100th Anniversary Special Paper:

Metal Concentrations in Crustal Fluids and Their Relationship to Ore Formation

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Abstract

A database of saline fluid compositions, including deep shield ground waters, sedimentary formation waters, geothermal brines, and fluids from metamorphic and igneous rocks and veins, is used to explore the controls on metal concentrations in crustal fluids. There are no systematic differences between analyses of fluids sampled by drilling and analyses of fluid inclusions. Over the wide range studied, temperature emerges as a dominant control on the concentrations of Fe, Mn, Zn, and Pb in solution, although the more limited data for Cu are equivocal. Chloride concentration is also important, with the mole ratio metal/chloride (Me/Cl) remaining reasonably constant at constant temperature over a wide range of chlorinities for all four metals considered in detail. There is no evidence for significant differences in transition-metal speciation with increasing chloride nor between low- and high-temperature fluids, although in the case of Zn, complexes with additional Cl may be important at low temperature. Plots of log Me/Cl versus 1/T for the transition metals considered each yield a linear correlation, with about five orders of magnitude variation in Me/Cl between diagenetic and magmatic temperatures. There is approximately two orders of magnitude variability at each temperature, which probably arises in large part from variations in pH. Limited data for low-salinity, CO_2-rich fluids indicate that they lie on the same trends, with transition-metal concentrations controlled by fluid salinity and temperature. Order of magnitude concentrations of Fe, Mn, Zn, and Pb in any chloride-dominated crustal fluid can be predicted with the following equations (T in K, concentration ratios are molar): $\log (Fe/Cl) = 1.4 - (1,943/T) \pm 1$; $\log (Mn/Cl) = 0.55 - (1,871/T) \pm 1$; $\log (Zn/Cl) = -(1,781/T) \pm 1$; $\log (Pb/Cl) = -1.2 - (1,533/T) \pm 1$.

The results demonstrate that crustal fluids are strongly buffered through interactions with the rocks (or melts) that host them. Thus, of the major variables influencing metal concentrations in solution, only temperature and chloride concentration can be considered as truly independent. The plots show that metal-rich fluids may arise through equilibration of chloride-rich waters with normal silicate rocks. Saline magmatic fluids, which may attain extremely high concentrations of transition metals, have clear ore-forming potential, as do formation brines from deep, hot basins; cooler basins do not permit such high concentrations of base metals to be attained. The results of this study emphasize the importance of the distribution and cycling of chloride in the crust for the distribution of base metal deposits; it is often the salinity of ore fluids that is the primary anomaly.

Introduction

THE IMPORTANCE of aqueous solutions for the formation of a wide range of both high- and low-temperature ore deposits has been recognized for many years, but our understanding of their role in the formation of hydrothermal ores was limited for many years by a lack of reliable information about metal concentrations in ore fluids. Twenty-five years ago, many researchers thought that ore fluids were very dilute; Fyfe et al. (1978, p. 45) wrote that "the concentration of minor elements (ore-forming elements) is generally in the ppm or less range," while Barnes (1979) suggested 10 ppm as a minimum threshold value for base metal ore fluids. As a result, there was an emphasis on identifying flow mechanisms capable of processing exceptionally large volumes of fluid for the formation of

orebodies. In recent years, it has become apparent that metal concentrations are commonly much higher than this (Carpenter et al., 1974; Bottrell and Yardley, 1988; Williams and McKibben, 1989) and as a result a more balanced approach is needed toward understanding the formation of large orebodies, taking into account both controls on fluid chemistry and the focusing of fluid flow.

The experimental databases of mineral solubilities and thermodynamic parameters provide an essential framework for the interpretation of hydrothermal ore formation and, in particular, for the understanding of the factors that control precipitation and dissolution of minerals. However the experimental and theoretical framework must be interfaced with an empirical knowledge of key compositional parameters for natural fluids derived from rocks and ores themselves. This is because some of the most important parameters

controlling metal contents in fluids, notably chloride concentration, are variables that are not constrained by pressure, temperature, or fluid-rock interaction and must be measured directly. Because the thermodynamic and experimental databases are not complete, they cannot always provide a reliable prediction of the metal contents of natural fluids. Uncertainties in activity models for concentrated solutions and lack of knowledge of the equilibrium constants for the formation of many metal complexes, especially those involving ligands other than chloride, remain important limitations on the effectiveness of a theoretical approach to predicting crustal fluid chemistry at the present time.

While our experimental and theoretical understanding of ore fluids has been greatly extended in recent years (Seward and Barnes, 1997; Sverjensky et al., 1997; Wood and Samson, 1998), so too has the database of natural fluid compositions. Some aspects of fluid chemistry can be inferred from mineral compositions, but the major advances have been in the increased range of fluids sampled by deep drilling and in fluid inclusion studies. Deep drilling and submersible sampling have both provided direct information about the fluids involved in the precipitation of minerals at submarine hydrothermal systems (e.g., de Ronde, 1995) and in a range of other settings, including deep basins (e.g. Carpenter et al., 1974) and igneous and metamorphic basement rock (e.g., Frape and Fritz, 1987; Möller et al., 1997). The development of techniques for high-precision bulk analysis of fluid inclusions (Bottrell et al., 1988) and for analysis of individual inclusions by techniques such as laser Raman spectroscopy, proton probe, synchrotron XRF, and especially laser ablation ICP-MS (Heinrich et al., 1992; Phillipot et al., 1998; Anderson and Mayanovic, 2003; Heinrich et al., 2003) give direct information about ore metal concentrations in natural fluids beyond the reach of drilling. This paper explores the implications of data from natural fluids sampled by drilling and from fluid inclusions on models for the origin of ore fluids and ore deposits.

In particular, this paper is concerned with fluids from sedimentary, metamorphic, and igneous environments where fluid-mineral interactions are likely to be important. Shallow geothermal systems in which phase separation and interactions with the hydrosphere and atmosphere may also play a major role in controlling fluid compositions are not considered here in detail. The main emphasis of the paper is on Fe, Mn, Zn, and Pb in saline fluids and, to a lesser extent, Cu. All the fluids considered here have chloride as the dominant anion and chlorinities that range from <15,000 to >400,000 ppm, although most are in the range 40,000 to 180,000 ppm. While this selection is partly dictated by the greater availability of data on natural brine compositions, it is also justified by the importance of brines in the genesis of a wide range of ore deposit types. Sedimentary brines are responsible for the formation of extensive low-temperature Pb-Zn mineralization (Carpenter et al., 1974; Sverjensky, 1986), whereas saline magmatic fluids (some containing >40–50 wt % salts) are implicated in porphyry mineralization (e.g., Hedenquist and Lowenstern, 1994). Both types of brines have been proposed as the source of hydrothermal iron mineralization (e.g. Barton and Johnson, 1996; Hitzman, 2000). In addition, brines generated by dissolution of evaporites at

elevated temperatures are responsible for the formation of some types of emerald deposits (Kozlowski et al., 1988, Banks et al., 2000), while evaporites are also implicated in the formation of Zambian copper belt ores and structures (Hudec and Jackson, 2002).

Metal Solubility in Crustal Fluids

Crustal fluids react with the rocks that host them, and so an equilibrium approach is a useful starting point to understand the range of crustal fluid chemistries that are possible. While equilibrium might be expected to be attained readily in magmatic and metamorphic systems (Eugster, 1981; Brimhall and Crerar, 1987; Eugster and Baumgartner, 1987), it also appears that mineral-fluid equilibrium is attained even at low temperatures in sedimentary basins (Hanor, 1994, 2001; Hutcheon, 2000).

Ore metal concentrations in solution can ultimately be linked to simple mineral dissolution reactions such as:
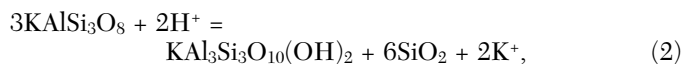
$$ZnS + 2H^+ = Zn^{2+} + H_2S^\circ, \qquad (1)$$

for which $\log K_1 = \log (a_{Zn^{2+}}/a_{2H^+}) + \log a_{H_2S^\circ}$. Thus, even for fluids saturated with sphalerite at a single pressure and temperature, the Zn^{2+} concentration can vary as a function of both pH and the concentration of reduced S. Furthermore the total Zn in solution is almost invariably dominated by Zn chloride complexes (Ruaya and Seward, 1986), the concentration of which will depend additionally on the salinity of the fluid. For many other transition metals, f_{O_2} is an additional variable with a major influence on their solubility.

Experimental studies of ore metal solubility have explored the effects of variations in many of these parameters, and a number of authors have calculated contoured activity diagrams to show the very wide ranges of metal concentrations that are possible as functions of pH, f_{O_2}, and total sulfur in particular (e.g. Barnes, 1979). In the laboratory it is desirable to be able to explore independently the variations in the parameters that control metal solubility, but in many natural systems there is much less scope for independent variation in most of the key parameters because their values are constrained by reaction with common rock-forming minerals. As a result, natural fluids in the crust may show a much more restricted range of compositions than would be possible for fluids that did not interact with surrounding rocks or melts. Thus, their metal concentrations should be much more predictable than in an unconstrained and unbuffered system. In the following section, the potential for independent variation (at constant pressure and temperature) in each of the main parameters that controls metal concentrations in solution will be discussed. The arguments are specifically directed at the limits to the compositions of fluids that have equilibrated with common silicate rock types; obviously a somewhat wider range of conditions may be experienced by fluids equilibrated with some other, less abundant lithological units.
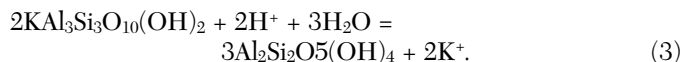
Parameters

pH: Crustal fluids equilibrated with aluminosilicate rocks most commonly have a pH limited by the presence of mica, through equilibria with Al silicate phases such as kaolinite or with feldspar, although in some rocks carbonate minerals will

also impose limits. Examples of the bounding reactions to muscovite stability include:

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

and

$$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O = \\ 3Al_2Si_2O5(OH)_4 + 2K^+. \qquad (3)$$

Each of these limits the ratio a_{K^+}/a_{H^+} rather than pH itself, and together they define a range of a_{K^+}/a_{H^+} values over which muscovite is stable. K-feldspar is stable at higher values of a_{K^+}/a_{H^+}, Al silicates such as kaolinite, pyrophyllite, or andalusite at lower values. The actual concentration of K in a crustal fluid, and hence a_{K^+}, is largely a function of salinity and Na-K mineral exchange equilibria (Eugster and Gunter, 1981; Henley et al., 1984, chap. 6). The concentration of K probably varies by around one order of magnitude between concentrated brines and fluids of near seawater salinity in equilibrium with the same assemblage, although lower values are possible in very dilute waters. The difference in log a_{K^+}/a_{H^+} buffered by these two reactions in the presence of quartz is around 2 log units at 150° and 5 kbars pressure, although it will be less under more normal P-T conditions of higher temperature at lower pressures, where the stability field of muscovite is diminished (Bowers et al., 1984). The relationship between fluid chlorinity, mineral assemblage, and pH is illustrated for two temperatures in Figure 1. This figure has been calculated using Geochemist's Workbench (Bethke, 1996) to take into account the nonideality of saline fluids and demonstrates that, at P-T conditions for which fluid densities are close to those of many ore fluids, the pH of a saline fluid equilibrated with kaolinite + muscovite + paragonite is unlikely to be more than ca. 2 log units lower than the pH of a low-salinity fluid equilibrated with K-feldspar + muscovite + albite at the same temperature. Thus, only a limited range of pH values is expected for most rock-hosted fluids at any given pressure and temperature, even though few rock systems act as true pH buffers. It will be demonstrated below that the effect of variations of salinity on pH is further reduced if divalent cations are present in the fluid to a significant degree.

