Capítol 3

MESCLA DE FLUIDS EN LA GÈNESI DELS DIPÒSITS DE TIPUS MISSISSIPPI VALLEY: MODELITZACIÓ DE FLUXOS I GEOQUÍMICA

RESUM

Els dipòsits minerals de tipus Mississippi Valley (MVT) es localitzen predominantment en zones de dissolució de l'encaixant carbonàtic. La reacció de precipitació de sulfurs metàl·lics no pot ser l'únic desencadenant de la generació de la porositat ja que no s'acompleix el balanç de massa entre la quantitat de sulfurs dipositats i la de carbonat dissolt, i a més, en els districtes miners apareixen moltes cavitats que no estan reblertes per sulfurs. Com que experimentalment és difícil transportar S i metalls base en la mateixa solució en concentracions suficients, la majoria de models genètics per als dipòsits MVT inclouen dos fluids, en què cadascun aporta un dels components dels sulfurs metàl·lics al lloc on es barregen i es dipositen. Nosaltres també fem ús d'un model de barreja per a explicar la formació dels MVT, però en aquest estudi mostrem com la mescla d'una aigua regional amb una salmorra calenta causa, a més, la dissolució de l'encaixant malgrat que totes dues estiguin equilibrades en carbonat.

Quantifiquem els fluxos de fluid i de calor en un districte tipus i la geoquímica del procés de barreja en un dipòsit mineral per mètodes numèrics. La circulació de fluxos il·lustra com fluids i calor arriben a un estat estacionari en uns pocs milers d'anys: s'estableix un règim convectiu i en les parts de pujada de fluids i calor és on es formen els cossos mineralitzats. Al voltant d'aquest lloc, en unes desenes de metres, la temperatura es pràcticament la de la salmorra calenta, i, per tant, la podem desacoblar de les simulacions de geoquímica considerant-la una constant. Els models de barreja de fluids

químicament diferents però equilibrats en calcita causen la seva dissolució i precipitació en zones separades però contigües. Aquestes zones presenten una forma de V semblant a les de les bretxes mineralitzades de molts districtes. Si els fluids mineralitzants aporten S i metalls en concentracions més grans que aproximadament 10^{-5} mol/kg, la seva mescla genera també la deposició de sulfurs metàl·lics; aleshores, es pot formar un dipòsit mineral sempre que la barreja de fluids duri prou temps.

Chapter 3

MISSISSIPPI VALLEY-TYPE DEPOSITS GENESIS DUE TO FLUID MIXING: NUMERICAL MODELING OF FLUX AND GEOCHEMISTRY

ABSTRACT

Mississippi Valley (MVT) ore deposits are predominantly located within dissolution zones of a carbonate host rock. The sulfide precipitation reaction cannot be the sole responsible of this porosity, as the mass balance between carbonate dissolved and sulfide precipitated is not achieved in most deposits; besides, some cavities are not filled by sulfides at all in MVT districts. Because metals and reduced sulfur are difficult to transport together in high enough concentration, most genetic models for MVTs involve two fluids that each carries one of the components to the site of mixing and deposition of metal sulfides. We also invoke a mixing model for the formation of MVTs, but go further and show in this paper that mixing a dilute groundwater with a hot brine may also be the cause of the dissolution of the carbonate host.

With the aid of numerical methods we quantify the fluid and heat flow in a type district and the geochemistry involved in the mixing process at an ore body. The flow modeling illustrates that after a few thousand years fluids and temperature reach a steady state: a convective circulation establishes and in the upflow and upheat plumes is where the ore bodies form. In the few tens of meters next to the site the temperature is essentially that of the brine, thus the temperature may be decoupled from the geochemical modeling. The simulations of mixing fluids, both saturated with calcite, but otherwise with different chemistry, cause dissolution and precipitation of calcite in contiguous zones, that is, at different proportions of the end-member fluids. The dissolution zone appears "V"-shaped, as the breccia bodies of many MVT districts. Whenever the mixing fluids carry sulfur and metals at concentrations higher than about

10^{-5} mol/kg sulfide precipitation occurs and an ore deposit may form if the encounter of fluids lasts long enough.

INTRODUCTION

Mississippi Valley-type (MVT) deposits are one of the world's major producers of zinc and lead and have, consequently, been studied extensively. At present, scientists understand most of the processes involved in the formation of such ore deposits, but do not quite agree on the main cause of metal precipitation. Several genetic models have been proposed through the years, but none of them completely explains the features observed and the geochemical data obtained from major districts such as the Upper Mississippi Valley (USA), Southeast Missouri (USA), or Silesia (Poland). One such feature is the ubiquitous dissolution of the carbonate host; another is the varied mineralogy filling that porosity.

The dissolution features described in carbonates that host MVTs range from vugs (Pine Point, Canada; Qing and Mountjoy, 1994), opened bedding planes and solution collapse breccias (Southeast Missouri and the Upper Mississippi Valley, USA; Kyle, 1976; Heyl, 1959) to karst caves (Central Colorado, USA; Tschauder et al., 1990) and karst breccias and hydrothermal ore breccias (Upper Silesia, Poland; Sass-Gustkiewicz, 1996). In some of these areas the dissolution features are thought to be temporarily unrelated, and therefore previous to the infilling material, while in others, it is believed the processes causing carbonates to dissolve were linked to those producing the precipitation of sulfides. Nevertheless, the amount of sulfide precipitated is usually much smaller than the amount of host carbonate dissolved, and in many districts there are gangue minerals filling the same cavity. What is more, in some districts, like the Upper Mississippi Valley (USA) or Silesia (Poland), there are cavities that are only filled with carbonates (Heyl et al. 1959; Leach et al. 1996), or cavities that are mainly filled by fluorite or barite, like the European Alpine, the English Penninnes, the Appalachian, the Irish or Polaris districts (Schroll, 1996; Dunham, 1983; Kesler, 1996; Hitzman and Beaty, 1996; Randell and Anderson, 1996).

Mixing of solutions was thought to be of importance in the formation of MVTs long ago (e.g. Brown, 1970; Ohle, 1980), nevertheless, quantifications of such a process has only recently been done. The reaction path calculations of Anderson and Garven (1987) lead to the description of MVTs as the site of mixing of the fluids responsible of carrying the different components of ore. Other reaction path simulations (Plumlee et al. 1994, for the Ozark region, USA) concluded that mixing of fluids with different $H_2S_{(g)}$ and metal content was a very efficient mechanism to deposit metal sulfides together with the replacement of limestone by dolostone. Opposite to this one, Appold and Garven (2000) run numerical experiments that included heat, fluid and solutes transport and suggested that mixing of two fluids that only differ in their metal and $H_2S_{(aq)}$ content, and travel along different aquifers, did not mix efficiently enough to build up the ores observed.

Dissolution of carbonates in low temperature environments is easily achieved by mixing of solutions of differing chemistry because of the intrinsic effects of geochemical mixing (Wigley and Plummer, 1976). The same effects seem to apply at hydrothermal temperatures (chapter 2): although both fluid end-members are initially saturated with respect to calcite, the saturation index of this mineral in the mixture is not that of the initial solutions because other chemical variables are different in both fluids, and their value in the mixture does not vary linearly. When the concentration of either calcium or carbonate ion is different in the extreme solutions the mixture tends to be oversaturated with respect to calcite (algebraic effect); when there is a salinity contrast between the two initial solutions calcite becomes subsaturated in the mixture, as salinity affects the activity coefficients of ions (salinity or ionic strength effect); finally, when there is a pH difference between the end member fluids, and this leads to a total carbon change in the mixture, the final solution becomes subsaturated again (pH-_C effect) unless the fluids are basic. All these effects occur simultaneously and compete with each other. How the effects combine in a particular system is what is difficult to predict a priori because of their non-linearity, thus the usefulness of numerical simulations of mixtures.

Contrarily to what had been predicted up to now by other modeling work (Plumlee et al. 1994; Appold and Garven, 2000), mixing alone might be a much more powerful process to produce carbonate dissolution, and precipitation in some cases, than the chemical reactions triggered by the mixing of solutions, according to the calculations presented in chapter 2. Previous quantifications of the problem focused on forming an MVT deposit, that is, precipitating sulfides, thus they mixed two brines of similar pH, pE and solute concentration but different metal content. Oppositely, our goal was to dissolve the carbonate host, so we mixed a dilute solution with a brine of distinct chemistry, although both were equilibrated with calcite, and obtained wide dissolution of the host rock; this would increase the interaction between solutions enhancing the effects of mixing. With the present paper we take this modeling further and anticipate that the mixing of warm MVT solutions, both saturated with carbonates, triggers both the dissolution and the precipitation of carbonates in different parts of the system. Sulfides may precipitate as a consequence of that mixing, once some porosity exist, which may encourage even more mixing to occur at the site, that may evolve in an MVT deposit.

The purpose of this paper is to evaluate the response of a 2D-systen to mixing solutions in the context of the hydrothermal environment of formation of MVT ore. More specifically, we employ numerical modeling to study the temperature and fluid flow in a type district, and in more detail, the geochemistry involved in the mixing of a brine and a groundwater at a constant rate. This would explain the formation of carbonate porosity and the shape and location of MVT ore bodies.

