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Role of fluid mixing in deep dissolution of carbonates

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ABSTRACT

The presence of cavities filled with new minerals in carbonate rocks is a common feature in oil reservoirs and lead-zinc deposits. Since groundwater equilibrates rapidly with carbonates, the presence of dissolution cavities in deep carbonate host rocks is a paradox. Two alternative geochemical processes have been proposed to dissolve carbonates at depth: hydrogen sulfide oxidation to sulfuric acid, and metal sulfide precipitation. With the aid of geochemical modeling we show that mixing two warm solutions saturated with carbonate results in a new solution that dissolves limestone. Variations in the proportion of the end-member fluids can also form a supersaturated mixture and fill the cavity with a new generation of carbonate. Mixing is in general more effective in dissolving carbonates than the aforementioned processes. Moreover, mixing is consistent with the wide set of textures and mineral proportions observed in cavity infillings.

KEYWORDS **Hydrothermal karst. MVT deposits. Reactive transport. Fluid mixing. Carbonate dissolution.**

INTRODUCTION

Carbonates have a fast dissolution kinetics. Thus, groundwater circulating over long distances in carbonate-hosted aquifers rapidly reaches equilibrium with calcite and/or dolomite (Back and Hanshaw, 1971; Deike, 1990; Mogollón et al., 1999). By contrast, dissolution of carbonate takes place in deep environments, where hydrocarbon traps or Mississippi Valley type (MVT) base metal deposits occur (Hill, 1995; Anderson, 1973). Furthermore, as carbonates have inverse solubility dependence with temperature, deep dissolution is not to be expected.

Two scenarios have been proposed to explain carbonate dissolution at such depths. The first scenario is hydrogen sulfide oxidation, which creates sulfuric acid speleogenesis and forms carbonate reservoirs (Hill 1990; 1995). A similar model was employed by Barnes (1983) to explain the dissolution of the carbonate host of MVTs in the Upper Mississippi Valley (UMV). The mixture of a reduced solution rich in hydrogen sulfide with a more oxidizing one leads to the oxidation of sulfide to sulfate, and the release of protons:

$$H_2S_{(aq)} + 2\,O_{2\,(aq)} = SO_4^{2-} + 2\,H^+ \,. \qquad (1)$$

When this reaction occurs in a carbonate host rock dissolution of carbonates takes place:

$$2\,H^+ + CaCO_{3\,(s)} = Ca^{2+} + CO_{2\,(aq)} + H_2O \,. \qquad (2)$$

The second scenario is based on sulfide precipitation (mainly sphalerite and galena) in MVT deposits (Anderson, 1975):

$$H_2S_{(aq)} + Zn^{2+} = ZnS_{(s)} + 2\,H^+ \,. \qquad (3)$$

As a result of proton release, reaction (2) takes place. The sulfur is added to the metal-bearing brine with the other solution or as a result of the “in situ” reduction from sulfate ions, which may require microbial catalysis at low temperature

(Ohmoto and Lasaga, 1982). According to reactions (1) to (3), a mole of carbonate is dissolved for each mole of hydrogen sulfide oxidized or metal sulfide precipitated.

However, the processes described above are difficult to reconcile with many observations in nature. First, the textures indicate that the minerals filling the cavities grew in open spaces (e.g. Heyl et al., 1959; Sass-Gustkiewicz et al., 1982; Leach et al., 1996). Therefore, part or the entire volume of the cavities was formed prior to the filling. Second, since sulfide minerals are not the only ones filling the cavity, the amount of sulfide precipitated is insufficient to meet the mass balance requirements of reaction (3). The volume of sulfides is usually greater than that of the rest of minerals, but some districts, like the UMV or Silesia-Cracow, include cavities only filled with carbonates (Heyl et al. 1959; Leach et al. 1996), and/or cavities that are mostly filled by fluorite or barite, like the European Alpine, the English Pennines, the Appalachian, the Irish or Polaris districts (Schroll, 1996; Dunham, 1983; Kesler, 1996; Hitzman and Beaty, 1996; Randell and Anderson, 1996). Third, gypsum, which could form from reactions (1) and (2), is only found in a few localities, and in very small amounts (e.g. Lu et al., 1995). All these observations suggest that at least some of the processes that generated the cavities are not related to those causing the precipitation of the infilling minerals. Therefore, additional processes not considered to date must account for these observations.