The significance of pH variation for metal concentrations in ore fluids is that mineral assemblages generally buffer ratios of transition metal (and most other ore metal) cations to hydrogen ions, through mineral dissolution reactions. For example, from reaction (1), all fluids equilibrated with sphalerite at the same pressure, temperature, and $a_{H_2S^o}$ will have the same value for $(a_{Zn^{2+}}/a_{2H^+})$, but the actual value of $a_{Zn^{2+}}$ will depend on pH and hence will increase with salinity (below).

f_{O_2}: The oxygen fugacity of most crustal rocks is constrained by the presence of Fe in both reduced and oxidized forms, either as oxides or as components of silicate mineral solid solutions, such as biotite (e.g., Giggenbach, 1997). Although oxygen fugacity varies greatly with temperature in absolute terms, values relative to the quartz-fayalite-magnetite buffer (ΔQFM) vary only by a few log units for a wide range of natural rock buffer assemblages. Using the equations of Frost et al. (1988), the maximum difference between the reduced QFM buffer and the relatively oxidized hematite-magnetite
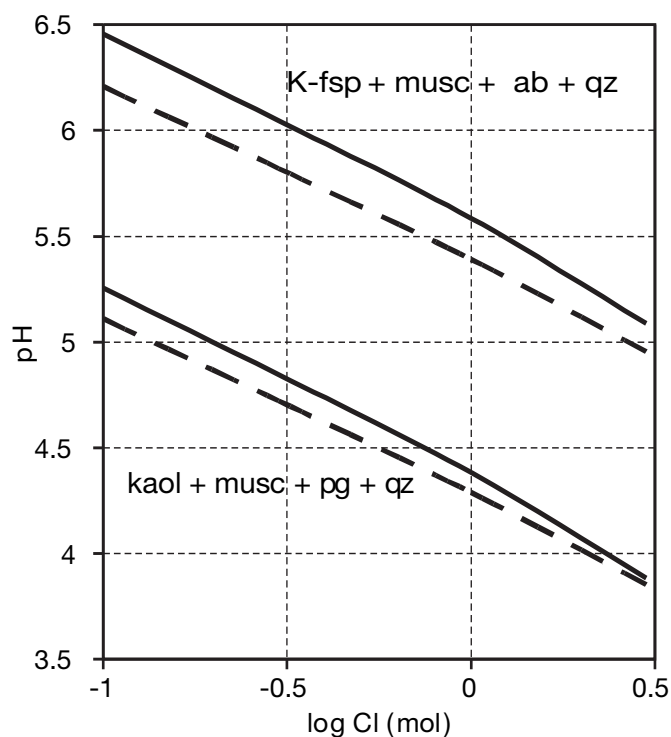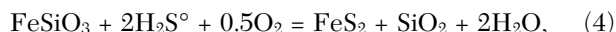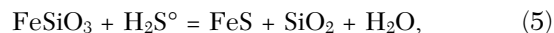

FIG. 1. Curves to show the pH of fluids ranging from 0.1 to 3.0 m Cl, equilibrated with K-feldspar + muscovite + albite + quartz (upper curves), and kaolinite + muscovite + paragonite + quartz (lower curves) at 275°C (solid lines) and 225°C (broken lines) and at pressures on the boiling curve of water. At these conditions neutral pH is ca. 5.6 and pyrophyllite and kaolinite yield very similar results for the lower curves. The calculations were performed using the Geochemist's Workbench code (Bethke, 1996).

(HM) buffer is 5.4 log f_{O_2} units at 300°C and 1,000 bars pressure, decreasing to 5.0 at 500°C. This means that fluids equilibrated with silicate rocks experience only a rather small part of the range of redox conditions that has been investigated experimentally and in calculations, and this lies close to the major mineral buffers. Changes in temperature along the flow path of a fluid can however induce significant changes in its oxidation state relative to QFM, provided it is unable to react with host rocks.

Reduced sulfur: The majority of crustal rocks contain a sulfide phase, most commonly pyrite or pyrrhotite, and an Fe-bearing silicate, and these provide a clear limit on the concentration of reduced S in solution, for example:

$$FeSiO_3 + 2H_2S° + 0.5O_2 = FeS_2 + SiO_2 + 2H_2O, \qquad (4)$$

and

$$FeSiO_3 + H_2S° = FeS + SiO_2 + H_2O, \qquad (5)$$

where $FeSiO_3$ represents the Fe-bearing component of the silicate phase. Not only do these equilibria constrain the H_2S concentrations in rock-buffered fluids, they also demonstrate the limitation of using activity diagrams constructed for a constant total S content of the fluid, for the interpretation of rock-buffered fluids. Equilibria 4 and 5 specifically define the activity of the $H_2S°$ species; however, other S species may predominate at higher pH or f_{O_2}, in which case the total S in the fluid may vary considerably. Both these equilibria define

$a_{H_2S^o}$ independently of pH, and hence at higher pH values, where HS^- is the dominant reduced S species in solution, HS^- must be present in addition to the constant (pH-independent) amount of H_2S^o. As a result, outside the field of H_2S^o predominance the total amount of reduced S in solution in equilibrium with the Fe silicate plus Fe sulfide increases rapidly with pH until the solid assemblage is no longer stable. This result, namely that pyrite solubility increases with pH, appears counterintuitive, but it is consistent with the observation that pyrite simply does not remain stable to pH values much beyond the H_2S^o field unless very high dissolved S levels are present. Note also that equations 4 and 5 do not say anything about Fe solubility in solution, and this will be expected to decrease with increasing pH.

A similar argument applies as conditions become more oxidizing. For pyrite equilibria (reaction 4), an increase in f_{O_2} of 2 log units will result in a drop in the log activity of H_2S^o of 0.5. However sulfide-sulfate equilibrium requires that, at constant pH, there is a four orders of magnitude increase in $(a_{SO_4^{2-}}/a_{H_2S^o})$ in response to this increase in O_2. Except where the initial $a_{SO_4^{2-}}$ was very low, this will be achieved primarily through dissolution of pyrite, rather than by oxidation of H_2S^o, and will result in an increase in the total S content of the fluid.

Chloride concentration: The importance of chloride as a master variable controlling metal concentration in fluids was emphasized by Helgeson (1970). Since solid chlorides are rare in rocks other than evaporites, the chloride content of crustal fluids is normally unbuffered and dictates the total cation load of the fluid through charge balance. Because chloride is partitioned so strongly into the fluid phase, mineral-fluid interactions have little effect on the amount of Cl present in crustal fluids; indeed, their main impact on chloride concentrations arises through changes in the quantity of water in the fluid, not the quantity of salt. In general magmatic or sedimentary fluids inherit a salinity that reflects their source and origin, and this is modified through subsequent fluid-rock interactions by dilution and hydration and/or dehydration reactions. Yardley and Graham (2002) showed that the salinity of fluids from metasedimentary rocks of all grades reflected the original environment of deposition of the sediments, rather than their metamorphic grade. Specifically, they found that continental margin sequences, likely to have originally contained evaporites, yield much more saline metamorphic fluids than are present in metamorphosed oceanic sediments.
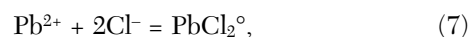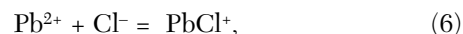
There are three ways in which chlorinity influences the balance of metals in rock-buffered fluids: by the formation of aqueous chloride complexes, by controlling the relative proportions of monovalent to divalent (or trivalent) cations (Eugster and Gunter, 1981), and by influencing the level at which a given mineral assemblage controls the pH.
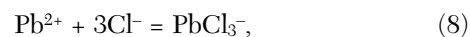
Formation of chloride complexes

Chloride is the most important complexing ligand for a wide range of metals, including most base metals, in part because of the stability of chloride complexes for the many metal cations that display hard behavior under hydrothermal conditions (Seward and Barnes, 1997) and also because of the massive predominance of chloride over other ligands in many

natural fluids. Of the hydrothermal ore metals commonly considered, it is likely that only Au, As, Sb, Tl, and Hg are normally complexed by other ligands (Seward, 1973; Seward and Barnes, 1997; Zotov et al,. 1995), although some metals may be complexed by either chloride or other ligands (e.g., Ag). Also, it is likely that Cl is unimportant for the transport of Al and some other light metals. Seward and Barnes (1997) have summarized experimental data on the formation constants of a range of metal chloride complexes, and Sverjensky et al. (1997) have presented predicted equilibrium constants for a very wide range of aqueous complexes. Wood and Samson (1998) presented a valuable comparison of these and other results.

For many metals there is a series of possible chloride complexes, for example:

$$Pb^{2+} + Cl^- = PbCl^+, \qquad (6)$$

$$Pb^{2+} + 2Cl^- = PbCl_2^o, \qquad (7)$$

and

$$Pb^{2+} + 3Cl^- = PbCl_3^-, \qquad (8)$$

for which $\log K_6 = \log a_{PbCl^+} - \log a_{Pb^{2+}} - \log a_{Cl^-}$, $\log K_7 = \log a_{PbCl_2o} - \log a_{Pb^{2+}} - 2 \log a_{Cl^-}$, and $\log K_8 = \log a_{PbCl3-} - \log a_{Pb2+} - 3 \log a_{Cl^-}$. These equilibrium constant expressions imply that the larger complexes are stabilized, if at all, at higher Cl^- activities. In experimental systems investigated at constant pH, the identity of the dominant chloride complex under any specified conditions can be determined from the slope of the measured fluid composition on a log Cl versus log Pb diagram, as shown for an ideal theoretical system in Figure 2a. This relationship does not, however, apply to a rock-buffered crustal fluid, where pH varies with chlorinity (above; Hanor, 1994). The effects of rock buffering by alkali feldspars, quartz, and muscovite on pH are taken into account in Figure 2b. Here, $m_{Na^+} + m_{K^+} = m_{Cl^+}$, so that pH decreases with increasing Cl, and this is accompanied by an increase in Pb^{2+} also. As a result the slopes of all the Pb chloride species in the rock-buffered system of Figure 2b are steeper than predicted by Figure 2a. These diagrams are constructed for comparative purposes and ignore nonideal behavior; they are intended to underline this important difference between experimental (constant pH) and natural (variable pH) systems.

Combined effects of chloride and pH on transition metal concentrations

Not only is pH coupled to salinity in crustal fluids, the relationship between pH and salinity will vary according to whether the dominant cations are monovalent or divalent.

