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The role of thermochemical sulfate reduction in the origin of Mississippi Valley-type deposits. II. Carbonate–sulfide relationships

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ABSTRACT

The two-dimensional (2D) reactive transport model of Corbella *et al.* [*Min. Deposita* 39 (2004) 344] of the classic 'mixing hypothesis', in which a solution containing reduced sulfur and a solution containing aqueous Zn are mixed, has been extended to the case where one brine contains sulfate rather than reduced sulfur, and H_2S is produced during the mixing process by thermochemical sulfate reduction (TSR), using a possible rate law and experimentally derived rate constants. It is shown that TSR can provide sufficient reduced sulfur to form an ore body in geologically reasonable times, using rate constants in the upper part of the experimental range, in agreement with the results of a constant stirring tank reactor model (Thom & Anderson in press). The results of the 2D model are also compared with the results of titration (zero dimensional) and one-dimensional models, showing that these models fail to adequately show the amount of carbonate precipitation. Although the 2D model qualitatively shows the distribution and amounts of carbonate precipitation and dissolution, these results are quantitatively inaccurate due to several factors that are intrinsically hard to define.

Key words: carbonates, kinetics, MVT, sulfate reduction, TSR

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INTRODUCTION

The relationship between carbonates and sulfides in carbonate-hosted Zn-Pb ore deposits is a complex problem, both in the field, where it is often difficult to establish whether carbonate dissolution or precipitation was or was not related to ore deposition, and in geochemical models, where results can depend critically on the assumptions made and parameters chosen. One such important assumption is the precipitation mechanism, which could depend on a number of factors. Because it is unlikely that metals such as Zn and Pb can be transported in any quantity in sulfide-bearing fluids, the most commonly accepted precipitation mechanism is the addition of sulfide to a metal bearing hydrothermal fluid (the 'mixing hypothesis'). This addition of sulfide might simply occur by mixing a pre-existing sulfide-bearing fluid with the metal-bearing fluid, or it might occur by reduction of sulfate in the metal-bearing fluid itself. It is these two mechanisms which are investigated in this contribution.

Anderson (1983) pointed out that the 'mixing hypothesis' of Beales & Jackson (1966), in which sulfides are precipitated by the mixing of a reduced sulfur-bearing solution and a metal-bearing solution, theoretically results in acid generation which will dissolve carbonate minerals. Anderson & Garven (1987) then illustrated this effect with a titration model calculation in which methane is titrated incrementally into a sulfate and Zn-bearing solution in equilibrium with dolomite and anhydrite at 100°C. This was the first attempt at the derivation of a model describing thermochemical sulfate reduction (TSR). This model illustrated the two main possible consequences for carbonate minerals when sulfate is reduced in a carbonate-dominated environment.

The first possible result is the TSR reaction:

$$SO_4^{2-} + CH_4 = H_2S + CO_3^{2-} + H_2O \qquad (1)$$

In a calcite-saturated environment, this results in calcite precipitation according to:

$$SO_4^{2-} + CH_4 + Ca^{2+} = H_2S + CaCO_3 + H_2O \quad (2)$$

If anhydrite is also present, the calcite will replace anhydrite:

$$CaSO_4 + CH_4 = H_2S + CaCO_3 + H_2O \quad (3)$$

The replacement of anhydrite by calcite is a common observation in sour gas petroleum studies (Worden & Smalley 1996; Worden *et al.* 2000). Dolomite rather than calcite can result in a dolomite environment, where Mg^{2+} is available:

$$2CaSO_4 + 2CH_4 + Mg^{2+} = 2H_2S + CaMg(CO_3)_2 + Ca^{2+} + 2H_2O \quad (4)$$

Equations (2)–(4) are simply variations of the first possibility: carbonate minerals are precipitated.

The second possibility results if the H_2S produced by TSR results in sulfide mineral precipitation. In this case, carbonate minerals are dissolved rather than precipitated. Using Zn^{2+} as an example:

$$SO_4^{2-} + CH_4 + Zn^{2+} = ZnS + H_2CO_3 + H_2O \quad (5)$$

The generation of CO_2 (or H_2CO_3, carbonic acid) results in some carbonate mineral dissolution, though far less than would be dissolved by the simple mixing of aqueous sulfide and metal-bearing solutions:

$$H_2S + Zn^{2+} = ZnS + 2H^+ \quad (6)$$

This was demonstrated by Anderson & Garven (1987), and one obvious conclusion that can be drawn from this fact is that a purely replacement deposit cannot be directly formed by TSR, although TSR might well generate the H_2S responsible for the later precipitation of the metals.