The mixing of two fluids saturated in a particular mineral may bring about changes in the saturation state of the new solution. Raup (1970) describes an experiment where halite precipitates at the interface of two brines in equilibrium with this mineral. Mixing of fresh and sea water has been interpreted as being responsible for carbonate corrosion at the salt intrusion front in coastal aquifers (Back et al., 1979; Sandford and Konikow, 1989; Wicks and Herman, 1996). Moreover, the mixing of two fluids at low temperature (10 to 25°C) is discussed by Wigley and Plummer (1976); they isolate the intrinsic factors that affect the dissolution and precipitation of calcite by mixing waters saturated with calcite.

We postulate that the mixing of two fluids in deep aquifers is much more important for carbonate dissolution-precipitation than the changes induced by the oxidation of H_2S or the precipitation of sulfides. The aim of this paper is to evaluate, by means of geochemical modeling, the effects of the chemical reactions described (1 to 3), and to compare them with the effect of pure mixing of the two solutions involved.

DESCRIPTION OF CALCULATIONS

We assume that deep mixing occurs between a basinal brine and a less saline groundwater in accordance with the conceptual models described for MVT deposits (e.g. Anderson, 1975; Garven and Freeze, 1984; Barnes, 1983; Sverjensky, 1986). The compositions of these solutions are given in Table 1 and Fig. 1.

TABLE 1 **Chemical composition of end-member solutions (1)**

Cases	1. Mixing		2. H_2S oxidation		3. H_2S addition		4. SO_4^{2-} addition and reduction	
	gw	**br**	**gw**	**br**	**gw**	**br**	**gw**	**br**
Cl	1.0	5.0	1.0	5.0	1.0	5.0	1.0	5.0
Na	0.99	3.5	0.99	3.5	0.99	3.5	0.99	3.5
Ca	0.05	0.5	0.05	0.5	0.05	0.5	0.05	0.5
$C_{inorganic}$(2)	$\underline{6\ 10^{-4}}$	$\underline{0.015}$	$\underline{3\ 10^{-4}}$	$\underline{0.015}$	$\underline{6\ 10^{-4}}$	$\underline{0.015}$	$\underline{3\ 10^{-4}}$	$\underline{0.015}$
$C_{organic}$	$5\ 10^{-4}$	0.013	$5\ 10^{-11}$	0.013	$5\ 10^{-4}$	0.013	$5\ 10^{-11}$	0.013
S	10^{-10}	10^{-10}	10^{-10}	10^{-3}	10^{-4}	10^{-10}	10^{-4}	10^{-10}
Fe	$2\ 10^{-7}$	10^{-10}	$2\ 10^{-7}$	10^{-10}	$2\ 10^{-7}$	10^{-10}	$2\ 10^{-7}$	10^{-10}
Zn	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-10}	10^{-4}	10^{-10}	10^{-4}
K	$2\ 10^{-4}$	0.3	$2\ 10^{-4}$	0.3	$2\ 10^{-4}$	0.3	$2\ 10^{-4}$	0.3
fO_2(bar)	10^{-51}	10^{-51}	10^{-42}	10^{-51}	10^{-51}	10^{-51}	10^{-42}	10^{-51}
pH	6.5	5.0	6.5	5.0	6.5	5.0	6.5	5.0

(1) Concentration units are mol/kg; gw: groundwater; br: brine.
(2) The underlined numbers have been calculated to fulfil the condition of calcite equilibrium.

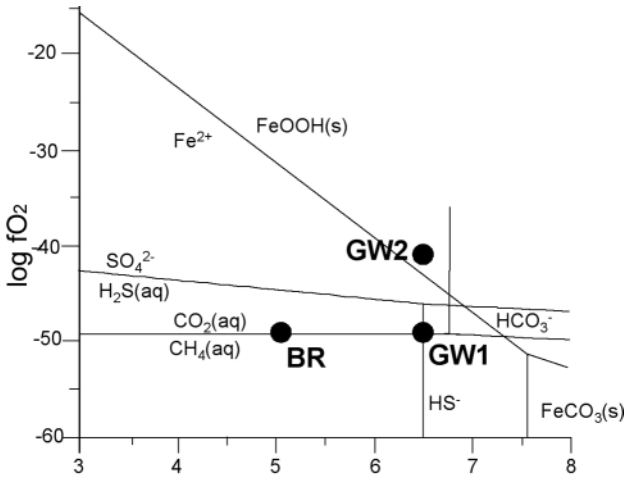

FIGURE 1 **Location of the brine (BR) and two possible regional groundwaters (GW1 and GW2) in a pH-log f_{O2}(bar) diagram at 150°C. Total concentrations of carbon and iron of 10^{-2} and 10^{-7} mol/kg, respectively, are used.**