Alkali-dominated brines: Mineral equilibria between feldspars and micas buffer or limit activity ratios such as a_{K^+}/a_{Na^+} and a_{K^+}/a_{H^+} in a wide variety of rock types through reactions such as (2) and (3), above. At the same time, in an alkali-dominated brine, it is approximately the case that $m_{K^+} + m_{Na^+} = m_{Cl^-}$. It follows that a unit increase in m_{Cl^-} leads to a unit increase in $m_{(K^+ + Na^+)}$. Since the mineral buffers (reactions 2 and 3) require that a_{H^+} increases linearly with an increase in a_{K^+}, while exchange with Na phases controls the ratio a_{K^+}/a_{Na^+}, it will be true to a first approximation that pH decreases linearly with an increase in $\log m_{Cl^+}$ (Fig. 2b).
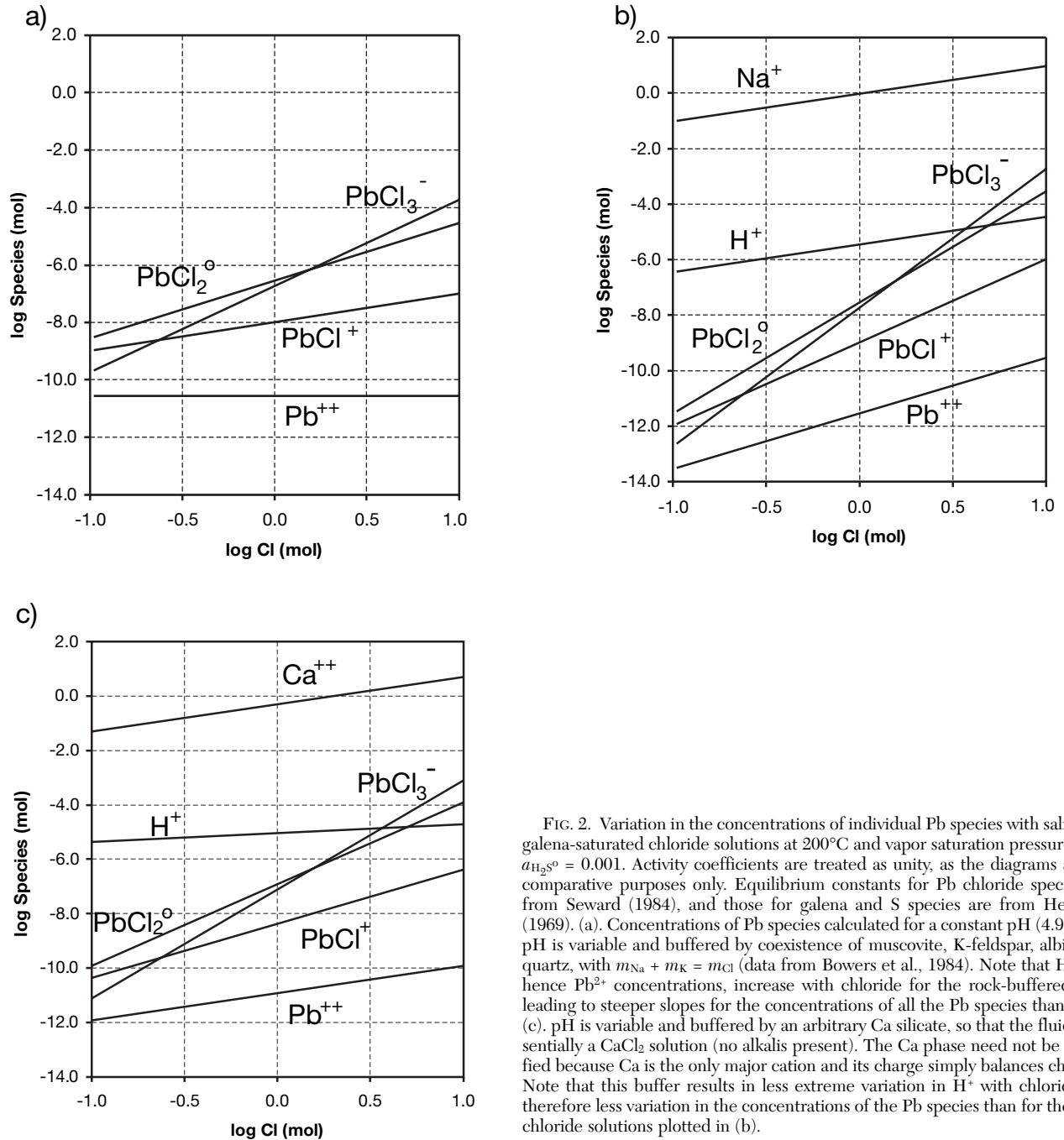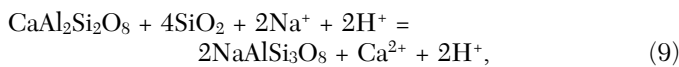
FIG. 2. Variation in the concentrations of individual Pb species with salinity in galena-saturated chloride solutions at 200°C and vapor saturation pressure, with $a_{H_2S^o} = 0.001$. Activity coefficients are treated as unity, as the diagrams are for comparative purposes only. Equilibrium constants for Pb chloride species are from Seward (1984), and those for galena and S species are from Helgeson (1969). (a). Concentrations of Pb species calculated for a constant pH (4.96). (b). pH is variable and buffered by coexistence of muscovite, K-feldspar, albite and quartz, with $m_{Na} + m_K = m_{Cl}$ (data from Bowers et al., 1984). Note that H⁺, and hence Pb²⁺ concentrations, increase with chloride for the rock-buffered case, leading to steeper slopes for the concentrations of all the Pb species than in (a). (c). pH is variable and buffered by an arbitrary Ca silicate, so that the fluid is essentially a CaCl₂ solution (no alkalis present). The Ca phase need not be identified because Ca is the only major cation and its charge simply balances chloride. Note that this buffer results in less extreme variation in H⁺ with chloride and therefore less variation in the concentrations of the Pb species than for the alkali chloride solutions plotted in (b).

Ca-dominated brines: In rocks that contain Ca silicate phases, the buffer reactions are more complex because of the valency difference between major cations. For example, plagioclase exchange equilibria in the presence of quartz may be written:

$$CaAl_2Si_2O_8 + 4SiO_2 + 2Na^+ + 2H^+ =$$
$$2NaAlSi_3O_8 + Ca^{2+} + 2H^+, \qquad (9)$$

for which $\log K_9 = \log (a_{Ca^{2+}}/(a_{H^+})^2) - 2 \log (a_{Na^+}/(a_{H^+})) = \log (a_{Ca^{2+}}/(a_{Na^+})^2)$. This equation demonstrates that the Ca/Na ratio of fluids equilibrated with a specific plagioclase composition will vary with fluid salinity, because it is $(a_{Ca^{2+}}/(a_{Na^+})^2)$, not $(a_{Ca^{2+}}/a_{Na^+})$ that is buffered by plagioclase-fluid equilib-

rium (Orville, 1972). A similar argument can be made for any fluid equilibrated with albite and a Ca silicate. It follows from reaction (9) that calcic mineral assemblages buffer $a_{Ca^{2+}}/(a_{H^+})^2$ so that there is no longer a simple linear relationship between cation and hydrogen ion activities. To a first approximation, $(a_{H^+})^2$, rather than a_{H^+}, increases linearly with increase in $m_{Ca^{2+}}$ in calcic fluids. At the same time, charge balance requires that $m_{Ca^{2+}} = 0.5\ m_{Cl^-}$ in the end-member case. It follows that a unit increase in m_{Cl^-} leads to only a 0.5 unit increase in $m_{Ca^{2+}}$ and therefore in $(a_{H^+})^2$. Hence large increases in Cl cause only modest decreases in pH. This effect is illustrated in Figure 2c.

The implication of this result for the relationship between transition metal concentrations and salinity is illustrated by comparing Figure 2b and c. Ore mineral dissolution equilibria constrain the ratio of the metal cation activity to hydrogen ion activity raised to the power of the cation valency, as in reaction (9). If an ore fluid is dominated by monovalent alkali cations, pH decreases more rapidly with increasing salinity than if it is dominated by divalent cations, and this is tracked by the Pb species. Thus, a high-salinity alkali-dominated fluid can show much greater ore metal enrichment than would be the case for calcic fluids.

Compositions of Natural Crustal Fluids

Although there is an extensive database on the major element chemistry of oil-field brines as well as of subaerial and sea-floor geothermal fluids, there are only sparse data on the compositions of natural fluids that have equilibrated with rocks at temperatures and/or depths beyond the reach of drilling. As a result, it has not been possible to evaluate systematically the compositions of fluids from a wide range of crustal residence environments. In this paper, I draw on the growing database of crustal fluid compositions, including analyses of inclusion fluids trapped at high temperature, to evaluate the controls on fluid composition through a wide range of crustal conditions. This empirical approach also provides insights into the factors that control metal transport and precipitation. The fluid compositions evaluated are selected as examples of fluids locally equilibrated with silicate rocks or magmas at specific pressure and temperature conditions; they are not ore fluids per se. The reason for this is to explore the ore-forming potential of crustal fluids; ore fluids by definition may reflect a fluid source distinct from the location at which they were sampled.

The emphasis of this study has been on fluids more saline than seawater (i.e., brines), with many analyses of fluids with >4 m chloride. Other anions are relatively minor, although they may dominate the solubility of some elements (above). The data sets included in the study are summarized below, and representative analyses are provided in Table 1.

Shield brines

Highly saline ground waters have been described from igneous and metamorphic basement rocks in various localities and are characterized by high concentrations of $CaCl_2$. In this study I have included those high-salinity waters compiled by Frape and Fritz (1987) that include data for transition metals.

Oil-field brines

Four sets of analyses of oil-field formation waters have been included, representing a range of temperatures and settings. Data from offshore oil fields comes from the study of Land et al. (1988) of offshore Louisiana and from the compilation by Warren and Smalley (1994) of data from North Sea oil fields. Not all are sufficiently saline to be categorized as brines, but we have included all the North Sea analyses for which data on Fe are given. Onshore formation waters are from the classic study of Mississippi oil-field brines by Carpenter et al. (1974), representing a relatively high temperature basin, and from the data set of Connolly et al. (1990) for Alberta basin brines.

Metamorphic brines

Sedimentary pore waters evolve continuously into metamorphic pore fluids (Yardley, 1997; Yardley and Graham, 2002) and so the distinction of this category is somewhat arbitrary. The data sets included here are examples of saline inclusion fluids extracted from quartz veins that developed during low-grade metamorphism or retrograde metamorphism. They are believed to represent the compositions of saline fluids that equilibrated with host lithologies in the crust, although they are not all metamorphic fluids in the sense of having been released from mineral lattices during heating. Temperatures have been estimated from associated mineral assemblages and fluid inclusion homogenization measurements, with pressure corrections where appropriate.