GEOLOGICAL FRAMEWORK OF MVT DEPOSITS

MVT deposits are usually clustered into districts of hundreds of square kilometers and are confined to some stratigraphic units, which are commonly dolomitized limestones. They are found all over the world and are hosted in rocks of different ages (Leach et al. 2001). The interpretation of geochemical data, mainly fluid inclusions and isotope analyses, leads to the conclusion that MVTs are formed by hot (80-200 ºC) and saline

(5-10 times that of seawater) basinal fluids, similar to those found in oil-field brines of present-day sedimentary basins, at shallow depths (less than 2 km).

The mineralization seems to be epigenetic, as the ore and gangue minerals are found occupying pre-existing open spaces: as cavity filling in fault breccias (figure 1), solution breccias or karst breccias, vugs or caverns, and as disseminations by replacement and impregnation, which is more usual in shaly strata. The minerals are also found in fractures as banded veins along the walls. Dripstones are encountered in lots of MVT cavities and some barren breccias exist in many districts.
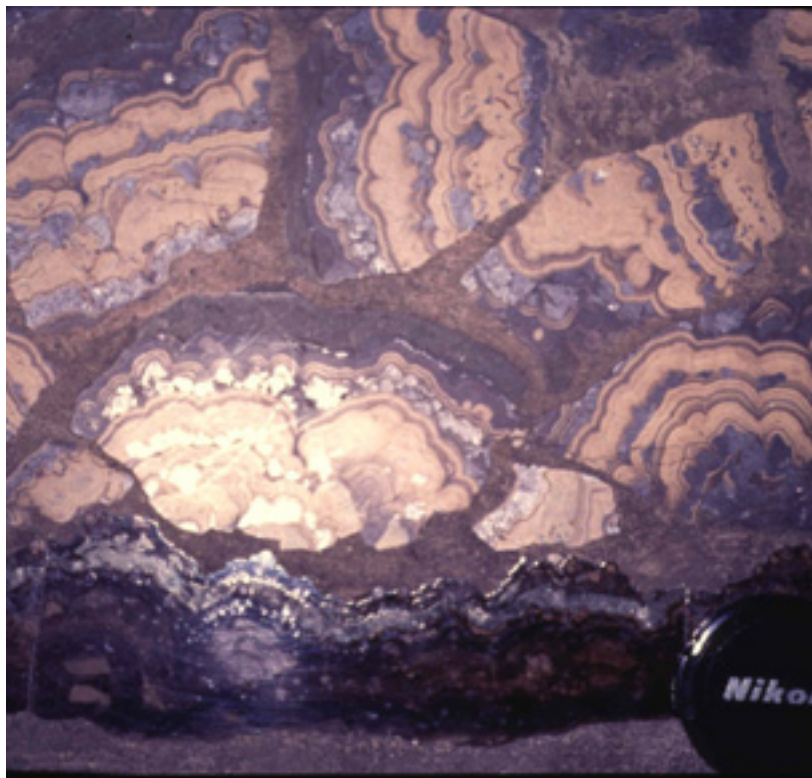

Figure 1. Carbonate and sulfide breccia of Pomarzany Mine, Silesia (Poland).

The mineral paragenesis includes quartz and dolomite, which deposit before the dissolution of the carbonate host in most ore districts. After widespread dissolution of

the carbonate host, and also simultaneously as in the Upper Mississippi Valley (UMV) district (Heyl et al. 1959), sulfides of Zn, Fe and Pb precipitate, together with barite and carbonates in some districts. In some deposits fluorite also precipitates after galena (e.g. Central Tennessee, USA), and most of them contain calcite and dolomite as carbonates. The last mineral to precipitate in many districts is calcite, although some of it is much younger than the ore: the sphalerite of the UMV district yielded an age of 270 ± 2 Ma, late Early Permian (Brannon et al., 1992), while U-Pb analyses in stage II calcite (after the main sulfide stage) provided an age of 159 ± 20 Ma (Brannon et al. 1993).

For the MVTs that appear in contintental basins such as the Mississippi River basin, it is widely agreed now that the ore-forming fluids migrated updip toward the shallow edge of the basin along its aquifers. Several mechanisms have been proposed to drive deep waters out of basins, but their quantification with hydrologic numerical models (Garven, 1985; Bethke, 1986; Garven et al., 1993) indicates that the one that explains most characteristics of basins is a gravity-driven flow, induced by an orogeny. Flow rates generated by compaction seem too small to transport heat efficiently to the edge of a basin unless the basin is shaly and rapidly subsiding, causing high enough overpressures. Tectonic compression, thrusting and seismic pumping provide flow of fluid masses that are either too small or in too short a period of time to precipitate enough mineralization. The uplift of the Appalachian and Ouachita Mountains provides the topographic relief, and a sufficient hydraulic head, to drive brines away from foreland basins into platform strata to precipitate the MVT deposits of the eastern interior of the United States. Paleomagnetic and isotopic ages of these districts are consistent with gravity driven models (Brannon et al., 1992; Symons and Sangster, 1994; Chesley et al., 1994; Leach et al. 2001).

The main controversy about MVT genesis concerns the conditions for metal precipitation, which are intimately related to the mode of metal transport in solution. Chloride and sulfide compounds have been suggested as complexing agents for metals in brines, but their contribution to the metal solubility at the pH range of such solutions is no more than 1 ppm (Giordano and Barnes, 1981; Sverjensky, 1986), which is insufficient for the formation of MVT deposits given the time span of the mineralization

process. Organic ligands have been proposed as an alternative (Giordano and Barnes, 1981; Sverjensky, 1986; Gize et al., 1991; Gize and Barnes, 1992), and although no evidence for their efficiency has yet been reported, some preliminary results look promising (Giordano, 1994; Sicree and Barnes, 1996).

The mechanisms of ore precipitation in MVTs can be synthesized in two general models. On the one hand, there is the one-solution model, which invokes a single brine that transports both metals and hydrogen sulfide in solution; metal sulfide precipitation may then occur by cooling, dilution of the brine by groundwater, by a pH change in the solution, by protonation of the metal complexing ligand or its oxidation. Although they are sometimes called non-mixing models, most possibilities of precipitation involve a second fluid. This type of models seems to suit places where the fine banding of the ore has been correlated across the district (UMV, Southeast Missouri), as this seems indicative of homogeneous precipitating conditions and apparently contrary to mixing of solutions. On the other hand, there is the mixing or two solutions model. This requires that the brine carries only metals, and the sulfide is added in situ, either because it was transported as sulfate ion in the same fluid and later reduced to sulfide at the site of deposition or because a source of sulfide is encountered. There is no agreement among the authors on any one model that fits all the observed characteristics of major MVTs.

Among these models, two proposals relate the dissolution of the carbonate host with the precipitation of sulfides. Bisulfide oxidation has been presented as a way to generate the acidity necessary to dissolve the host carbonate, that would also be linked to metal sulfide precipitation (Barnes, 1983). Nevertheless, with the small concentrations of oxygen available at depth such an oxidation reaction does not occur (chapter 2). Precipitation of metal sulfides was proposed by Anderson (1975) and Randell and Anderson (1996) as another process that releases hydrogen ions thus producing dissolution of the host carbonates. The mass balance of the reaction would require the same amount of carbonates should dissolve than sulfides precipitate.
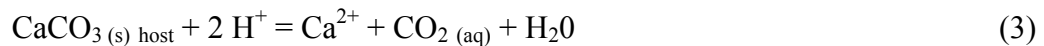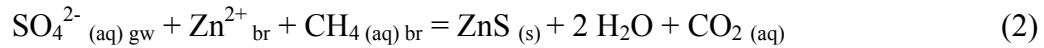
There are features that point to some form of mixing having occurred during the precipitation of sulfides in many MVT districts. First of all, the intergrowth of sulfides and barite in the Irish deposits was interpreted as the result of mixing two incompatible fluids (Hitzman and Beaty, 1996). Secondly, stable isotope data indicate that there are contributions from at least two sources to the sulfur, as the sulfate signature of barite differs from that of sulfides in the UMV, the Appalachian or the Silesian districts (Ohmoto et al. 1985; Kesler, 1996; Leach et al. 1996) and it is heavier further away from the feeding faults in Southeast Missouri (Ohmoto et al., 1985). Finally, fluid inclusion analyses delineate a temperature decrease towards the surface in Silesia (Leach et al. 1996), or depict a variation in salinity in Central Tennessee (Misra et al. 1996).

Besides, some characteristics of MVTs are more easily explainable by mixing than by any other process. The skeletal galena crystals intergrown in botrioidal sphalerite suggest that the precipitation was a rapid phenomenon. The excess of H_2S found in fluid inclusion decrepitates of sphalerite from Pine Point was also interpreted by Haynes and Kesler (1987) as a sign the mineral formed by mixing of an H_2S-rich fluid with a metal-rich brine. The presence of dolomite interbands in sulfides, with dissolution of dolomite, that was thought to be caused by pH fluctuations by Hitzmann and Beaty (1996), may very well be due to variations in the relative contribution of the two fluids mixing. Finally, the diverse mineralogy of gangue minerals that precipitate in varying proportions in different ore bodies of even the same district suggests that there must be at least two solutions involved in the formation of such varied deposits.