Anderson & Garven (1987) concluded that carbonate and sulfide minerals cannot precipitate together, but as the titration model used had no spatial coordinates, this refers to precipitation together *at the same place*. The aqueous Ca^{2+} generated by carbonate dissolution as a result of reactions (5) or (6) must diffuse, or be carried, away from the site of sulfide precipitation, and in a carbonate-saturated environment, will inevitably reprecipitate somewhere.

A final point about these reactions, mentioned in Thom & Anderson (in press), is that the TSR reaction (1) contains the assumption that the reduced carbon (C^{4-}) in methane is oxidized all the way to C^{4+} in CO_2. This has not been experimentally established. Possibly, the methane is partially oxidized to other (metastable) organic compounds, instead of, or as well as, some CO_2. In the petroleum sour gas environment, at least some CO_2 is produced, as shown by the replacement of anhydrite by calcite, but the MVT situation may be different. The reason that this is important is because TSR combined with sulfide deposition will cause carbonate dissolution only to the extent that CO_2 is produced. If no CO_2 is produced, no carbonate is dissolved, and simultaneous precipitation of carbonate and sulfide at the same place is then theoretically possible.

In this contribution we (i) use the TSR reaction in a reactive transport model in one and two dimensions (assuming complete reaction of CH_4 with CO_2); (ii) compare the amount of sulfide precipitation using reactive transport models with that obtained from the 'constant stirring tank reactor' (CSTR), model discussed in many chemical engineering texts, for example Schmidt (2005, Chapter 3) used in Thom & Anderson (in press); and (iii) show that although the two-dimensional (2D) model is far more informative than the zero-dimensional (0D) and one-dimensional (1D) models in that it shows that carbonate dissolution can occur for two different reasons, and that precipitation and dissolution can happen simultaneously, several factors combine to cast doubt on any quantitative relationship.

MODEL CALCULATIONS

All calculations were carried out using the USGS programs Phreeqc (Parkhurst & Appelo 1999) for titration and 1D transport, and Phast (Parkhurst *et al.* 2004) for 2D transport. Both programs use the databases llnl.dat and pitzer.dat.

Titration model

Anderson & Garven (1987) used a titration model, which has no spatial coordinates and no kinetics. That is, after every increment of methane added to the sulfate and Zn solution, the solution reaches equilibrium. The pH was set initially to 5.5, and though not fixed, did not change greatly throughout the titration. The results conform to those described by Anderson (1983), but it should be realized that, as is common in geochemical modeling, only part of the complete picture was captured. Many variations are possible. For example, if the pH is set at a more basic value such as 7.5 or 8, sulfide precipitation begins at much lower CH_4 concentrations, and in this case carbonate and sphalerite can precipitate together, but only at the very lowest CH_4 and sulfide levels. More serious is the lack of spatial coordinates, which precludes determination of several interesting aspects of sulfide–carbonate mineral relationships, specifically the fact that carbonate precipitation and dissolution might occur simultaneously in different parts of the system. Anderson (1983) predicted that this would occur but titration models cannot demonstrate this spatial relationship.

One-dimensional reactive transport

We have used the box model from Thom & Anderson (in press) for both 1 and 2 dimensional reactive transport

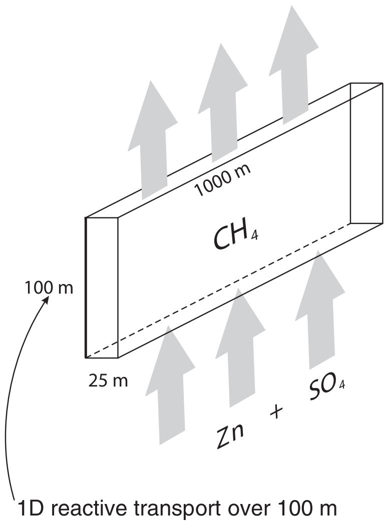

Fig. 1. The box representing a vein from Part I (Thom & Anderson in press). The 100 m height of the box is used in the 1D reactive transport simulations shown in Fig. 2. The 25 × 100 m cross-section has almost the same dimensions as the 26.5 × 110 m 2D section used by Corbella *et al.* (2004) and in Figs. 4, 5 and 6. The methane is assumed to be generated by heating of kerogen in the wall rocks.

modeling. In the box (Fig. 1) methane reduces incoming sulfate, precipitating sulfide, at a rate controlled by TSR, as detailed in Thom & Anderson (in press). In that contribution, the box (representing a vein) was simply a volume, which could have any shape, in which sulfide is deposited. Again, there were no spatial coordinates, the objective being simply to determine the amount of sulfide deposited as a function of rate constant, time and flow parameters. In the 1D reactive transport model, we look at the sulfide deposited over the 100 m vein height (Fig. 1), using various rate constants and flow parameters. Regional groundwater modeling indicates that reasonable specific discharge values in this situation are about 1 to 10 $m^3\ m^{-2}\ year^{-1}$ (Bethke & Marshak 1990; Garven *et al.* 1993; Garven 1995).