Veins from the Variscan of southwest Ireland (Meere et al., 1997) and the Colombian emerald deposits (Banks et al., 2000) are interpreted to represent pervasive peak metamorphic fluids in low-grade metasediments. Fluids from veins associated with Alpine thrusting of the Pyrenees (Banks et al., 1991; McCaig et al., 2000) are interpreted as brines that had experienced an extended residence in a sedimentary sequence before being remobilized during thrusting. They come from a particularly wide range of host rock lithological units including limestones, red beds, and igneous and metamorphic basement rocks. Temperature estimates from the original study have been revised upward based on the chlorite geothermometer of Cathelineau and Nieva (1985) applied to chlorite compositions reported by Grant (1989). Veins from basement rocks at Modum, Norway (Munz et al., 1995, 2002; Gleeson et al., 2003) contain deep basin brines that infiltrated the underlying high-grade basement. Their temperature structure is complex in detail (Gleeson et al., 2003) and is based in part on chlorite geothermometry and bitumen reflectance (Munz et al., 2002), as well as on fluid inclusion data. At higher metamorphic grades, primary fluid inclusions are generally absent from quartz and no data base suitable for inclusion in this compilation currently exists.

Magmatic and geothermal fluids

These data include both brines sampled by drilling and fluid inclusion samples. Most geothermal fluids are too dilute to be included in this compilation, but the Salton Sea geothermal brines (Williams and McKibben, 1989) are an important exception. They are not directly of magmatic origin (McKibben and Hardie, 1997) but are included here because they circulate in response to magmatic heating and interact with igneous rocks. A unique example of a magmatic brine sampled at high temperature is included from the Kakkonda geothermal system, Japan (Kasai et al., 1996). All other data consist of analyses of inclusion fluids. Analyses of fluids from the Mole Granite, southwestern Australia (Heinrich et al., 1992; Audetat et al., 2000) and from the Industrialnoe tin deposit of northeast Russia (Kamenetsky et al., 2002) are single inclusion analyses (see below), whereas the data from Cornwall (Bottrell and Yardley, 1988; Smith et al., 1996) and the Capitan pluton, New Mexico (Campbell et al., 1995) are bulk crush-leach analyses. Note that the fluids from the Capitan pluton are strictly wet salt melts and were shown by Campbell et al. (1995) to have evolved at a late stage in the emplacement

history when remobilized evaporite material mingled with the magma; this may have influenced the degree to which they equilibrated with silicate melt.

Data Quality

In general, analyses of oil-field and geothermal waters are not subject to large analytical errors but may be prone to problems of contamination or precipitation during sampling. This is particularly a problem for Fe, and for the North Sea compilation of Warren and Smalley (1994) it is not clear how valid all the Fe data may be (E. Warren, pers. commun., 2002). Fluid inclusion analyses are for the most part from published studies. Most analyses are bulk crush-leach determinations of the total fluid composition in a few hundred milligrams of vein host. In each example used, detailed microthermometry had first been employed to demonstrate that all the inclusions belonged to a reasonably homogeneous population, and the analyses reported both cations and anions, providing a check on charge balance (which was required to be within a few percent). Recent developments in proton probe (PIXE) and LA-ICPMS analysis have produced data from single fluid inclusions (Heinrich et al., 1992; Gunther et al., 1998; Heinrich et al., 2003) although with larger analytical uncertainties than bulk crush-leach analyses. We included LA-ICPMS analyses from Audetat et al. (2000) for magmatic brines from the Mole Granite, although some individual analyses were rejected as a result of large excess positive charges coupled to extremely high levels of Fe. PIXE analyses from Heinrich et al. (1992) and Kamenetsky et al. (2002) are included in the data set, although the results of Kamenetsky et al. (2002) do not include data for Na, making it impossible to test for charge balance or estimate molalities.

Downhole temperature estimates of formation waters may be subject to uncertainty depending on the sampling and measurement strategy. For a number of the metamorphic fluid examples, the temperatures are approximations, with a single value being used for an entire suite of (closely related) samples. Some of the magmatic fluids were trapped as inclusions at subsolidus temperatures and, therefore, may represent fluid compositions derived at higher temperatures than the trapping temperatures against which they have been plotted.

Results

The compiled data have been plotted to evaluate the importance of temperature, salinity, and oxidation state on ore metal concentrations in chloride fluids. By inference, the remaining unaccounted variability in the data is likely to be due primarily to pH variations, although in the case of minor element analyses of inclusion fluids, analytical errors may also produce significant scatter. Sulfide buffering cannot be evaluated independently for most of the analyses. Note that in the following sections, all element ratios considered are mole ratios, but for element concentrations results are plotted in parts per million, so that the incomplete data from Industrialnoe (Kamenetsky et al. 2002) could be included, except where otherwise noted. The main emphasis of this paper is on controls on Fe, Mn, Zn, and Pb in solution, because there is a sufficiently extensive data base for these elements. Although copper is also of considerable interest, it has not been possible

to demonstrate the major controls on Cu in solution, due to the paucity of good quality data and possibly more complex behavior of Cu (e.g. Heinrich et al., 1992).

Temperature

Figure 3 shows the concentrations of Zn, Pb, Fe, Mn, and Cu from the entire data set as a function of the inferred fluid temperature. The use of log concentration and reciprocal temperature is intended to identify the linear relationships that might arise if concentrations are dictated by mineral buffering. Remarkably, for Fe, Mn, Zn, and Pb, metal concentrations correlate linearly with 1/T across the entire range of fluid types and temperatures, and there is no systematic difference between analyses of fluids sampled by drilling and fluid inclusion analyses. Although there is a significant (ca. two orders of magnitude) spread in the data at a given temperature, reflecting variability in T-independent factors such as pH, the spread in the data set as a whole is so large that the correlation between metal contents and temperature is unambiguous. A few data sets do appear to be somewhat anomalous relative to the overall trend. Low-temperature Canadian shield brines are relatively rich in Fe and Mn, and Mississippi Valley formation waters are rather rich in Zn. At the high-temperature end of the spectrum, there is probably a significant uncertainty in the temperature of equilibration of analyzed inclusion fluids, and the apparent temperature difference between the Mole Granite fluids and the fluids from the Industrialnoe tin deposit may be partly an artifact of the different criteria used to estimate temperature. In contrast, the Cu data do not show such a clear trend, with large differences in Cu concentrations between Salton Sea brines and fluids from the Colombian emerald deposits, despite similar temperatures. Metamorphic and magmatic fluids also show considerable overlap in Cu concentrations. These deviations from a simple correlation between temperature and Cu concentration cannot be accounted for by variations in salinity, suggesting that the Cu database must be improved and expanded before it can be understood and interpreted further.

The data shown in Figure 3 do not imply that the absolute solubilities of these metals are a simple function of temperature, but they do mean that silicate rocks buffer the other factors that influence metal concentrations in natural waters in such a way as to produce this strong temperature effect. Thus, temperature emerges as a first-order control on metal concentrations in crustal fluids, a result that is in line with the instincts of many economic geologists but is not always apparent from theoretical and experimental studies that extend beyond the conditions encountered in rock-buffered environments.

Chlorinity

Part of the spread in the data at each temperature seen in Figure 3 may arise from variations in the chlorinity of the fluids, although all the fluids considered are of relatively high salinity. The relationship between metal concentration and chlorinity in natural fluids has the potential to shed considerable light on metal chloride complexing, as discussed above, and this part of the study follows the pioneering approach of McKibben and Williams (1989) who interrogate their Salton Sea data set in this way.

TABLE 1. Representative Analyses of Crustal Fluids from the Data Sets Discussed in the Text[1]

	Shield brine	Sedimentary formation waters								Metamorphic fluids			
Fluid type													
Data set	Canadian Shield	North Sea	North Sea	Central Mississippi	Central Mississippi	Central Mississippi	Offshore Louisiana	Alberta	Alberta	Pyrenees	Pyrenees	Columbia	Columbia
Location	Yellowknife	Miller	Buchan	West Clara	Raleigh Field	Raleigh Field		Rock Creek	Leduc	La Glere	Pic de Port Vieux	Cincho	Chivor
Sample no.	4500-6C	Brae	Old Red	Well 15	Well 66	F/60	E/Ai	Well 1	Well 5	55137	50182	Emerald GG-7	Quartz GG-20
Temp (°C)	22.5	120	105	129	135	68	96	75	63	300	345	320	320
Element concentrations (ppm)													
Na	32,600	28,780	56,700	54,200	76,200	25,900	52,660	8,470	50,000	56,303	41,772	94,823	68,344
K	495	1,830	1,525	863	979	173	244	119	3,640	7,747	1,630	18,813	8,796
Li	1.67	115		12		3.4	9.6	4	50	810	456	1,261	2,549
Mg	920	1,060	1,250	2,550	2,400	530	531	46	5,035	692	919	5,424	1,435
Ca	57,300	1,050	16,075	41,200	36,500	1,970	2,680	123	30,000	49,946	28,187	16,821	31,855
Sr	1640	110	938	1,360	2,260	70	444	26	1,190	1,964	1,228	228	1,524
Ba		14	23	20	109	53	274	14	7	450	1,028	303	1,503
Fe	18.6		100	335	294	7	11.9	0.15	17.48	1,334	1,516	10,772	4,579
Mn	21.8			110	102	1.2	2.3	0.09	0.49	647	176	1,005	1,025
Zn	0.59			108	342	0.06	0.12	0.06	0.83	191	75	199	950
Pb	2.42			2.3	96						3	60	315
Cu	0.81									107			
B	9.19					40	85	15	142	84	100		
F	26.9												
Cl	142,000	47,660	121,600	169,000	193,400	44,000	86,590	12,700	144,000	179,561	129,282	224,306	183,208
Br	1,520	1,520		1,680	1,510	61	126	28	1260	4,363	1034	39.7	42.8
As												370	48
SO_4^{2-}	1	8	220			9.6	3.6	11	294			166	
HCO_3^-	2	2,090	200		3	195	218						
Borehole/ inclusion	B	B	B	B	B	B	B	B	B	FI	FI	FI	FI
Reference	Frape and Fritz (1987)	Warren and Smalley (1994)		Carpenter et al. (1974)			Land et al. (1988)	Connolly et al. (1990)		Banks et al. (1991); McCaig et al. (2000)		Banks et al. (2000)	

TABLE 1 (*cont.*)