FLUID MIXING MODELING FOR MVTS

The simplest conceptual models for generating MVT deposits are those in which metals and sulfur travel in different fluids. The mixing of the two causes not only the precipitation of metal sulfides but also the dissolution of the host carbonate (Anderson, 1975). This problem was already analyzed from the geochemical point of view (chapter 2), so this chapter will couple the geochemistry with the steady flow of the mixing

solutions and the transient changes this produces to a 2D section around an ideal MVT orebody. We compare what results from mixing a regional groundwater with a brine in the case they are sulfur-poor and metal-poor (pure mixing), sulfide-rich and metal-rich (sulfide addition, reactions 1 and 3) and sulfate-rich and metal-rich (sulfate addition, reactions 2 and 3) respectively.

$$H_2S_{(aq)\ gw} + Zn^{2+}_{\ br} = ZnS_{(s)} + 2\ H^+ \tag{1}$$

$$SO_4^{2-}_{\ (aq)\ gw} + Zn^{2+}_{\ br} + CH_{4\ (aq)\ br} = ZnS_{(s)} + 2\ H_2O + CO_{2\ (aq)} \tag{2}$$

$$CaCO_{3\ (s)\ host} + 2\ H^+ = Ca^{2+} + CO_{2\ (aq)} + H_2 0 \tag{3}$$

The problem of hydrothermal fluid mixing is a threefold one. First of all, there is the phenomenon of fluid movement, that is the fluid flow; secondly, there is the variation of temperatures in the country rock and the two solutions, or heat flow; and finally, the changes in concentrations that occur among the fluids and rock components while they mix, that is the chemical reactions.

The chemical reactions we are concerned with, those leading to dissolution and precipitation of carbonates and sulfides, occur mainly at the ore body and next to it, in the case of MVT deposits. Thus, the geochemical simulations need only be done at that scale. Nevertheless, the fluid and heat distribution at the ore body scale is not evident, and we still need it in order to evaluate mixing phenomena. Some numerical models have been run (Bethke, 1986; Garven et al. 1993; Appold and Garven, 1999) at a basin scale that include both, heat and fluid flow. Therefore, with the results of these previous large-scale simulations, we perform some exercises at an ore district scale that include heat and fluid transport; these serve as a starting point for the geochemical simulations, where heat and fluid distribution are incorporated as boundary conditions.

DISTRICT WIDE MODEL FOR HEAT AND FLUID FLOW

For fluid flow and heat transport calculations we use CODE-BRIGHT (COupled DEformation, BRIne, Gas and Heat Transport), a Fortran code developed by Olivella et al. (1994), that is capable of simulating heat and fluid flow in a transient system. The

experiments are two-dimensional, in a cross section that is representative of an MVT district, like that of the UMV, that has a simple geology, mineralogy and was one of the bigger producers of Zn until the 70's. The 2D section then, is 100 km long and 1400 m thick, the approximate reconstructed depth of deposition of the ore bodies in the UMV district; at that depth, it has and aquifer (a well sorted sandstone, Heyl et al. 1959) invaded by a hydrothermal brine. The system also contains a shaly bed (Heyl et al. 1959) 150 m above the basal aquifer; short (100 m high) vertical fractures connecting the basal aquifer with the carbonates overlying it, are included in some simulations. Permeability, porosity and thermal conductivity data are calculated or inferred from the equations and data presented or collected by Bethke et al. (1991) and Young (1992). The mesh is composed of 5964 nodes and 11320 rectangular triangles. The brine temperature (varying from 100 to 200ºC depending on the run), as well as the brine velocity at the bottom boundary of 5 m yr^{-1} , are held constant throughout each experiment (figure 2 A). The lateral boundaries are no flow boundaries for both heat and fluid, and the top boundary is held at a constant temperature of 20ºC and free to fluid flow, that is held at a constant atmospheric pressure.

The results (figure 2 B) show that a few large heat convection cells are well established after some 20,000 years whenever the brine temperature is higher than 130ºC. Moreover, the temperature above the basal aquifer is approximately constant in the first hundred or so meters where the heat-plumes occur (there, temperatures of 120ºC are reached 400 m above the basal aquifer). The regional groundwater travels at velocities that are on the order of 10^{-9} m s^{-1} (~0.30 m yr^{-1}) just above the bottom boundary and along faults. An increase in the depth of the section results in convection occurring earlier and more vigorously. Changes in the permeability of the shale unit do not produce major changes in the convection pattern, but the decrease in its permeability induces the general velocity to increase. The existence of the short faults evenly distributed at the bottom of the section facilitates the onset of convection but do not change the overall pattern of heat and fluid velocities.
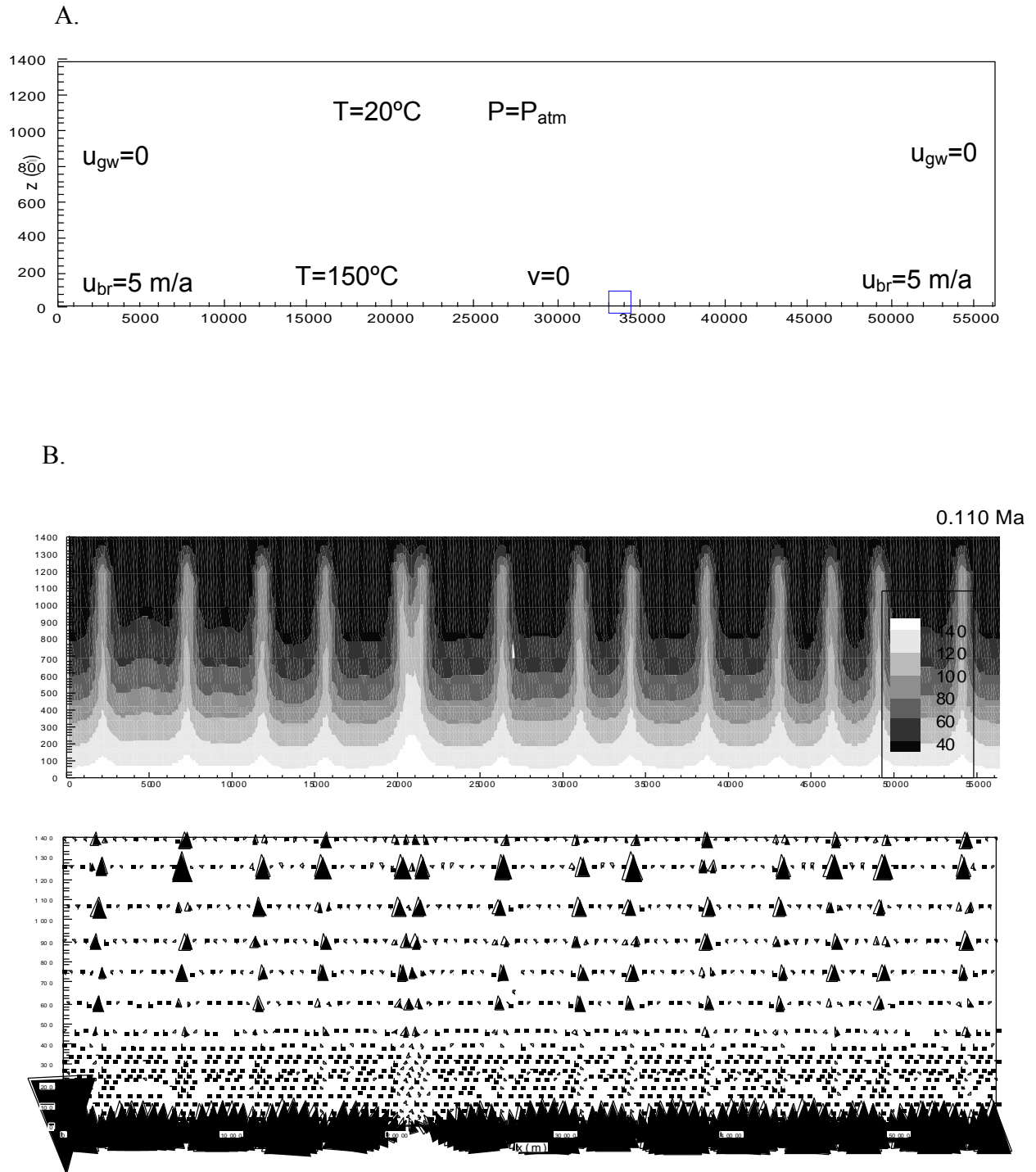
A.

B.

Figure 2. A. Heat and flow transport simulations system with their boundary conditions. The small square at the bottom represents the system of figure 3.

B. Convective cells in a MVT district as reflected in isotherms and velocity vector plots after 0.1 Ma of simulation time. Maximum velocities are 10^{-8} m/s at the bottom boundary, and 10^{-9} m/s in the upflow zones.

The main conclusion extracted from this modeling is that the temperature variation on the 100 m above the bottom boundary is about 10ºC, and less than that at heat and fluid plumes, that is the upflow zones. Moreover, the heat and fluid circulation becomes almost evenly distributed along the section, in the form of convection cells, with ascending plumes every 4000 m that may or may not coincide with preexisting faults.