The model (in Phreeqc) has 40 cells, each 2.5 m long, initially containing a 0.1 M NaCl solution in equilibrium with dolomite at 150°C. Some simulations had the cells also saturated with anhydrite, better simulating a sour gas environment. A 3 M NaCl solution with 0.01 m Zn (about 650 ppm) and 0.028 m sulfate at the same temperature is introduced into the first cell, equilibrates, and is 'shifted' into the next and succeeding cells, with a time step which controls the simulated fluid velocity. For example, a time step of 0.5 year and a cell length of 2.5 m gives a fluid pore velocity of 2.5/0.5 = 5 m $year^{-1}$, or a specific discharge of 1 $m^3\ m^{-2}\ year^{-1}$ assuming a porosity of 0.2. The number of shifts from one cell to the next controls the total time of fluid flow. In this case, 1000 shifts simulates 1000 × 0.5 year = 500 years. During the (simulated) fluid flow, methane is added to each cell, generating H_2S, at a rate controlled by the TSR data detailed in Thom & Anderson (in press), simulating reduction of the sulfate in the incoming Zn-bearing brine. ZnS precipitates and dolomite dissolves (or precipitates) in each cell as a result, and dispersivity values control the mixing of solutions between cells. The model temperature chosen (150°C) is typical of MVT deposits, and changing it by ± 50°C has little effect. The Zn concentration was chosen rather arbitrarily such that sulfide precipitation would not be 'Zn limited', i.e. that the limiting factor in the amount of ore formation would be the amount of H_2S generated, not the amount of Zn entering the vein. As it turned out, the Zn concentration would need to be much greater, and probably unrealistic, for this to be true in all the cases considered. The sulfate concentration is that of seawater, and the NaCl concentration, although fairly typical, has no effect on the results.

Figure 2 shows some typical results. Note that although the time periods are short (500 years), longer (more

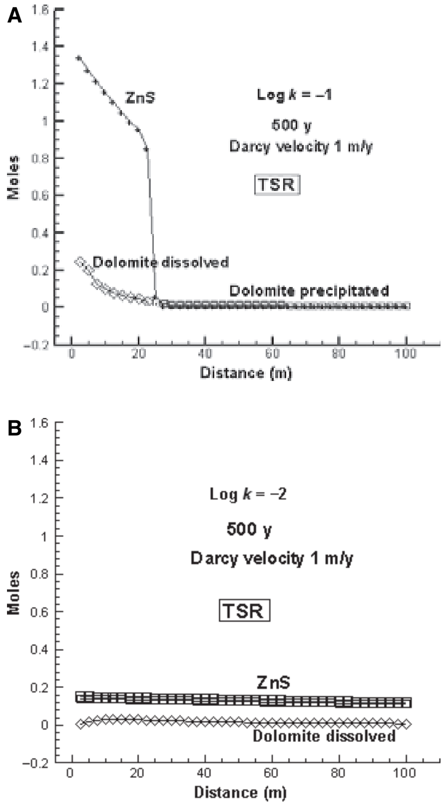

Fig. 2. Sphalerite precipitation and dolomite dissolution and precipitation along the 100 m vein height shown in Fig. 1. Specific discharge 1 $m^3\ m^{-2}\ year^{-1}$ in each case. Duration 500 years. (A) With a TSR rate constant $10^{-1}\ year^{-1}$ all aqueous Zn is precipitated within about 20 m of the flow path. Dolomite is precipitated ahead of the ZnS precipitation due to forward mixing, but is far less than shown by a 2D model. The effect of adding anhydrite is to keep the sulfate level high, increasing the rate of TSR. (B) With a TSR rate constant of $10^{-2}\ year^{-1}$, ZnS precipitation is spread out over the 100 m vein height. No dolomite precipitation is observed.

realistic) times do not change the patterns shown. Realistic mineralization times are approximately 10^4 to 10^6 years (Garven *et al.* 1993; Lewchuk & Symons 1995; Rowan & Goldhaber 1995; Lavery & Barnes 1971). Only the quantities dissolved or precipitated change, and these change in a perfectly linear fashion. Figure 2A shows ZnS precipitating and dolomite dissolving, as in the titration model. The rate constant is 10^{-1} year^{-1} .and the flow is 1 m^3 m^{-2} year^{-1}. With these parameters, the incoming 650 ppm Zn is completely precipitated in the first 20 m along the flow path, showing in a sense how fast TSR really is. A very small amount of dolomite is precipitated in the cells ahead of the precipitated ZnS, due to forward mixing. The pattern shown by ZnS in Fig. 2A is not an ‘advancing wave’ of precipitation, which would extend over the 100 m flowpath given longer durations. Longer durations (i.e., more than 500 years) simply repeat exactly the same pattern, but with greater amounts of ZnS.

