Transport of Pb and Zn by carboxylate complexes in basin ore fluids and related petroleum-field brines at 100 °C: the influence of pH and oxygen fugacity

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It is well established through field observations, experiments, and chemical models that oxidation (redox) state and pH exert a strong influence on the speciation of dissolved components and the solubility of minerals in hydrothermal fluids. log $f_{O_2}$–pH diagrams were used to depict the influence of oxygen fugacity and pH on monocarboxylate- and dicarboxylate-transport of Pb and Zn in low-temperature (100 °C) hydrothermal ore fluids that are related to diagenetic processes in deep sedimentary basins, and allow a first-order comparison of Pb and Zn transport among proposed model fluids for Mississippi Valley-type (MVT) and red-bed related base metal (RBRBM) deposits in terms of their approximate pH and $f_{O_2}$ conditions. To construct these diagrams, total Pb and Zn concentrations and Pb and Zn speciation were calculated as a function of log $f_{O_2}$ and pH for a composite ore-brine with concentrations of major elements, total sulfur, and total carbonate that approximate the composition of MVT and RBRBM model ore fluids and modern basinal brines. In addition to acetate and malonate complexation, complexes involving the ligands Cl$^-$, HS$^-$, H$_2$S, and OH$^-$ were included in the model for calculated total metal concentration and metal speciation. Also, in the model, Zn and Pb are competing with the common-rock forming metals Ca, Mg, Na, Fe, and Al for the same ligands. Calculated total Pb concentration and calculated total Zn concentration are constrained by galena and sphalerite solubility, respectively. Isotherms, in log $f_{O_2}$–pH space, of the concentration of Pb and concentration of Zn in carboxylate (acetate + malonate) complexes illustrate that the oxidized model fluids of T. H. Giordano (in Organic Acids in Geological Processes, ed. E. D. Pittman and M. D. Lewan, Springer-Verlag, New York, 1994, pp. 319–354) and G. M. Anderson (Econ. Geol., 1975, 70, 937–942) are capable of transporting sufficient amounts of Pb (up to 10 ppm) and Zn (up to 100 ppm) in the form of carboxylate complexes to form economic deposits of these metals. On the other hand, the reduced ore fluid models of D. A. Sverjensky (Econ. Geol., 1984, 79, 23–37) and T. H. Giordano and H. L. Barnes (Econ. Geol., 1981, 76, 2200–2211) can at best transport amounts of Pb and Zn, as carboxylate complexes, that are many orders of magnitude below the 1 to 10 ppm minimum required to form economic deposits. Lead and zinc speciation (mol% of total Pb or Zn) in the model ore fluid was calculated at specific log $f_{O_2}$–pH conditions along the 100, 0.01, and 0.001 ppm total Pb and total Zn isopleths. Along the 100 ppm isopleth conditions are oxidized ($\Sigma SO_4 \gg \Sigma H_2S$) with Pb and Zn predominantly in the form of chloride complexes under acid to mildly alkaline conditions (pH from 3 to approximately 7.5), while hydroxide complexes dominate Pb and Zn speciation under more alkaline conditions. Sulfide complexes are insignificant under these oxidized conditions. For more reduced conditions along the 0.01 and 0.001 ppm isopleths chloride complexes dominate Pb and Zn speciation in the SO$_4^{2-}$ field and near the SO$_4^{2-}$–sulfur boundary from pH $= 4$ to approximately 7.5, while hydroxide complexes dominate Pb and Zn speciation under alkaline conditions above pH $= 7.5$ in the SO$_4^{2-}$ field. In the most reduced fluids ($\Sigma H_2S \gg \Sigma SO_4$) along the 0.01 and 0.001 isopleths, sulfide complexes account for almost 100% of the Pb and Zn in the model fluid. Acetate (monocarboxylate) complexation is significant only under conditions of chloride and hydroxide complex dominance and its effect is maximized in the pH range 3 to 7, where it complexes 2 to 2.6% of the total Pb and 1 to 1.25% of the total Zn. Malonate (dicarboxylate) complexes are insignificant along all isopleths. The speciation results from this study show that deep formation waters characterized by temperatures near 100 °C, high oxidation states and $\Sigma H_2S < 0.03$ mg L$^{-1}$, high chlorinities ($\sim 100 000$ mg L$^{-1}$), and high but reasonable concentrations of carboxylate anions can mobilize up to 3% of the total Pb and up to 1.3% of the total Zn as carboxylate complexes. Furthermore, these percentages, under the most favorable conditions, correspond to approximately 1 to 100 ppm of these metals in solution; concentrations that are adequate to form economic deposits of these metals. However, the field evidence suggests that all of these optimum conditions for carboxylate complexation are rarely met at the same time. A comparison of the composite ore fluid compositions from this study and modern brine data shows that the ore brines, corresponding to log $f_{O_2}$–pH conditions based on the Anderson (1975) and Giordano (1994) model fluids, are similar in many respects to modern, high trace-metal petroleum-field brines. The principal differences between modern high trace-metal brines and the composite ore fluids of Anderson (1975) and Giordano (1994) relate to their carboxylate anion content. The reported concentrations of monocarboxylate anions ($\Sigma$ mono$\chi$) and dicarboxylate anions ($\Sigma$ dic$\chi$) in high trace-metal petroleum-field brines (less than 1 to 300 mg L$^{-1}$ and less than 1 mg L$^{-1}$, respectively) are significantly lower than the concentrations assumed in the modelled brines of this study.
Introduction

It is well established through field observations, experiments, and chemical models that oxidation (redox) state and pH exert a strong influence on the speciation of dissolved components and the solubility of minerals in hydrothermal fluids. These parameters are also known to act as major constraints on the stability of specific minerals and mineral assemblages in hydrothermal systems and to control sulfur and carbon isotope systematics in these systems. Of particular interest to this study is the influence of pH and redox state on the speciation of metals, ligands, and metal complexes. For example, in the model presented below, zinc monocarboxylate, as represented by the reaction

\[ \text{Zn}^{2+} + \text{CH}_3\text{COO}^- \rightarrow \text{Zn}(\text{CH}_3\text{COO})^+ \]

directly influences by pH through the control of acetate activity by protonation,

\[ \text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} \]  

(acetate)

and the control of \( \text{Zn}^{2+} \) activity by sphalerite solubility,

\[ \text{ZnS}(s) + \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{HS}^- \]  

(sphalerite)

The oxygen fugacity indirectly affects reaction (1) because \( \text{HS}^- \) in reaction (3) is constrained, assuming constant total dissolved sulfur, constant pH, and equilibrium, by the \( \text{SO}_4^{2-} / \text{H}^+ \) ratio of the fluid through the reaction,

\[ \text{HS}^- + 2\text{O}_2(g) \rightarrow \text{SO}_4^{2-} + \text{H}^+ \]

and corresponding mass action condition at equilibrium:

\[ K = \frac{[\text{SO}_4^{2-}][\text{H}^+]}{[\text{HS}^-][\text{O}_2(g)]} \]

In eqn. (5), the bracketed species represent the activity of the enclosed species and \( f_o2 \) is the fugacity of oxygen gas in equilibrium with the fluid. It has been suggested (cf. Shock,1,3 Helgeson et al.4) that dissolved acetate is coupled to dissolved carbonate in basinal fluids via metastable redox equilibria including the oxidation of acetate by molecular oxygen,

\[ \text{CH}_3\text{COO}^- + 2\text{O}_2(g) \rightarrow 2\text{HCO}_3^- + \text{H}^+ \]

This type of metastable link between carboxylate species and carbonate is not assumed in the model described below. In this model total acetate and total malonate concentrations are independent of total carbonate.

Oxygen fugacity (or activity) is the most commonly used redox variable for describing the oxidation state of hydrothermal systems. Its common use stems from the convenience of writing many hydrothermal reactions in terms of oxygen gas as a reactant or product and the generally close approach to (or actual attainment of) stable or metastable equilibrium under hydrothermal conditions. Consequently, \( f_o2-p\text{H} \) (or \( a_o2-p\text{H} \)) diagrams have become the most widely used approach to illustrate the combined effects of \( p\text{H} \) and redox state in the control of hydrothermal aqueous speciation and related phase equilibria (Barnes and Kullerud,2 Barnes and Czamanske,2 Ripley and Ohimoto,3 Henley et al.,4 McPhail,5 Wood6). These diagrams can also be employed to graphically represent aqueous carbon and sulfur isotope systematics (Ohimoto,11 Ohimoto and Rye,12 Zhang13) and organic matter composition (Helgeson et al.,4 Gize14) under hydrothermal conditions. In addition to \( f_o2-p\text{H} \) diagrams, other graphical depictions of hydrothermal redox dependency are used, including: (a) plots in log (\( \Sigma\text{SO}_4/\Sigma\text{H}_2\text{S} \))–pH and log (\( \Sigma\text{SO}_4/ \Sigma\text{H}_2\text{S} \))–T space (Ripley and Ohimoto,7,15 Ahmad et al.,16 Ohimoto and Goldhaber,17), (b) log \( f_o2-T \) and log \( f_s2-1/T \) diagrams (Ripley and Ohimoto,15 Ohimoto et al.,18 Henley et al.19), (c) log \( f_o2-T \), log \( f_s2-1/T \), and log \( (f_{\text{H}_2\text{S}/f_o2})-T \) diagrams (Ripley and Ohimoto,15 Ohimoto and Rye,12 Eugster,19 Helgeson et al.,2 Ohimoto and Goldhaber,17 Giggenbach,20 Cooke et al.,21 Wood and Samson22), (d) plots in \( p\text{H} \)-pe–pH space (Rose,23,24 Wintsch,25 Henley et al.,26 Pound et al.,26 Pourbaix and Pourbaix27), (e) log \( f_s2-T \) diagrams (Shock3), and (f) the activity diagrams log \( a_o2 \)–log \( d\text{CO}_3 \) (Helgeson et al.), log \( f_o2- \log \text{aqS} \) (Kettler et al.28), log \( d\text{SO}_4-\log \text{aqS} \) (Ohimoto et al.19), and log \( f_o2- \log f_s2 \) (Barton et al.,29 Casadevall and Ohimoto,30 Ohimoto et al.,31 Henley et al.,32 Eugster,19 Sverjensky,31,32 Ahmad et al.19).