CHEMISTRY SOLVER AND 2D SYSTEM

The computer program utilized for the chemical exercises is RETRASO (REactive TRAnsport of SOlutes), which is able to couple multicomponent solute transport with chemical reactions between 0 and 300ºC. It can handle complexation, adsorption and precipitation/dissolution of minerals, either under local equilibrium or kinetic laws (Saaltink et al. 1998; Ayora et al. 1998).

RETRASO uses Garlekin finite element discretization in space and fully implicit finite differences discretization in time. It employs the 'direct-substitution approach' (Yeh and Tripathi, 1989), or 'global implicit method' (Steefel and MacQuarrie, 1996), to solve the initial set of nonlinear equations: transport and chemical equations are solved simultaneously applying a Newton-Raphson scheme. In order to avoid the need for large amounts of computer memory, the species of constant activity are eliminated from the list of unknowns, that is, the number of variables is reduced. To ensure numerical stability, a set of primary species with the higher concentration must be chosen. The physical parameters of the system are updated after each time-step: porosity, volume fraction of each mineral, permeability, diffusion coefficients, mechanical dispersion and reactive surface area of minerals.

The code includes two sets of databases compiled from the literature: one for equilibrium constants of chemical reactions, mostly taken from the EQ3NR datafiles (Wolery, 1992), the other for available reaction rates; both of them include data from 0 to 300 ºC. The user is in charge of selecting the one that applies to each reaction of the system.

The physical system chosen to conduct the reactive transport model is a narrow 2D section around one of the faults at the bottom of the previous CODE-BRIGHT simulations. More specifically, the section is a fragment of the bottom part of figure 1 from the top of the bottom boundary to the bottom of the shale strata, that is, 110 m high, as would have been in the UMV district (Heyl et al. 1959). In the x-direction, the section ranges from where the flow lines are orthogonal to one of the faults to another fault or 26.5 m long (figure 3 A). The ore body is located on top of the fault.

With this system we plan to observe the interaction between the brine, which moves upward through the fault on the right hand side, and the regional groundwater that is slowly moving through the country rock.

MESH, TEMPERATURE AND VELOCITY FIELD

The section is discretized into a mesh of triangular elements with 9 nodes in the x-direction and 23 nodes in the z-direction (figure 3 B). It is not a homogeneous grid as we focus on the reaction between groundwater and brine that must occur in or next to the fault, that is, on the right hand side of the section, where the elements become much finer.

As the temperature variation around the faults of the district-wide exercises was rather small (less than 10 ºC) it iss maintained as a constant of 150 ºC in the geochemical calculations. The fluid flow conditions imposed are also extracted from the previous simulations: the brine enters the system through the fault, at the bottom-right corner, at a flow rate of 1 $m^3\, m^{-2}\, a^{-1}$; groundwater is recharged through the left boundary at a flow rate of 0.1 $m^3\, m^{-2}\, a^{-1}$; the fluid comes out of the system through the right-hand side upper boundary (figure 3 A). With these conditions the resulting steady flow in the 2D section is shown in figure 3 C).

We divide the system in two parts: in the lower one the fault is assumed to be a 1D system with no hydraulic connection with the surrounding carbonate; in the upper part the fracture and the carbonate nodes are hydraulically connected. As seen in figure 3 C the hydraulic connection between the fracture and the wall rock alters significantly the flow system.
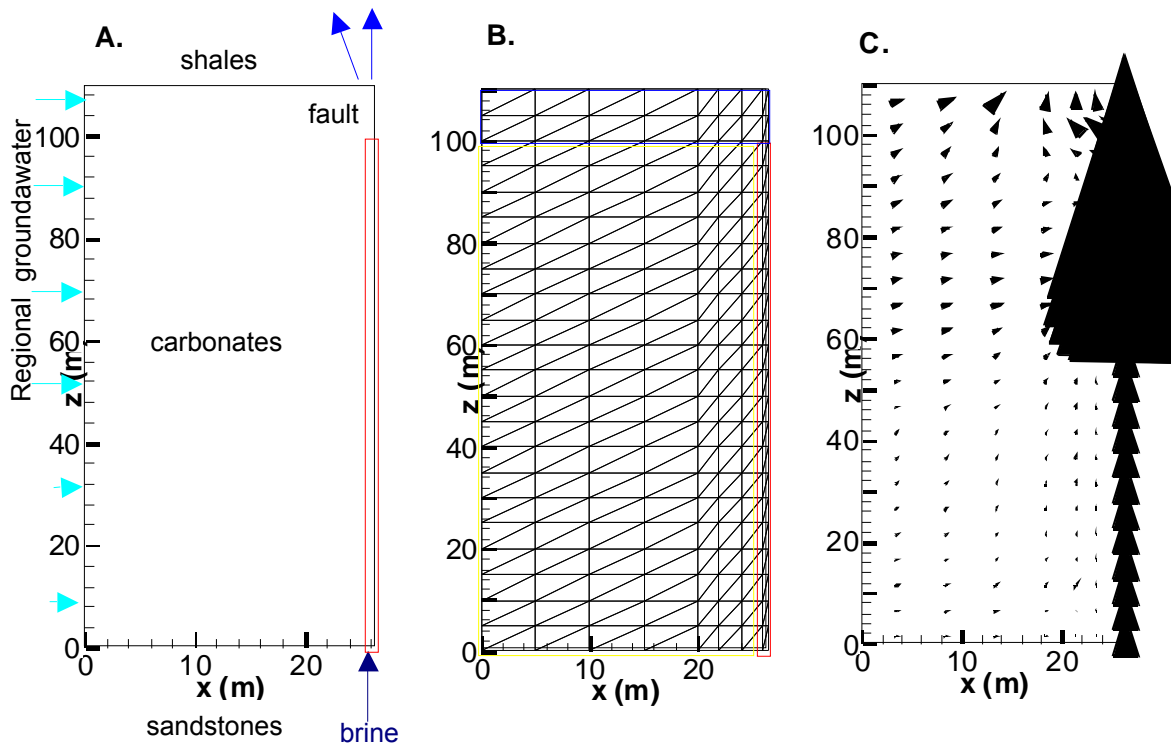

Figure 3. A. Physical system for the geochemical simulations. B. Mesh with the materials of the system. Yellow: K_x=0.25 m/a, K_y=0.16 m/a. Blue: K_x=0.25 m/a, K_y=0.16 m/a. Red: K_x=500.0 m/a, K_y=5000.0 m/a. Longitudinal and transversal dispersivity coefficients are 5.0 and 2.5 respectively, except for the red material where the trasnversal is equal to 0.5 . C. Steady state flow in the system shown in a velocity vector plot where the length of the vector is proportional to the logarithm of the velocity.

INITIAL AND BOUNDARY CONDITIONS

The set of aqueous primary species, and their concentrations, are chosen in accordance to the geological environment of MVTs and the available geochemical data. The initial water in the system is assumed to be groundwater, homogeneous in the whole section.

The boundary waters are two: on the left-hand side, a groundwater water enters the system, and on the bottom right-hand corner of the section a brine is recharged through the fault (table 1, figure 3)

The principal solutes of the whole system are assumed to be those found in fluid inclusions of ore minerals of the UMV deposits (McLimans, 1977) and the ones relevant to possible reactions between them, that is, Cl^-, Na^+, $CO_{2(aq)}$, Ca^{2+}, SO_4^{2-}, $ZnOH^+$, K^+, $SiO_{2(aq)}$, $Al(OH)_4^-$, H^+ and e^-. 22 additional aqueous complexes ($O_{2(aq)}$, OH^-, $CH_{4(aq)}$, HCO_3^-, $NaCl_{(aq)}$, $CaCl_{2(aq)}$, $CaCl^+$, $CaHCO_3^+$, $NaHCO_{3(aq)}$, $H_2S_{(aq)}$, HS^-, HSO_4^-, $CaSO_{4(aq)}$, CO_3^{2-}, $ZnHCO_3^+$, Zn^{2+}, $KCl(aq)$, $NaHSiO_{3(aq)}$, $HSiO_3^-$, Al^{+3} and $Al(OH)_{3(aq)}$) are included in the calculations. Each solute is specied in every fluid using the equilibrium constants of EQ3NR (Wolery, 1972). The only minerals allowed to precipitate or dissolve are calcite and sphalerite, which are assumed to do so under equilibrium, and are considered a proxy of carbonate rocks and ore respectively.

The groundwater chemistry is primarily extrapolated from the supposed composition of the stratigraphy of the UMV district at Permian time, the time where those deposits formed. The total concentration of chlorine, sodium and calcium are chosen as those of a typical groundwater that fulfils Hanor (2001) empirical data for basinal solutions; the total sulfur is varied between 10^{-10} and 10^{-3} mol/kg. Total carbonate concentration is calculated in equilibrium with calcite, and a pH of 6.5 is initially tested. The oxidation state is also varied according to the conceptual model: it is in the sulfide field for the sulfide addition model and in the sulfate field for the sulfate addition model (table 1).

The total concentration of chlorine, sodium, calcium and potassium of the hydrothermal brine are approximated directly from the fluid inclusion study of McLimans (1977).

Table 1. Chemical composition of end-member solutions.