Figure 2B shows the effect of changing the rate constant of the TSR reaction from 10^{-1} to 10^{-2} year^{-1}. Slowing the rate of reduction results in sphalerite precipitating over the whole 100 m flow path. Approximately the same effect is achieved by increasing the Darcy velocity from 1 to 10 m^3 m^{-2} year^{-1}. Changing the Zn and/or sulfate concentrations or the rate constant gives predictable results. The dispersivity value used in most runs was 1 m, but changing this to 5 m had little effect.

The results from the 1D transport models are instructive in some senses, but they fail in one important respect. Carbonate precipitation, in addition to dissolution, is only shown using the fastest rate constants, $k = 10^0$ and 10^{-1} year^{-1}. These results give no sense of the importance of carbonate precipitation, as shown by 2D models.

Two-dimensional reactive transport

The 2D calculations take as their starting point the 2D model of Corbella *et al.* (2004). We use all their hydrologic parameters, but use a different transport code and slightly different solution compositions in order to compare with the results in Part I (Thom & Anderson in press). The 2D model is intended to investigate sulfide-carbonate relationships, not to model any particular ore deposit. Nevertheless, the general configuration of the 2D model in which a solution rising along a fault mineralizes one unit in a carbonate sequence does fit aspects of the classic Upper Mississippi Valley district (Heyl *et al.* 1959), as well as the Polaris deposit (Randell & Anderson 1996) and virtually all the Irish deposits (Hitzman & Beaty 1996).

Corbella *et al.* (2004) used a 26.5 × 110 m section in which a 5 M NaCl brine is injected along a fault into a limestone unit containing 1 M NaCl groundwater. Both aqueous solutions are initially saturated with calcite at 150°C. The mixing produces calcite dissolution near the mixing interface, and calcite precipitation farther out. The dissolution is caused by the differing brine chemistries, discussed in the next section. The carbonate precipitation results from the diffusion of the dissolved calcium away from the mixing zone into solutions already saturated with calcite. Corbella *et al.* (2004) then showed that if the limestone pore solution contains H_2S and the introduced solution contains dissolved Zn, sulfide is precipitated where the calcite is dissolved, causing additional calcite dissolution and precipitation. This important contribution shows both the importance of dissolution due to mixing in addition to dissolution due to the acid generated by sulfide deposition, and the importance of carbonate precipitation away from the mixing zone. We extend this work by adding the effect of TSR, which changes the nature of carbonate–sulfide relationships, as mentioned in the introduction.

CALCITE SATURATION INDEX

The mixing of two solutions having different compositions, each in equilibrium with the same carbonate mineral, can result in dissolution or precipitation for several reasons, fully investigated theoretically by Wigley & Plummer (1976) and others. In the present case, the reason is the non-linear dependence of activity coefficients with ionic strength, and if the two solutions are brines, both initially saturated with calcite, the result is dissolution of calcite. This is made clear, as shown by Wigley & Plummer (1976), by calculating the saturation index (SI) of calcite for solutions having compositions intermediate between the two end members. For the case considered by Corbella *et al.* (2004), in which one solution is a 5 M NaCl brine and the other a 1 M NaCl brine, both at 150°C, the result from Phreeqc, using ion-pair speciation and the extended Debye-Hückel (DH) model for activity coefficients, is shown in Fig. 3. This result gives a calcite SI of about –0.4 for a solution having 93% of the 1 M brine. The problem with this is that the extended DH model is notoriously inaccurate at high ionic strengths such as used in this case. An example of this inaccuracy is given by Anderson (2005, p. 458).

