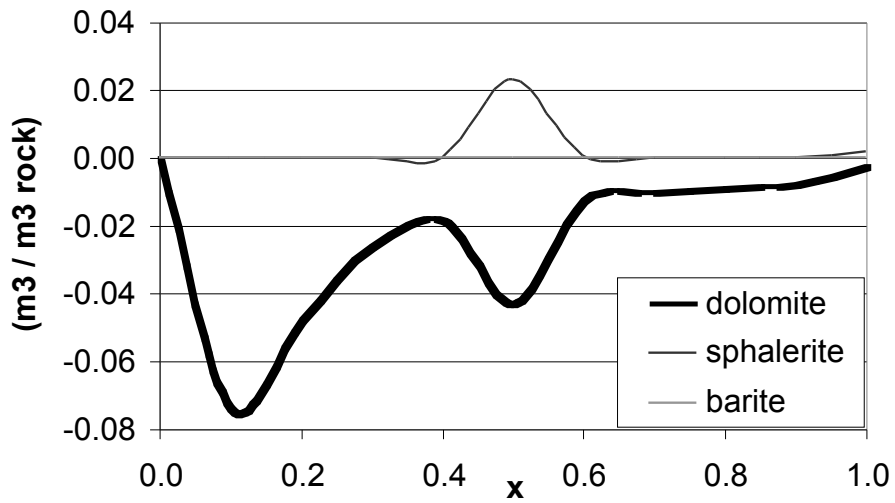
*Figure 7. Precipitation and dissolution of dolomite, sphalerite and barite because of the mixing of a sulfate-rich groundwater with a zinc and barium-rich brine after 0.5 Ma of simulation time.*
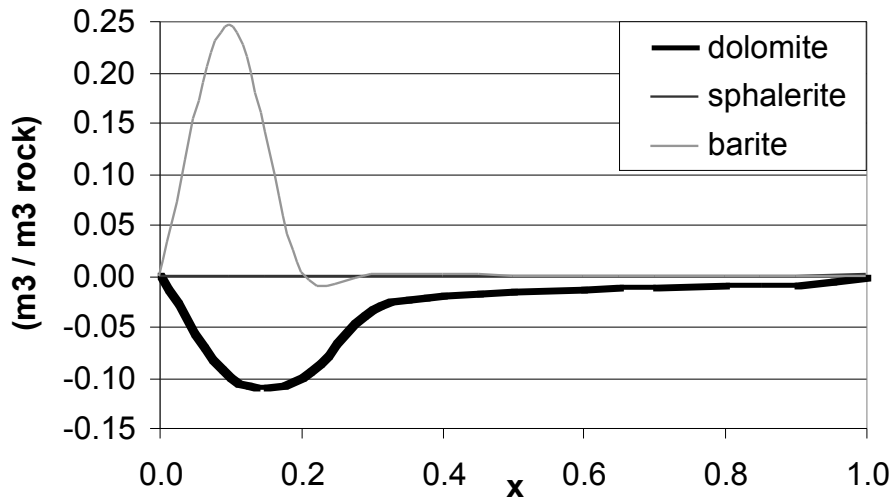


*Figure 8. Dissolution and precipitation of dolomite, sphalerite and barite due to the mixing of a $SO_4^{2-}$-rich groundwater and a zinc and barium-rich brine, slightly oxidized, after 0.5 Ma of simulation time.*

reduced (figure 9 A);  barite starts precipitating when the brine has an oxygen fugacity of more than $10^{-50}$ bar (figure 9 B), where barite can coexist with sulfides;  and sulfide do not form at the concentrations of our example when the oxygen fugacity of the brine is larger than $10^{-48}$ bar (figure 9 C).