Cases	1. Sulfide precipitation: H_2S addition		2. Mixing		3. Sulfide precipitation		4. Sulfide precipitation: SO_4^{2-} addition and reduction	
	gw	br	gw	br	br	br	gw	br
Cl	1.0	5.0	1.0	5.0	5.0	5.0	1.0	5.0
Na	0.99	3.5	0.99	3.5	3.5	3.5	0.99	3.5
Ca	0.05	0.5	0.05	0.5	0.5	0.5	0.05	0.5
$C_{inorganic}$	$\underline{7\ 10^{-4}}$	$\underline{0.04}$	$\underline{7\ 10^{-4}}$	$\underline{0.04}$	$\underline{0.04}$	$\underline{0.04}$	$\underline{2\ 10^{-4}}$	$\underline{0.04}$
$C_{organic}$	$5\ 10^{-4}$	0.02	$5\ 10^{-4}$	0.02	0.02	0.02	$5\ 10^{-22}$	0.02
S	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-4}	10^{-10}	10^{-4}	10^{-10}
Zn	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-4}	10^{-10}	10^{-4}
K	$5\ 10^{-3}$	0.3	$5\ 10^{-3}$	0.3	0.3	0.3	$5\ 10^{-3}$	0.3
fO_2 (bar)	10^{-51}	10^{-51}	10^{-51}	10^{-51}	10^{-51}	10^{-51}	10^{-42}	10^{-51}
pH	6.5	5.0	6.5	5.0	5.0	5.0	6.5	5.0

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

The total amounts of sulfide and carbon are those of a typical hydrothermal brine (e.g. Giordano and Barnes, 1981), but carbon also has to be in equilibrium with calcite. The oxygen fugacity or oxidation state of the brine is considered to be in the hydrocarbon field, and the pH is calculated to 5.0 from the paragenesis muscovite-quartz-K-feldspar observed by Heyl et al. (1959) along faults, with a fixed concentration of potassium ion of 0.3 mol/kg, value that agrees with fluid inclusion data and the reported ion contents by Hanor (2001).

RESULTS OF THE H₂S ADDITION MODEL

Most solutes concentration reach steady state in less than 10,000 years in all mixing simulations. The chlorine concentration contour plot at the steady state (figure 4 A) shows how the mixing of the two fluids occurs, as chlorine is a conservative solute. It is well apparent that at the lower 40 m of the section the regional groundwater is not affected by the encounter of the brine. The concentration pattern of this conservative solute depends on two factors: 1) the flow imposed by the total flux and the boundary conditions, as represented in figure 3, and 2) the hydraulic connection between fracture an wall rock. Cl transport in the upper part of the system is in part due to numerical dispersion; as a consequence, the extent of Cl mixing is reduced if a more refined grid
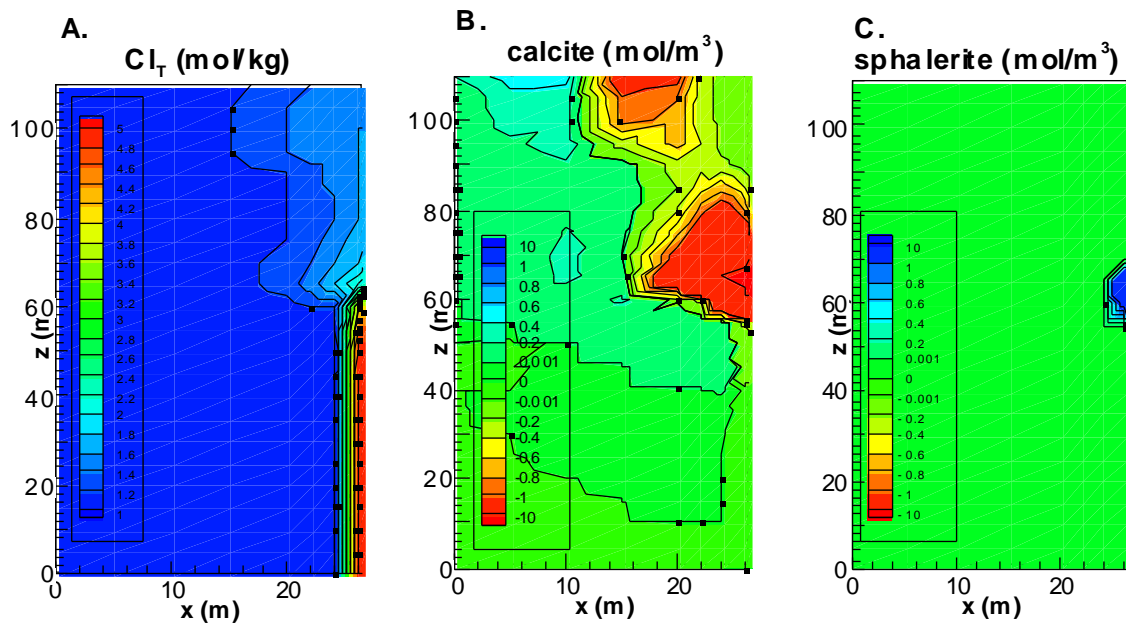

Figure 4. Results of the H₂S addition model after 150,000 years of simulation time. A. Chlorine concentration contour plot; it illustrates the mixing mode between a regional sulfide-rich groundwater and a metal-rich brine that have the composition described in table 1. B.. Contour plot of amount of calcite precipitated (blue) or dissolved (red). C. Contour plot of amount of sphalerite precipitated.

is used (not represented). In the lower part of the system, and because of the absence of hydraulic connection, no dispersion is observed between fracture and wall rock. Therefore, due to numerical dispersion, the distribution patterns of the reactive transport modeling should only be considered on a qualitative basis.

The mixing of a metal-rich brine and a sulfide-rich groundwater (table 1), that are both initially in equilibrium with respect to calcite, produces major dissolution of calcite, as predicted in chapter 2, together with some precipitation of the mineral (figure 4 B). The dissolution mainly occurs on the upper part of the fault and next to it, as can be seen in figure 4 B for calcite contours at 0.150 Ma of simulation time. If composed with a mirror image of the section, the dissolution zone shape is a narrow "V", with a wider "V" around it of calcite precipitation.

Calcite dissolves and precipitates throughout the experiment, as groundwater and brine are continuously entering the system, in separate zones (figure 5 A, B and C). The time-evolution of the system is such that only the amount of calcite precipitated or dissolved increases with time, but not the area over which it dissolves or precipitates.

Sphalerite is used as a proxy of all metal sulfides of MVT deposits. Figure 4 C illustrates how sphalerite precipitates in a very localized area that coincides with that of the strongest carbonate dissolution, right where the two fluids meet. However, the extent of sphalerite precipitation is much smaller than the extent of carbonate dissolution, that is, the mass balance between reaction (1) and (3) is not achieved. This is more clearly pictured in figure 6, where the contributions to calcite dissolution and precipitation of the pure mixing and the sulfide precipitation processes are separated.
Two fluids of different compositions, but both poor in sulfur and metals and equilibrated with calcite, are mixed in order to see the pure mixing part (table 1, case 2 and figure 6 A); two brines of identical composition except for sulfur and metal content are mixed to quantify the effect of sulfide precipitation (table 1, case 3, and figure 6 B). The comparison of figure 4 B with figure 6 point out that most precipitation and dissolution of calcite is due to the pure mixing of solutions, and that the contribution of

the sulfide precipitation reaction (1) only adds to the dissolution of the host rock in a reduced area.
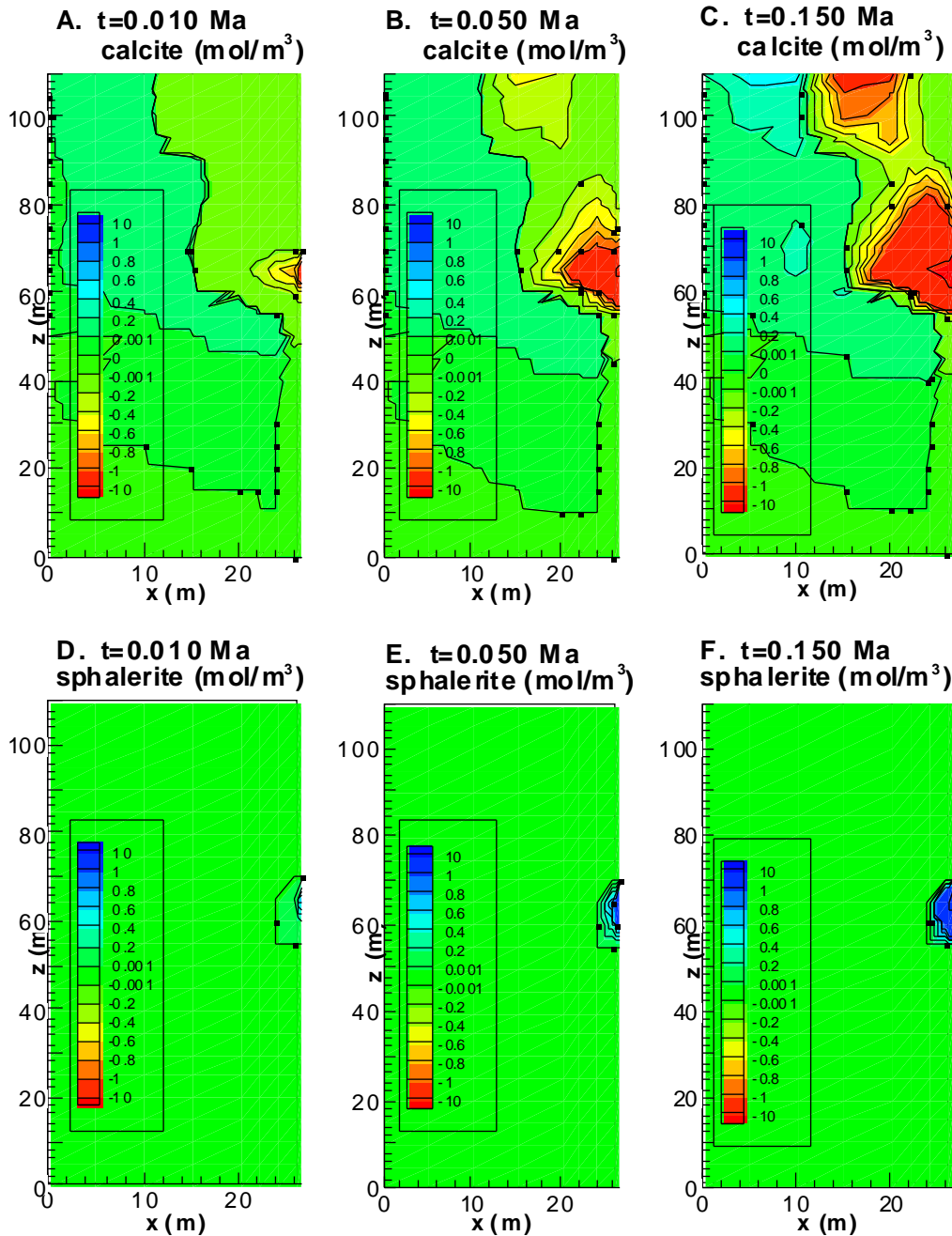