	Metamorphic fluids		Geothermal fluids			Magmatic fluids							CO_2–H_2O fluids	
Data set	Modum	Irish Variscan	Salton Sea	Salton Sea	Kakkonda	Mole	Mole	Cornwall	East Vitifer	Capitan	Industrialnoe	Industrialnoe	Muiane	Brusson
Location			Magmax 1	IID Well 1		Yankee	Gol 1							
Sample no.	DOV-1	Vein 2	1977	1968	WD-1a	2	B	54435	SW-89-155	FN-qtz	2.3	5.5	50700	LD886
Temp (°C)	220	260	250	340	500	528	420	400	500	570	800	800	500	280
Element concentrations (ppm)														
Na	17,118	16,824	38,300	50,400	75,000	73,000	65,000	24,559	70,054	173,686	44,400	36,100	11,236	16,752
K	1,032	1,497	10,400	17,500	35,000	35,000	63,000	5,795	13,100	68,902			882	985
Li	13	326	175	215		1,500	530	336	392	297			6,647	239
Mg	27	446						664	182					129
Ca	5,457	19,046	21,100	28,000	15,000			4,347	28,828	37,342	4,600	6,900		665
Sr	83	841					69		504	1361		120		54
Ba	31	130						164	148	767			188	43
Fe	53	178.3	280	2,290	32,000	40,200	93,000	3,848	5,940	14,347	46,200	27,400	125	120
Mn	26	291	635	1,400	8,000	14,000	12,000	1,155	3,475	17,143	7,000	5,800	17	5
Zn	3	63.9	290	540		3,200	2,800	190	686	2,067	3,400	3,200	469	34.3
Pb		118	44	102		2,600	1,700		190	680	4,400	1,300	133	
Cu	1	89	0.5	8		600	200	547	35		310	76	47	25.1
B	24	193				2,400		1,913	967	192			2,064	560
F									899	3,157				242
Cl	35,661	67,113	128,700	155,000	220,000	210,000	210,000	39,321	172,333	402,066	319,000	127,000	23,893	19,112
Br	221	169						51	329	122	250	339	118	70
As									98			45	1,814	147
SO_4^{2-}	86							995	876	15,892			1,420	102
HCO_3^-		2,382		5.4										
Borehole/ inclusion	FI	FI	B	B	B	FI	FI	FI	FI	FI	FI	FI	FI	FI
Reference	Munz et al. (1995)	Meere et al. (1997)	Williams and McKibben (1989)		Kasai et al. (1996)	Heinrich et al. (1992)		Smith et al. (1996)	Campbell et al. (1995)		Kamenetsky et al. (2002)		Pike (1993)	Yardley et al. (1993)

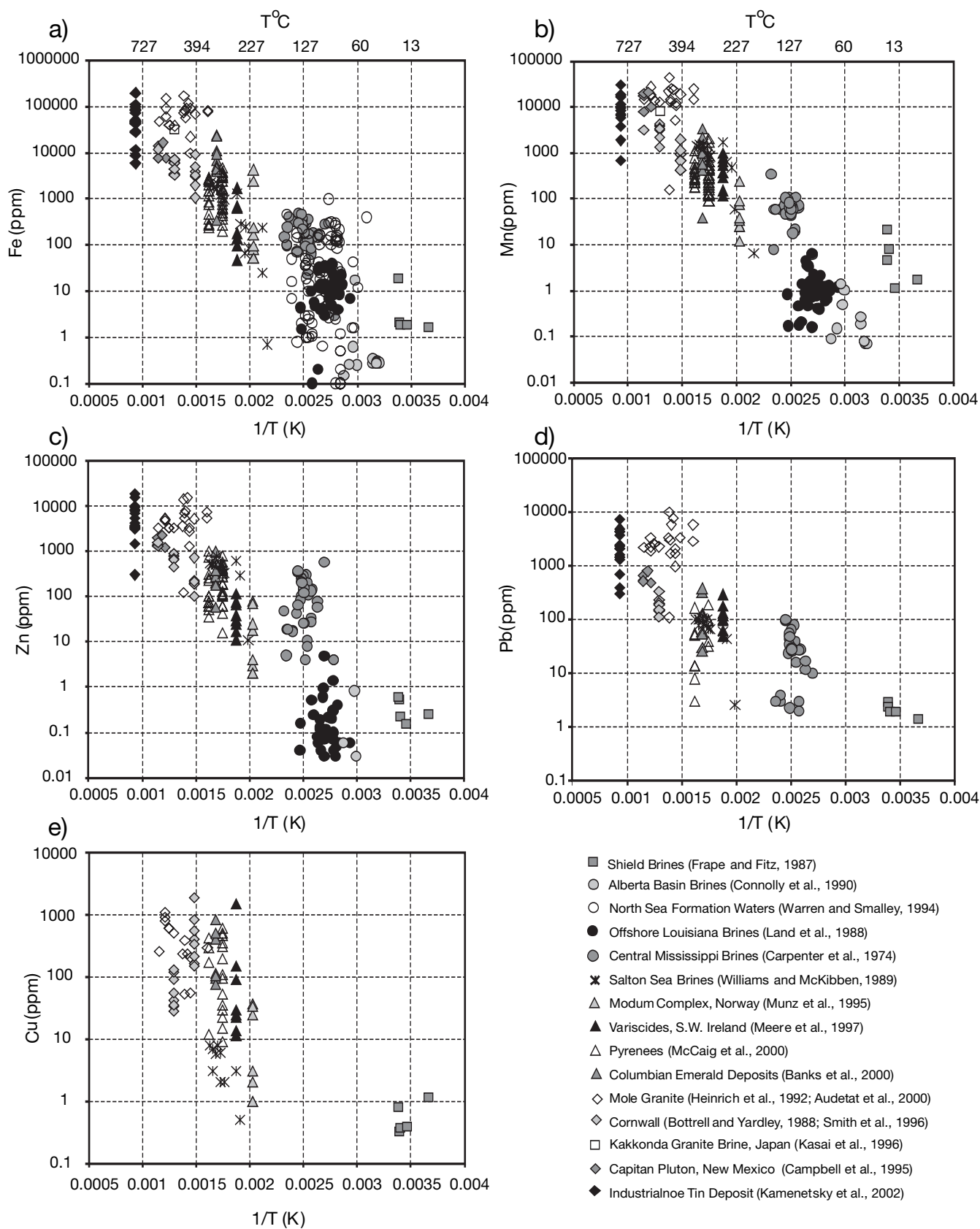[1] Blank entries may denote not analyzed or below detection, consult the original references for detail

FIG. 3. Concentrations of transition metals in crustal fluids from the data sets discussed in the text (note logarithmic scale) vs. 1/T (Kelvin) showing the major control that temperature exerts on rock-buffered crustal fluids. (a). Iron. (b). Manganese. (c). Zinc. (d). Lead. (e). Copper.

Figure 4 investigates the relationships between Cl and transition metal concentrations for the data sets that display the largest ranges in Cl concentration. Each dataset can be considered isothermal to a first approximation, and each defines a trend across the figure, with higher temperature data sets defining trends at higher metal concentrations. Concentration data in this figure are in weight units, and therefore the slopes are not comparable to those shown in Figure 2. Iron, manganese, zinc, and lead all display similar trends in Figure 4, although the Pb plot has more scatter than the others due to the paucity of data and often low concentrations.

The widest range of chloride concentrations is represented by the magmatic fluids, the low-temperature oil-field brines, and the Salton Sea brines, and Figure 5 shows the concentrations for these data sets plotted as molalities, where the data permit. Figure 5 provides two important insights into transition metal behavior in brines. First, for each element considered the slope of each data set appears to be approximately constant, suggesting that there are no significant changes in speciation over the range of salinities investigated. For all elements, the slope of the data for the high-temperature fluids is about 1 to 1.5. This cannot be taken as a direct indication of the metal chloride complexing, both because of the systematic pH variation that will be present (Fig. 1b, c) and because very large deviations from ideality must be expected for Cl$^-$ ion activity at these salinities. However the activity coefficient effects are likely to be very similar for each metal, since it is chloride activity that is crucial. The plots confirm our understanding from theoretical and experimental considerations, and from the Salton Sea case study by McKibben and Williams (1989), that each of these metals in chloride solutions is likely to form similar complexes (Seward and Barnes 1997, Wood and Samson 1998). Furthermore, the results are consistent with the dominant complexes being neutral dichloride complexes once allowance is made for nonideality as proposed by Seward and Barnes (1997).

A second point of interest is the effect of temperature on metal chloride speciation and therefore the slopes in Figure 5. It appears that, within the uncertainty of the data, the slope obtained from the low-temperature (formation water) data sets is indistinguishable from that for the high-temperature (magmatic) data, except possibly for Zn. Experimental results suggest that, for Zn at least, larger complexes may predominate at low-temperature and high-salinity ZnCl$_3^-$ and ZnCl$_4^{2-}$ (Seward, 1984). Hanor (1996) reported evidence for a threshold chlorinity near 100g/L, above which high concentrations of Zn were possible in oil-field waters and suggested that this reflects the increasing predominance of the larger complexes. Basuki and Spooner (2002) provided support for the existence of such a threshold from analyses of Mississippi Valley-type ore fluids, but there is little evidence to support it in this study. Figure 6a and b are plots of the mol ratios Zn/Cl and Zn/Cl^2, respectively, against chloride concentration. If the stoichiometry of the dominant Zn-Cl complex is either ZnCl or ZnCl$_2$, then data from a single isothermal suite will plot on a horizontal trend in these respective figures. On the other hand, if there is a change in the complexing with salinity, the slope of the data will change. Only the magmatic fluids show clear trends, reflecting the larger range of chlorinities and the smaller analytical uncertainties. These data fit best to the 1:1

Zn:Cl stoichiometry, although this may reflect nonideality of chloride rather than the actual complexing. Most of the lower temperature data do not have clear trends, however there is no evidence for any threshold, and the differences between different data sets are in accordance with their temperatures. Salinity tends to increase with depth and temperature in many oil fields, and it is possible that the underlying temperature trend, although not evident within individual data sets spanning a small temperature range, has reinforced the effects of high salinities.

The relationship between metal concentrations and chlorinity deduced from Figures 5 and 6 can be used to refine the relationship between temperature and metal concentrations. The molar ratio Me/Cl has been taken to be independent of Cl (as in Fig. 6a) and used to remove the effects of chlorinity from the evaluation of the relationship between metal concentrations and temperature. Figure 7 is a plot of log mol ratios Me/Cl versus 1/T and provides, as expected, a somewhat better fit between metal concentrations and temperature than Figure 3, although not surprisingly order of magnitude variations remain across the temperature spectrum. As noted previously, these most likely reflect different pH-limiting assemblages and analytical error, although redox will also be important for Fe (below). The Cu data have been included for completeness in Figure 7, although it is clear that, even after making allowance for the effect of Cl, the correlation with temperature is weak with large differences between data sets at similar temperatures.