Over the past forty years these diagrams, particularly log \( f_o2-p\text{H} \) diagrams, have been used to investigate transport and deposition mechanism of metals in hydrothermal ore fluids. In the majority of these studies, the principal focus is on inorganic complexation mechanisms that mobilize metals in solution and associated processes that cause complex destabilization and concomitant ore deposition. Although a large number of inorganic ligands are known to be complexing agents in hydrothermal ore fluids, inorganic transport and deposition processes have been commonly evaluated using concentration contours of metal complexes involving these ligands in log \( f_o2-p\text{H} \) space. This approach has been particularly fruitful in developing or evaluating genetic models for a wide variety of hydrothermal deposit-types, including mercury deposits (Wells and Gliorso,33 Barnes and Seward,34 Fein and Williams-Jones35), Mississippi Valley-type (MVT) deposits (Anderson36,37).
Giordano and Barnes,39 Barnes,40 Sverjensky41), red-bed related base metal (RBBRM) deposits (Sverjensky31,32), McArthur-type and Selwyn-type sedex deposits (Cooke et al.42), porphyry copper deposits (Cerar and Barnes43), gold and silver deposits (Barton et al.44, Casadevall and Ohmoto,45 Ahmad et al.46, Gammons and Williams-Jones47), and the special category of the more exotic metals including the platinum group elements (Mountain and Wood,48 Wood et al.49, Gammons et al.50).

Although inorganic transport mechanisms adequately account for the genesis of many medium- and high-temperature hydrothermal deposits (e.g., porphyry Cu–Mo–W deposits; skarn deposits; and epithermal base metal, Hg, Au, and Ag deposits) it is less certain that such mechanisms can fully account for most lower-temperature hydrothermal deposits formed in the 50 to 200 °C temperature range, especially those deposits intimately associated with organic matter and formed by basinal diagenetic processes (e.g., MVT and RBBRM deposits). As a means of addressing metal transport in these lower-temperature hydrothermal ore systems, alternative complexing mechanisms have been tested including organic transport, involving transport of metals via organic ligands in the form of metal-organic complexes (cf. Giordano and Barnes,49 Giordano,47 Drumm and Palmer,48 Manning,49 Hennet et al.,50 Giordano and Khara,51 Sicree and Barnes,52 Giordano53) and via pressure-sensitive species such as metal-thiocarbonate complexes (Hennet et al.54). Furthermore, many epithermal precious metal and mercury deposits contain organic matter with paragenetic relationships closely related to the timing of ore-formation. This observation has sparked speculation that a significant role for organic complexing may supplement or dominate apparently viable inorganic mechan-isms of metal transport in these systems (cf. Fein and Williams-Jones,56 Leventhal and Giordano57).

Giordano53 gives an overview of those investigations conducted during the past 25 years and designed to evaluate organic transport in hydrothermal ore systems. The majority of these investigations (experimental and theoretical) have focused on Pb and Zn transport in MVT and RBBRM deposits and deep sedimentary basin brines, generally thought to be ore fluids for these deposits. In all of these studies Pb and Zn concentrations and speciation are either measured or calculated for very restricted fluid compositions in terms of $f_{O_2}$, pH, and other solute activities. This approach is fine for evaluating the significance of complexing mechanisms under specific ore-fluid conditions. More useful, however, would be an evaluation based on metal concentration contours in $\log f_{O_2}$–pH space. This is the method employed in those studies mentioned above in which $\log f_{O_2}$–pH diagrams were used to develop transport and deposition models based on inorganic complexing. This approach allows a broad-based evaluation of a particular complexing mechanism over a wider range of possible $f_{O_2}$–pH conditions and the simultaneous evaluation of deposition processes as a function of $f_{O_2}$ and pH. The author is not aware of any published studies that take this approach in evaluating organic-transport mechanisms of base or precious metals in lower-temperature hydrothermal ore fluids. However, organic transport of mercury has been evaluated in $\log f_{O_2}$–pH space for hydrothermal ore-forming systems (Wells and Ghiorsa,58 Fein and Williams-Jones59). These authors found that methyl mercury as well as acetate and oxalate complexes of mercury do not contribute significantly to Hg transport in the formation of hydrothermal mercury deposits.

The purpose of this paper is to present a preliminary evaluation of the influence of oxygen fugacity and pH on monocarboxylate- and dicarboxylate-transport of Pb and Zn in low-temperature (100 °C) hydrothermal ore fluids that are related to diagenetic processes in deep sedimentary basins. First a description of the chemical model used in this study will be presented. This is followed by a presentation of model results illustrating Pb and Zn solubility and speciation and a discussion of these results in terms of fluid parameters and the compositional characteristics of modern petroleum-field brines. Finally, some conclusions will be presented regarding (a) the similarities between modern petroleum-field brines and ore fluid models of MVT and RBBRM deposits and (b) the systematics of Zn and Pb transport by carboxylate complexation in these basinal brines.

**Chemical model**

**Model ore fluids**

Over the past half century, geochemical studies of sedimentary basins, petroleum fields, and ore deposits related to these features have resulted in the general consensus that ore fluids responsible for a wide range of low- to medium-temperature (50 to 200 °C) hydrothermal deposits were in fact Na–Cl–Ca–Cl basinal brines (Beales and Jackson60, Carpenter et al.61, Hitchen62, Hano63, 50, 60, 61, 62 Anderson and McQueen,64 Lyndon,65 Sverjensky31, 32, Sangster,66 Force et al.67, Heijnjen et al.68). These fluids became enriched in metals as a result of diagenetic processes and migrated from hot, deep basin interiors to more peripheral and structurally active parts of the basin where metals were deposited in host rocks to form a variety of ore deposits ranging from purely epigenetic carbonate-hosted and siliciclastic-hosted deposits to those with a significant sedimentary exhalative component (Bjorlykke and Sangster,69 Gustafson and Williams70, Sangster,71 Cooke et al.72). Within this wide range of deposit-types, two important categories of epigenetic ores are carbonate-hosted MVT deposits and RBBRM deposits, base metal ores associated with siliciclastic continental/marginal marine host rocks. Both of these ore-types have been extensively studied in terms of their geology and genesis (cf. Kivisvarsny et al.73, Sverjensky74, Haynes and Bloom75, Boeing et al.76, Leach and Goldhaber,77 Sicree and Barnes78). Detailed ore-fluid models have also been proposed for each of these deposit-types and with respect to the ore fluids in these models, there is general agreement among researchers regarding temperature of transport and deposition, total sulfur and total carbonate concentration, and major element composition. For RBBRM deposits (Rose79, Sverjensky31, 32, Branan and Ripley80), there is also general agreement that the metal-transporting fluids were oxidized, very low in reduced sulfur (reduced sulfur is here defined as $2m_{SO_2} = m_{SO_2} + m_{SO_3} + m_{SO_4}$), and slightly acidic. Parameters for a composite RBBRM ore fluid (Giordano81) are shown in Table 1 and Fig. 1. Unlike RBBRM deposits, three very different sets of $\log f_{O_2}$–pH conditions have been proposed for MVT ore fluids (Table 1; Fig. 1): (1) reduced and acidic (Sverjensky82), (2) reduced and alkaline (Giordano and Barnes83), and (3) oxidized/ slightly acidic (Anderson37, 38, 39) similar to RBBRM ore fluids and many sulfide-poor petroleum–field brines.

**Carboxylate ligands**

It is well known that some petroleum-related brines from deep sedimentary basins contain measurable quantities (x to xxx mg L$^{-1}$) of base metals (Pb, Zn, Cu) and that many petroleum-field brines contain measurable concentrations ($x$ to xxx mg L$^{-1}$) of discrete, polar organic molecules (particularly carboxylic acid anions) capable of complexing Pb, Zn, and Cu, as well as the more common rock-forming metals mobilized in basin diagenetic environments. The nature of Pb–Zn rich brines from sedimentary basins will be summarized in the Discussion section of this paper. Lundegard and Kharaka,78 Giordano and Kharaka,79 and Kharaka et al.80 summarize the available data concerning the nature and distribution of discrete organic ligands in diagenetic environments. Based on
log pH 5.7 to 6.7 6.8 to 7.8 4.5 to 5.5 5.5 to 6.5 variable

log \( \Sigma_{\text{DMS}} \) -2 -2
log \( \Sigma_{\text{carbonate}} \) -1.37 -2 to -4 
\( \Sigma_{\text{C}^-} \) (acetic) 3.0 (2.0) 2.76 (1.4) 2.0 3.0
\( \Sigma_{\text{C}^-} \) (malonic) 3.0 (1.5) 1.67 (1.0) (1.0) 2.81
\( \Sigma_{\text{MgC}^-} \) (malonic) 0.1 (0.05) 0.491 (0.074) (0.01) 0.2
\( \Sigma_{\text{MgC}^-} \) (gluconic) 0.1 (0.02) 0.056 (0.013) (0.005) 0.1
Chlorinity\(^a\) 99 530 99 530 93 450 69 050 97 450
Salinity\(^b\) 169 200 169 200 158 865 132 480 179 270

Saturation

Galena x x x x x
Sphalerite x x x x x
Pyrite x x x x \( x^d \)
Hematite x x x \( x^e \)
Magnetite x x x \( x^e \)
Calcite x x x x
Dolomite x
Quartz x x x x x
K-Feldspar x x x x
Muscovite x x x x
Kaoilinite x

\(^a\) The composition of this model ore fluid is a composite based on parameter values proposed by Rose, Sverjensky, and Branam and Ripley.\(^b\) Chlorinity = Cl\(^-\) concentration in mg L\(^{-1}\). Calculated from \( \Sigma_{\text{Cl}^-} \) and assuming a fluid density of 1.1 g cm\(^{-3}\).\(^c\) Salinity = total dissolved solids (TDS) in mg L\(^{-1}\). Calculated assuming a fluid density of 1.1 g cm\(^{-3}\).\(^d\) Pyrite stability field only.\(^e\) Hematite stability field only.\(^f\) Magnetite stability field only.