The chlorine, sodium and calcium concentrations of the brine (BR in Fig. 1) are estimated from the fluid inclusions trapped in the precipitated minerals (McLimans, 1977). The total amounts of iron, zinc and sulfide are those of typical hydrothermal brines (Giordano and Barnes, 1981; Sverjensky, 1987; Anderson and Garven, 1987; Plumlee et al. 1994). The assemblage K-feldspar-muscovite-quartz, observed in fractures of the UMV district (Heyl et al., 1959), constrains the pH of the brine, although we test the response to other values as well. The concentration of potassium is taken from fluid inclusion data (McLimans, 1977). The total carbon concentration is calculated in equilibrium with calcite also following the MVT conceptual models (Anderson, 1975). The pH and solute concentrations are consistent with the data for basinal saline fluids (Hanor, 2001). Following Anderson and Garven (1987), Sverjensky (1987), Plumlee et al. (1994) and Appold and Garven (2000), the oxidation state of the brine is considered to be in the field of hydrocarbon species, represented here by methane (Fig. 1). The oxygen fugacity (fO_2) is further constrained to 10^{-51} bar to meet the concentration of C_{org} measured in the inclusion fluids (McLimans, 1977).

The other end fluid (GW1 and GW2 in Fig. 1) consists of slightly saline groundwater. Total carbon is again calculated in equilibrium with calcite. A closed system behavior is assumed (no exchange of CO_2 with any external reservoir). The pH is not constrained and may vary between 6.0 and 7.5 for a chlorinity of 1.0 in accordance with the analyses of dilute basinal fluids (Hanor, 2001). We work with a pH value of 6.5 and subsequently analyze the sensitivity of the results with respect to pH. Two oxidation states are assumed to account for two different scenarios: H_2S-bearing water with a fO_2 value similar to that of the brine described above (GW1), and a SO_4-bearing water, with fO_2 of 10^{-42} bar in equilibrium with goethite (GW2). Variations in fO_2 of GW2 do not significantly affect the results of the calculations provided that sulfate is the predominant S species. A temperature of 150°C, commonly reported in fluid inclusion microthermometry (McLimans, 1977), was assumed for both brine and groundwater.

The geochemical calculations are performed with the simulator RETRASO. This is a Fortran code capable of handling multicomponent solute transport coupled with chemical reactions (Ayora et al., 1998). Mixing is simulated assuming diffusion between two end-member solutions of fixed composition, in a closed system. The aqueous species included in the calculations are: Cl^-, Na^+, $CO_2(aq)$, Ca^{2+}, SO_4^{2-}, $ZnOH^+$, K^+, $SiO_2(aq)$, $Al(OH)_4^-$, H^+ and e^- as primary species, and $O_2(aq)$, 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+}, $ZnCl^+$, $KCl(aq)$, $NaHSiO_3(aq)$, $HSiO_3^-$, Al^{+3} and $Al(OH)_3(aq)$ as additional aqueous complexes. The incorporation of Zn-sulfide and Zn- hydroxide- sulfide complexes of Hayashi et al. (1990) does not change the result of the calculations. The thermodynamic data for chemical reactions were those compiled in the EQ3NR database (Wolery, 1992), which allow calculations from 0 to 300°C. The activity coefficients of aqueous species are calculated according to the B-dot expression (4) (Helgeson and Kirkham, 1974):

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B \mathring{a}_i \sqrt{I}} + \mathring{b}\, I , \tag{4}$$

where γ represents the activity coefficients of an ion *i*, z is the ion charge, I is the ionic strength, A and B are the parameters of the Debye-Hückel expression, $\mathring{b}$ is a fitting parameter which varies with temperature, and $\mathring{a}$ is the ionic radius of *i* in solution, which is considered constant.

