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Origin of 'exotic' minerals in Mississippi salt dome cap rocks: results of reaction-path modeling

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Abstract—Shallow salt domes in central Mississippi pierce Mesozoic formations hosting regionally extensive metal-rich brines. This association, coupled with the multiple fluid-migration pathways around salt domes, suggests that these brines were the source of Fe and base-metal sulfide, Sr, and Ba minerals in salt dome cap rocks. Fluid inclusions in barite and celestite indicate that the brines had a relatively constant average composition of approximately 200,000 mg/l total dissolved solids, which is similar to present-day oil field brines from central Mississippi. Geochemical reaction-path modeling indicates that the suite of observed cap rock minerals can be produced by alternating periods of biogenic SO_4 reduction with inorganic anhydrite dissolution (or by mixing with seawater). Sulfide-rich portions of cap rock at Hazlehurst salt dome have molar Fe:Pb and Fe:Zn ratios similar to present-day oil field brines, indicating that mixing of brines with abundant amounts of H_2S produced by biogenic SO_4 reduction led to rapid precipitation of virtually all dissolved metals as relatively insoluble sulfide minerals. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

Gulf Coast salt dome cap rocks locally contain a variety of sulfide, sulfate, and carbonate minerals in addition to the common cap rock constituents anhydrite, gypsum, calcite, and native sulfur. These include pyrite and marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), acanthite (Ag_2S), alabandite (MnS), hauerite (MnS_2), barite ($BaSO_4$), celestite ($SrSO_4$), and strontianite ($SrCO_3$; Hanna and Wolf, 1934; Kyle and Price, 1986). Locally, abundances of some of these minerals approach economic concentrations. For example, cap rock at Hockley dome, Texas contains approximately 12 million tons of 4.2% Zn + Pb with significant amounts of associated Ag and barite (Price *et al.*, 1983; Kyle and Price, 1986; Agee, 1990; and Kyle and Posey, 1991). The presence of Fe, Zn, Pb, Mn, Ba, and Sr minerals in cap rocks, the proximity of salt domes to sedimentary brines enriched in the same elements, and fluid-migration pathways provided by salt-piercement structures have led many to propose that oil field brines were the source of the 'exotic' cap rock constituents (Price *et al.*, 1983; Ulrich *et al.*, 1984; Kyle and Price, 1986; Saunders *et al.*, 1988; Kyle and Agee, 1988; Agee, 1990; Hallager *et al.*, 1990 and Kyle and Posey, 1991). Recently, Saunders and Swann (1994) presented fluid inclusion evidence of brine involvement in cap rock development at Hazlehurst salt dome, Mississippi.

In this paper, the oil field brine-cap rock genetic connection is evaluated using geochemical reaction-path modeling. Metal-rich Na-Ca-Cl oil field brines occur throughout central Mississippi (Carpenter *et al.*, 1974; Kharaka *et al.*, 1987; Saunders and Swann, 1990) and representative brine samples were chosen as the initial fluid composition for modeling. Oil field brines in central Mississippi are hosted by Jurassic and Cretaceous formations and typically exceed 100°C, have total dissolved solids (TDS) contents of 200,000 to > 300,000 mg/l (resulting in densities of 1.1–1.25), and contain 1000–2000 mg/l Sr. In addition, where dissolved H_2S contents are low, combined Pb + Zn values of several hundred mg/l are common. The modeling described here tests several hypothesized processes involving the movement of the brine from a deep reservoir into the relatively shallow cap rock setting. These include: (1) cooling of the brine as it moves upward; (2) dissolution of cap rock anhydrite; (3) mixing of brines with seawater; and (4) biogenic SO_4 reduction. Model-precipitated minerals and their relative abundances compare favorably with those in cap rock from 2 well-documented Mississippi salt domes (Tatum and Hazlehurst; Fig. 1), which provides further support for a genetic link between cap rock mineralogy, anhydrite dissolution, *in situ* SO_4 reduction, and oil field brines.

GEOLOGY OF SALT DOME CAP ROCKS

Gulf Coast salt-dome cap rock geology and genesis have been studied extensively in recent years (see Halbouty, 1979; Light *et al.*, 1987; Posey *et al.*, 1987; Prikryl *et al.*, 1988; Kyle and Posey, 1991 for excellent summaries) and only an overview of current ideas is presented here. Where cap rocks occur on salt stocks,

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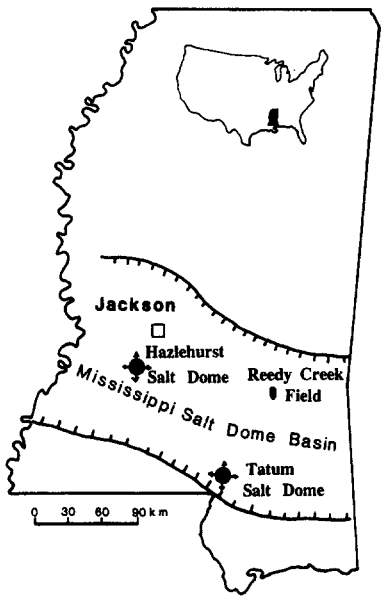


Fig. 1. Map showing location of Hazlehurst and Tatum salt domes and Reedy Creek oil field.