Fig. 1 Approximate log \( \phi_{\text{O}_2} \)-pH conditions of Mississippi Valley-type (MVT) and red-bed related base metal (RBRBM) model ore fluids at 100 °C (regions bounded by heavy lines). The stability fields of Cu–Fe–S–O minerals constructed for total sulfur of 10 and aqueous sulfur species are delineated by the light and medium boundaries, respectively. Abbreviations: Bn = bornite; Cp = chalcopyrite; Hem = hematite; Mt = magnetite; Po = pyrrhotite; Py = pyrite. Neutral pH is indicated by the vertical arrow.

A critical evaluation of the available analyses of dissolved organic species in petroleum-related brines, these authors conclude that the only clearly identified group of significant organic ligands in oil- and gas-field brines are short-chain aliphatic carboxylate anions. Furthermore, Kharaka et al.\(^{29}\) give recommended maximum concentrations for the most abundant carboxylate anions found in these fluids (Table 2). Acetate is the dominant monocarboxylate anion in brines with temperatures greater than 85 °C followed by propionate, butyrate, and valerate, while the dominant dicarboxylate species are succinate, glutarate, and malonate. Kharaka et al.\(^{79}\) do not rule out the possibility of other important groups of organic ligands but the observational data are not available to support their importance in modern basinal brines and ancient ore fluids. In the model ore fluid evaluated in this paper, acetate with a concentration of 7 700 mg L\(^{-1}\) (0.13 m) represents the four dominant monocarboxylate ligands and malonate with a concentration of 300 mg L\(^{-1}\) (0.0029 m) is used to represent the three dominant dicarboxylate ligands (Table 2). This approach was taken because there is a lack of experimental thermodynamic data for complexation equilibria involving the ligands propionate, butyrate, valerate, succinate, and glutarate. Based on experimental data at 25 °C (Smith et al.,\(^{20}\) and predicted constants at elevated temperatures (Shock and Koretsky,\(^{81}\) Sverjensky et al.,\(^{82}\) Prapaipong et al.\(^{83}\)) it appears that malonate, succinate, and glutarate form metal complexes with similar stabilities and that metal acetate complexes are similar in terms of stability to corresponding complexes formed by propionate, butyrate, and valerate. Metal dicarboxylate complexes are generally one to two orders of magnitude stronger than metal monocarboxylate complexes because of the chelate effect. Thus, for a given total carboxylate ligand content, metal carboxylate complexation increases with increasing proportion of dicarboxylate ligand species, or decreasing concentration ratio of total monocarboxylate to total dicarboxylate.

Composite ore fluid

In this paper a composite ore fluid (column 6 in Table 1) is tested for Pb and Zn transport at 100 °C as a function of pH and log \( \phi_{\text{O}_2} \). Concentrations of the major elements, total sulfur, and total carbonate of this hypothetical ore fluid only approximate the proposed concentrations given in columns 2 through 5 of Table 1 for the four model ore-fluids.
Nevertheless, the concentrations of the major elements, total carbonate, and total sulfur of this composite ore fluid are sufficiently close to those of the other model fluids, as well as many petroleum-field brines, to allow a first-order comparison of Pb and Zn transport among the proposed model fluids in terms of their approximate pH and \( f_{O_2} \) conditions. The primary purpose of this paper is to evaluate the influence of these two parameters on Zn and Pb transport by monocarboxylate and dicarboxylate ligands represented by acetate complexation and dicarboxylate ligands represented by malonate complexation. The stability constants used in this study to describe malonate and acetate protonation and malonate and acetate complexation of Pb and Zn are given in Table 3. Reliable 100 °C constants are available for the protonation equilibria and acetate complexation of Pb and Zn. However, the author is not aware of reliable 100 °C data for malonate complexation of Pb and Zn and, therefore, the available 25 °C data are used. Although thermodynamic data are available for Cu – acetate complexes between 50 and 150 °C (Liu et al.91), the lack of thermodynamic data for Cu – dicarboxylate complexes (Martell and Smith,9293 Smith and Martell,94 Smith et al.95) precluded the possibility of adequately modeling Cu complexation in this study. It should be noted that Sverjensky’s1984 model MVT-fluid41 has a temperature of 125 °C and, therefore, the \( f_{O_2} \) and pH boundaries defined by Sverjensky41 were used in this study to estimatecorrelativelog \( f_{O_2} \) and pH boundaries at 100 °C (Fig. 1 and Table 1).

Total Pb and Zn concentrations and Pb and Zn speciation were calculated as a function of log \( f_{O_2} \) and pH for the composite ore-brine described in Table 1. In addition to acetate and malonate complexation, complexes involving the ligands Cl−, HS−, \( H_2S \), and \( OH^- \) were included in the model of calculated total metal concentration and metal speciation. Also, in the model calculations, Zn and Pb are competing with the common-rock forming metals Ca, Mg, Na, Fe, and Al for the same ligands. Calculated total Pb concentration and calculated total Zn concentration are constrained by galena and sphalerite solubility, respectively. It was assumed that the brine is saturated with respect to quartz and K-feldspar at all \( f_{O_2} \) – pH conditions and that total Fe concentration is controlled by either pyrite, hematite or magnetite solubility, depending on the given \( f_{O_2} \) – pH condition. The stability fields for pyrite, hematite, and magnetite are shown in Fig. 1. K-Feldspar is the stable aluminum phase throughout only part of the \( f_{O_2} \) – pH conditions represented in Fig. 1. Because the calculated Pb and Zn values are not significantly affected by Al speciation, the assumption of K-feldspar saturation has little influence on Pb and Zn solubility in this model. The model does not constrain the activities of Ca2+ and Mg2+ by calcite or dolomite solubility. Although these cations affect the speciation of carboxylate ligands, their overall influence on Pb and Zn speciation, in the model, is negligible. Pb and Zn isopleths in \( f_{O_2} \) – pH space are presented in Fig. 2 through 5, while speciation of Pb and Zn along specific isopleths is presented in Tables 4 through 9 and Fig. 6 through 11.

### Results

#### Isopleths

It is generally assumed that an ore fluid must transport, at a minimum, between 1 and 10 ppm of a base metal to form an ore deposit of that metal (Barnes and Czamanske,6 Barnes40,95 Anderson,38 Rooderkerk,96 Ohmoto,97 Seward and Barnes39). Examination of the Pb isopleths (representing galena solubility) in Fig. 2 shows that sufficient lead in the model ore fluid can only be transported under \( f_{O_2} \) – pH conditions corresponding to low total sulfide (\( \Sigma_{S_{\text{sol}}} > \Sigma_{m(S)} \)); for example, the relatively oxidized RBRBM ore fluid of Giordano94 and the MVT ore fluid of Anderson.37 The MVT ore fluids of Sverjensky41 and Giordano and Barnes39 are capable of

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### Table 2

**Most abundant monocarboxylate and dicarboxylate anions observed in petroleum-field brines, their most likely maximum concentration in these fluids, and their concentrations used in the composite ore-fluid model of this study**

| Acid anion | Common | Petroleum-field brine concentration (likely maximum, mg L\(^{-1}\)) | Model ore-fluid concentration | /mg L\(^{-1}\) | /mol kg\(^{-1}\) |
|-----------|--------|---------------------------------------------------------------|-------------------------------|-----------------|-----------------|
| Ethanoate | Acetate | 5000                                                          |                               | 7700            | 0.13            |
| Propanoate | Propionate | 2000                                                          |                               | 0.10            | 0.10            |
| Butanoate | Butyrate | 500                                                          |                               | 0.13            | 0.13            |
| Pentanoate | Valerate | 200                                                          |                               | 0.10            | 0.10            |

### Table 3

**Equilibrium constants for acetate and malonate complexes of Pb and Zn used in model calculations**

| Reaction | log \( K \) | °C | Ref. | Reaction | log \( K \) | °C | Ref. |
|----------|-------------|----|------|----------|-------------|----|------|
| \( H^+ + Ac^- \rightarrow HAc \) | 4.94 | 100 | 1 | \( H^+ + HMa^+ \rightarrow H_2Ma \) | 3.02 | 100 | 5 |
| \( Pb^{2+} + Ac^- \rightarrow PbAc^{2+} \) | 3.00 | 100 | 2 | \( Pb^{2+} + Ma^{2+} \rightarrow PbMa \) | 2.79 | 25 | 6 |
| \( Pb^{2+} + 2Ac^- \rightarrow Pb(Ac)_2 \) | 4.69 | 100 | 2 | \( Pb^{2+} + 2Ma^{2+} \rightarrow Pb(Ma)_2^{2+} \) | 5.70 | 25 | 6 |
| \( Pb^{2+} + Ac^- + Pb(Ac)_2 \) | 3.66 | 100 | 3 | \( Pb^{2+} + Ma^{2+} \rightarrow PbMa \) | 2.40 | 25 | 6 |
| \( Zn^{2+} + Ac^- + ZnAc^{2+} \) | 2.30 | 100 | 4 | \( Pb^{2+} + 2Ma^{2+} \rightarrow Pb(Ma)_2^{2+} \) | 2.40 | 25 | 6 |
| \( Zn^{2+} + 2Ac^- \rightarrow Zn(Ac)_2 \) | 4.00 | 100 | 4 | \( Pb^{2+} + PbMa \) | 2.79 | 25 | 6 |
| \( Zn^{2+} + 3Ac^- \rightarrow Zn(Ac)_3 \) | 4.70 | 100 | 4 | \( Zn^{2+} + Ma^{2+} \rightarrow ZnMa \) | 3.84 | 25 | 7 |
| \( Zn^{2+} + 2Ma^{2+} \rightarrow Zn(Ma)_2^{2+} \) | 5.40 | 25 | 7 | \( Zn^{2+} + Ma^{2+} \rightarrow ZnMa \) | 3.84 | 25 | 7 |
| \( Zn^{2+} + Ma^{2+} \rightarrow ZnMa \) | 1.00 | 25 | 7 | \( Zn^{2+} + Ma^{2+} \rightarrow ZnMa \) | 3.84 | 25 | 7 |

*Ref. | Kharaka et al.79*
transporting maximum amounts of lead that are 2 to 5 orders of magnitude below the 1 to 10 ppm minimum. It should be noted that Sverjensky’s 1984 model ore fluid was developed for a temperature of 125 °C and that the model fluid could barely transport 1 ppm Pb at that temperature. The total Zn isopleths (representing sphalerite solubility) shown in Fig. 3 illustrate model results similar to those for Pb. The ore fluids of Sverjensky and Giordano and Barnes are not capable of transporting sufficient Zn at 100 °C. However, the oxidized RBRBM ore fluid of Giordano and the Anderson MVT ore fluid can clearly mobilize 100s of ppm Zn, several orders of magnitude greater than the minimum required to form economic deposits of Zn.