An alternative calculation method is to use the Pitzer ion-interaction model, which is accurate to high ionic strengths but at present can only be used in most cases at 25°C. This model has no data for Zn and many other elements, and cannot do redox calculations. The result using this model is also shown in Fig. 3, along with the DH result for 25°C. The minimum SI using the Pitzer model is –0.07 in a solution having 69% of the 1 M brine (called groundwater by Corbella *et al.*). We can conclude only that maximum dissolution will occur in solutions towards the groundwater side of the spectrum, and that using the DH model will greatly over-estimate the amount of

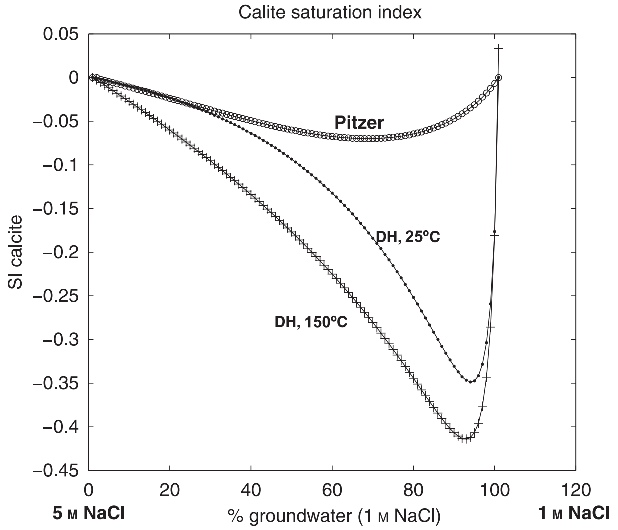

Fig. 3. The saturation index (SI) of calcite on mixing 1 and 5 M NaCl brines, both initially saturated with calcite. All three curves calculated with PHREEQC (Parkhurst & Appelo 1999), using the Pitzer model (at 25°C) and the extended Debye-Hückel (DH) model for activity coefficients. The *x*-axis shows the volume % of the 1 M brine, which is called groundwater.

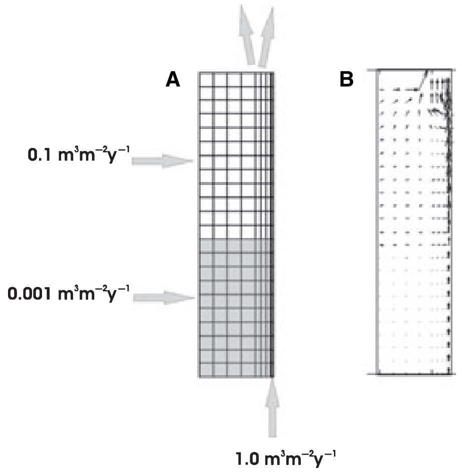

Fig. 4. The 26.5 × 110 m grid used by Corbella *et al.* (2004) and in this work, representing a limestone section. The lower 50 m is relatively impermeable, the upper 60 m permeable. A 0.5 m fault is on the right side. (A) Groundwater containing sulfate flows towards the fault at the rates shown and Zn bearing brine flows rapidly up the fault at 1.0 $m^3\ m^{-2}$ $year^{-1}$. TSR occurs in the limestone during the simulation. Fluid exits from the upper right corner. (B) Vectors proportional to the pore velocities in most simulations.

carbonate dissolution. Using the same input parameters, we find that at 25°C, using the DH activity coefficients results in cells (in the 2D section described below) having from eight to 740 times more calcite dissolved than does the Pitzer formulation. The average over all the cells is a factor of about 108.

A further complication is the fact that, as shown by Rezaei *et al.* (2005), the zone of maximum dissolution is not usually at the minimum of the SI curve, because the interaction between transport processes and chemical reactions significantly affects dissolution patterns. Maximum dissolution will take place close to the 'groundwater' side of Fig. 3, but calculated quantitative relationships between mixing, sulfide precipitation and carbonate dissolution are not likely to be accurate for due to largely unconstrained reaction-transport effects and the poorly defined activity coefficients described earlier.

A final problem is that, as mentioned in the introduction, it is not known to what extent CO_2 is produced by the TSR reaction while it is active in the ore deposition system.

The 2D section

To investigate the effect of TSR in 2D, we have used the same section used by Corbella *et al.* (2004), shown in Fig. 4. This 26.5 × 110 m grid is almost the same size as the 25 × 100 m section of the vein shown in Fig. 1, and used in our previous calculations. The section should be visualized as one-half of a symmetrical pattern, with the fault running up the center. Calculations for both halves are identical, so only one half is shown. Program PHAST (Parkhurst *et al.* 2004) actually requires a 3D grid, so for 2D modeling we used a 26.5 × 110 × 1 m grid.

Various properties of the simulation are shown in Table 1. The lower 50 m is relatively impermeable, the upper 60 m permeable. A 0.5 m fault lies along the right side. Groundwater containing sulfate flows towards the fault and Zn bearing brine flows rapidly up the fault, mixes with the limestone pore water in the permeable zone, and exits from the upper right corner. TSR occurs in the limestone, generating H_2S and precipitating ZnS during the simulation. Solution compositions were initially identical to those used by Corbella *et al.* (2004), but in most of the new simulations reported here the Zn and sulfate

Table 1 Model parameters, from Corbella *et al.* (2004).