they generally consist of an anhydrite zone up to several hundred feet thick overlain by a thinner calcite zone. Anhydrite typically comprises 1–3% of the salt massif itself and accumulates when halite-undersaturated waters dissolve the upper part of the salt stock. Locally, gypsum derived from the hydration of anhydrite may lie between anhydrite and the overlying calcite zone. Dissolution of the top of the anhydrite zone in the presence of hydrocarbons leads to biogenic SO_4 reduction and calcite precipitation by the following reaction (e.g. Feely and Kulp, 1957):

$$CH_4 + CaSO_4 \rightarrow CaCO_3 + H_2S\ (\text{aq. or gas}) + H_2O \quad (1)$$

H_2S gas generated by the process may escape from the cap rock, *in situ* oxidation of H_2S may produce native sulfur, or dissolved H_2S might react with dissolved metals to precipitate sulfide minerals. The progressive downward dissolution of halite and accumulation of anhydrite residue, and subsequent replacement of anhydrite by calcite, leads to an inverted stratigraphy in both the anhydrite and calcite zones (Ulrich *et al.*, 1984; Posey *et al.*, 1987; Prikryl *et al.*, 1988; Hallager *et al.*, 1990). For example, the earliest-formed anhydrite lies at the top of the anhydrite zone, and the oldest calcite lies at the top of the calcite zone.

Cap rock from the Tatum salt dome consists of an anhydrite zone ~150 m thick, overlain by an irregularly distributed gypsum zone up to 20 m thick, which is overlain by calcite cap rock that is ~30 m thick (Saunders, 1988; Saunders *et al.*, 1988). Calcite cap rock exhibits horizontal banding that is typical of many calcite cap rocks in the Gulf Coast. Banding is defined by alternating dark- and light-colored layers of calcite that formed along the prevailing anhydrite-calcite contact during dissolution of anhydrite coupled with SO_4 reduction (e.g. Posey *et al.*, 1987; Prikryl *et al.*, 1988). Dark bands consist of fine-grained and typically pelletoidal calcite containing minor amounts of Fe, Zn, and Pb sulfides and bitumen. Light-colored bands consist of coarse-grained euhedral calcite that apparently precipitated in open spaces. In the lower 6 m of the calcite cap rock, massive amounts of the Sr minerals celestite and strontianite (Fig. 2) occurs along with minor amounts of barite, primarily in the light-colored bands. Strontium isotopic data and mass balance considerations indicate that the bulk of the Sr in celestite and strontianite from Tatum dome did not originate from cap rock anhydrite (Saunders *et al.*, 1988). Instead, Saunders *et al.* (1988) proposed that the observed $^{87}Sr/^{86}Sr$ ratios in cap rock minerals are consistent with the addition of an external, more radiogenic Sr source such as the Sr-rich oil field brines in Mississippi.

Calcite cap rock at the Hazlehurst salt dome is approximately 30 m thick in the 2 drill holes that fully penetrate it (Swann and Saunders, 1992). The upper half of the cap rock consists of banded calcite similar to Tatum and other Gulf Coast salt domes. Numerous near-vertical banded calcite-sulfide veins are also present in this part of the cap rock (Saunders and Swann, 1994). The lower part of the calcite cap rock consists of horizontal sulfide + calcite bands that alternate with coarse-grained (white) calcite bands. Locally, sulfide-rich zones are > 1 m thick and consist principally of marcasite and pyrite, with minor amounts of sphalerite, galena, pyrrhotite, celestite, barite and strontianite. The sulfate minerals are commonly intergrown with sulfides (Fig. 3). Fluid inclusion data indicate that barite and celestite precipitated at temperatures < ~60°C from brines averaging approximately 200,000 mg/l total dissolved solids (~18% NaCl equiv.; Saunders and Swann, 1994; this study). Fluid inclusion salinities do not vary significantly with depth (Fig. 4), suggesting that brine salinity did not change dramatically over time. Sulfur and C isotopic evidence supports a biogenic origin for both carbonate and sulfide minerals in the calcite cap rock at Hazlehurst dome (Saunders and Swann, 1994).

GEOCHEMICAL MODELING

The computer programs SOLVEQ and CHILLER (Reed, 1982; Spycher and Reed, 1989) were employed to test the hypothesis that water–rock interactions between Fe-Zn-Pb-Sr-Ba-rich brines and principal cap rock minerals can produce the observed suite of exotic cap rock minerals in the 2 Mississippi salt domes. In this study, the chemical evolution of brines along the calcite/anhydrite interface are investigated. In other Gulf Coast salt domes, it appears that brines

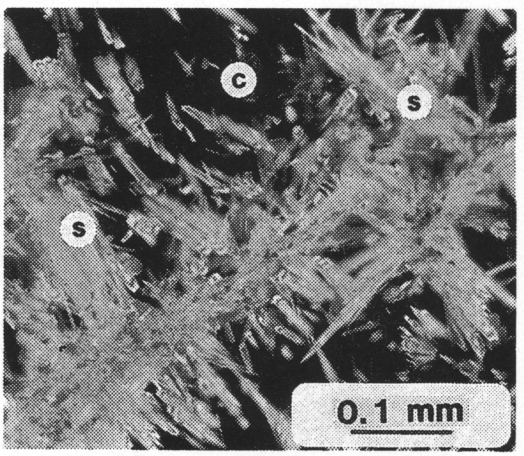


Fig. 2. Photomicrograph (transmitted light) of the intergrowth between strontianite (S) and celestite (C) from the Sr-rich lower part of the calcite cap rock at the Tatum salt dome.