Redox

The solubility of many transition metals is strongly influenced by the redox environment. This is not something that can be rigorously evaluated for the data sets that are compiled here, but some relationships are evident for Fe. Bottrell and Yardley (1990) reported that the Mn/Fe ratios of inclusion fluids equilibrated with chlorites having similar Mn/Fe ratios, but from different redox environments, were distinct. More oxidized fluids had higher Mn/Fe than more reduced fluids, in accordance with the predictions of Boctor (1985). Fluids from a range of crustal redox environments have been included in our data compilation, for example the Colombian emeralds are associated with black shales, whereas some of the fluid samples from the Pyrenees are from veins in red beds. It follows that part of the variation in Fe/Cl at any particular temperature in Figure 7a is most likely due to variable redox, and if the ratio Mn/Fe is in part a monitor of the redox environment, then it follows that this ratio should correlate with Fe concentration at constant temperature. This is evaluated in Figure 8, which is a plot of Fe/Cl versus Mn/Fe, for those data sets for which there is a reasonable spread in Mn/Fe. It is notable that lines of regression through each data set slope down to the right, indicating systematically lower Fe/Cl in the more oxidized (high Mn/Fe) fluids, although there is too much noise in the data to attach any significance to the slope. A similar plot for Zn yields random slopes. Figure 8 is interpreted as indicating that the effect of redox on the Fe/Cl ratio of the fluids is similar over a wide range of geologic environments; in general it appears that about an order of magnitude variation in Fe/Cl may exist between the most reduced (highest Fe/Cl ratios) and most oxidized fluids from any suite.
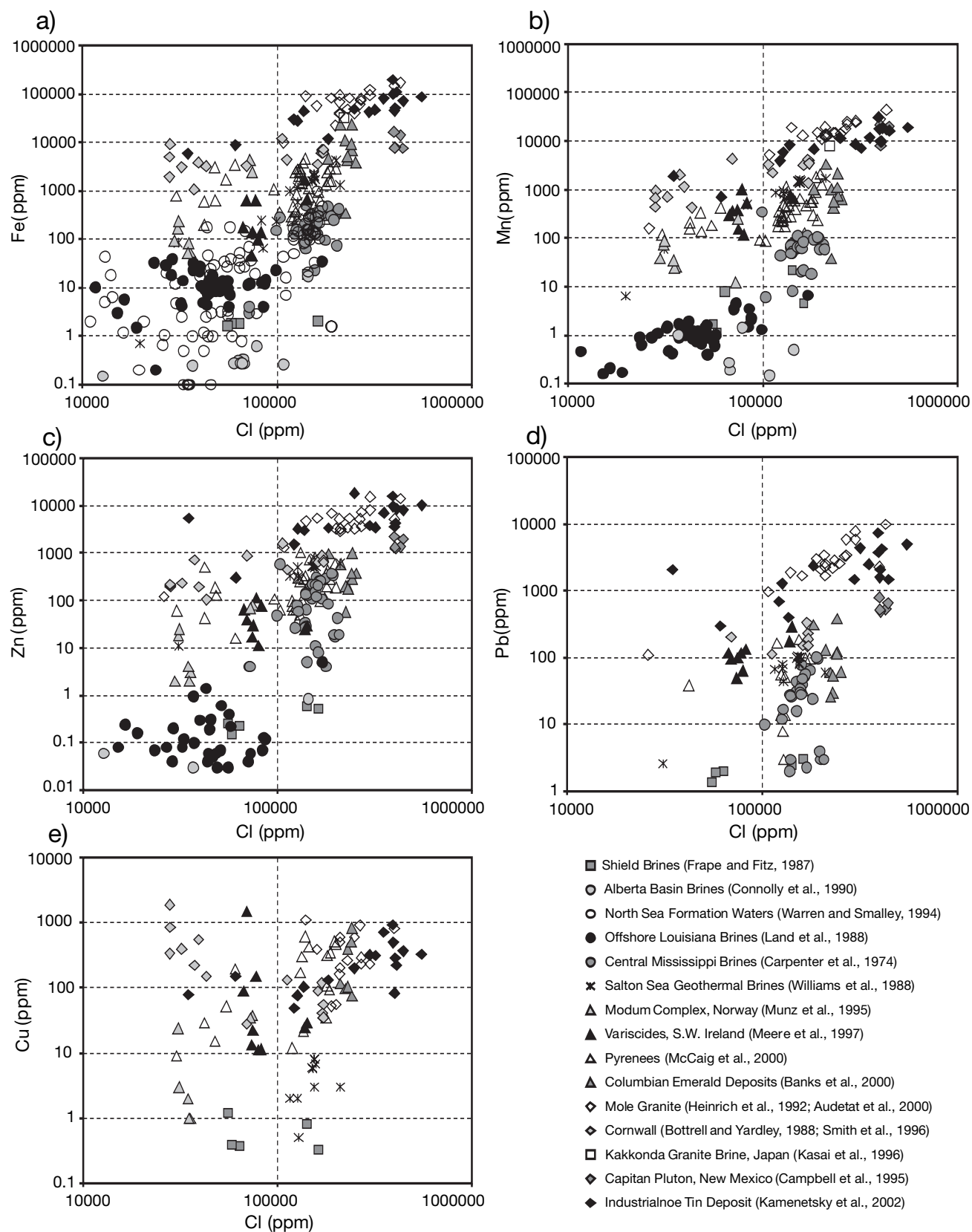
FIG. 4. Concentrations of transition metals in crustal fluids from the data sets discussed in the text vs. chloride concentations (logarithmic scales, units are ppm). (a). Iron. (b). Manganese. (c). Zinc. (d). Lead. (e). Copper. Arrays of data points from individual data sets that are approximately isothermal define a series of approximately parallel trends (increasing metal concentration with increasing chloride), with higher metal concentrations for the higher temperature data sets.
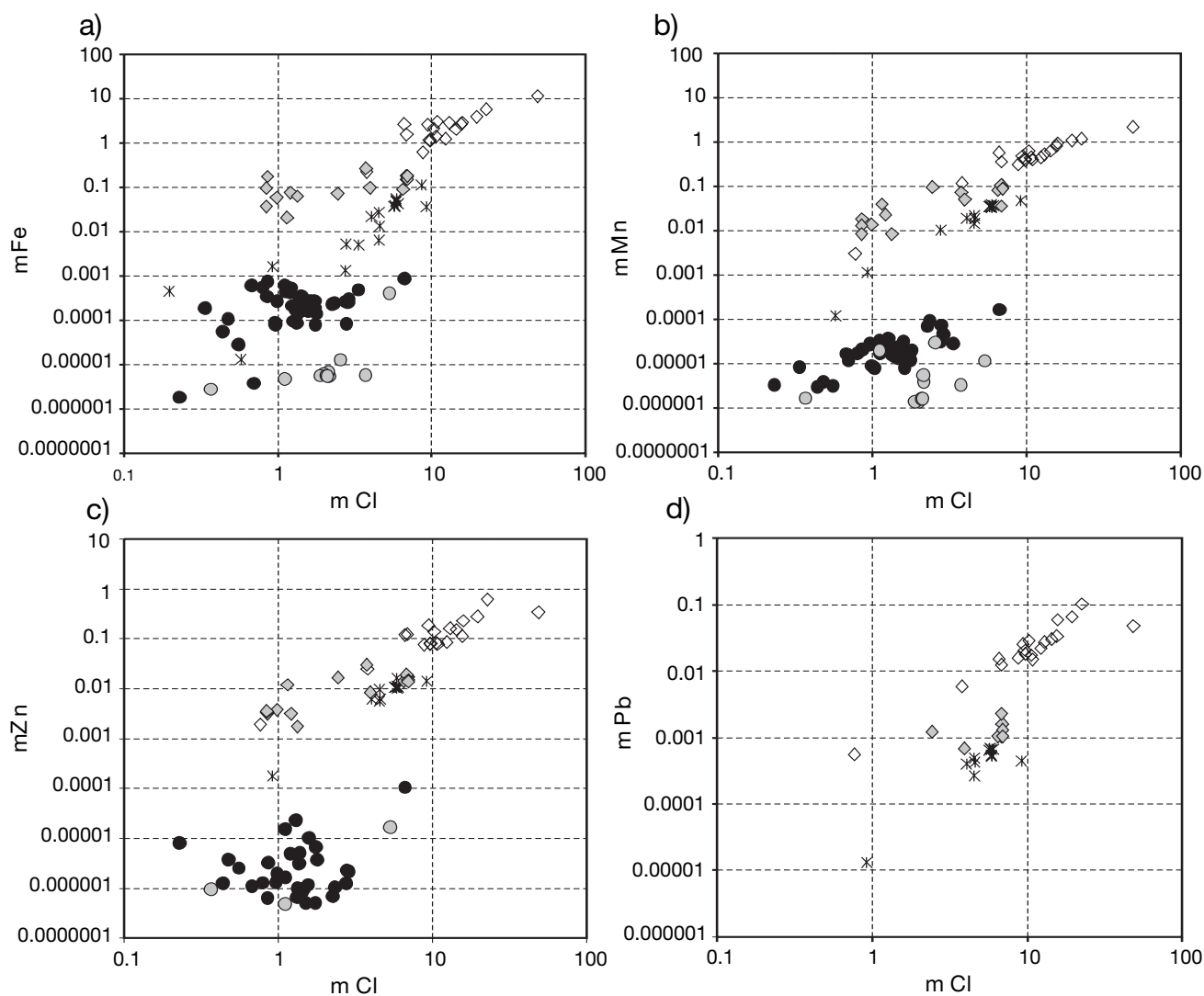
Fɪɢ. 5. Selected data sets from Figure 4, chosen for their relatively large range of Cl concentrations, plotted as transition metal molalities against chloride molality. (a). Iron. (b). Manganese. (c). Zinc. (d). Lead. Symbols as in Figure 4. In this figure it is apparent that, within the uncertainties of the data, the slope of the data for each metal appears to be between 1 and 1.5, irrespective of temperature or chloride concentration.

Other factors affecting transition metals in solution

Unfortunately, the nature of the data sets available does not allow $a_{H_2S^o}$ or pH values to be assigned to fluid analyses. The frequent occurrence of pyrite in their source rocks makes it unlikely that $a_{H_2S^o}$ is an important independent variable because, as discussed above, pyrite-Fe silicate assemblages buffer $a_{H_2S^o}$. Much of the scatter in the chloride-corrected plots (Fig. 7) is most likely to reflect pH variations between different host-rock environments, introducing an uncertainty of about an order of magnitude plus or minus in the metal concentrations that can be predicted at a given temperature and salinity. The significance of pH variations on Fe solubility was emphasized by Heinrich and Seward (1990), who showed that at relatively low temperatures the difference in pH between alkali-feldspar–buffered assemblages and those buffered by Al silicates with mica could cause order-of-magnitude

variations in the solubility of Fe, as seen in the data presented here.