	Units	Low *k* limestone	High *k* limestone	Fault
*k*x	m $year^{-1}$	0.18	0.25	500
*k*y	m $year^{-1}$	0.03	0.16	5000
*k*z	m $year^{-1}$	0.03	0.16	500
Porosity		0.1	0.1	0.5
Specific storage	m^{-1}	0	0	0
Long. dispersivity	M	5	5	5
Horiz. dispersivity	M	2.5	2.5	0.5
Vert. dispersivity	M	1	1	1
Flux	$m^3\ m^{-2}\ year^{-1}$	0.001	0.1	1

*k*x and long. dispersivity refer to the length (1000 m); *k*y and horiz. dispersivity refer to the width (25 m); *k*z and vert. dispersivity refer to the height (100 m) (see Fig. 1).

concentrations were changed (increased) to be the same as in our other calculations (Thom & Anderson in press), for comparison.

Program PHAST produces voluminous output in numerous files. A PERL program was written to extract from these files the quantities of carbonate dissolved and precipitated, the ZnS precipitated, and the pH, calcite SI, CO_2 pressure, sulfate and methane concentrations, the proportion of groundwater, and the fluid velocity vector components for each cell in the section, and to format these data for plotting in Matlab. Most simulations were for a flow duration of only 1500 years, because it was found that the pattern of dissolution and precipitation did not change much with longer times, and the quantities were quite linear with time.

Some typical results are shown in Fig. 5. As in the 1D models (Fig. 2) rate constants in the upper part of the experimental range result in virtually all the Zn (0.01 m, or 650 ppm) precipitating within the 100 m flowpath. This is shown in Fig. 5C by the fact that the ZnS contours do not extend to the top of the section. This remains true for even greater Zn concentrations. The percentage of Zn that is precipitated varies from near 100% in these cases to only a few percent for TSR rate constants in the lower part of the range. It is not useful to give these results in more detail until the rate constant and rate law are more definitively established. It is sufficient to establish here that TSR is not particularly slow.

The patterns of calcite precipitation and dissolution and ZnS precipitation are similar but not exactly the same as those shown by Corbella *et al.* (2004), because of the differences in carbonate–sulfide relationships between TSR and the simple mixing of sulfide and metal-bearing solutions that they used. For example Fig. 5B shows a maximum in carbonate precipitation at the groundwater inlet