The minerals considered are: calcite as a representative of the carbonate host, sphalerite as a representative of the metal sulfides that precipitate in MVT deposits, and K-feldspar, muscovite, quartz and kaolinite, as found in the country rocks. For the flux rates expected in deep aquifers (~ 1m/y, Garven and Freeze, 1984), and the temperatures modeled (150°C), the mineral-solution reactions are assumed to be fast enough to reach equilibrium.

We present the results as the saturation index of the mixture with respect to calcite; this mineral is not allowed to dissolve or to precipitate because we are only interested in showing the potential of the mixture to dissolve/precipitate calcite. The exact locus of dissolution and precipitation depends on the relative values of the fluxes of the two fluids. Since this depends on each site, the results for particular flow systems will be analyzed elsewhere through reactive transport modeling.

THE EFFECTS OF TWO MIXING FLUIDS

Mixing of fluids with different salinity

The result of mixing two calcite saturated solutions that only differ in their salinity is a new solution subsaturated in calcite. The subsaturation increases with the difference in salinity (Fig. 2A). This occurs because calcium activity coefficients are lower in solutions of intermediate salinities than in solutions of extreme salinities (Fig. 2B); therefore, after the definition of the saturation index of calcite (5), it diminishes together with the activity coefficients:

$$SI = \log\left(\frac{IAP}{K_{eq}}\right) = \log\left(\frac{m_{Ca^{2+}} m_{CO_3^{2-}} \gamma_{Ca^{2+}} \gamma_{CO_3^{2-}}}{K_{eq}}\right), \quad (5)$$

where IAP is the Ion Activity Product in solution and K_{eq} is the solubility product constant for calcite.

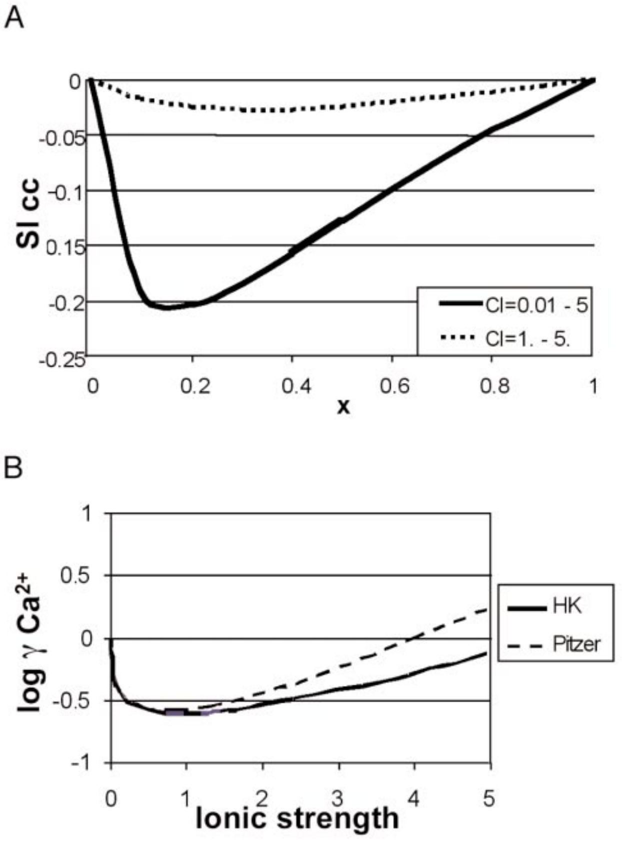

FIGURE 2 **Mixing of two fluids with different salinity. A) Saturation index of calcite in mixtures composed of a dilute groundwater (x=0.0) and a more saline fluid (x=1.0). The subsaturation of the mixture increases with the difference in salinity of the end member fluids. B) Activity coefficients for Ca^{2+} in solutions of different ionic strength at 25ºC calculated with the models of Helgeson and Kirkham (1974) and Pitzer.**

Mixing of fluids with different Ca concentration

Two fluids that are both equilibrated with calcite but have a different Ca concentration must also have different CO_3^{2-} concentration. The resulting mixtures are always supersaturated in calcite. This occurs because of the so-called algebraic effect described by Wigley and Plummer (1976). Let us assume a fluid equilibrated with a mineral that is composed of two ions, A and B (Ca^{2+} and CO_3^{2-}). The ion activity product is:

$$IAP = A \cdot B = K_{eq}\ . \quad (6)$$

A different fluid that contains b-times of ion A will also be equilibrated with the same mineral if equation (7) holds:

$$IAP = b \cdot A \cdot B / b = K_{eq}\ . \quad (7)$$

It is easily demonstrated that the IAP of any linear mixture of these two fluids is always higher than K_{eq}, indicating that the mixture is supersaturated. The maximum supersaturation occurs for equal proportions of the two fluids, and IAP increases with increasing b, i.e., the difference in Ca concentrations in the original solutions (Fig. 3).