In Fig. 4 and 5, respectively, isopleths of the total concentration of Pb and total concentration of Zn in carboxylate (acetate + malonate) complexes are plotted for the model ore fluid. The 1 to 10 ppm Pb isopleths shown in Fig. 4 illustrate that the oxidized model fluids of Giordano and Anderson are capable of transporting sufficient amounts of Pb in the form of carboxylate complexes to form economic deposits of lead. On the other hand, the reduced ore models of Sverjensky and Giordano and Barnes can at best transport amounts of Pb, as carboxylate complexes, that are many orders of magnitude below the 1 to 10 ppm minimum. Similar to Pb, the 1 and 10 ppm Zn isopleths in Fig. 5 coincide with the log $f_{O_2}$–pH conditions of the RBRBM and Anderson MVT ore fluids and demonstrate that these brines can transport sufficient Zn, as carboxylate complexes at 100 °C, to form economic deposits of Zn. However, the more reduced Sverjensky and Giordano and Barnes’ ore fluids are incapable of transporting sufficient Zn, as carboxylate complexes, to form economically viable deposits of Zn. The isopleths in Fig. 4 and 5 curve upward on the left side of the diagram because protonation of acetate and malonate becomes significant at pH below 5, thereby reducing the activities of these ligands in solution and

Table 4 Lead speciation, as a function of pH and log $f_{O_2}$ along the 100 ppm Pb isopleth of the model composite ore-brine at 100 °C

| pH  | Log $f_{O_2}$ | Iron phase | Cation | Chloride complexes | Sulfide complexes | Hydroxide complexes | Acetate complexes | Malonate complexes | Data set |
|-----|--------------|------------|--------|-------------------|-------------------|---------------------|-------------------|-------------------|---------|
| 8.00 | −50.20       | Hm         | 0.06   | 23.60             | 2.5 $\times$ 10$^{-14}$ | 74.47               | 0.80               | 2.6 $\times$ 10$^{-3}$ | 5       |
| 7.00 | −49.95       | Hm         | 0.17   | 72.64             | 6.9 $\times$ 10$^{-13}$ | 22.38               | 2.59               | 8.3 $\times$ 10$^{-3}$ | 4       |
| 5.00 | −49.90       | Hm         | 0.23   | 97.25             | 5.9 $\times$ 10$^{-9}$ | 0.30                | 2.19               | 9.9 $\times$ 10$^{-3}$ | 3       |
| 4.00 | −49.90       | Py         | 0.24   | 99.21             | 6.0 $\times$ 10$^{-7}$ | 0.03                | 0.51               | 8.9 $\times$ 10$^{-3}$ | 2       |
| 3.00 | −49.90       | Py         | 0.24   | 99.69             | 6.0 $\times$ 10$^{-5}$ | 3.2 $\times$ 10$^{-3}$ | 0.05               | 6.3 $\times$ 10$^{-3}$ | 1       |

Speciation for the indicated complexes is given as mol% of total Pb. The 100 ppm isopleth is illustrated in Fig. 2. Saturated with respect to hematite (Hm), pyrite (Py), or magnetite (Mt).
Fig. 5 Isopleths of total ppm Zn in carboxylate complexes as a function of log $f_{O_2}$ and pH for the model composite ore-brine. Neutral pH, log $f_{O_2}$, pH conditions for model ore fluids, regions of mineral stability, and regions of dominance for sulfur species are the same as illustrated in Fig. 1. The small arrows indicate the direction of increasing concentration.

Fig. 6 Percent of total Pb in chloride complexes and hydroxide complexes as a function of pH–log $f_{O_2}$ conditions along the 100 ppm total Pb isopleth in Fig. 2. Specific pH–log $f_{O_2}$ conditions (pH, log $f_{O_2}$) are given in Table 4, along with corresponding % of total Pb values for various forms of Pb, and begin at the right end of the 100 ppm isopleth with data set #5 (8, –50.20), followed by #4 (7, –49.95), #3 (5, –49.90), #2 (4, –49.90), and #1 (3, –49.90).

the complexation of lead and zinc by them. Under conditions deep within the H$_2$S field (Fig. 4 and 5) Pb$^{2+}$ and Zn$^{2+}$ activities are constant at a given pH. Therefore, the concentration of individual carboxylate complexes is also constant; thus producing the vertical 0.0001 ppm isopleths in Fig. 4 and 5.

Table 5 Lead speciation, as a function of pH and log $f_{O_2}$ along the 0.01 ppm Pb isopleth of the model composite ore-brine at 100 °C

| pH   | Log $f_{O_2}$ | Iron phase$^a$ | Cation | Chloride complexes | Sulfide complexes | Hydroxide complexes | Acetate complexes | Malonate complexes | Data set |
|------|---------------|----------------|-------|--------------------|-------------------|---------------------|-------------------|-------------------|---------|
| 8.00 | –52.20        | Hm             | 5.6 x 10$^{-2}$ | 23.6 | 2.3 x 10$^{-6}$   | 73.47              | 0.80              | 2.6 x 10$^{-3}$   | 8       |
| 7.00 | –51.95        | Hm             | 0.17 | 72.64              | 7.6 x 10$^{-5}$   | 22.37              | 2.58              | 8.3 x 10$^{-3}$   | 7       |
| 5.00 | –51.90        | Py             | 0.23 | 96.68              | 0.59              | 0.30               | 2.18              | 0.01              | 6       |
| 4.00 | –51.90        | Py             | 0.17 | 71.75              | 27.67             | 0.02               | 0.37              | 6.4 x 10$^{-3}$   | 5       |
| 4.20 | –52.00        | Py             | 0.17 | 68.42              | 30.85             | 0.03               | 0.52              | 6.3 x 10$^{-3}$   | 4       |
| 4.75 | –52.90        | Py             | 4.1 x 10$^{-3}$ | 1.70 | 98.26             | 3.0 x 10$^{-3}$   | 0.03              | 1.7 x 10$^{-4}$   | 3       |
| 5.80 | –54.00        | Py             | 3.5 x 10$^{-5}$ | 0.02 | 99.98             | 2.9 x 10$^{-4}$   | 4.6 x 10$^{-4}$   | 1.6 x 10$^{-6}$   | 2       |
| 6.30 | –55.00        | Py             | 3.2 x 10$^{-6}$ | 1.4 x 10$^{-3}$ | 99.99             | 8.4 x 10$^{-5}$   | 4.6 x 10$^{-5}$   | 1.5 x 10$^{-7}$   | 1       |

$^a$Speciation for the indicated complexes is given as mol% of total Pb. $^b$The 0.01 ppm isopleth is illustrated in Fig. 2. $^c$Saturation with respect to hematite (Hm), pyrite (Py), malonate (Ml).

Fig. 7 Percent of total Pb in chloride, hydroxide, and sulfide complexes as a function of pH–log $f_{O_2}$ conditions along the 0.01 ppm total Pb isopleth in Fig. 2. Specific pH–log $f_{O_2}$ conditions (pH, log $f_{O_2}$) are given in Table 5, along with corresponding % of total Pb values for various forms of Pb, and begin at the right end of the 0.01 ppm isopleth with data set #8 (8, –52.20), followed by #7 (7, –51.95), #6 (5, –51.90), #5 (4, –51.90), #4 (4.2, –52.00), #3 (4.75, –52.90), #2 (5.8, –54.00), and #1 (6.3, –55.00).

**Speciation**

Lead speciation (mol% of total Pb) in the model ore fluid was calculated at specific log $f_{O_2}$–pH conditions along the 100, 0.01, and 0.001 ppm total Pb isopleths shown in Fig. 2. These speciation results are presented in Table 4 and Fig. 2, Table 5 and Fig. 7, and Table 6 and Fig. 8 for the 100, 0.01 and 0.001 ppm isopleths, respectively. Along the 100 ppm isopleth (Fig. 2 and 6, Table 4) conditions are oxidized and lead is predominantly in the form of chloride complexes under acid to mildly alkaline conditions (pH from 3 to approximately 7.5), while hydroxide complexes dominate lead speciation under more alkaline conditions (Table 4 and Fig. 6). Sulfide complexes are insignificant under these oxidized conditions. Acetate (monocarboxylate) complexation accounts for up to 2.6% of the total Pb in the pH range 5 to 7, while malonate (dicarboxylate) complexes are insignificant along the isopleth. For the 0.01 ppm isopleth (Fig. 2 and 7, Table 5), chloride complexes dominate lead speciation in the SO$_4^{2-}$ field and near the SO$_4^{2-}$–reduced sulfur boundary from pH ~ 4 to approximately 7.5, while hydroxide complexes dominate lead speciation under alkaline conditions above pH = 7.5 in the SO$_4^{2-}$ field. In the most reduced fluids along the 0.01 isopleth, lead sulfide complexes account for almost 100% of the Pb in the model fluid. Acetate (monocarboxylate) complexation is significant only under conditions of chloride and hydroxide complex dominance and its effect is maximized in the pH range 5 to 7, where it complexes 2 to 2.6% of the total Pb. Malonate (dicarboxylate) complexes are insignificant along the 0.01 isopleth. The lead speciation systematics along the 0.001 isopleth (Fig. 2 and 8, Table 6) are similar to those for the 0.01
isolement. Chloride and hydroxide complexation dominate the speciation of Pb in the SO₄²⁻ field and near the SO₄²⁻-reduced sulfur boundary, while sulfide complexes account for most of the Pb under reduced conditions below the SO₄²⁻-reduced sulfur boundary. Acetate (monocarboxylate) complexes comprise a significant portion of the Pb (up to 3%) in oxidized, weakly acid to mildly alkaline (6 to 8 pH range) fluids, while malonate (dicarboxylate) complexes are insignificant under all conditions along the 0.001 isopleth.