The sulfate ions incorporated in barite comes principally from the regional groundwater as it contains more total sulfur, but part of them come from the brine which also contain some sulfur.  At an oxygen fugacity of $10^{-46}$ bar, the redox state considered in our simulations for the stage of barite precipitation, most S atoms of the brine are in an oxidized state.  Even if the brine is not rich in sulfur, its mixture with groundwater may explain the varying isotopic signature (14 to 19‰) measured by Canals et al. (1999). This may have also been the case for the sulfide deposition stage, because even though the sulfur isotopic data of sulfide minerals are scarce they show a wide variability.

SENSITIVITY ANALYSIS WITH RESPECT TO pH

Fluid inclusion analyses of ore minerals would have been of great help to constrain not only the temperature of precipitation but also the composition of the ore fluid. Variations of up to 50ºC in the temperature of deposition in this case would not significantly affect the overall pattern of dissolution and precipitation of carbonates, sulfides and sulfates; we believe so because all solutes and minerals involved in our calculations behave similarly at the range of temperatures between 100º and 200ºC. Nevertheless, the composition of groundwater and brine completely determine the ratio of dissolution versus precipitation of the minerals;  among these variables, one that is expected to affect dissolution and precipitation of minerals (chapter 2) is the pH, that is only constrained from Hanor's (2001) data.  Therefore we have tested the effects of other ph values for both, brine and groundwater, over the formation of Rocabruna's ore bodies.

The precipitation of sulfide and sulfate is not essentially affected by the variations in the pH of the end-member fluids of the mixture, as shown in  figure 10 for the sulfide stage.
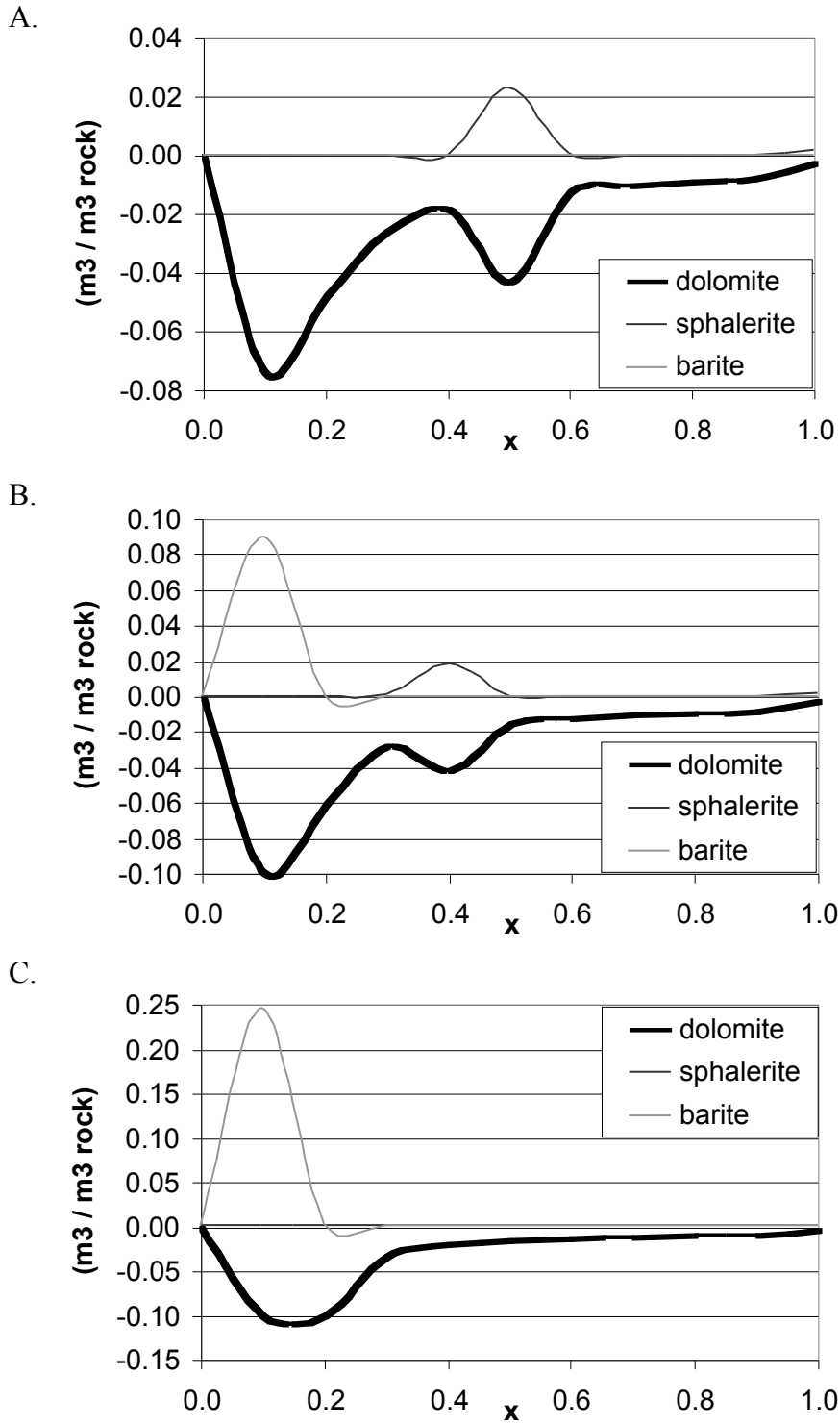
A.