Apart from Fe and Mn, which are important components of common rock-forming minerals, other transition metals may occur as trace components of minerals in the source regions of ore fluids or as trace amounts of an ore phase. If a crustal fluid is a saturated solution of its host rock, then the identity and composition of these metal-saturating phases will determine the metal concentrations in solution. For example, Pb concentrations might reflect Pb concentrations in feldspar or galena saturation. Where hydrothermal convection cells invade a cooling pluton or other crystalline rocks formed initially at higher temperatures, the apparent saturating phases are often metastable and the activities of trace components in solution may instead be saturated by the breakdown products of the primary minerals, even if these are present only in trace amounts. The importance of metal-saturating phases in
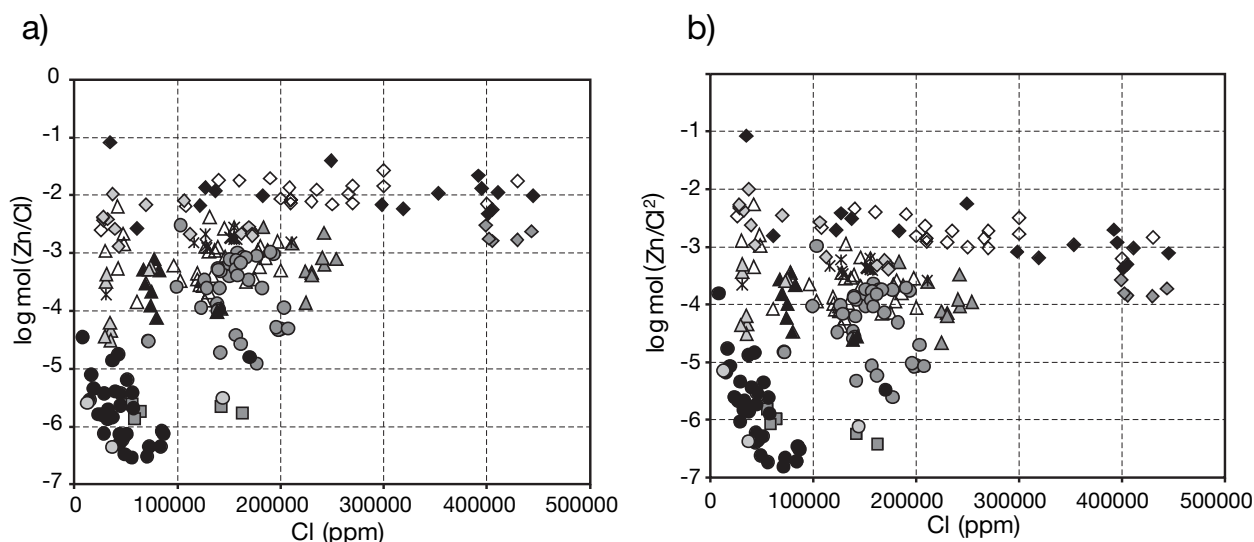
FIG. 6. Further evaluation of the relationship between Zn and Cl. (a). Molar ratio Zn/Cl vs. Cl concentration (symbols as in Fig. 4). This plot should result in a horizontal trend for each approximately isothermal data set if the data in Figure 5c are best fit by a slope of 1. (b). Molar ratio Zn/Cl^2 is plotted similarly and should provide a better horizontal trend if the data in Figure 4c have a slope that is significantly steeper than 1. It is evident that the high-temperature data points yield constant Zn/Cl for all Cl concentrations. Considering the high-salinity fluids from Colombian emerald fields together with the lower salinity fluids from the Pyrenees also give a better horizontal trend in (a).

controlling fluid compositions is illustrated by the plot of Pb against Zn (Fig. 9). Initially, it seems remarkable that so many analyses of oil-field, geothermal, and magmatic brines should all lie along a precise trend of correlated Pb and Zn values. However it is most likely that this trend reflects saturation of a wide range of crustal fluids with traces of both sphalerite and galena. Analyses that lie off the trend most likely arise where one or both of the saturating sulfides are absent from the source rock.

Low-Salinity, Gas-Rich Fluids

The data set considered here is dominated by brines with very low concentrations of dissolved gases, but in most crustal settings it is possible to find examples where the fluid phase is less saline (though seldom much below seawater salinity) and contains significant dissolved carbon dioxide or other gases (Roedder, 1988). Examples include orogenic gold fluids, some pegmatite fluids, and some metamorphic fluids. Metal behavior in these fluids might differ significantly if the gas species play an important role. Therefore, two contrasting examples of low-salinity, gas-rich fluids are compared below with the trends identified for brines.

High-temperature pegmatite fluid, Muiane, Mozambique: Fluid inclusions in the quartz core of Li pegmatites from the Muiane deposit were studied by Pike (1993) using the collections of O. von Knorring. One sample contained exceptionally large inclusions with CO_2 liquid and vapor phases as well as water and sparse Al silicate daughter crystals. An arsenic daughter phase (native element or oxide) with minor antimony was also commonly present. The crush-leach analysis of this fluid (Table 1) is notable for the very high Li (>K) and almost 1,000 ppm Cs. The temperature of formation of the pegmatite is not well constrained, but the analysis of this fluid

is included in the Cl-corrected plots (Fig. 7), assuming a temperature of 500°C.

Mesothermal Au quartz fluid, Brusson, Italy: Yardley et al. (1993) presented analyses of H_2O-CO_2 fluid inclusions described by Diamond (1990) from postorogenic Au quartz veins of the western Alps. These are also low-salinity fluids, relatively rich in arsenic, but with a formation temperature below 300°C. They are also included in Figure 7.

Both of the gas-rich fluids plot within the spread of the brine data in Figure 7, with the exception of the Mn/Cl and Fe/Cl values for the Muiane pegmatite, which are low. If bicarbonate ions or other ligands derived from dissolved gases made an important contribution to the complexation of these metals, then this should result in higher Me/Cl ratios for which there is no evidence. Lower ratios could arise because of different activity-composition relationships for the dilute, gas-rich fluids, but this should affect all the metals equally. Instead, it is possible that the low concentrations of Fe and Mn in the Muiane pegmatite may be due to unusually oxidized conditions, indicated by the very high Mn/Fe ratio.

Thus it appears that Figure 7 may be a useful indicator of transition metal concentrations in a wide range of Cl-bearing crustal fluids, not just the brines on which it is based. Although, as noted earlier, data for Cu appears to scatter too widely to be usefully interpreted with the presently available information, it is nevertheless of interest that the data from gas-bearing fluids lie centrally within the brine data in Figure 7e.

Discussion: Crustal Fluids as Ore Fluids

This study has demonstrated that there are large and systematic variations with salinity and temperature in the transition metal concentrations of crustal fluids. The consistency of
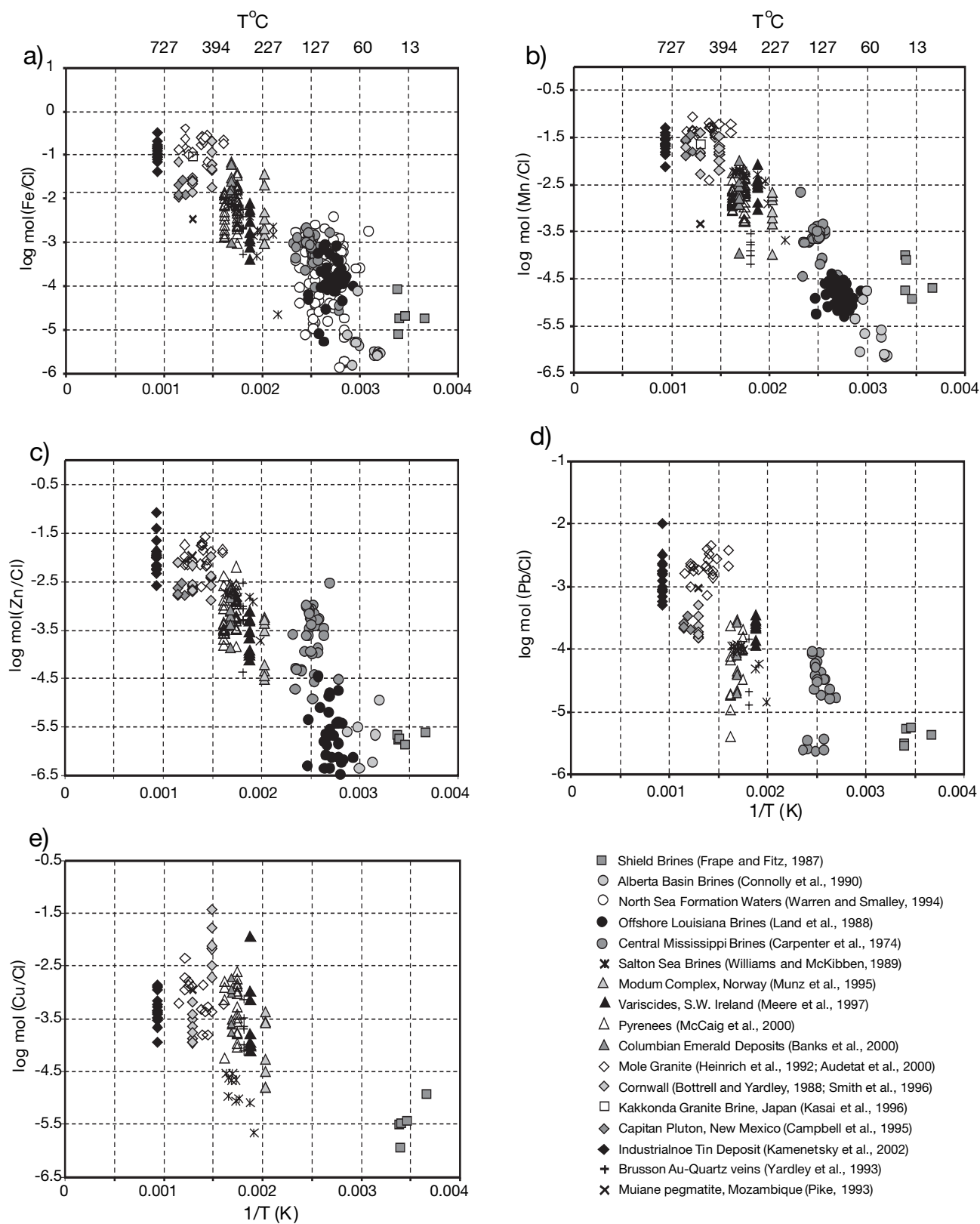
FIG. 7. Evaluation of the combined effect of salinity and temperature on transition metal concentrations. The mol ratio of metal to chloride (based on the conservative estimate of the slopes in Fig. 5 as being approximately 1 is plotted vs. 1/T (Kelvin) to provide a tighter data array than Fig. 3). Also included in this figure are examples of low-salinity, gas-rich fluids for comparison (see key). (a). Iron. (b). Manganese. (c). Zinc. (d). Lead. (e). Copper.
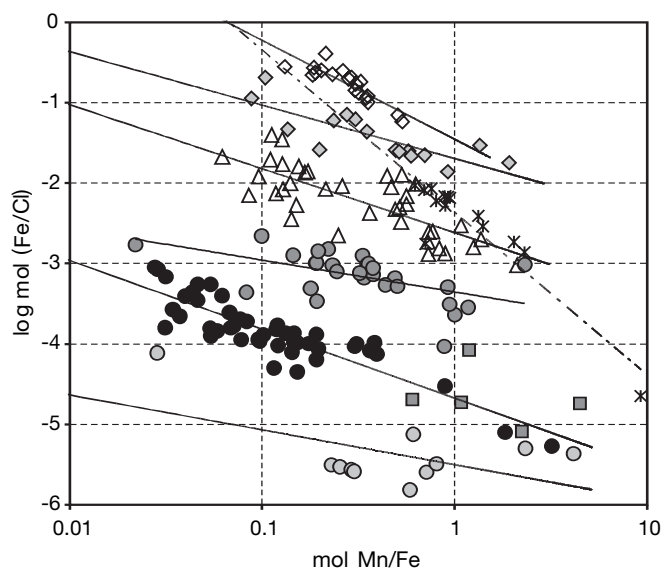
FIG. 8. The effect of redox on the Fe content of crustal fluids, demonstrated approximately by plotting the mol ratio Fe/Cl against Fe/Mn (reflecting oxidation state) for data sets with a suitably wide range of data (symbols used are as in Fig. 7). Linear trend lines are fitted through the data sets (the steeper, broken line is fit to the Salton Sea data) and all slope to the right, demonstrating a decrease in Fe/Cl with increasing oxidation. Based on this figure, about one order of magnitude of the scatter in Fe/Cl seen in Figure 7a at any temperature can be ascribed to redox variation.