The speciation systematics for Zn in the model fluid are, in general, similar to those for Pb. Zinc speciation (mol% of total Zn) in the model ore fluid was calculated at specific log fO₂ conditions along the 0.001 ppm Pb isopleth with data set #7 (8, −52.70), followed by #6 (6, −52.40), #5 (6, −53.55), #4 (6.45, −54.00), #3 (7, −54.60), #2 (7.3, −55.00), and #1 (7.55, −57.00).

Table 6 Lead speciation, as a function of pH and log fO₂ along the 0.001 ppm Pb isopleth of the model composite ore-brine at 100 °C

Table 7 Zinc speciation, as a function of pH and log fO₂ along the 0.01 ppm Zn isopleth of the model composite ore-brine at 100 °C

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near the SO\(_4^{2-}\)−reduced sulfur boundary at pHs ranging from approximately 5 to 7.5, while zinc sulfide complexes account for approximately 87 to near 100% of the total Zn under reduced conditions in the pH range 4.8 to 6.5. Acetate (monocarboxylate) complexation is significant only in oxidized, weakly acid to mildly alkaline solutions and accounts for approximately 1.25 to 1.3% of the total Zn under these conditions. Malonate (dicarboxylate) complexation is maximized, but insignificant, under the same conditions. For the 0.001 isopleth, hydroxide complexation, again, dominates under alkaline conditions in the SO\(_4^{2-}\)− field and chloride complexes are dominant under acidic to mildly alkaline conditions in the SO\(_4^{2-}\)− field and near the SO\(_4^{2-}\)−reduced sulfur boundary, while 90 to nearly 100% of the zinc is complexed by sulfide ligands under reduced conditions below the SO\(_4^{2-}\)−reduced sulfur boundary.

**Table 8 Zinc speciation, as a function of pH and log fo\(_3\) along the 0.01 ppm Zn isopleth of the model composite ore-brine at 100 °C**

| pH     | Log fo\(_3\) | Iron phase\(^a\) | Cation | Chloride complexes | Sulfide complexes | Hydroxide complexes | Acetate complexes | Malonate complexes | Data set |
|--------|---------------|-------------------|--------|--------------------|-------------------|---------------------|-------------------|-------------------|---------|
| 8.00   | −52.55        | Hm                 | 0.11   | 31.53              | \(9.3 \times 10^{-6}\) | 67.90               | 0.45              | 9.0 \times 10^{-3} | 7       |
| 7.00   | −52.35        | Hm                 | 0.28   | 81.15              | \(3.8 \times 10^{-4}\) | 17.30               | 1.22              | 0.02              | 6       |
| 6.00   | −52.30        | Py                 | 0.34   | 96.19              | 0.03              | 2.07                | 1.33              | 0.03              | 5       |
| 4.75   | −52.90        | Py                 | 0.04   | 12.36              | 87.48             | 0.02               | 0.10              | 2.5 \times 10^{-3} | 4       |
| 5.78   | −54.00        | Py                 | 3.9 \times 10^{-4} | 0.11 | 99.89 | 1.4 \times 10^{-3} | 1.5 \times 10^{-3} | 3.0 \times 10^{-3} | 3       |
| 6.40   | −55.00        | Py                 | 2.4 \times 10^{-4} | 6.7 \times 10^{-3} | 99.99 | 3.6 \times 10^{-4} | 9.6 \times 10^{-4} | 1.9 \times 10^{-4} | 2       |
| 6.50   | −56.00        | Py                 | 1.7 \times 10^{-5} | 4.8 \times 10^{-3} | 99.99 | 3.2 \times 10^{-4} | 6.9 \times 10^{-5} | 1.4 \times 10^{-4} | 1       |

* Speciation for the indicated complexes is given as mol% of total Zn. *The 0.01 ppm isopleth is illustrated in Fig. 3. *Saturation with respect to hematite (H), pyrite (Py), or magnetite (Mt).

**Discussion**

Percentage of total Pb and Zn in carboxylate complexes: key determinants

The percent of dissolved Zn or Pb complexed by carboxylate ligands in a basinal brine will depend on four key variables, assuming a systems remains invariant with respect to temperature and pressure, total sulfur and total carbonate of the brine, major cation ratios of the brine, and mineralogy of the aquifer. The four variables are (1) the total chloride molality to total carboxylate ligand molality (\(\Sigma m_{\text{Cl}} / \Sigma m_{\text{L,bas}}\)), (2) the mix of specific carboxylate ligands, for example the monocarboxylate to dicarboxylate ratio (\(\Sigma m_{\text{monoc}} / \Sigma m_{\text{dic}}\)), (3) the concentration of total inorganic sulfide (\(\Sigma m_{\text{H,S}} = m_{\text{H,S}} + m_{\text{HS}}\)), and (4) the pH. Values for these four parameters are

**Table 9 Zinc speciation, as a function of pH and log fo\(_3\) along the 0.001 ppm Zn isopleth of the model composite ore-brine at 100 °C**

| pH     | Log fo\(_3\) | Iron phase\(^a\) | Cation | Chloride complexes | Sulfide complexes | Hydroxide complexes | Acetate complexes | Malonate complexes | Data set |
|--------|---------------|-------------------|--------|--------------------|-------------------|---------------------|-------------------|-------------------|---------|
| 8.00   | −53.05        | Mt                 | 0.11   | 31.53              | \(9.3 \times 10^{-4}\) | 67.90               | 0.45              | 9.0 \times 10^{-3} | 8       |
| 7.00   | −52.85        | Mt                 | 0.28   | 81.11              | 0.04              | 17.30               | 1.22              | 0.02              | 7       |
| 6.00   | −52.80        | Py                 | 0.33   | 93.57              | 2.75              | 2.01                | 1.29              | 0.03              | 6       |
| 6.00   | −53.55        | Py                 | 0.01   | 3.73               | 96.12             | 0.08                | 0.05              | 1.0 \times 10^{-3} | 5       |
| 6.40   | −54.00        | Py                 | 1.5 \times 10^{-5} | 0.43 | 99.54 | 0.02 \times 10^{-4} | 6.2 \times 10^{-5} | 1.3 \times 10^{-4} | 4       |
| 7.00   | −54.60        | Py                 | 1.3 \times 10^{-4} | 0.04 | 99.95 | 7.9 \times 10^{-3} | 5.5 \times 10^{-4} | 1.1 \times 10^{-5} | 3       |
| 7.30   | −55.00        | Py                 | 2.8 \times 10^{-3} | 8.0 \times 10^{-3} | 99.99 | 3.4 \times 10^{-3} | 1.2 \times 10^{-4} | 2.3 \times 10^{-6} | 2       |
| 7.70   | −56.00        | Py                 | 6.8 \times 10^{-6} | 1.9 \times 10^{-3} | 99.99 | 2.1 \times 10^{-3} | 2.8 \times 10^{-5} | 5.5 \times 10^{-7} | 1       |

* Speciation for the indicated complexes is given as mol% of total Zn. *The 0.001 ppm isopleth is illustrated in Fig. 3. *Saturation with respect to hematite (H), pyrite (Py), or magnetite (Mt).
Table 10 Comparison of model ore fluids with modern Na–Cl and Na–Ca–Cl basinal brines

| Parameter | MVT Anderson (1975) | MVT Giordano and Barnes (1981) | MVT Sverjensky (1984) | RBRBM Giordano (1994) |
|-----------|---------------------|-------------------------------|------------------------|------------------------|
| T/°C | 100 | 100 | 100 | 100 |
| TDS/mg L⁻¹ | 179270 | 179270 | 179270 | 179270 |
| ΣCl/mg L⁻¹ | 97450 | 97450 | 97450 | 97450 |
| pH | 6.0 | 7.5 | 4.6 | 6.0 |
| ΣH₂S/mg L⁻¹ | 10⁻⁵.⁴ | 340 | 3.4 | 10⁻⁵.³ |
| ΣH₂S/mg L⁻¹ | 10⁻⁵.⁸ | 10⁻² | 10⁻³ | 10⁻⁶.³ |
| ΣSO₄²⁻/mg L⁻¹ | 960 | 960 | 960 | 960 |
| ΣH₂SO₄⁻/mg L⁻¹ | 10⁻² | 10⁻² | 10⁻² | 10⁻² |
| ΣH₂S/cmol L⁻¹ | 7700 | 7700 | 7700 | 7700 |
| ΣH₂S/cmol L⁻¹ | 0.13 | 0.13 | 0.13 | 0.13 |
| ΣH₂S/cmol L⁻¹ | 300 | 300 | 300 | 300 |
| ΣH₂S/cmol L⁻¹ | 0.0029 | 0.0029 | 0.0029 | 0.0029 |
| ΣH₂S/cmol L⁻¹ | 23 | 23 | 23 | 23 |
| Pb/mg L⁻¹ range/ | 45 | 45 | 45 | 45 |
| Pb/mg L⁻¹ range/ | 65 | 0.001 | 0.02 | 65 |
| Zn/mg L⁻¹ | 420 | 0.002 | 0.02 | 420 |
| Zn/mg L⁻¹ range/ | Fig. 3 | Fig. 3 | Fig. 3 | Fig. 3 |

Modern petroleum field brines

| Parameter | Low ΣH₂S, high trace metal content | Low ΣH₂S, low trace metal content | High ΣH₂S, low trace metal content |
|-----------|-----------------------------------|-----------------------------------|-----------------------------------|
| T/°C | 50 to 250 | 50 to 250 | 50 to 250 |
| TDS/mg L⁻¹ | 100000 to 330000 | 12000 to 210000 | 20000 to 330000 |
| ΣCl/mg L⁻¹ | 600000 to 210000 | 12000 to 210000 | 12000 to 210000 |
| pH | 4 to 6.5 | 4 to 8 | 4 to 8 |
| ΣH₂S/mg L⁻¹ | <0.1 | <1.0 | <1.0 |
| ΣH₂S/cmol L⁻¹ | <10⁻⁵.⁴ | <10⁻⁵.⁴ | <10⁻⁵.⁴ |
| ΣSO₄²⁻/mg L⁻¹ | 0.1 to 1000 | 0.1 to 1000 | 0.1 to 1000 |
| ΣH₂SO₄⁻/mg L⁻¹ | 10⁻⁵ to 10⁻² | 10⁻⁴ to 0.15 | 10⁻⁴ to 0.15 |
| ΣH₂S/cmol L⁻¹ | <1.0 | <10⁻² to 10⁻⁵ | <10⁻² to 10⁻⁵ |
| ΣH₂S/cmol L⁻¹ | <0.1 to 300 | <10⁻⁵ to 0.005 | <10⁻⁵ to 0.005 |
| Pb/mg L⁻¹ range/ | 5 to 70 (cluster) | 0.01 | 0.01 |
| Zn/mg L⁻¹ | 15 to 250 (cluster) | <0.1 (cluster) | <0.1 (cluster) |
| Zn/mg L⁻¹ | 1 to 575 | BDL to 0.9 | BDL to 0.9 |

SUMMARIZED

Summarized in Table 10 for modern petroleum-field brines and for the four-modelled ore fluids considered in this study. The ΣH₂S of the system will of course be controlled by the log fO₂–pH conditions of the brine, assuming sulfate–sulfide equilibrium among the sulfur-bearing species of the system.