B.

C.

*Figure 9. Dissolution and precipitation of dolomite, sphalerite and barite due to the mixing of a sulfate-rich groundwater and a zinc and barium-rich brine, with different redox states after 0.5 Ma of simulation time. A. $Log(fO_2)_{br}= 10^{-50}$ bar. B. $Log(fO_2)_{br}= 10^{-49.5}$ bar. C. $Log(fO_2)_{br}= 10^{-48}$ bar.*

Similarly, changes of 0.5 units in the value of groundwater pH does not seem to substantially vary the amount of dolomite dissolved from the mixture (figure 10 A and B);  however, brine pH variations in 0.5 units do.  When the pH of the brine is simulated more acidic than the example of figure 4, more dissolution of dolomite is obtained (figure 10 C).  When the pH of the brine is increased most dissolution of dolomite occurs as a consequence of the sulfide precipitation effect, and more significantly, dolomite clearly precipitates in the dilute terms of the mixture (figure 10 D).  This last case is the only one that is not effective enough to create cavities in dolostones.  The sensitivity of the system to the brine pH is due to the changes in speciation of the carbon species induced by the varying pH from the dilute to the saline mixture, as explained above and in chapter 2.
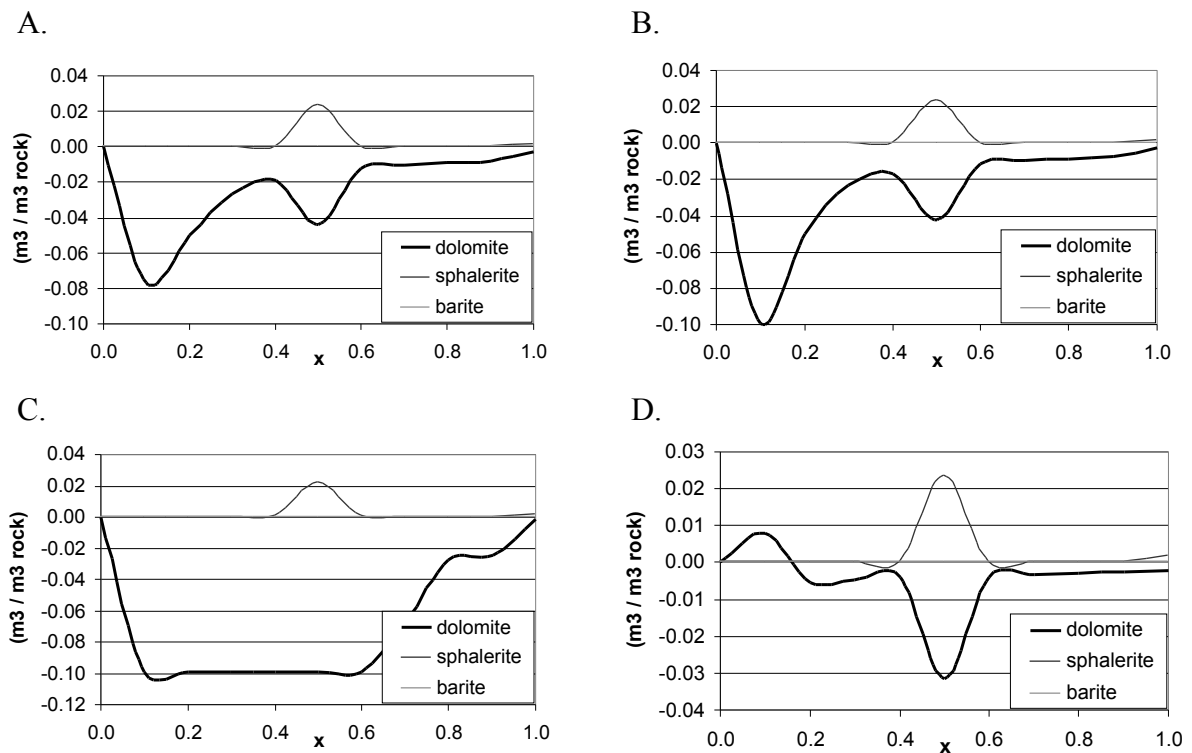
A.