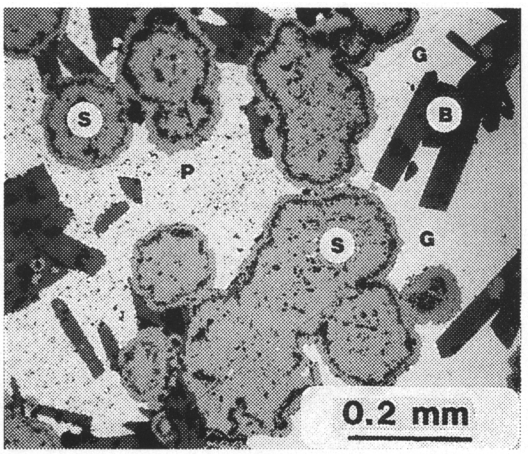


Fig. 3. Photomicrograph (reflected light) of a sulfide-rich zone from the calcite cap rock of the Hazlehurst dome. G = galena, P = pyrite, S = sphalerite, and B = barite.

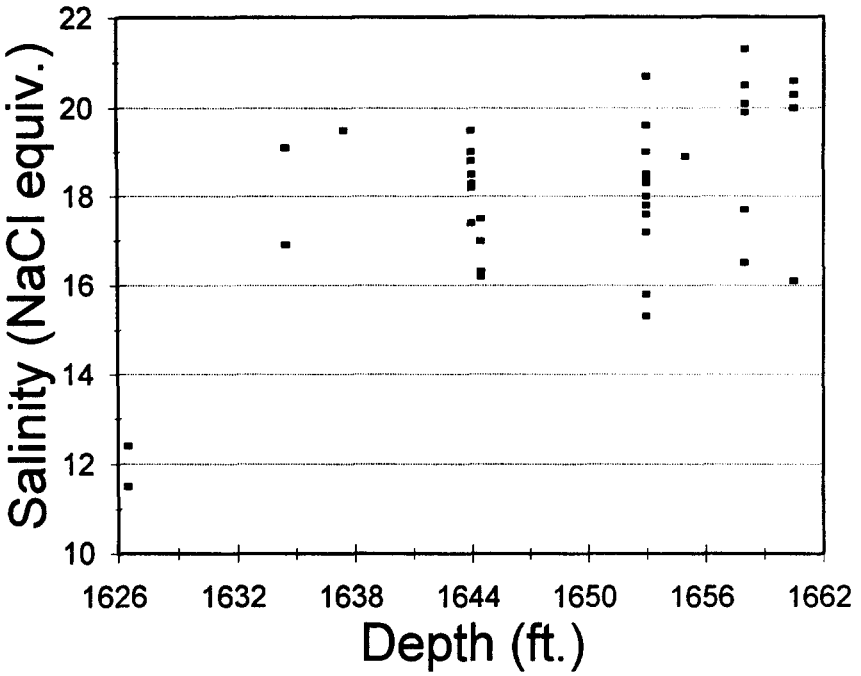


Fig. 4. Plot of fluid inclusion salinities in barite and celestite in calcite cap rock versus depth.

have also moved along the salt/anhydrite contact (Ulrich *et al.*, 1984; Kyle and Price, 1986; Hallager *et al.*, 1990) causing many of the same minerals to precipitate. SOLVEQ is an aqueous speciation program, capable of calculating chemical equilibrium conditions over a wide range of temperature and pressure. CHILLER is an equilibrium reaction-path modeling program applicable to heterogeneous systems; the program solves a series of mass balance and mass action equations by a Newton-Raphson numerical method. CHILLER computes the heterogeneous equilibrium conditions (aqueous speciation and amounts of minerals precipitated) as a reaction progress variable (e.g. composition or temperature) is changed incrementally.

Application of quantitative geochemical models to high ionic strength solutions has many uncertainties, the most important of which is the procedure used to calculate ion activity coefficients. Kharaka *et al.* (1987) presented geochemical modeling results of metal speciation in Mississippi oil field brines using the computer program SOLMINEQ.87 (later updated to the widely used SOLMINEQ.88), which incorporates equations from the Pitzer ion-interaction model to calculate activity coefficients for 9 major ions. The Pitzer ion-interaction model works well in predicting mineral solubilities in brines, but only for the minerals derived from the major ions for which the required parameters have been measured (Kharaka *et al.*, 1988). For minor constituents, an operational approach is taken where activity coefficients calculated for Na^+ and Ca^{2+} from the Pitzer equations serve as an approximation for values for univalent and divalent metals, respectively (e.g. Kharaka *et al.*, 1988). SOLVEQ and CHILLER use the algorithm of Helgeson *et al.* (1981) for calculating activity coefficients for both major and minor constituents on an ion-specific basis. The latter procedure is applicable for solutions with true ionic strengths up to 5 (Helgeson *et al.*, 1981).

A brine from the Reedy Creek Oil Field (Fig. 1), Mississippi (sample 84-MS-11 from Kharaka *et al.*, 1987), was chosen as a starting solution for modeling. This Na-Ca-Cl brine is generally representative of the Zn- and Pb-rich brines in central Mississippi (Fig. 5; Carpenter *et al.*, 1974; Kharaka *et al.*, 1987) and it

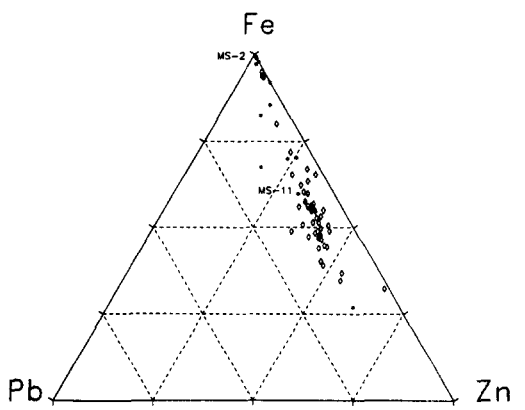


Fig. 5. Plot of normalized molar abundances of Fe, Pb, and Zn from Mississippi oil field brines that contain > 50 mg/l Fe + Pb + Zn. Data is from Carpenter *et al.* (1974) (diamond symbol) and Kharaka *et al.* (1987) (star symbols). Brines used for modeling in this study are identified.