Modern petroleum-field brines: composition and types

Excellent summaries of the origin of sedimentary basin brines and their chemical evolution are given by Carpenter,115 Hanor,160,161 Karhaka,162,163 Kharaka et al.,148 and Kharaka.147 The compositional data gathered over the past 40 years from sedimentary basins worldwide provide unequivocal evidence that deep formation waters, in particular petroleum-field brines, vary widely in composition. (White,171 Billings et al.99 Hitchon et al.,100 Collins,102 Carpenter,115 Hanor,160,161 Kharaka,162,163 Kharaka et al.,148 Land et al.,107 McManus and Hanor,119 Wilson and Long,120 Kyle,110 Land,113 Palandri and Reed114.) This diversity is particularly evident for those variables that significantly influence carbonate complexation of metals in these fluids. Of particular interest to this study are those modern formation waters classified as Na–Cl and Na–Ca–Cl brines, because of their compositional similarity to those modern formation waters classified as Na–Cl and Na–Ca–Cl brines, because of their compositional similarity to inclusion fluids from Mississippi Valley-type and red-bed related base metal deposits (Roedder,66 Heijen et al.65). In Table 10, the model ore fluids considered in this paper are compared to modern Na–Cl and Na–Ca–Cl brines in terms of specific fluid parameters that influence the concentration of Pb and Zn in these waters. In the discussion that follows salinity is defined as total dissolved solids, TDS, in units of milligrams per liter and chlorinity is defined as total chloride in units of milligrams per liter. The salinity of a Na–Cl or Na–Ca–Cl brine
can be estimated from its chlorinity by the relation salinity = 1.7 chlorinity (Hanor\textsuperscript{79}). This relation is based on the Cl to NaCl mass ratio of the brine and, therefore, with decreasing Na/Ca values, this estimate becomes less accurate. Nevertheless, it provides a quick conversion between salinity and chlorinity for the brines considered in this study.

Chloride is the dominant anion in formation waters with salinities greater than 20,000 mg L\textsuperscript{-1}. While a transition zone between 20,000 and 10,000 mg L\textsuperscript{-1} defines a TDS boundary below which the dominant anion is either bicarbonate, sulfate, or acetate (Hanor\textsuperscript{8,111}). Sodium is the dominant cation in basinal brines with salinities less than 300,000 mg L\textsuperscript{-1}. In general, the relative proportion of Na to K, Ca, or Mg decreases in these waters with increasing salinity and Ca is the dominant cation in basinal brines having salinities in excess of 330,000 mg L\textsuperscript{-1}. TDS. Between 300,000 and 330,000 mg L\textsuperscript{-1} TDS, the dominant cation is either Na or Ca. Although salinities generally increase with depth in a sedimentary basin, there are many exceptions to this trend. Thus, the salinity of a formation water is not necessarily related to temperature or pressure.

True in situ pHs of deep subsurface brines are not well known (Hanor\textsuperscript{8}) and must be estimated from field pH measurements or calculated using a field pH and various assumptions regarding the mineral saturation state of the fluid and loss of volatiles (e.g., H\textsubscript{2}S and CO\textsubscript{2}) during sampling (Kharaka et al.,\textsuperscript{103,116} Aggarwal et al.,\textsuperscript{115} Palandri and Reed\textsuperscript{114}). In general, the pH of formation waters decreases with increasing salinity from values of approximately 8 for salinities near 20,000 mg L\textsuperscript{-1} to values between 3 and 4 for halite-saturated brines with salinities near 330,000 mg L\textsuperscript{-1} (Hanor\textsuperscript{9,61}). The available field evidence suggests that most Na-Ca and Na-Ca-Cl brines have a pH in the 4-8 range.

The distribution of modern petroleum-field brines in terms of total reduced sulfur content ($\Sigma$H\textsubscript{2}S) is bimodal in character (Table 10). Low H\textsubscript{2}S brines have $\Sigma$H\textsubscript{2}S values less than 1.0 mg L\textsuperscript{-1}, however, most have $\Sigma$H\textsubscript{2}S concentrations less than 0.02 mg L\textsuperscript{-1} and often have values below the detection limit of the analytical instrument used (Kharaka et al.,\textsuperscript{106} Moldovanii and Walter,\textsuperscript{108} Hanor\textsuperscript{111}). High H\textsubscript{2}S brines have $\Sigma$H\textsubscript{2}S concentrations greater than 1.0 mg L\textsuperscript{-1} with the highest concentrations approaching 10000 mg L\textsuperscript{-1} (Wade et al.,\textsuperscript{112} Moldovanii and Walter\textsuperscript{109}). The most commonly observed $\Sigma$H\textsubscript{2}S concentrations from high H\textsubscript{2}S formation waters appear to be in the 1 to 600 mg L\textsuperscript{-1} range. Total sulfate concentrations in modern petroleum-field brines (Table 10) rarely exceed 1000 mg L\textsuperscript{-1} and are more typically in the 0.1 to 250 mg L\textsuperscript{-1} range (Kharaka et al.,\textsuperscript{106} Hanor\textsuperscript{111}). Although there appears to be a rough inverse correlation between $\Sigma$H\textsubscript{2}S and $\Sigma$SO\textsubscript{4}, there is no statistical correlation between the concentration of SO\textsubscript{4}\textsuperscript{2-} and chlorinity or salinity (Hanor\textsuperscript{9,111}).

Monocarboxylic anions (mainly acetate, propionate, butyrate, valerate) and dicarboxylic anions (mainly malonate, succinate, glutarate, maleate) are the dominant organic acid species in basinal brines. These species are commonly detected in formation waters associated with petroleum and obtained from petroleum formations having temperatures from 20 to 200 \degree C (Kharaka et al.\textsuperscript{79}). Concentrations of carboxylic acid anions in modern petroleum-field brines (Tables 2 and 10) are highly variable with respect to their major known controls, including age and temperature of reservoir rocks, type and amount of kerogen in source rocks, and the nature of metastable equilibria that characterized organic-matter interactions in the reservoir (Kharaka,\textsuperscript{106} Shock,\textsuperscript{112} Lundegard and Kharaka,\textsuperscript{78} Giordano and Kharaka,\textsuperscript{51} Franks et al.,\textsuperscript{124} Seewald\textsuperscript{123}). Although concentrations vary with temperature and reservoir depth for any given petroleum field, maximum values are generally present in Cenozoic-age reservoir rocks in the temperature range 80 to 120 \degree C (Hanor,\textsuperscript{111} Kharaka et al.,\textsuperscript{78} Lundegard and Kharaka\textsuperscript{78}). Based on carboxylate anion concentration versus salinity relationships for petroleum-field brines worldwide, Hanor\textsuperscript{111} has shown that there is a pronounced decrease in carboxylate anion concentration with increasing salinity. The highest concentrations of carboxylic acid anions are found in waters having salinities less than about 30,000 mg L\textsuperscript{-1}, while these species do not appear to be major constituents of petroleum-field brines having salinities greater than 100,000 mg L\textsuperscript{-1}.

The total concentration of monocarboxylic anions ($\Sigma$monocbx) in modern petroleum-field brines is generally less than 100 mg L\textsuperscript{-1}, however, many brines have concentrations in the 100 to 5000 mg L\textsuperscript{-1} range. The dominant monocarboxylate anion in most petroleum-field brines is acetate, followed in order of decreasing concentration by propionate, butyrate, and valerate (Table 2). The highest concentration of acetate reported is 10000 mg L\textsuperscript{-1} but values higher than 5000 mg L\textsuperscript{-1} are very rare (Lundegard and Kharaka,\textsuperscript{114} Kharaka et al.\textsuperscript{78}). Typically acetate comprises 80 to 90% of the total monocarboxylic species (Giordano and Kharaka\textsuperscript{9}). The dominant dicarboxylic species in modern petroleum-field brines are malonate, succinate, and glutarate. Each of these species is not likely to have concentrations greater than about 100 mg L\textsuperscript{-1} (Table 2), but controversially high values for oxalate (494 mg L\textsuperscript{-1}) and malonate (2540 mg L\textsuperscript{-1}) have been reported (MacGowan and Surdam\textsuperscript{26}). Reported total dicarboxylic anion concentrations ($\Sigma$dicbx) range from 0 to 2640 mg L\textsuperscript{-1} but values higher than 300 mg L\textsuperscript{-1} are very rare.

Typically, brines high in dicarboxylic anions are also high in monocarboxylic anions; however, brines high in monocarboxylic species are not always enriched in dicarboxylic anions. The total dicarboxylate anion concentration is typically less than 5% of the total carboxylate concentration for modern petroleum-field brines. Thus, the ratio of total monocarboxylic anions to total dicarboxylic anions ($\Sigma$monocbx/$\Sigma$dicbx) for modern basinal brines is nearly always greater than 20.