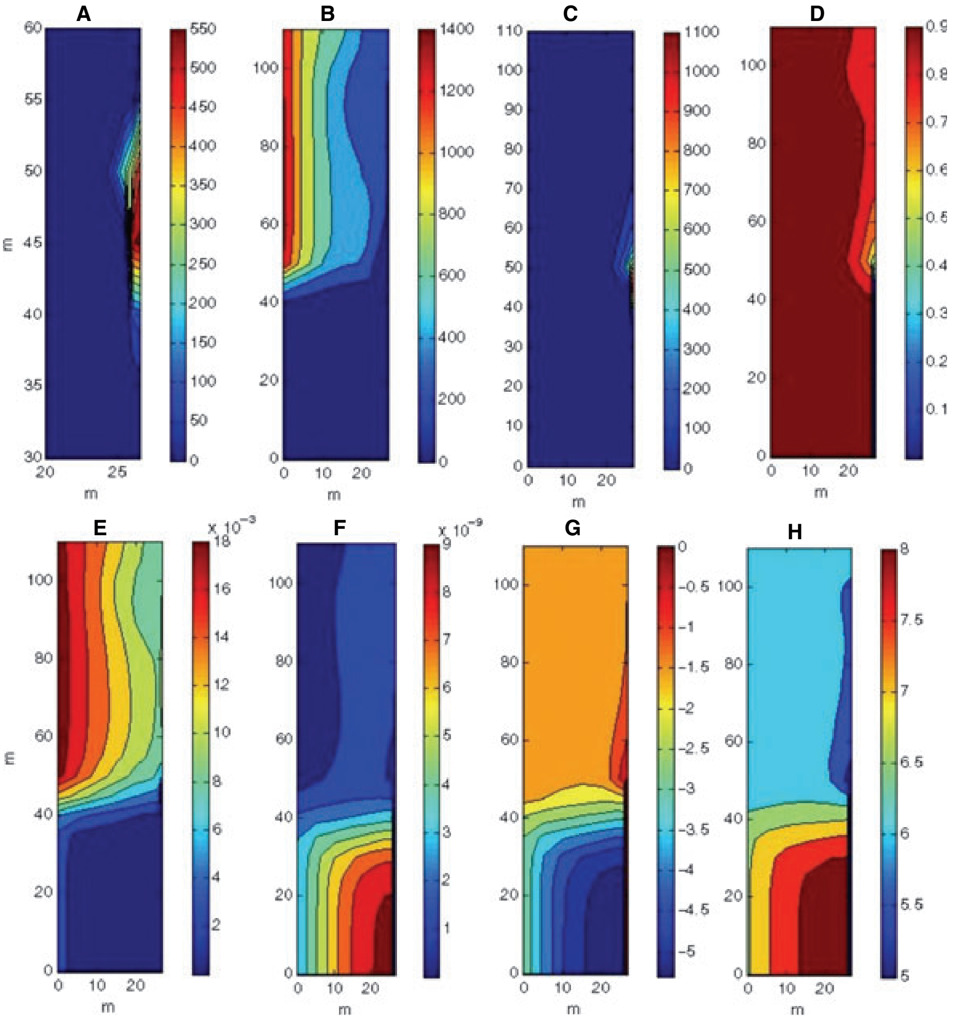

Fig. 5. A 2D section of limestone, as described in the text. ZnS precipitation by thermochemical sulfate reduction in the limestone, rate constant log *k* = –1, duration 1500 years. (A) Moles calcite dissolved per m^3. (B) Moles calcite precipitated per m^3. (C) Moles ZnS precipitated per m^3. (D) Proportion of groundwater. (E) Sulfate molality. (F) Methane molality. (G) $\log(pCO_2)$. (H) pH. Note that (A) shows only part of the section in order to better see the contours.

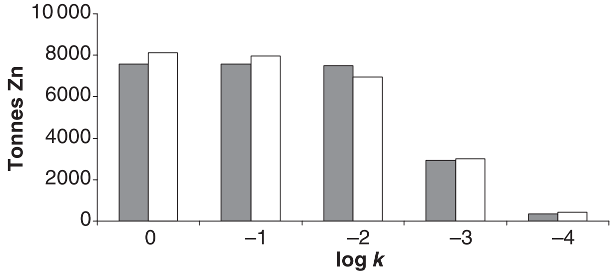

Fig. 6. Comparison of the amount of Zn precipitated (tonnes) in 10 000 years as calculated by the CSTR model (Thom & Anderson, in press; white bars) and by the 2D reactive transport model in this contribution (gray bars) for various possible values of the rate constant for the TSR reaction. Flow parameters shown in Table 1. Tonnes Zn for log $k = 0$ to -2 are about the same because virtually all the incoming Zn is precipitated. For log $k = -3$ and -4, most of the Zn in solution passes through the vein unprecipitated.

side of the section, rather than near the carbonate dissolution zone. This is because in TSR, carbonate precipitation occurs where sulfate is reduced, as long as sulfide is not simultaneously precipitated, as explained in the introduction. In Fig. 5B, most of the carbonate precipitation is due to sulfate reduction, and is maximum, where sulfide precipitation is least. Reprecipitation of dissolved carbonate also occurs, nearer to the zone of sulfide precipitation as shown by Corbella *et al.* (2004), but TSR provides an additional and more effective reason for carbonate precipitation.

The amount of ZnS precipitation is very close to that given by the CSTR model (Thom & Anderson in press) when the same conditions are used (Fig. 6). No general relationship between the amount of ZnS precipitated and the amount of carbonate dissolution could be discerned, but any such relationship would be suspect for the reasons mentioned above (activity coefficient problems, precise TSR rate poorly defined). Generally speaking, maximum carbonate dissolution occurs where the proportion of groundwater is about 60–80% (as shown in Fig. 5A,D), showing that simple mixing, quite apart from sulfide deposition, is an important factor, as shown by Corbella *et al.* (2004). The distribution of several other parameters is also influenced by the mixing pattern.

CONCLUSIONS

- The TSR reaction results in carbonate precipitation if sulfides are not precipitated, and carbonate dissolution if they are.
- The amount of carbonate mineral dissolution during TSR and MVT deposit formation is much less than is produced by mixing of a sulfide solution and a metal-bearing solution (the classic 'mixing hypothesis').
- Carbonate dissolution is also caused by the mixing itself, independent of sulfide precipitation, as shown by Corbella *et al.* (2004).
- The amount of carbonate dissolution and its relationship to the amount of sulfide precipitation cannot be accurately determined at present, because of unknown activity coefficients (only serious in very concentrated solutions), the unknown amount of CO_2 produced by the TSR reaction, and because the interaction between transport processes and chemical reactions significantly affects the dissolution (Rezaei *et al.* 2005).
- Titration and 1D reactive transport models do not adequately represent carbonate precipitation.
- The CSTR model and the 2D reactive transport model give about the same results for the amount of sulfide precipitated by the TSR reaction as a function of time.
- Finally, it is emphasized that these results are based on the present knowledge of the TSR reaction. Much remains to be learned about this reaction.