B.

C.

D.



*Figure 10.   Dissolution and precipitation of dolomite, spahlerite and barium caused by the mixing of a sulfide-rich groundwater and a zinc and barium-rich brine at different pHs after 0.5 Ma of simulation time.  A.  pH=7.0 – 5.0.  B.  pH=6.0 – 5.0.  C.  pH=6.5 – 4.5.  D.  pH=6.5 - 5.5.*

SENSITIVITY ANALYSIS WITH RESPECT TO Ca AND Mg CONCENTRATIONS

The algebraic effect of the mixing (chapter 2) is caused by the contrast in Ca and Mg concentration in the two end-member solutions.   The previous simulations were performed with Ca and Mg concentrations in both groundwater and brine that are in the lower side of the range given by Hanor (2001) for basinal fluids.   The results of the mixing using the higher values (0.1 and 1.8 mol/L of Ca and 0.05 and 0.5 mol/L of Mg for groundwater and brine respectively) of Hanor (2001) for basinal waters are shown in figure 11.   They illustrate that mixing of Ca and Mg-rich fluids yields mostly precipitation of dolomite, except where the precipitation of sulfides induces dissolution of dolomite (at x=0.5 in figure 11).   In this case cavities will not necessarily form as a result of mixing.   Obviously, intermediate situations may occur where Ca and/or Mg concentrations in the primary fluids are not as high so that dissolution and precipitation of dolomite happen from the same mixture.
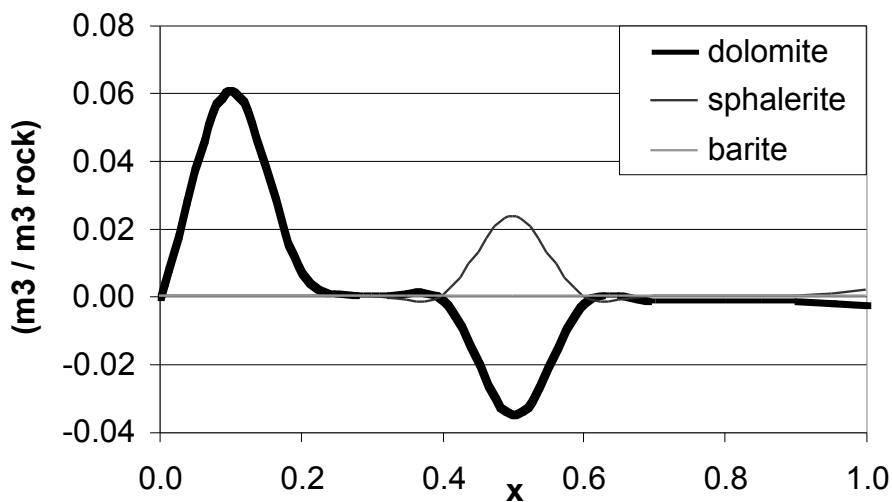