Table 1. Model brine composition, Reedy Creek field, Mississippi

Na	61,700	Fe	465
K	990	Mn	212
Mg	3050	Pb	70.2
Ca	48,600	Zn	243
Sr	1920	Al	0.37
Ba	60	Cd	0.99
B	59	Cu	0.021
SiO_2	27.8		
F	1.5		
Cl	198,000		
Br	2020		
I	17	Temp. (°C)	102
SO_4	64	pH	4.93
HCO_3	206		

Note: data from Kharaka *et al.* (1987). All values for dissolved constituents are reported as mg/l. The value for pH was calculated by Kharaka *et al.* (1987) by adding the coproduced gases back into the solution under reservoir conditions.

contains >300 mg/l Zn + Pb, 1920 mg/l Sr, and 60 mg/l Ba at a reservoir temperature of 102°C (Table 1). The dissolved H_2S content of this sample was less than the lower detection limit of 0.02 mg/l. Therefore, SOLVEQ was used to calculate a dissolved sulfide content of approximately 10^{-7} m by equilibrating the model brine under reservoir conditions with pyrite. Calculated true ionic strength for the model brine is approximately 4.4. The pH of 4.93 for the brine was calculated by Kharaka *et al.* (1987) by adjusting the measured pH to reflect the contribution of the coproduced (gas phase) CO_2 to the solution acidity under reservoir conditions. Measured pHs of Mississippi oil field brines typically range between approximately 4.8 and 6 (Carpenter *et al.*, 1974; Kharaka *et al.*, 1987).

Based on the geologic setting of salt domes, their major cap rock minerals, permeability and porosity of cap rock at the calcite/anhydrite contact, isotopic and fluid inclusion data, and previous proposals for cap-rock-forming hypotheses, the following processes were modeled: (1) cooling of the brine to reflect the upward movement from reservoir to shallow cap rock; (2) dissolution of anhydrite followed by biogenic SO_4 reduction; (3) inorganic dissolution of anhydrite without SO_4 reduction; and (4) seawater mixing.

Cooling

CHILLER was used to cool the model brine from the reservoir temperature of 102° to a temperature of 52°C, which is consistent with maximum fluid inclusion homogenization temperatures in cap-rock barite and celestite at the Hazlehurst salt dome. CHILLER calculations indicate that cooling leads to the precipitation of minor amounts of quartz, barite, and galena. Interestingly, cooling due to pumping of present-day oil field brines pumped from oil-producing formations in central Mississippi commonly leads to the precipitation of Sr-rich barite and galena in well pipe (Carpenter *et al.*, 1974; Saunders and Rowan, 1990). During cooling, solution pH drops slightly to 4.8 as carbonic acid dissociates to a greater extent at lower temperatures. In addition, anhydrite and calcite become more soluble because of their retrograde solubility. Many Gulf Coast salt dome cap rocks show evidence of extensive calcite dissolution (e.g. Prikryl *et al.*, 1988) and modeling indicates that cooled oil field brines could have been one such calcite-dissolving solution.

Anhydrite dissolution with SO_4 reduction

Because the model brine is well undersaturated with respect to anhydrite, movement of the solution into the cap rock along the calcite/anhydrite interface dissolves anhydrite. If hydrocarbons were also present, then biogenic SO_4 reduction would accompany anhydrite dissolution. Production of biogenic dissolved sulfide would lead to precipitation of most metals from the brine because of the low solubility of sulfide minerals. For example, geochemical modeling by Kharaka *et al.* (1987) showed that mixing of a typical metal-rich and sulfide-poor Mississippi oil field brine with a solution containing abundant sulfide leads to the precipitation of virtually all of the contained Zn and Pb.

To model anhydrite dissolution and biogenic SO_4 reduction, equation (1) can be rewritten as:

$$CaSO_4 + CH_4 \rightarrow Ca^{2+} + HCO_3^- + HS^- + H_2O \quad (2)$$

to reflect the probable aqueous species when SO_4 reduction occurs in the circum-neutral pH range. Textural evidence from the Hazlehurst dome (Thomas, 1995) indicates solution pH during SO_4 reduction probably ranged between 5 and 6 based on the pH-dependent precipitation of low-temperature pyrite and marcasite (e.g. Schoonen and Barnes, 1991a, 1991b). Therefore, CHILLER was used to titrate a hypothetical solution having a pH of 7 and containing equimolar concentrations of HS^- and HCO_3, charged balanced by Ca^{2+}, (aqueous products of reaction 2) into the model brine at 52°C. Modeling results (Fig. 6) show the relative amounts of minerals precipitated along with solution composition as a function of reaction progress. Modeling indicates that strontianite, pyrrhotite, galena, sphalerite, alabandite, calcite, and a minor amount of chalcopyrite (not plotted in Fig. 6) precipitate during biogenic SO_4 reduction. Pyrrhotite was selected as the FeS phase to use in the modeling based on textural evidence from the Hazlehurst dome indicating that an amorphous FeS phase recrystallized to form much of the observed pyrite and marcasite (Saunders and Swann, 1994). Model results do not differ significantly if pyrite is allowed to precipitate instead of pyrrhotite. Because most sulfides precipitate early in the modeled reaction,