Mixing of fluids with different pH and pCO_2

The mixture of two fluids in equilibrium with calcite that differ in their pH and pCO_2 and have the same concentration of Ca^{2+} is a solution subsaturated with respect to calcite at acidic to neutral pH. The pH variation of the mixture is not linear although the pCO_2 or the total carbon concentration variation between the two end-term solutions is linear (Fig. 4A and 4B). This is due to the speciation of carbon: when the pCO_2 is low the pH drops steeply due to the low buffering capacity of the carbonic system. However, as the total carbon increases, a higher amount of

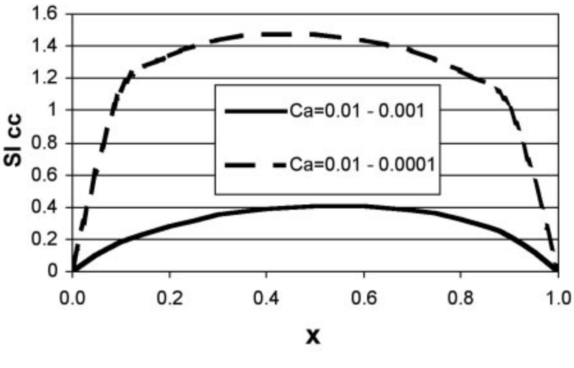

FIGURE 3 **Mixing of two fluids with different Ca (and CO_3^{2-}) concentration. The supersaturation of the mixture increases with the difference in calcium concentration in the two end-member solutions, that are both saturated with respect to calcite.**

H^+ is consumed in carbonic speciation reactions (HCO_3^- to $CO_{2(aq)}$), and the pH decrease is more gradual. The concentration of CO_3^{2-} also follows a non-linear pattern (Fig. 4C): it decreases initially because of the drop in pH, but recovers as total carbon increases and the pH decrease slows. The evolution of calcite saturation parallels that of the CO_3^{2-} concentration since Ca^{2+} is constant (Fig. 4D).

Mixing of fluids with different temperature

The behavior of the system at different temperature depends on the property that varies to ensure the calcite saturation of the end-members. Thus, if the pCO_2 remains constant, the variation in pH and/or Ca will lead to supersaturated mixtures. If the pCO_2 varies together with pH, subsaturation may appear. However, according to convection experiments and theory (Nield and Bejan, 1992), if we assume that the warm brine acts as a heat source in deep environments, temperature variations exceeding 10ºC are not expected within the range of a few meters (the scale of the carbonate cavities). For these differences in temperature, the variations in the saturation of the mixtures are negligible and were ignored in our calculations.

General case: mixing fluids with different parameters

As shown in Fig. 5, case A, the mixing effect of the two fluids selected as brine and groundwater (case 1 of Table 1) causes subsaturation in calcite along the entire mixture. According to the literature, there is a range of variation in the parameters listed in Table 1, among which the pH is the more significant one. On the one hand, the pH value of the brine is calculated from the muscovite-quartz-K feldspar equilibrium (8):

$$KAl_3Si_3O_{10}(OH)_2 + 6\,SiO_2 + 2\,K^+ = 3\,KAlSi_3O_8 + 2\,H^+ \,. \quad (8)$$

Although abundant, there is no evidence that these minerals coexist in equilibrium everywhere. In addition to this uncertainty, variations in the potassium concentration also affect the pH value obtained for the brine. On the other hand, the pH of groundwater remains broadly unconstrained. Therefore, the saturation index of calcite will be calculated for other pH values of the two end fluids. A more acidic brine (pH 4.5) leads to an increasing subsaturation (case B, Fig. 5) due to the more important pH-pCO_2 effect. A more acidic groundwater (pH 6) leads to a similar subsaturation pattern (case C, Fig. 5) due to the fewer