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REFERENCES

Anderson GM (1983) Some geochemical aspects of the deposition of sulfides in carbonate rocks. In: *International Conference on Mississippi Valley-Type Lead-Zinc Deposits, Proceedings volume*, pp. 61–76. University of Missouri, Rolla, MO.

Anderson GM (ed.) (2005) *Thermodynamics of Natural Systems*, 2nd edn. Cambridge University Press, New York, 648 pp.

Anderson GM, Garven G (1987) Sulfate-sulfide-carbonate associations in Mississippi Valley-type lead-zinc deposits. *Economic Geology*, **82**, 482–88.

Beales FW, Jackson SA (1966) Precipitation of lead-zinc ores in carbonate reservoirs as illustrated by pine point ore field. *Canadian Institute of Mining and Metallurgy Transactions, Sec. B*, B8278–85.

Bethke CM, Marshak S (1990) Brine migrations across North America: the plate tectonics of groundwater. *Annual Review of Earth and Planetary Sciences*, **18**, 287–315.

Corbella M, Ayora C, Cardellach E (2004) Hydrothermal mixing, carbonate dissolution and sulfide precipitation in Mississippi Valley-type deposits. *Mineralium Deposita*, **39**, 344–57.

Garven G, Ge S, Person MA, Sverjensky DA (1993) Genesis of stratabound ore deposits in the midcontinent basins of North America: the role of regional groundwater flow. *American Journal of Science*, **293**, 497–658.

Garven G (1995) Continental-scale groundwater flow and geologic processes. *Annual Review of Earth and Planetary Sciences*, **24**, 89–117.

Heyl AV, Agnew AF, Lyons EJ, Behre CH (1959) The geology of the upper Mississippi Valley zinc-lead district. *USGS Professional Paper*, **309**, 310p.

Hitzman MW, Beaty DW (1996) The Irish Zn-Pb-(Ba-Ag) orefield. Society of Economic Geologists Special Publication No. 4, pp. 112–43.

Lavery NG, Barnes HL (1971) Zinc dispersion in the Wisconsin zinc-lead district. *Economic Geology*, **66**, 226–42.

Lewchuk MT, Symons DTA (1995) Age and duration of Mississippi Valley-type ore-mineralizing events. *Geology*, **23**, 233–6.

Parkhurst DL, Appelo CAJ (1999) *User's Guide to phreeqc (version 2) – a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations.* USGS Water-Resources Investigations Report 99-4259, 312 pp.

Parkhurst DL, Kipp KL, Engesgaard P, Charlton SR (2004) *phast – a program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions.* USGS Techniques and Methods 6-A8, 154 pp.

Randell RN, Anderson GM (1996) *Geology of the Polaris Zn-Pb deposit and surrounding area, Canadian arctic archipelago.* Society of Economic Geologists Special Publication No. 4, pp. 304–19.

Rezaei M, Sanz E, Raeisi E, Ayora C, Vázquez-Suñé E, Carrera B (2005) Reactive transport modeling of calcite dissolution in the fresh-salt water mixing zone. *Journal of Hydrology*, **311**, 282–98.

Rowan EL, Goldhaber MB (1995) Duration of mineralization and fluid flow history of the Upper Mississippi Valley zinc-lead district. *Geology*, **23**, 609–12.

Schmidt LD (2005) *The Engineering of Chemical Reactions*, 2nd edn. Oxford University Press, New York, 618 pp.

Thom J, Anderson GM (2007) The role of thermochemical sulfate reduction in the origin of MVT deposits. I. Experimental results. *Geofluids* (in press).

Wigley TML, Plummer LN (1976) Mixing of carbonate waters. *Geochimica et Cosmochimica Acta*, **40**, 989–95.

Worden RH, Smalley PC (1996) H_2S-producing reactions in deep carbonate gas reservoirs: Khuff formation, Abu Dhabi. *Chemical Geology*, **133**, 157–71.

Worden RH, Smalley PC, Cross MM (2000) The influence of rock fabric and mineralogy on thermochemical sulfate reduction: Khuff formation, Abu Dhabi. *Journal of Sedimentary Research*, **70**, 1210–21.