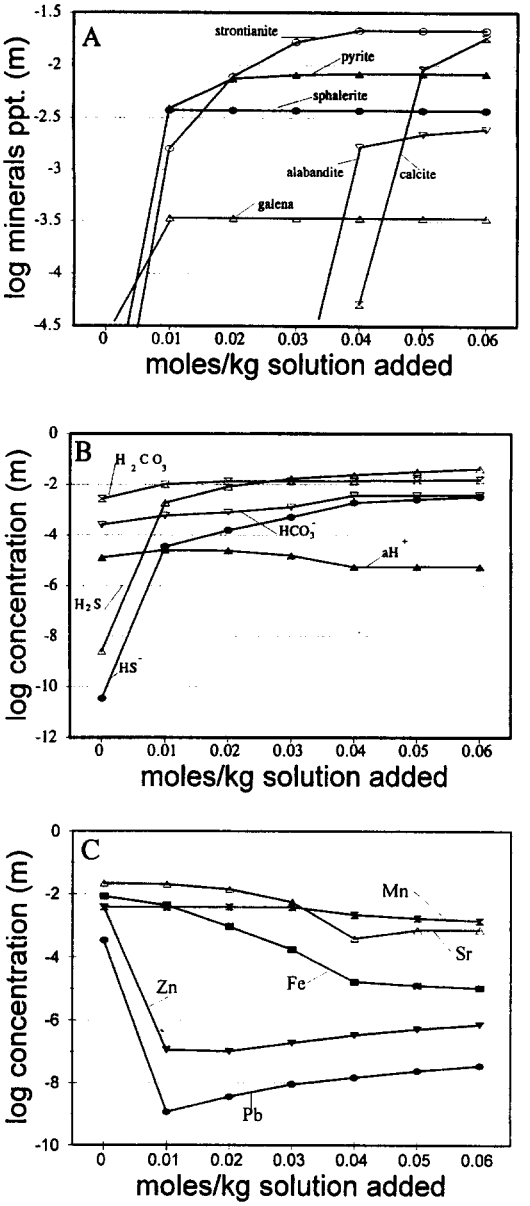


Fig. 6. Model results for biogenic SO_4 reduction showing the effects of mixing increasing amounts of the solution containing the products of anhydrite dissolution and SO_4 reduction (1 mole each of HCO_3^-, HS^-, and Ca^{2+}) with 1 kg of brine 84-MS-11 of Kharaka *et al.* (1987). Reaction progress increases toward the right. (A) Cumulative amounts of minerals precipitated, (B,C) concentration of aqueous species (total molalities). Line segments that plot off the scale of the figures do not have data points plotted where they 'enter' the figure.

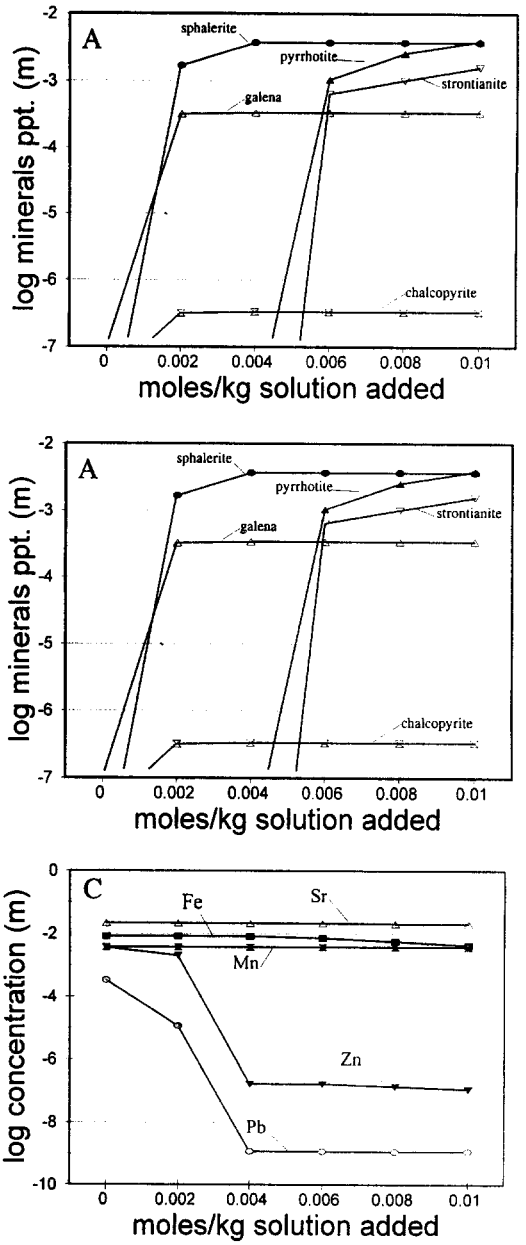


Fig. 7. Details of the early stages of biogenic SO_4 reduction model, corresponding to the 0–0.01 increment of Fig. 6.

an expanded view of model results between the 0 and 0.01 increments are shown in Fig. 7.