Figure 5. Time-evolution of the sulfide addition model results in terms of amount of calcite and sphalerite precipitated (blue) or dissolved (red). A. Calcite after 10,000 years. B. Calcite after 50,000 years. C. Calcite after 150,000 years. D. Sphalerite after 10,000years. E. Sphalerite after 50,000 years. F. Sphalerite after 150,000 years of simulation time.

Similarly to the temporal evolution of calcite, the area of sphalerite precipitation does not grow with time. The time effect is only in the amount of sphalerite precipitated (figure 5 D, E and F).
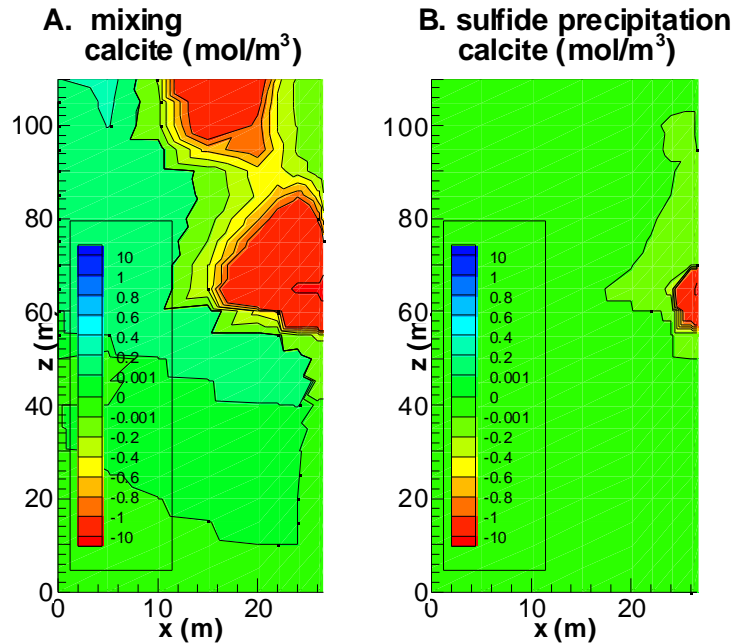

Figure 6. Contour plots of amount of calcite dissolved and precipitated after 150,000 years of simulation time due to: A. mixing effects, and B. sulfide precipitation.

RESULTS OF THE SO_4^{2-} ADDITION MODEL

The pattern of mixing is the same for the sulfate-rich groundwater mixture with a metal-rich brine as for the sulfide addition model because the flow conditions of the mixing solutions involved are the same. A zone of carbonate dissolution also appears in the section, which, as before, is due to the mixing of the now slightly oxidizing groundwater with the more reduced brine (figure 7 B), as reaction (3) does not produce acidity. The mixing also brings about precipitation of calcite (figure 7 A), and more of

it than in the pure mixing case or the sulfide addition case. The zones of dissolution and precipitation appear located similarly to the previous examples.

Sphalerite precipitation also occurs in this case, and with similar amounts as in the previous model (figure 7 B), and with a comparable areal extent.
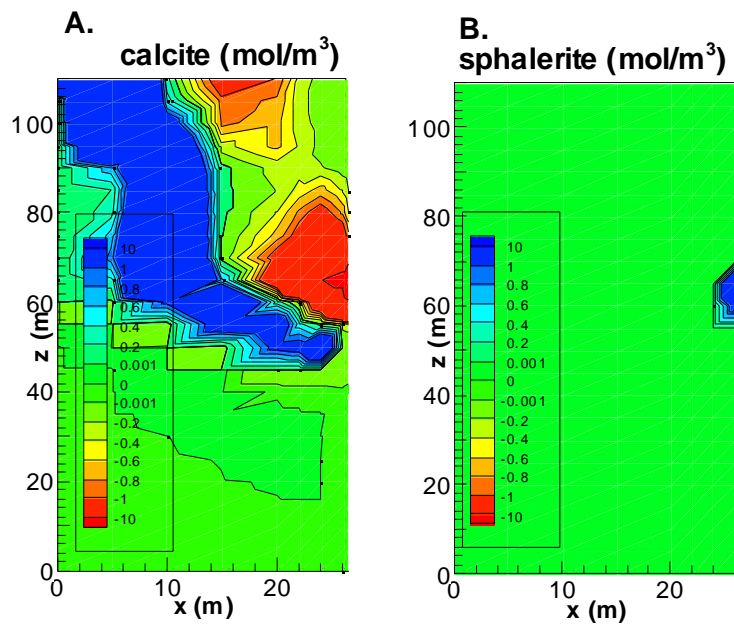

Figure 7. Results of the SO_4 addition model after 150,000 years of simulation time. A. Amount of calcite precipitated (blue) and dissolved (red) contour plot. B. Amount of sphalerite precipitated contour plot.

SENSITIVITY ANALYSIS WITH RESPECT TO S AND Zn CONCENTRATION

The higher the concentration of S and Zn in groundwater and brine respectively, the larger the amount of sphalerite that precipitates from reaction (1) and the larger the amount of calcite that dissolves from reaction (2). Therefore, when concentrations are on the order of 10^{-5} mol kg^{-1}, the plot of calcite contours is similar to that of the mixing

case (figure 8 A). Nevertheless, the concentration of S and Zn also intervenes in the mixing because their speciation is pH dependent. As the pH of the mixture decreases
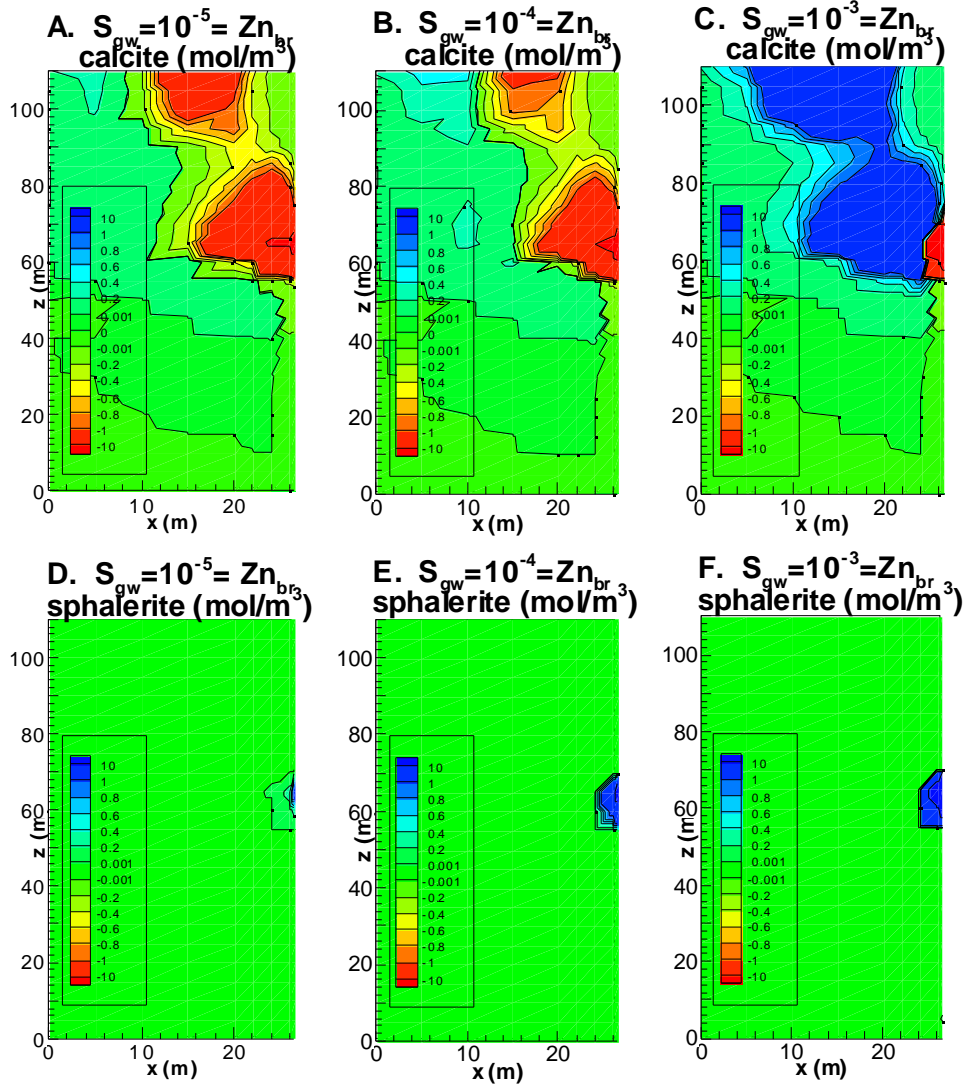