**Modern petroleum-field brines: Pb and Zn content**

The speciation results from this study show that deep formation waters characterized by temperatures near 100 \degree C, high oxidation states (i.e., low $\Sigma$gH\textsubscript{2}S), high chlorinities ($\sim$100 000 mg L\textsuperscript{-1}), and high but reasonable concentrations of carboxylic acid anions can mobilize up to 3% of the total Pb and up to 1.3% of the total Zn as carboxylate complexes. Furthermore, these processes are expected to occur over a range of pHs corresponding to approximately 1 to 100 ppm of these metals in solution; concentrations that are adequate to form economic deposits of these metals. However, the field evidence suggests that all of these optimum conditions for carboxylate complexation are rarely met at the same time and that total concentrations of Pb and Zn are typically below 0.1 mg L\textsuperscript{-1} in most oil-field brines (Kharaka et al.,\textsuperscript{105,106}). Nevertheless, as indicated in Table 10, formation waters high in trace metal content are common in a dozen or so localities worldwide (Carpenter et al.,\textsuperscript{57} Kharaka,\textsuperscript{114} Kharaka et al.,\textsuperscript{103,105,106} Saunders and Swann,\textsuperscript{2,108} Moldovanii and Walter,\textsuperscript{108} Kyle,\textsuperscript{108} Lund,\textsuperscript{33} Hanor,\textsuperscript{9,61,62} Hitchon et al.,\textsuperscript{106}). These brines typically have concentrations of Pb and Zn in the 1 to 250 mg L\textsuperscript{-1} range, with maximum reported concentrations of 111 mg L\textsuperscript{-1} and 575 mg L\textsuperscript{-1} for Pb and Zn, respectively (Table 10).

To ascertain the factors influencing base metal concentrations in deep formation waters, the compositional data from a large number of modern petroleum-field brines, worldwide, have been evaluated by many investigators using a variety of correlation and chemical modelling methods (Sverjensky,\textsuperscript{31,41} Kharaka et al.,\textsuperscript{106,116,127} Lundegard and Kharaka,\textsuperscript{114} Giordano and Kharaka,\textsuperscript{9} Giordano and Kharaka,\textsuperscript{51} Hanor,\textsuperscript{62,111,112} Hitchon et al.,\textsuperscript{106} Palandri and Reed\textsuperscript{114}). Based on these studies as well as others, it is now well established that three principal factors control Pb and Zn concentrations in modern basinal brines: (1) the availability of Pb and Zn in the basin system, (2) the total reduced sulfide...
content ($\Sigma H_2S$) of the brine, and (3) the chlorinity of the brine ($\Sigma Cl^{-}$). The field evidence for modern petroleum-field brines, as summarized in Table 10, suggests an inverse relationship between total sulfide content and the concentration of Pb and Zn. All high $\Sigma H_2S$ brines have low concentrations of these metals, while all brines with elevated Pb and Zn values have low concentrations of total sulfide. General details of this inverse relation are presented by Kharaka et al.\textsuperscript{106} Moldovanyi and Walter,\textsuperscript{109} and Hanor.\textsuperscript{61} Hanor\textsuperscript{61} also reports a pronounced covariation in Zn and Pb corresponding to a mass ratio of approximately 5:1 for brines with dissolved Zn concentrations greater than a few mg L\textsuperscript{-1}, while there is considerable scatter in Zn to Pb ratios for brines having Zn and Pb concentrations below 1 mg L\textsuperscript{-1}. These relationships (Zn + Pb vs. $\Sigma H_2S$ and Zn vs. Pb) support the conclusion that one control of Pb concentration and Zn concentration in high trace-metal brines is mineral buffering, possibly equilibrium with galena and sphalerite, respectively (Kharaka et al.\textsuperscript{106}, Hanor\textsuperscript{61}).

However, because most low $\Sigma H_2S$ petroleum-field brines also have low concentrations of trace metals (e.g., Pb and Zn < 1.0 mg L\textsuperscript{-1} each, see Table 10) and highly variable Zn to Pb ratios, the availability of Pb and Zn in the brines must also be a major control on the concentration these metals. Because galena and sphalerite are normally not present as components of basinal sediments, it seems more likely that Pb and Zn in most petroleum-field waters (as well as related ore fluids) were ultimately leached from other sources including metal oxides and hydroxides associated with red-beds sediments, organic matter, K-feldspar in sandstone, carbonate phases, or shales (Sverjensky,\textsuperscript{51,41} Kharaka et al.\textsuperscript{106}, Hanor\textsuperscript{61}). If such is the case, then it is not surprising that most low $\Sigma H_2S$ formation waters with low concentration of Pb and Zn are also characterized by variable Zn to Pb ratios.

Both field and modelling evidence demonstrate that chlorinity has a strong influence on the trace metal content of petroleum-field brines (Lundegard and Kharaka,\textsuperscript{128} Hanor,\textsuperscript{60,61,111} Kharaka et al.\textsuperscript{7}). The relationship of chlorinity versus Zn concentration for Gulf Coast saline waters (Hanor\textsuperscript{61}) shows unequivocally that petroleum-field brines which have Pb and Zn concentrations in excess of 1.0 mg L\textsuperscript{-1} nearly always have chlorinities in excess of approximately 100 000 mg L\textsuperscript{-1} (salinity $\approx$ 170 000 mg L\textsuperscript{-1}). There is a $\Sigma Cl^{-}$ transition zone between 60 000 mg L\textsuperscript{-1} (salinity $\approx$ 100 000 mg L\textsuperscript{-1}) and 100 000 mg L\textsuperscript{-1} in which a few brines have Pb or Zn in excess of 1 mg L\textsuperscript{-1}. As mentioned by Hanor,\textsuperscript{61,111} these results strongly suggest a threshold chlorinity of roughly 100 000 mg L\textsuperscript{-1} below which formation waters are typically poor solvents of Pb and Zn and above which Pb and Zn, in concentrations capable of forming economic deposits of these metals, can be mobilized by formation waters. These field relationships are consistent with modelling results, including those of this study. There are also major differences in the corresponding total chloride to carboxylate ratio ($\Sigma Cl^{-}$/2$\Sigma CBX$). Most modern high trace-metal brines have much higher $\Sigma Cl^{-}$/2$\Sigma CBX$ and, therefore, the contribution carboxylate complexes to the total Pb and Zn content in these modern brines is likely to be significantly less than the 1 to 3 percent for the composite ore fluids of Anderson\textsuperscript{37} and Giordano\textsuperscript{76}. The ratio of monocarboxylate acid anions to dicarboxylate ligand species ($\Sigma MOCB$/$\Sigma CBX$) appears to be higher in modern high trace-metal brines compared to the composite ore fluid. These systematics in organic acid content suggest that carboxylate complexation of Pb and Zn in modern brines should be less than predicted by the composite brine modal in this study. There are also major differences in the corresponding total chloride to carboxylate ratio ($\Sigma Cl^{-}$/2$\Sigma CBX$). Modern high trace-metal brines have much higher $\Sigma Cl^{-}$/2$\Sigma CBX$ and, therefore, the contribution carboxylate complexes to the total Pb and Zn content in these modern brines is likely to be significantly less than the 1 to 3 percent for the composite ore fluids of Anderson\textsuperscript{37} and Giordano\textsuperscript{76} (\textsuperscript{1}). This is consistent with the prediction of Giordano and Drummond\textsuperscript{87} that zinc chloride complexes dominate over acetate complexes of Zn if $\Sigma MOCB$/2$\Sigma MCT$ is greater than 10 at temperatures near 100 °C.

In contrast to these ore solutions, the composite ore-brine based on the Giordano and Barnes\textsuperscript{59} MVT ore fluid (Table 10, Fig. 2 and 3) is comparable to the high salinity (> 170 000 mg L\textsuperscript{-1} TDS) subset of modern brines characterized by low trace-metal content and high total reduced sulfur ($\Sigma H_2S$) (Table 10, bottom half). The Giordano\textsuperscript{39} composite fluid is saturated with respect to galena and sphalerite and Pb and Zn speciation is dominated by sulfide complexes (Tables 6, 5, 8, 9). Thus, it is likely that concentrations of Pb and Zn in modern low trace-metal brines, with high sulfide content and slightly acidic to alkaline in pH, are also controlled by galena and sphalerite solubility and sulfide complexation of Pb\textsuperscript{2+} and Zn\textsuperscript{2+}. Overall concentrations of Pb and Zn are low because of the high sulfide content and, hence, the activities of Pb\textsuperscript{2+} and Zn\textsuperscript{2+} are suppressed because of mass action effects. It is likely that carbonate complexation of Pb and Zn is insignificant in these fluids because of the presumably low concentration of carbonate ligands and because Pb\textsuperscript{2+} and Zn\textsuperscript{2+} activities are low, thus suppressing the formation of Pb and Zn in high trace-metal brines is consistent with the 1 ppm Pb and 1 ppm Zn isopleths in Fig. 2 and 3, that are not far from the lower boundary of the Anderson\textsuperscript{37} and Giordano\textsuperscript{76} ore-regions.

The modelled fluids in this study are in equilibrium with galena and sphalerite. Hence, the above similarities in Pb and Zn content between the composite ore fluids and modern high trace-metal brines is consistent with the above assertion that an important control of Pb and Zn content in high trace-metal brines is mineral buffering, possibly equilibrium with galena and sphalerite.