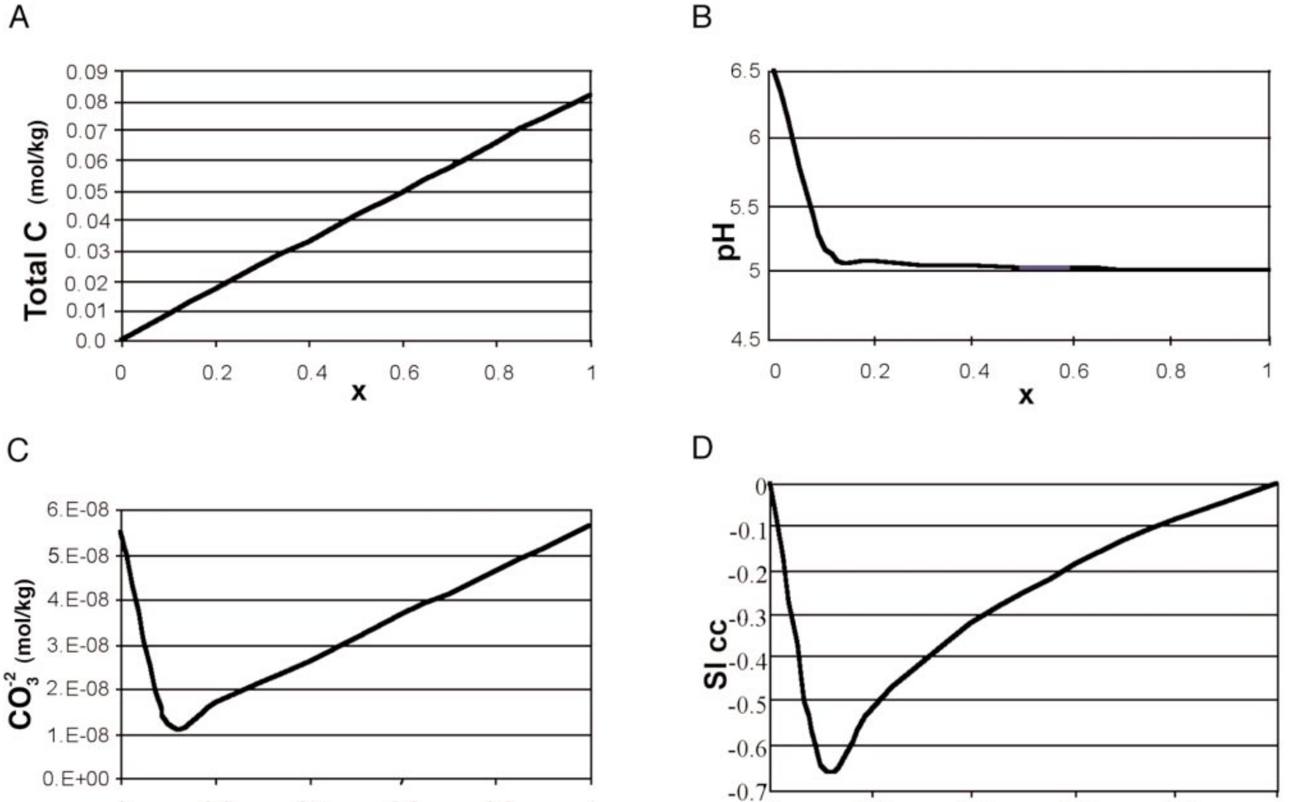

FIGURE 4 **Mixing of two fluids with different pH and pCO_2 (total Ca concentration is 0.05 mol/kg in both end-members). A) Linear variation in total C concentration in the mixture. B) pH variation in the mixture. C) Concentration of CO_3^{2-} in the mixture. D) Saturation index of calcite, which parallels that of CO_3^{2-} concentration since Ca^{2+} concentration is constant (pH- pCO_2 effect).**