*Figure 11.   Dissolution and precipitation of dolomite, spahlerite and barium caused by the mixing of a sulfide-rich groundwater and a zinc and barium-rich brine both rich in Ca and Mg ($Ca_{gw}$=0.1mol/L, $Ca_{br}$=1.8 mol/L, $Mg_{gw}$=0.05mol/L, $Mg_{br}$=0.5 mol/L) after 0.5 Ma of simulation time.*

Coll de Pal fluid inclusions reveal that the resulting mixture of mineralizing solutions for these deposits was rich in calcium. This coincides with the presence of abundant dolomite in Coll de Pal cavities (Canals et al. 1999). Our simulations are in accordance with such observations, and infer that Rocabruna's mineralizing solutions were much poorer in Ca than Coll de Pal fluids.

SENSITIVITY ANALYSIS WITH RESPECT TO SALINITY

Without analyses of the inclusion fluids in the minerals from Rocabruna, the salinity is only constrained by data from the similar deposits of Coll de Pal and Hanor's (2001) work. Therefore, we tested the volumetric changes of dolomite dissolution induced by the salinity effect (chapter 2) when combined with the other mixing effects in Rocabruna.

The total concentration of chlorine was varied in both, groundwater and brine in 2 mol/L covering the following cases: $Cl_{gw}$=1.0 mol/L and $Cl_{br}$=7.0 mol/L; $Cl_{gw}$=3.0 mol/L and $Cl_{br}$=3.0 mol/L; $Cl_{gw}$=1.0 mol/L and $Cl_{br}$=3.0 mol/L. All simulations resulted in a volume of dolomite dissolved almost identical to the volume of dolomite dissolved when the initial solutions contained 1.0 mol/L and 5.0 mol/L of chlorine respectively, as in the previous examples.

**CONCLUSIONS**

Cavities in Rocabruna may have formed as a result of mixing a dilute groundwater with a brine, both saturated with respect to the dolomitic host rock, at hydrothermal temperatures. The intrinsic effects of mixing are responsible not only for the dissolution of the host rock but also for a scarce precipitation of dolomite.

Sulfides may precipitate as a consequence of the mixing whenever the brine is reduced. This process helps to the enlargement of the cavity but is not the sole responsible, as the proportion of 2 moles of sulfides precipitated for each mole of dolomite dissolved is not preserved in Rocabruna. On the contrary, the volume of sulfides precipitated from the mixing is much smaller than the volume of dolomite dissolved.

The maximum dissolution of host dolomite is produced at large proportions of groundwater in the mixture. As sulfides in Rocabruna deposited at the dissolution front, the proportion of groundwater to brine in the mineralization must have been the same. Consequently, the total concentration of sulfur in groundwater must have been much smaller than the total concentration of metals in the brine.

The redox potential of the dilute fluid is not significant in the first stage of cavity formation and sulfide precipitation, as long as it is kept in the sulfide or sulfate field. The redox potential of the brine has to be reduced for this stage, or in other words, hydrocarbons must predominate over carbonate species.

Sulfates may also precipitate as a consequence of the mixing whenever both end-member fluids are slightly oxidizing. That is, groundwater has to carry sulfate for the second stage of sulfate precipitation, and the brine has to be free of hydrocarbons.

The volume of sulfate precipitated at the second stage of the mixing is much larger than the volume of host dolomite dissolved, so that the cavity may end up completely full of barite. Textures evidencing large barite crystals filling an open space are consistent with these results.