Modeling indicates that solution pH initially drops to ~4.6 as sulfide minerals precipitate by reactions similar to:

$$Zn^{2+} + HS^- \rightarrow ZnS + H^+. \quad (3)$$

After the brine is depleted of most of its metals, pH gradually rises as addition of HCO_3 consumes protons to produce H_2CO_3 in this pH range. Ultimately, pH and dissolved CO_3 content rise to the point at which calcite precipitates (pH = ~5.25), where pH begins to drop slightly as a result of the following reaction:

$$Ca^{2+} + HCO_3^- = CaCO_3\ (cal.) + H^+. \quad (4)$$

Note that the precipitation of pyrrhotite and strontianite at a mixing increment of 0.006 causes pH to drop slightly (Fig. 7) by reactions analogous to reactions 4 and 5, respectively.

In the model, dissolved CO_3^{2-} and S^{2-} equilibria, coupled with mineral dissolution and precipitation, buffer pH of the model solution to the 4.60 to 5.25 range.

The calculated mineral assemblage of Fe-Zn-Pb-Mn sulfides, calcite, and strontianite closely approximates the observed minerals present in sulfide-rich portions of Hazlehurst and other Gulf Coast salt domes. Furthermore, the model is also consistent with textural observations that sulfides replace calcite locally, but more commonly appear to have coprecipitated with calcite (Thomas, 1995). The model also predicts the general lack of Ag- and Cu-sulfides in Gulf Coast salt dome cap rock (e.g. Kyle and Saunders, 1995) which is primarily a function of the low Ag and Cu content of the brines.

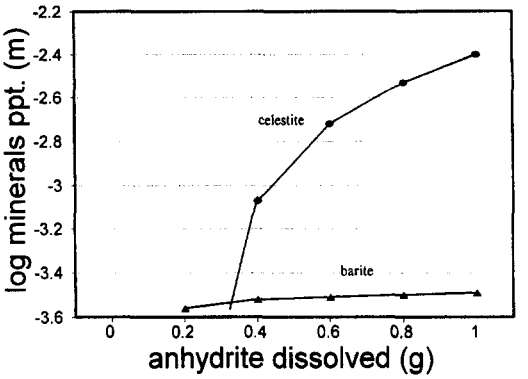


Fig. 8. Model-predicted mineral precipitation as a function of dissolving anhydrite into 1 kg of brine.

Anhydrite dissolution/seawater mixing

One aspect of the cap rock mineralization not accounted for by biogenic SO_4 reduction is the presence of locally abundant barite and celestite. The association of celestite with barite in the Mississippi domes argues against simple cooling as a precipitation mechanism due to the retrograde solubility of celestite (e.g. Saunders *et al.*, 1988). Barite in Gulf Coast salt dome cap rocks typically is isotopically heavy, with $\delta^{34}S$ values generally ranging from +30 to 60% with some values as high as +78‰ (Kyle and Price, 1986; Posey *et al.*, 1987; Saunders and Swann, 1994). This suggests that at least some of the SO_4 incorporated into barite was derived from an isotopically heavy S reservoir remaining after a cycle of biogenic SO_4 reduction (Posey *et al.*, 1987). Modeling with CHILLER indicates that the model brine is undersaturated with respect to anhydrite upon cooling to 52°C, and SO_4 reduction would lead to increased anhydrite undersaturation as SO_4 is consumed if the rate of SO_4 reduction is greater than the rate of anhydrite dissolution. If sulfate reduction ceases or slows dramatically at the anhydrite–calcite interface, then anhydrite dissolution would increase the dissolved SO_4 content. This in turn would lead to the precipitation of the more insoluble SO_4 minerals, barite and celestite, by the common ion effect (Saunders *et al.*, 1988; Saunders, 1992).

To model this possibility, a solution with composition representing a brine actively precipitating sulfides, (0.01 m titration mix; Fig. 6) was chosen for a starting model composition. CHILLER was used to dissolve anhydrite into the brine, which results in the precipitation of significant amounts of barite and then celestite (Fig. 8). Model results compare favorably (including relative abundances) with the observed minerals in the SO_4-rich parts of Tatum and Hazlehurst salt domes. Because salt dome cap rocks probably formed at shallow depths below the sea floor (e.g. Kyle and Posey, 1991) CHILLER was used to model the mixing of the same brine with seawater containing 2710 mg/l SO_4 (e.g. Drever, 1988). Model results yield the same paragenesis of barite followed by celestite.

Sensitivity analysis

Geologic, geochemical, fluid-inclusion, and isotopic evidence indicates that saline formation waters and hydrocarbons entered the cap rock of the Mississippi salt domes studied, leading to at least episodic biogenic SO_4 reduction. The numerical simulations of this process only provide affirmation as to whether the hypothesized process is feasible from a thermodynamic standpoint. The correspondence between the relative amounts of cap rock minerals precipitated in the model and what actually is observed can be viewed as support for the general conceptual model, but does not prove it. Model results can be non-unique. For example, both anhydrite dissolution and mixing with seawater can lead to the precipitation of barite and celestite after a SO_4 reduction cycle. Both of these possibilities can be reconciled with available fluid-inclusion and S isotope data from the Hazlehurst dome. Similarly, we have also modeled proposed processes by Kyle and Agee (1988) and Kyle and Posey (1991) that also may be important in the genesis of cap-rock sulfide mineralization: (1) mixing of metal-rich brines with H_2S produced by *in situ* thermochemical SO_4 reduction in the cap rock at a temperature >100°C; and (2) mixing of brines with external sources of H_2S derived from thermochemical SO_4 reduction deep in the basin. In both cases, model-precipitated sulfide minerals and their relative abundances closely match the biogenic SO_4 reduction scenario at lower temperature. However, we feel that at least at the Hazlehurst dome, biogenic SO_4 reduction is most consistent with isotopic and fluid-inclusion evidence. Hence, we have chosen to present the numerical modeling results based on this process.