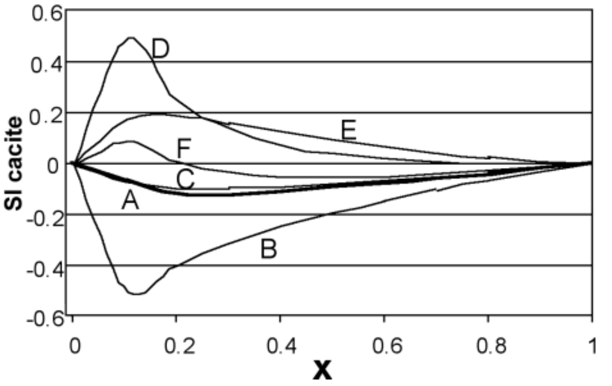

FIGURE 5 **Calcite saturation index of the mixture of a groundwater (left hand side) and a brine (right hand side) of different pH and salinity. A: composition of the end members as case 1 in Table 1; B: pH of 6.5 and 4.5; C: pH of 6 and 5; D: pH of 7 and 5; E: pH of 6.5 and 5.5; F: Cl concentration of 0.25 and 5 mol/kg; Ca concentration of 0.006 and 0.5 mol/kg, respectively.**

differences between groundwater and brine. As expected, for a more basic groundwater (pH 7) or brine (pH 6) there is supersaturation along the entire mixing (case D and E, Fig 5). Finally, a more diluted groundwater can lead to supersaturation and subsaturation (case F, Fig. 5) owing to the increasing role of the algebraic effect.

Therefore, the combination of the different non-linear effects described above leads to trends that are impossible to predict ‘a priori’: calcite subsaturation, supersaturation or both. When both occur, supersaturation takes place in the higher pH terms, which correlate with more diluted solutions (Hanor, 2001), whereas subsaturation predominates in the more acidic and more saline solutions. Henceforth, we will employ a reference case where the effect of mixing is moderate (case A in Fig. 5).

THE EFFECTS OF CHEMICAL REACTIONS

Mixing of fluids with H_2S oxidation

In this model, H_2S carried by the brine is oxidized when mixing with groundwater. The oxidation state of the resulting mixture depends on the amount of H_2S in the brine and on the concentration of oxidant agents in the groundwater. Barnes (1983) proposed $O_{2(aq)}$ as the oxidant agent. However, water from many aquifers lacks detectable oxygen; in such cases, the oxidizing capacity of water is controlled by redox pairs, such as Fe(III)-Fe(II), U(VI)-U(IV), $SO_4{}^{2}$-H_2S, etc. (Grenthe et al., 1992). Owing to the assumed reducing conditions of the groundwater, dissolved oxygen will obviously play no role as an oxidant.

We model the effect of oxidation of H_2S by Fe(III). The total Fe concentration is assumed to be 10^{-7} mol/kg, from the equilibrium with goethite (GW2 in Fig. 1). This concentration is low but it still is a possible oxidant in groundwater. Compared with pure mixing (case A, Fig. 5 or heavy line of Fig. 6, calcite subsaturation increases slightly, but the effect of H_2S oxidation is very minor (Fig. 6, H_2S oxidation). It is interesting to note, however, that this effect is not dependent on Fe concentration or on fO_2 but on pH and H_2S concentration. This is so because the increase in calcite subsaturation is not attributed to H_2S oxidation to SO_4, but to hydrogen sulfide deprotonation (9):

$$H_2S_{(aq)} = H^+ + HS^- . \qquad (9)$$

Since S is only present in the brine and H_2S is the predominant species at the pH of the brine (x=1.0), H_2S acts as a reserve of acidity and reaction (9) releases additional protons to the mixture, increasing the calcite subsaturation.

Mixing of fluids with sulfide precipitation

In this case, the brine is assumed to carry Zn but is sulfur-free (Anderson, 1975). Thus, Zn-sulfide precipitates when mixing with a sulfide-rich groundwater (GW1 in Fig. 1). One consequence of sulfide precipitation is calcite subsaturation via pH decrease (reaction 3). According to our calculations, however, this subsaturation is smaller than that obtained from the pure mixing effect (Fig. 6, H_2S addition), and depends on the brine-groundwater proportions. Where there is an excess of sulfur, i.e., in the groundwater-rich terms of the mixture (x=0.0), the pH decreases less than in the pure mixing case because of the buffering effect of sulfide species. Thus, HS^- is the predominant S species at the pH of the groundwater and the reverse of reaction (9) favors the consumption of hydrogen ions in the alkaline groundwater-rich terms of the mixture, increasing the saturation index of calcite (Fig. 6). Subsaturation of calcite increases at even proportions of S and Zn (at x=0.5 in our example) due to the precipitation of sulfides. Furthermore, in the Zn-rich terms of the mixture the formation of $ZnOH^+$ slightly increases the amount of free H^+ in solution, enhancing the subsaturation of calcite. Higher or lower concentrations of S and Zn in the end-member solutions lead to mixtures with a more or less pronounced effect over the saturation of calcite.