Figure 8. Contour plots of amount of calcite and sphalerite precipitated (blue) and dissolved (red) after 150,000 years of simulation time at different S and Zn concentrations in the initial solutions. A. Calcite plot when S in groundwater and Zn in brine are both 10^{-5} mol/kg . B. Calcite plot when S in groundwater and Zn in brine are both 10^{-4} mol/kg. C. Calcite plot when S in groundwater and Zn in brine are both 10^{-3} mol/kg. D. Sphalerite plot when S in groundwater and Zn in brine are both 10^{-5} mol/kg. E. Sphalerite plot when S in groundwater and Zn in brine are both 10^{-4} mol/kg. F. Sphalerite plot when S in groundwater and Zn in brine are both 10^{-3} mol/kg.

from the groundwater rich-terms to the brine-rich terms, and in a non-linear manner according to chapter 2, the proportions of HS^--H_2S and $ZnOH^+-Zn^{+2}$ also decrease non-linearly along the mixture. When the concentration of sulfur is higher there are less H^+ free in solution and the mixture becomes more alkaline, so that it is more easily supersaturated with respect to calcite and more precipitation of this mineral occurs (figure 7 B and C). The area of sphalerite precipitation does not seem to vary with the concentration of S and Zn in the end-member solutions (figure 8 D, E and F).

SENSITIVITY ANALYSIS WITH RESPECT TO GROUNDWATER FLUX

The influence that the uncertainty on the velocity of the regional groundwater, as well as the presence of an aquitard on the upper part of the section have over the dissolution of carbonates and the precipitation of sphalerite is described below.

The effect of increasing the overall flux of groundwater or its velocity in one order of magnitude (v_{gw}=1 m a^{-1}) with respect to the reference case of figure 4 at the left boundary is pictured in figure 9. The chlorine concentration contour plot, that depicts the amount of mixing between solutions, is biased towards the groundwater in much of the system, including the upper part of the fault (figure 9 B). As the more dilute solution has the higher pH, the more of it in the mixture implies that most of the mixture has a basic pH; thus it tends to be supersaturated for more terms of the mixture and calcite precipitates from it (figure 9 C).

A different pattern of groundwater circulation was devised in order to see the role of the top shale: if it acted as an aquitard, as seems to be the case in districts like Pine Point (Anderson, 1983), the outflow zone of the system would not be through it but on the left side of the section as well (figure 10 A). This type of simulations result in a mixing interface that is closer to the left boundary of the system (figure 10 B); therefore the zone of carbonate dissolution equivalent to that of previous exercises, has a wider "V" shape (figure 10 C).
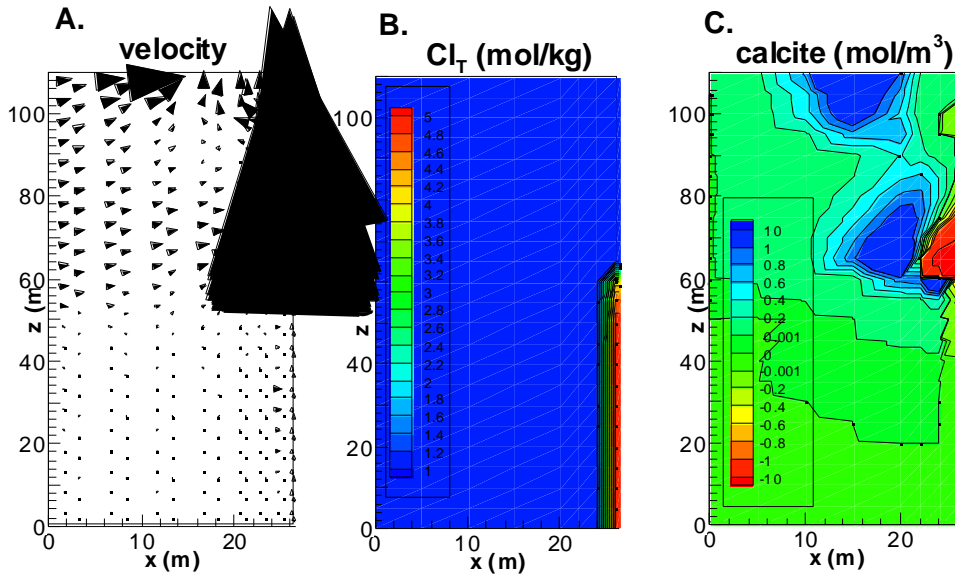
Figure 9. Results of the mixing model when groundwater velocity is increased in one order of magnitude. A. Constant velocity field in the section, where arrowheads are proportional to the logarithm of velocity. B. Chlorine concentration contour plot at steady state illustrating the mode of mixing. C. Contour plot of amount of calcite precipitated (blue) and dissolved (red) after 150,000 years of simulation time.

SENSITIVITY ANALYSIS WITH RESPECT TO pH

The pH affects the saturation of the mixture with respect to calcite because the speciation of the most abundant solutes depends on it, but it has no major effect over the precipitation of sphalerite. When the two solutions are closer in pH than the above cases, there appears to be less calcite dissolution (figure 11 A and B). If this is because the pH of brine is more basic than our type case of figure 4, then calcite dissolution is reduced to the fault zone and an ample zone of calcite precipitation appears instead (figure 11 A); but if it is because the groundwater pH is more acidic, then no calcite precipitation occurs (figure 11 B). Oppositely, when the pH difference between the two solutions is higher, calcite dissolution appears enhanced (figure 11 C and D). When groundwater pH is more basic, calcite precipitation is also stronger and two separate but contiguous zones form, one of strong precipitation and one of strong dissolution (figure

11 C); when the brine pH gets more acidic almost no calcite precipitation occurs (figure 11 D), and the zone of calcite dissolution extends over a wider area.
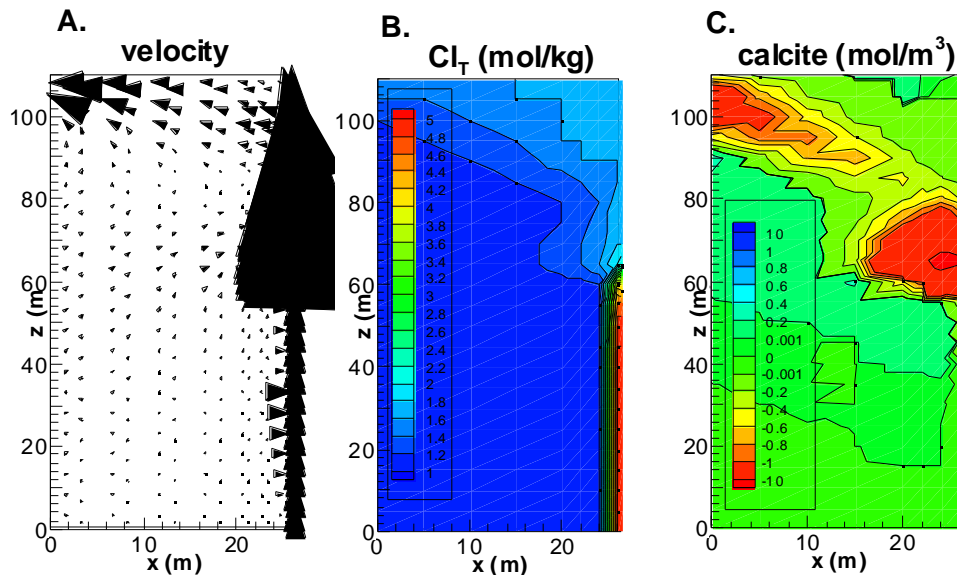

Figure 10. Results of the mixing model with an aquitard on top that doesn't allow flow through it. A. Constant velocity field in the section, where the arrowhead is proportional to the logarithm of the velocity. B. Chlorine concentration contour plot indicative of the mixing mode and interface. C. Amount of calcite precipitation (blue) and dissolution (red) contour plot after 150,000 years of simulation time.