The principal adjustable parameter in our model is the brine composition. A representative Zn- and Pb-rich brine was chosen (Fig. 5) primarily to test the hypothesis that such a brine could account for the Pb- and Zn-rich zones of the cap rock at the Hazlehurst dome. However, Fe sulfide minerals are more abundant throughout most of the sulfide-rich cap rock. Therefore, we chose an Fe-rich brine (Fig. 5 Kharaka

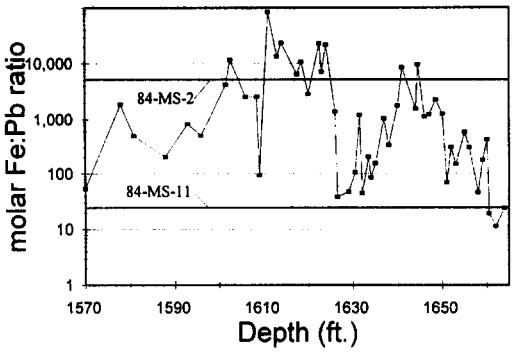


Fig. 9. Plot of molar Fe:Pb ratios of massive sulfide samples from calcite cap rock core. Also shown are the molar Fe:Pb ratios for the 2 brines used in reaction-path modeling.

et al. (1987) sample 84-MS-2) and re-ran the biogenic SO_4-reduction modeling schemes discussed above. Results were very similar, with the exception that Fe sulfides were much more abundant than when the Zn + Pb-rich brine was used in the model.

This study demonstrates a general correspondence between brine composition, model-precipitated minerals and elemental abundances (e.g. Fe, Pb, and Zn), and observed composition of cap rock. For example molar Fe:Pb and Fe:Zn ratios of the 2 brines used in the modeling (Figs 9 and 10, respectively) essentially bracket the observed ranges of these ratios in the cap rock core. That the sulfide-rich portions of the cap rock can reflect the composition of the metal-rich brines involved in its genesis indicates that there had to have been excess H_2S in the system, so that *all* of the dissolved metals are precipitated.

SUMMARY AND CONCLUSIONS

Geochemical modeling shows that metal-rich oil field brines are undersaturated with respect to both halite and anhydrite. This indicates that similar formation waters could have played an active role in calcite cap rock formation. More dilute solutions such as groundwater or seawater generally are considered the principal agent in anhydrite cap rock genesis (e.g. Halbouty, 1979), although any halite undersaturated solution could have been important (e.g. Posey *et al.*, 1987). Geochemical modeling suggests that simple mixing with seawater or the inorganic dissolution of anhydrite by brines containing Ba and Sr will lead to barite and celestite precipitation. Modeling also indicates that anhydrite dissolution by metal-rich brines, coupled with biogenic SO_4 reduction, can lead to the precipitation of Fe- and base-metal sulfide minerals, calcite and strontianite. The correspondence of model-precipitated minerals to those in the 2 Mississippi salt domes strongly implicates metal-rich brines as the source of exotic cap rock minerals. Furthermore, modeling supports interpretations from textural observations that biogenic SO_4 reduction must have occurred episodically during cap rock formation.

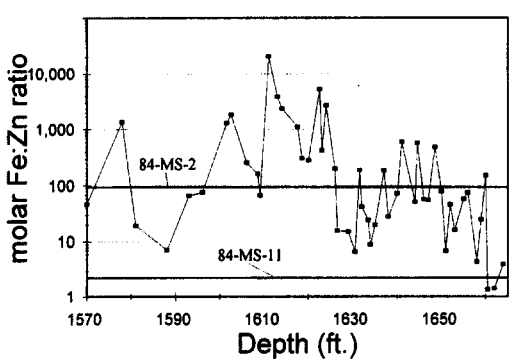


Fig. 10. Plot of molar Fe:Zn ratios of massive sulfide samples from calcite cap rock core. Also shown are the molar Fe:Zn ratios for the 2 brines used in reaction-path modeling.

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REFERENCES

Agee W. N., Jr (1990) Relation of metal sulfide mineralization to anhydrite cap rock formation at Hockley salt dome, Harris County, Texas, Unpub. M. Sc. thesis, Univ. Texas. 255.

Carpenter A. B., Trout M. L. and Pickett E. E. (1974) Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in central Mississippi. *Econ. Geol.* **69**, 1191–1206.

Drever J. I. (1988) *Geochemistry of Natural Waters* (2nd edn). Prentice-Hall, Englewood Cliffs, NJ.

Feely H. W. and Kulp J. L. (1957) Origin of Gulf Coast salt-dome sulphur deposits. *AAPG Bull.* **41**, 1802–1853.

Halbouty M. F. (1979) *Salt Domes, Gulf Region, United States and Mexico* (2nd edn). Gulf Publishing Co., Houston.

Hallager W. S., Ulrich M. R., Kyle J. R., Price P. E. and Gose W. A. (1990) Evidence for episodic basin dewatering in salt-dome cap rocks. *Geology* **18**, 716–719.

Hanna M. A. and Wolf A. G. (1934) Texas and Louisiana salt-dome caprock minerals. *AAPG Bull.* **18**, 212–225.

Helgeson H. C., Kirkham D. H. and Flowers G. C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressure and temperatures. IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 Kb. *Am. J. Sci.* **281**, 1249–1516.

Kharaka Y. K., Maest A. S., Carothers W. W., Law L. M., Lamothe P. J. and Fries T. L. (1987) Geochemistry of metal-rich brines from central Mississippi Salt Dome Basin, USA. *Appl. Geochem.* **2**, 543–561.