The evolution of a brine from the hydrocarbon field, in the first stage, to the carbonate and sulfate field, in the second stage of cavity filling, may be due to the exhaustion of organic matter in the source rocks after certain time. A transition from one stage to the other is observed in Rocabruna deposits where sulfides and sulfates coexist. Simulations with intermediate oxidation states also yield precipitation of sulfides and sulfates from the same mixture.

The pH of the groundwater and the brine that conform the corrosive mixture need to be basic (more than 5.5 at 150ºC) and acidic respectively. Cavities are not generated from the mixture if the brine pH is neutral to basic at the temperature of formation of the deposits.

Low concentrations of Ca and Mg in the end-member solutions of the mixture are more effective in generating cavities. At very high concentrations of these elements only precipitation of dolomite would occur. Rocabruna seems to have formed by low Ca and Mg fluids, whereas Coll de Pal must have formed by fluids richer in Ca and Mg ions.

There is a wide salinity range from which cavities may be formed due to mixing of fluids. The pH-pCO2 effect of the mixing is dominant over the salinity effect with the concentrations chosen for our mixtures.

There are three situations where the mixing of chemically distinct hydrothermal solutions saturated in dolomite may not yield to dissolution of this mineral but to its precipitation. These are: high concentration of total sulfur in the basic fluid, neutral to basic pH in the acidic solution, and large amounts of calcium and/or magnesium in the the initial waters. One of them is enough to preclude the formation of cavities in deep carbonate terrains.

As the cavities in the host dolostone of Rocabruna may have been developed by a mixing of hydrothermal solutions, there is no need for them to be related to a paleosurface, neither in time nor in space. Then, the karst of Rocabruna may not have been formed during an emergence period, either Triassic or early Tertiary.

The mixing model of Rocabruna links three processes that had been considered unrelated until now: karst formation, sulfide precipitation and sulfate deposition. Our model is in concordance with the amounts of host dissolved and sulfide and barite precipitated in the Rocabruna barite deposits.

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# CONCLUSIONS GENERALS

Les mescles de solucions hidrotermals saturades en carbonat es comporten de manera semblant a les de solucions fredes. S'hi produeixen els mateixos efectes de salinitat, algebraic i de pH, que competeixen per produir la subsaturació o sobresaturació en carbonat de la barreja final.

La mescla de fluids calents saturats en calcita o dolomita pot generar porositat i cavitats en roques carbonàtiques profundes, que poden servir de trampa per a l'acumulació d'hidrocarburs o de minerals d'interès econòmic. La mateixa barreja, però a proporcions diferents de les solucions inicials, pot produir també la precipitació de carbonat.

La reactivitat dels components de les solucions hidrotermals amb els seus encaixants carbonàtics no és tan efectiva en la generació de cavitats com ho és la mescla de les solucions equilibrades en carbonats.

La temperatura de les solucions inicials d'una mescla pot ser considerada constant i igual. Aquesta afirmació se sustenta en el fet que, per una banda, l'efecte del contrast de temperatures dels components fluids de la mescla és molt inferior a la dels altres efectes de mescla, i per l'altra, les simulacions de fluxos de calor i aigua en un districte tipus de MVT demostren que a les zones de flux ascendent on es formen les mineralitzacions la temperatura és pràcticament la de la salmorra.

Els càlculs de transport reactiu per als dipòsits de MVT, que simulen la mescla de solucions calentes saturades en calcita a temperatura i fluxos de fluids constants, resulten en una zona de dissolució de l'encaixant carbonàtic que té una forma similar a l'observada en aquestes mineralitzacions.

La modelització geoquímica de mescla de fluids saturats en dolomita pels dipòsits de baixa temperatura de tipus sòcol-cobertora encaixats en dolomies reprodueix la formació de la cavitat, la precipitació de sulfurs i el rebliment de sulfats tal i com s'observa a Rocabruna (Pirineus Orientals).

Els dipòsits minerals encaixats en roques carbonàtiques i de característiques epigenètiques poden haver-se format simultàniament a la cavitat que els acull per la mescla de solucions hidrotermals.