DISCUSSION

The mixing of groundwater and brine of table 1 principally results in calcite dissolution, as was expected from the modeling of chapter 2: the algebraic, salinity and pH-_C effect occur simultaneously and combine, as both initial solutions have different total calcium, salinity, pH and total carbon. The sulfide and sulfate addition models also lead to calcite dissolution, but this is mainly due to the mixing effects, as is clearly shown in figure 6. The contribution of the geochemical reactions of the models is more

noticeable in the enhancement of calcite precipitation next to the zone of dissolution. This is even more significant for the sulfate addition model, were calcite dissolution is diminished with respect to the mixing model because the sulfate reduction reaction is already pH independent.
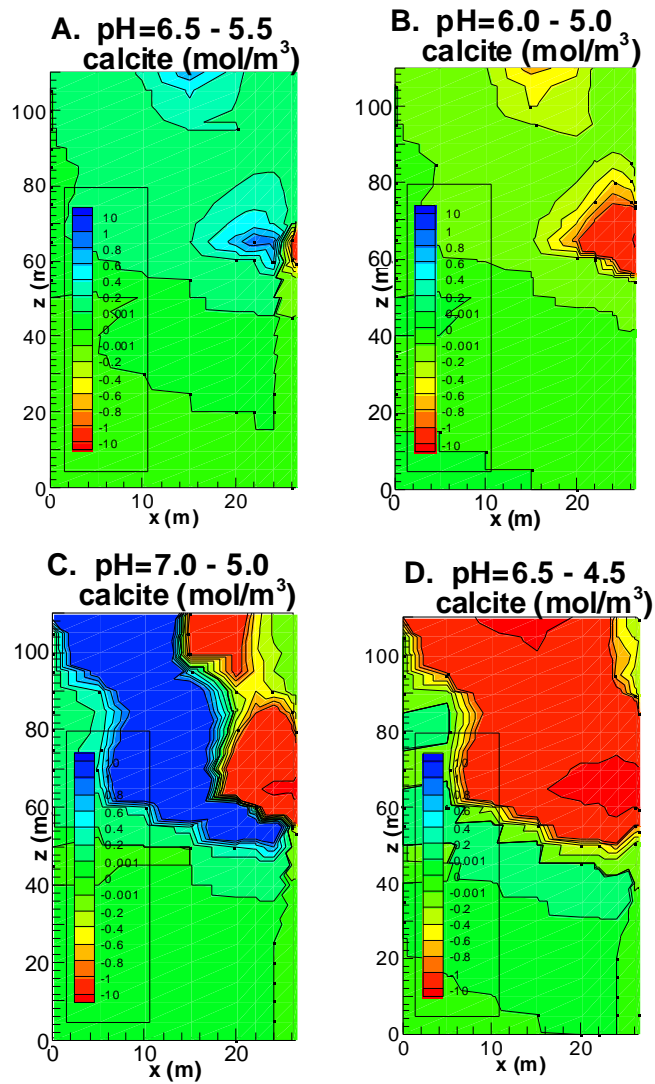

Figure 11. Results of the sensitivity analyses with respect to pH in contour plots of amount of calcite precipitated (blue) and dissolved (red). A. Mixing fluids of pHs 6.5 and 5.5. B. Mixing fluids of pHs 6.0 and 5.0. C. Mixing fluids of pHs 7.0 and 5.0. D. Mixing fluids of pHs 6.5 and 4.5.

In every simulation performed, the dissolution zones of calcite (and the precipitation zones as well when they appear) display a "Y" or "V" shape when reconstructing the whole section with its mirror image on the right hand side of the fault. This is the shape of the interface between the two mixing fluids that originally travelled perpendicular to one another, as is seen in the chlorine contour plots. Depending on the relative fluxes of the contributing solutions the "V" appears narrower or wider (figure 4 and figure 9). Interestingly, this is the shape described for the classic MVT ore bodies of the UMV (Heyl et al. 1959), the Tri-State (Hagni, 1976) or the SE Lennard Shelf, Australia, (Vearncombe et al. 1996) districts. This is not a mere coincidence but the result of mixing two fluids that travel along orthogonal conduits.

Sphalerite precipitation occurs in similar amounts from both, sulfide and sulfate addition models (figure 4 and 7). Sulfides seem to deposit in a very localised area, of approximately circular shape, coincident with the zone of maximum dissolution of calcite, that is, where the two fluids first 'see' each other. The extent of the sulfide precipitation area is much reduced than that of host dissolution. Although not appreciable in the plots, similar or more moles of calcite dissolve than sphalerite precipitate in every node of the simulation mesh. Therefore, as long as the sulfides precipitating have a molar volume smaller than that of the carbonate host, as sphalerite or pyrite, sulfide precipitation will never seal the porosity. From the point of view of equilibrium geochemistry, both mechanisms of sulfide precipitation, that is sulfide and sulfate addition, are able to lead to the formation of an ore-body given sufficient time, metals and sulfur.

An increase in the velocity of the regional water that enters through the left boundary, produces an increase in the proportion of groundwater in the mixture in much of the section (figure 9). This causes the zones of calcite dissolution and of calcite precipitation to form closer to the fault, that is, the interface of fluids moves to the right hand side. The resultant dissolution "V" is then much narrower than when groundwater velocity is smaller.

The simulations performed with the top shaly beds acting as an aquitard result in cavities located at similar depths, and with approximately similar "V" forms although wider, as when the shaly beds let some fluids through (figure 4 and 10). Consequently, the location of the dissolution zone depends on the site the brine encounters the suitable groundwater, and the shape depends solely on the velocity proportions and directions of the contributing fluids. Anderson (1983) believed a shale cover on the district was necessary in order to restrict groundwater circulation in the ore zone and to prevent the upward movement of the brine, so that H_2S and metals would mix more effectively. Our results show that this was not necessary at all; indeed, the location and shape of the cavities formed by mixing of fluids are independent of the permeability of the beds on top of it, that is, the existence of aquitards in the district that restrict the upward movement of fluids. It has not been possible to predict the size of the deposits because of the dispersion of the numerical equations.

Dissolution of the host carbonate tends to occur at the brine-rich terms of the mixture, while precipitation of calcite seems to predominate on the groundwater-rich terms. This is principally due to the pH of the mixture, which is more acidic in the brine-side, making the solution rather subsaturated with respect to calcite; the mixture is more alkaline in the groundwater side becoming there more easily supersaturated.

The formation of an MVT ore body depicts a steady temporal evolution whenever the fluxes of fluids remain constant. The zones of host dissolution, carbonate precipitation and sulfide deposition are already delineated in a few thousand years (figure 5); their time dependence is only in increasing the amount of precipitation or dissolution, but not in the extent of the zone. Therefore, the refilling of carbonate porosity by carbonate gangue minerals, which is so common in MVT deposits, must be caused by the variation of fluxes through time. This varies the contribution of the two mixing fluids in one particular point, so that a zone of carbonate dissolution may become a zone of carbonate precipitation when a higher proportion of regional water enters the system.

The dissolution of calcite as predicted by the mixing process alone may also explain the occurrence of barren carbonate breccias that are found in many MVT districts (UMV,

SE Missouri, Central Tennessee). These breccias may have formed as a consequence of the encounter of groundwater and brine, the same two fluids that are believed to generate the Zn-Pb deposits, once they have been depleted of either sulfur or metals. It is also possible that the so called barren breccia still have a little zone with sulfides in their interior, as the extent of the dissolution zone is calculated to be much larger than that of sulfide precipitation.

CONCLUSIONS

The formation of dissolution features of the carbonate host associated with MVT ore deposits is easily explained by mixing of fluids with distinct chemistry and equal temperature.

Since variations in temperature are not important at the ore deposit scale, we actually save lots of computer power and time by not coupling the heat flow with the geochemical simulations.

The mixing of hydrothermal fluids of differing chemistry although both saturated with respect to calcite generates dissolution and precipitation of that mineral in separate but contiguous zones. Both processes occur simultaneously, by the same two solutions, but at different proportions of the end-member fluids.

The zone of country rock dissolution of our calculations appears as a "V"-shaped area. This agrees with the observations of the breccia bodies of many MVT districts, and is precisely the shape of the interface between the two mixing fluids that have orthogonal velocities. Depending on their relative fluxes the "V" is wider or narrower.

The zones of carbonate dissolution and precipitation remain separate in time as long as the fluxes of the initial solutions remain constant. Nevertheless, as soon as one of them declines the proportion of fluids in the mixture change and the zones of dissolution and

precipitation move accordingly. This explains the filling of calcite and dolomite of the carbonate breccia.

The presence of aquitards in the stratigraphic section is not directly significant for the formation of MVT ore bodies, since the confinement of the mixing fluids is not necessary to trigger the dissolution of the host nor the precipitation of sulfides. These processes happen at the mixing interface between the two initial solutions.

Precipitation of metal sulfides is one of the consequences of mixing whenever the fluids carry enough sulfur and metals. As most base-metal sulfides have a smaller molar volume than that of carbonates, sulfide precipitation does not occlude porosity completely, and the mixing may carry on while the two fluids last. Mixing of such fluids may then lead to the formation of an MVT ore deposit.

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