Model ore fluids
A comparison of the composite ore fluid compositions from this study (Table 10 and related isopleths in Fig. 2 and 3) and the modern brine data in Table 10 shows that the ore brines, corresponding to log $fO_2$-pH conditions based on the Anderson\textsuperscript{37} and Giordano\textsuperscript{76} model fluids, are similar in many respects to modern, high trace-metal petroleum-field brines. Both sets of fluids have the following characteristics in common: (a) chlorinities ($\Sigma Cl^{-}$) near 100 000 mg L\textsuperscript{-1} or higher, (b) pH in the 4–6.5 range, (c) less than 0.1 mg L\textsuperscript{-1} total sulfide ($\Sigma H_2S$), (d) total sulfate ($SO_4^{2-}$) in the 0.1 to 1000 mg L\textsuperscript{-1} range, and (e) Pb concentrations in the 1 to 100 mg L\textsuperscript{-1} range and Zn concentrations in the 1 to 1000 mg L\textsuperscript{-1} range. Note that the Pb and Zn isopleths transecting the more reduced log $fO_2$–pH regions of the Anderson\textsuperscript{37} and Giordano\textsuperscript{76} ore fluids in Figs. 2 and 3, as well as the Pb isopleth corresponding to the 1 ppm Pb content (420 mg L\textsuperscript{-1}) for the corresponding composite fluids in Table 10, are close to the highest concentrations reported for these metals in petroleum-field brines (Pb, 111 mg L\textsuperscript{-1}; Zn, 575 mg L\textsuperscript{-1}). Also note that the 1 mg L\textsuperscript{-1} minimum for Pb and Zn in high trace-metal brines is consistent with the 1 ppm Pb and 1 ppm Zn isopleths in Figs. 2 and 3, that are not far from the lower boundary of the Anderson\textsuperscript{37} and Giordano\textsuperscript{76} ore-regions.
geochemical complexes, which are significantly weaker that sulfide complexes. Although high concentrations of carboxylate anions have been observed in certain high ΣH₂S petroleum-field brines, these high concentrations are always from brines with salinities much lower than 170 000 mg L⁻¹.

A comparison of the Sverjensky composite ore-brine with modern petroleum-field brines in terms of ΣH₂S and Zn content, reveals that this ore fluid holds a border position between modern high trace-metal brines and those with low trace-metal content and high ΣH₂S (Table 10). The composite Sverjensky fluid, as represented by the model results in Table 10 and Fig. 2 and 3, barely qualifies as a modern low trace-metal/high ΣH₂S brine and it is not far removed from modern high trace-metal brines that have total Zn content and ΣH₂S near the lower limit (1 mg L⁻¹) and upper limit (0.1 mg L⁻¹), respectively, for this brine category. As mentioned above, both of these modern brine-types are probably saturated, or close to saturation, with respect to galena and sphalerite. Also, these two modern brine-types generally coincide when ΣH₂S, Zn, and/or Pb all have values within or near the 1 to 10 mg L⁻¹ range. Thus, modern brines having these characteristics are referred to below as border-type brines.

Based on brine-composition data from numerous references cited in this paper, border-type brines do exist but are rare. Hanor41 discusses the variation of total Zn with ΣH₂S in Gulf Coast formation waters and suggests that brines which contain both dissolved Zn and dissolved total reduced sulfur in the 1 to 10 mg L⁻¹ range are probable. He also implies that these brines are likely to be saturated with respect to galena and sphalerite. Hanor41 also conducted computer simulations of sphalerite solubility, at 100 °C, in hypothetical basin brines and reports that at chlorinities in excess of 150 000 mg L⁻¹ (TDS = 250 000 mg L⁻¹) it may be possible for concentrations of Pb and Zn in excess of 1 mg L⁻¹ to coexist in solution with comparable concentrations of dissolved inorganic sulfide. It is interesting to note that the original MVT ore fluid of Sverjensky41 is initially saturated with respect to galena, but undersaturated with respect to sphalerite and contains 1.3 mg L⁻¹ Zn, 2 mg L⁻¹ Pb, and approximately 1 mg L⁻¹ dissolved sulfide (ΣH₂S). Thus, Sverjensky’s initial MVT ore fluid also corresponds to a border-type brine, as defined above.

The principal compositional difference between the original Sverjensky MVT fluid and the composite Sverjensky brine modelled in this study is in the total sulfur content. The original ore fluid has a total sulfur content of approximately 10⁻⁴.6 molal (1 mg L⁻¹ as H₂S), while total sulfur content in the composite fluid of this study is 10⁻² molal (340 mg L⁻¹ as H₂S or 960 mg L⁻¹ as SO₄²⁻). Thus, for the most oxidized and acidic conditions of the composite Sverjensky model, pH near 4.6 and log fO₂ near 51.8 (Table 10, Fig. 2 and 3), both ore fluid models, yield similar total Zn and ΣH₂S values, close to those of a border-type brine. However, as log fO₂–pH conditions deviate from this point in terms of log fO₂, but still remain in the delimited ore-fluid region, the composite fluid yields values for ΣH₂S and concentrations of Zn and Pb that are more in line with modern brines, with only a few percent of the total Pb and Zn being transported by carboxylate complexes. Under more reduced conditions, sulfide complexation of Pb and Zn dominates transport of these metals and, once again, carboxylate complexes are insignificant.

**Geochemical modelling of petroleum-field brines**

The model results and field evidence presented above are consistent with chemical simulation studies of carboxylate complexation in modern petroleum-field brines (cf. Hanor, cf. Kharaka, cf. Lundegard and Kharaka, cf. Giordano and Kharaka). The results from these studies indicated (1) that concentrations of Pb and Zn in carboxylate complexes form only a small percentage of the total Pb and Zn in metal-rich petroleum-field brines, (2) chloride complexation dominates Pb and Zn speciation in these brines, and (3) significant amounts of Ca, Mg, Fe, and Al can be complexed by carboxylate ligands in petroleum-field brines. The influence of pH and oxygen fugacity on the solubilization of Ca, Mg, Al, and Fe by carboxylate complexes in fluids similar to those modelled in this study is currently being investigated by the author and results of this study will be the topic of a forthcoming paper.

**Conclusions**

The chemical simulation results from this study and the comparisons made between proposed ore fluids and modern brines lead to several important conclusions regarding the role of carboxylate complexation of Pb and Zn in Mississippi Valley-type (MVT) ore fluids, ore fluids responsible for red-bed related base metal (RBRBM) deposits, and modern petroleum-field brines.

1. A comparison of dissolved Pb, Zn and sulfur content of modern petroleum-field brines with Pb and Zn solubility systematics in log fO₂–pH space for the composite ore-brine in this study reveals good correlations between modern brine-types and proposed ore fluid models for Mississippi Valley-type deposits and red-bed related base metal (RBRBM) deposits.

2. Based on analyses of formation waters worldwide and the modeling results of this study, modern petroleum-field brines and the model ore fluids can be divided into four main categories:

   a. High trace-metal, low total sulfide brines which are similar to the 1975 model MVT fluid of Anderson and the 1994 RBRBM ore fluid of Giordano. Total sulfide is less than 0.1 mg L⁻¹, while total Pb and Zn have values between 1 and 100 mg L⁻¹, and 1 and 1000 mg L⁻¹, respectively.

   b. Low trace-metal, high total sulfide brines which are similar to the 1981 MVT ore fluid of Giordano and Barnes. Total sulfide is between 1 and 1000 mg L⁻¹, while total Pb and Zn are normally less than 0.1 mg L⁻¹.

   c. Low trace-metal, low total sulfide brines which may correlate to spent ore fluids or to basinal fluids not sufficiently enriched in Pb or Zn to be ore fluids of these metals.

   d. Border-type brines that in terms of reduced sulfur and trace-metal content are on the border between high trace-metal brines and brines low in trace metals but high in sulfide. Brine-types (a) and (b) above coincide when total sulfide, total Pb, and/or total Zn all have values near or within the 1 to 10 mg L⁻¹ range. Brines of this type are rare and generally correspond to the 1984 model ore fluid of Sverjensky.41

3. In modern basinal brines and related ore fluids with chlorinates near 100 000 mg L⁻¹, chloride complexes dominate the speciation of Pb and Zn under log fO₂–pH conditions most favorable for the complexation of these metals by carboxylate ligands.

4. The model results at 100 °C indicate that, for these basinal brines under the most favorable conditions, up to 3% of the total Pb and up to 1.3% of the total Zn can be mobilized by
carboxylate complexes, principally those involving the acetate ligand.

(5) The percent of dissolved Zn and Pb complexed by carboxylate ligands in a basinal brine will depend primarily on four key variables, assuming a system remains invariant with respect to temperature, total sulfur content of the brine, and mineralogy of the aquifer. The four variables are (a) the ratio of total chloride molality to total carboxylate ligand molality, (b) the mix of specific carboxylate ligands, for example the molar ratio of monocarboxylate ligands to dicarboxylate ligands, (c) the concentration of total sulfide, which is controlled by the log $f_{O_2}$–$pH$ conditions of the brine, assuming sulfate–sulfide equilibrium among the sulfur-bearing species of the system, and (d) pH.

(6) Optimum brine conditions, at 100 °C, for carboxylate complexation include (a) high oxidation state, reflecting a high total sulfate to total sulfide ratio and total sulfide concentrations less than $10^{-6}$ molal (i.e., dissolved H$_2$S), (b) high but reasonable concentrations of carboxylate anions, near 7000 mg L$^{-1}$ for total monocarboxylate species and 300 mg L$^{-1}$ for total dicarboxylate ligands, and (c) pH in the 4–8 range.

(7) At 100 °C, under optimum brine conditions for carboxylate complexation, approximately 1 to 100 mg L$^{-1}$ and 0.1 to 10 mg L$^{-1}$ of Zn and Pb, respectively, can be mobilized as carboxylate complexes, principally those involving acetate.

(8) However, the field evidence based on analyses of petroleum-field brines worldwide, suggests that all of these optimum conditions are rarely, if ever, met at the same time, particularly with regard to the requisite carboxylate ligand content. Thus, it appears that carboxylate complexation plays a minor, if not insignificant, role as a transport mechanism for Pb and Zn in high salinity Na–Cl and Na–Ca–Cl basinal brines and related ore fluids.

(9) More refined simulations of base-metal solubility and speciation in basinal brines can be conducted by making the following modifications of the model used in this study: (a) the use of reliable 100 °C thermodynamic data for Pb$^{2+}$ and Zn$^{2+}$ monolactate complexes, (b) the inclusion of Cu$^{2+}$ complexation in the model, (c) better estimates of log $f_{O_2}$ and pH conditions for the modelled ore fluids and modern petroleum-field brines, and (d) the use of mineral solubility constraints to control the activities of Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ in the model.

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