Kharaka Y. K., Gunter W. D., Aggarwaal P. K., Perkins E.

H. and DeBraal J. D. (1988) SOLMINEQ.88: a computer program for geochemical modeling of water-rock interactions. U.S. Geological Survey Water Res. Inv. Rept., **88-4227**, 420.

Kyle J. R. and Price P. E. (1986) Metallic sulphide mineralization in salt-dome caprocks Gulf Coast, USA . *Instit. Mining Metall. Trans.* **95**, B6–B16.

Kyle J. R. and Agee W. N. (1988) Evolution of metal ratios and $\delta^{34}S$ composition of sulfide mineralization during anhydrite cap rock formation Hockley Dome, Texas, USA . *Chem. Geol.* **74**, 37–56.

Kyle J. R. and Posey H. H. (1991) Halokinesis, cap rock development, and salt dome mineral resources. In *Evaporites, Petroleum, and Mineral Resources* (ed. J. L. Melvin), pp. 413–474. Elsevier, New York.

Kyle J. R. and Saunders J. A. (1995) Metallic mineralization in the Gulf Coast Basin of southern North America. In *Proc. Int. Conf. on Carbonate-Hosted Lead-Zinc Deposits, St Louis, MO*, pp. 167–170.

Light M. P. R., Posey H. H., Kyle J. R. and Price P. E. (1987) Integrated hydrothermal model for the Texas Gulf Coast Basin; origins of geopressured brines and lead-zinc, uranium, hydrocarbon, and caprock deposits. In *Dynamical Geology of Salt Domes and Related Structures* (eds I. Lerche and J. J. O'Brien), pp. 787–830. Academic Press, Austin, TX.

Posey H. H., Price P. E. and Kyle J. R. (1987) Mixed carbon sources for calcite cap rocks of Gulf Coast Salt Domes. In *Dynamical Geology of Salt Domes and Related Structures* (eds I. Lerche and J. J. O'Brien), pp. 593–630. Academic Press, Austin, TX.

Price P. E., Kyle J. R. and Wessel G. R. (1983) Salt dome related lead-zinc deposits. In *Proc. Int. Conf. on Mississippi Valley Type Lead-Zinc Deposits, University of Missouri, Rolla, MO* (eds G. Kisvarsanyi, S. K. Grant, W. P. Pratt and J. W. Koenig), pp. 558–571.

Prikryl J. D., Posey H. H. and Kyle J. R. (1988) A petrographic and geochemical model for the origin of calcite cap rock at Damon Mound salt dome Texas. *Chem. Geol.* **74**, 67–98.

Reed M. H. (1982) Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases, and an aqueous phase. *Geochim. Cosmochim. Acta* **46**, 513–528.

Saunders J. A. (1988) Pb-Zn-Sr mineralization in limestone caprock, Tatum salt dome Mississippi. *Trans. Gulf Coast Assoc. Geol. Soc.* **38**, 569–576.

Saunders J. A. (1992) Geochemical modeling of salt dome cap rock-brine reactions. In *Proc. Int. Symp. on Water-Rock Interaction, Park City, Utah*, pp. 1121–1124.

Saunders J. A. and Rowan E. L. (1990) Mineralogy and geochemistry of metallic well scale, Raleigh and Boykin Church oil fields Mississippi, USA. *Instit. Mining Metall. Trans.* **99**, B54–B58.

Saunders J. A. and Swann C. T. (1990) Trace metal content of Mississippi oil field brines. *J. Geochem. Explor.* **37**, 171–183.

Saunders J. A. and Swann C. T. (1994) Mineralogy and geochemistry of cap rock Zn-Pb-Sr-Ba mineralization at Hazlehurst salt dome Mississippi. *Econ. Geol.* **89**, 381–390.

Saunders J. A., Prikryl J. D. and Posey H. H. (1988) Mineralogic and isotopic constraints on the origin of Sr-rich caprock Tatum salt dome, Mississippi, USA. *Chem. Geol.* **74**, 137–152.

Schoonen M. A. A. and Barnes H. L. (1991a) Reactions forming pyrite and marcasite from solution: I. Nucleation of FeS_2 below 100°C. *Geochim. Cosmochim. Acta* **55**, 1496–1504.

Schoonen M. A. A. and Barnes H. L. (1991b) Reactions forming pyrite and marcasite from solution: II. Via FeS precursors below 100°C. *Geochim. Cosmochim. Acta* **55**, 1505–1515.

Spycher N. F. and Reed M. H. (1989) Evolution of a Broadlands-type epithermal ore fluid along alternative paths: implications for the transport and deposition of base, precious, and volatile metals. *Econ. Geol.* **84**, 328–359.

Swann C. T. and Saunders J. A. (1992) Cap rock geology of Hazlehurst salt dome, Copiah County Mississippi. *Trans. Gulf Coast Assoc. Geol. Soc.* **42**, 697–705.

Thomas R. C. (1995) Geochemistry and genesis of sulfide-rich calcite cap rock at Hazlehurst salt dome, Copiah County, Mississippi. Unpubl. M. Sc. thesis, Auburn University, 1995, 340.

Ulrich M. R., Kyle J. R. and Price P. E. (1984) Metallic sulfide deposits in the Winnfield salt dome, Louisiana: evidence for episodic introduction of metalliferous brines during cap rock formation. *Trans. Gulf Coast Assoc. Geol. Soc.* **34**, 435–442.