In an alternative hypothesis H_2S could be generated by reduction of SO_4^{2-} supplied by groundwater (GW2) at the expense of the organic matter from the brine (Jackson and Beales, 1967; Anderson, 1975). Unlike the previous case, the mixture becomes less subsaturated, and even supersaturated for some proportions of fluids, as metal sulfide pre-

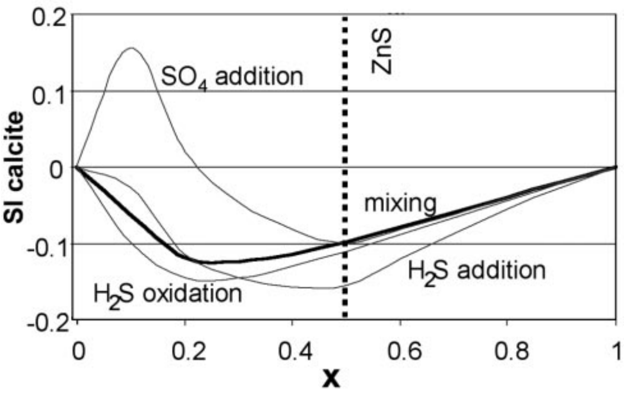

FIGURE 6 **Comparison of the effects of mixing H_2S oxidation, H_2S addition and SO_4^{2-} addition on the calcite saturation index with different mixing proportions between a groundwater (left hand side) and a brine (right hand side). The compositions of the end member fluids are found in Table 1, cases 1, 2, 3 and 4. The vertical dotted line marks the proportions of groundwater and brine where most sphalerite precipitates in cases 3 and 4.**

cipitates (Fig. 6, SO_4 addition). This is due to the proton consumption in the organic matter oxidation reaction (10):

$$CH_4\,(aq) + SO_4^{2-} + 2H^+ = CO_2\,(aq) + 2\,H_2O + H_2S\,. \quad (10)$$

Nothing is known on the kinetic feasibility of this reaction at high temperatures and confined environments. In the Zn-rich terms of the mixture, the H^+ ions freed in the formation of $ZnOH^+$ compensate the ones consumed in reaction (9) with the result that the final pH and subsaturation of the mixture is very similar to that in the pure mixing case.

Gypsum saturation is never reached during the simulations tested. This is in accordance with the scarcity of this mineral in MVT deposits.

CONCLUSIONS

According to our calculations, the mixing of warm solutions has effects on calcite solubility similar to those described by Wigley and Plummer (1976) for low temperature fluids and also to the synergy effects discussed by Mogollón et al. (1999). Three competing effects over calcite saturation could occur simultaneously when mixing two calcite-saturated solutions of high temperature and disparate chemistry. The algebraic effect causes supersaturation of the mixture, and the salinity and the pH-pCO_2 effects result in subsaturation of calcite in the final solution. The combination of these effects could lead to supersaturation or subsaturation.

Our calculations confirm the dissolution of carbonates when a reduced brine mixes with a more diluted and more oxidizing water. This is not attributed to the H_2S oxidation (Barnes, 1983; Hill, 1990), but is essentially due to the mixing effect.

When H_2S is supplied by the groundwater, our results corroborate the hypothesis that sulfide precipitation promotes calcite dissolution (Anderson, 1975). However, they again show that dissolution mainly occurs because of the mixing effect. Moreover, subsaturation increases with respect to the pure mixing only where a sulfide-rich fluid meets a zinc-rich brine. When H_2S is produced from the reduction of sulfate by organic matter, less calcite is dissolved (and sometimes precipitates) compared with the pure mixing case.

Therefore, with respect to carbonate dissolution, mixing is in general more effective than chemical reactivity between the components of the solutions. Mixing can form cavities regardless of H_2S oxidation and sulfide precipitation. Mixing explains the textures that demonstrate the filling of open cavities, and the wide variety of minerals and proportions encountered.

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