FIG. 9. Plot of Zn vs. Pb for a wide range of crustal fluid types. The remarkable continuity of the trend through most of the data sets is inferred to arise from buffering by trace sphalerite and galena in most source rocks. Symbols used are as in Figure 7.

the trends is indicative of systematic buffering of other factors influencing their metal contents, probably through the widespread occurrence of quartz, mica, feldspars, and pyrite in the crust. As a result, many of the variations in pH, f_{O_2}, and ΣS that are commonly explored in activity diagrams are actually not relevant to rock-equilibrated fluids. Furthermore, there is

little indication that the dominant chloride complexing of the metals investigated varies markedly over the range of temperatures and fluid salinities of the data set. Therefore, the concentrations of many transition metals in rock- (or silicate melt-) saturated crustal fluids are remarkably predictable. The effects of temperature and m_{Cl} can be inferred directly from Figure 6 for Fe, Mn, Zn, and Pb. The remaining variability is probably due to differences in the pH-limiting assemblage, and while this cannot be quantified as yet, it is possible to use the data presented to make inferences for other crustal fluids of interest.

Whether ore deposits are formed from fluids with anomalously high concentrations of dissolved ore metals, or from normal crustal fluids that migrate into environments where metal solubilities are greatly reduced, has been a subject of discussion for many years. The results presented here show unequivocally that metal-rich fluids which have been widely accepted as ore fluids, such as those from the Mole Granite (Heinrich et al., 1992; Audetat et al., 2000) or the Mississippi oil-field brines described in the classic study of Carpenter et al (1974), are in fact chemically indistinguishable from other crustal fluids, plotting on the same trends in plots of log(Me/Cl) versus 1/T as fluids with no known relationship to economic mineralization. Fluids equilibrated with normal crustal rocks at relatively high temperatures and/or low pH have the potential to form hydrothermal orebodies of the transition metals if they migrate to regions of lower temperature or if the pH is raised by mineral-fluid interactions, provided a source of sulfide is available.

Dilution has been suggested as a first-order mechanism for precipitation of metals from brines, but our results cast some doubt on its effectiveness. It has been widely assumed that the formation of neutral or negatively charged metal chloride complexes under supercritical conditions must mean that metal concentrations in solution rise rapidly with Cl at high salinity, following the types of theoretical trends illustrated in Figure 2. However our empirical compilation shows that the concentration ratios of Fe, Mn, Zn, and Pb to Cl appear to remain constant independent of chlorinity over a wide range of temperatures. If the solutions were ideal, this would imply that the $MeCl^+$ complex predominated. However it is more likely that strong departures from ideality for chloride ions in these concentrated solutions simply mean that the chloride ion activity increases only slowly with chloride concentration, and the slope in the plot is not truly representative of the complex stoichiometry. In any event, a consequence of the approximately 1/1 Me/Cl relationship is that the effect of dilution on equilibrium metal concentrations will be small. In contrast, temperature emerges as a much more important control on transition metal concentrations than has been generally recognized, although the precise precipitation mechanisms that would enable fluids to adjust composition to remain on the buffered fluid trends defined here have not been explored.

The major conclusion of this study is that normal saline crustal fluids have the potential to act as ore fluids as they migrate. This does not preclude the possibility that distinctive metal-enriched fluids may occur also, for example, in shallow settings, where fluid-fluid interactions such as phase separation may proceed more rapidly than mineral-fluid interactions, leading to unbuffered compositions. It is also understood that

secondary processes may result in fluids with high levels of enrichment in ore metals beyond the concentrations required for primary formation of the ore.

The conclusion that there is nothing very special about ore fluids compared to crustal fluids in general appears to be incompatible with the evidence that some parts of the crust have experienced repeated episodes of ore formation through geologic time, whereas others are barren. Results of this analysis suggest that the key to the greater fertility of some parts of the crust is the presence of chloride, since this is the essential ligand that allows most metals to be mobilized into solution. Where chloride-rich evaporites or brines are present within the rock column, they are surprisingly difficult to remove; brines are dense and less easily expelled than fresh waters, and evaporite bodies are of very low permeability and only slowly dissolved away once they are entombed in a fluid-poor rock mass. Bittern brines sink into the sediment column as halite beds form from evaporation and can remain as pore fluids at depth even if the halite beds themselves are subsequently dissolved away by marine incursions. It seems counterintuitive for a fluid to have a greater geologic preservation potential than a solid, but Br/Cl studies of paleofluids have demonstrated that bitterns are indeed more widespread than halite evaporites (e.g., Rittenhouse, 1967). Thus, repeated episodes of base metal mineralization may reflect continued presence of chloride in the rock column, rather than any special characteristics of the ore metals themselves. Examples of major base metal terranes with evidence for evaporates in the original sedimentary sequences include the Mary Kathleen district of Queensland (Oliver et al., 1992) and the Zambian copper belt (Hudec and Jackson, 2002). Although the salt has now been dissolved out of these sequences, chloride may remain in scapolite at appropriate metamorphic grades (making mariolitic scapolite a potential pathfinder mineral), and the chloride may have been involved in multiple episodes of mineralization before being largely expelled.

The Practicalities:
Which Crustal Fluids Have Ore-Forming Potential?

The main conclusion of this study is that the hotter and more saline a crustal fluid is, the more likely it is to form an orebody, but this result must be tempered by considerations of fluid abundance. For example, brines formed by the progressive removal of water from crustal fluids as they participate in mineral hydration reactions are unlikely to be present in ore-forming quantities, even though extreme metal enrichment may be present (e.g., Svensen et al., 1999).

Hydrothermal ore formation requires the precipitation of a large amount of metal from the fluid within a small rock volume. Implicitly, the time period over which this takes place must be limited, because it is unlikely that the same fluid-flow pathway will be sustained over geologic time periods. Very high metal concentrations are evidently present in high-salinity magmatic fluids, making magmas with a high Cl/H_2O ratio important sources of ore fluids. The data summarized here suggest that Fe/Cl ratios may exceed 0.2 for a highly saline magmatic hydrothermal fluid. It follows that a pluton with a volume of 1 km^3, containing ca. 1 percent Cl (Webster and DeVivo, 2002) may give off on the order of 3×10^7 t Cl in hydrothermal solution, transporting around 1×10^7 t

hydrothermal Fe. If the Fe is removed from solution by oxidation, magmatic fluids derived from just a 10-km^3 pluton will be sufficient to give rise to over 100 Mt of hydrothermal Fe oxides. A similar case can be made for high concentrations of other transition metals in magmatic ore fluids, but the very high concentrations of Fe, making it a major brine component, are exceptional, and this probably accounts for the abundance of Fe minerals in most orebodies formed from saline hydrothermal fluids.

At the other end of the temperature spectrum, saline sedimentary formation waters are also an important source of ore fluids. Here, the very large volumes of formation brines available in some basins are a key factor for ore formation, but the brines must also be metal rich. An aquifer extending over an area of 100 km^2 and with a thickness of 100 m and a porosity of 10 percent may contain approximately 1.2×10^9 t of brine. If this brine has an Fe concentration of about 300 mg/kg (implying a source temperature approaching 200°C), then it has the potential to precipitate almost 5 Mt of hydrothermal iron oxide. Draining the same aquifer from an area 50 × 40 km could potentially give rise to 100 Mt of Fe oxides. The results presented here can identify which basins are most likely to generate brines with sufficiently high metal concentrations to have ore-forming potential. The temperature effects illustrated in Figures 3 and 7 are particularly important over the lower part of the temperature range. Whereas brines at temperatures significantly below 100°C sometimes contain appreciable transition metals and could precipitate them as sulfides, the quantities are less likely to be significant than for hotter brines. On the other hand superficially similar formation brines from deeper, hot basins, or brines which circulate into underlying hot basement as in the Irish Pb-Zn deposits (Russell, 1978), may attain orders of magnitude greater concentrations of transition elements and have the potential to form orebodies given a suitable geochemical trap.

Metamorphic fluids, since they have high transition metal concentrations, might also seem to have ore-forming potential. However, during metamorphism, rocks must recrystallize to very low porosity and permeability because there is widespread evidence that they support fluid pressures approaching lithostatic values. The rate at which fluid is generated during metamorphism is low, because it is limited by the rate of heat supply due to the strongly endothermic character of dehydration reactions (Yardley, 1986). Rates of fluid escaping from rocks undergoing metamorphism must be equally low to sustain the elevated fluid pressures. Hence true metamorphic fluids, in the sense of those released by mineral breakdown reactions, are generated over many millions of years and are very unlikely to remain to be focused to form orebodies, irrespective of their metal contents. More voluminous fluids of various possible origins that equilibrate with metamorphic rocks may, however, have ore-forming potential.

Conclusions

This study has made possible a series of generalizations about the compositions of crustal fluids and their potential to form base metal orebodies. High-quality fluid inclusion analyses produce results that are closely comparable with bulk analyses of fluids sampled by deep drilling and, if

gathered with care, are clearly of great value for understanding crustal fluid compositions.

The compositions of crustal fluids vary systematically and within well-defined ranges, indicating that many of the important variables that influence metal concentrations are buffered by mineral-fluid equilibria. Temperature and chloride are the main independent controls on transition metal concentrations in saline fluids, although variations in pH with rock type and salinity can also account for around two orders-of-magnitude variation in metal concentrations at constant temperature.

Concentrations of Fe, Mn, Zn, and Pb increase with chloride concentration in a similar way. Furthermore, within the limitations of the data, it is not possible to demonstrate a difference between the trends in low- and high-temperature sample suites, suggesting a rather similar nature of chloride complexing over the crustal temperature range.

The ratios of metal to chloride ($\log (Me/Cl)$) plot on a linear trend against $1/T$. As a result, concentrations of Fe, Mn, Zn, and Pb in any chloride-dominated crustal fluid can be predicted with the following equations (T in Kelvin, concentration ratios are molar): $\log (Fe/Cl) = 1.4 - (1943/T) \pm 1$; $\log (Mn/Cl) = 0.55 - (1871/T) \pm 1$; and $\log (Zn/Cl) = - (1781/T) \pm 1$; $\log (Pb/Cl) = -1.2 - (1533/T) \pm 1$.

These relationships include the effects of variations in pH and f_{O_2} in the uncertainty, and it is apparent that large ranges of conditions that are commonly plotted in pH-redox diagrams are simply not accessible to rock-buffered fluids. It is a corollary of these systematic variations in fluid composition with temperature, in particular, that the migration of fluids across isotherms in the crust has the potential to form orebodies. The greatest potential arises when the fluids are highly saline, and many base metal deposits are associated with highly saline fluids. It is likely that repeated episodes of base metal mineralization in a district arise not because of intrinsically anomalous metal concentrations, but because of chloride anomalies resulting, for example, from the presence of evaporites in an original sedimentary sequence.

Ore formation is particularly associated with either magmatic brines, present in limited amounts but with extremely high metal concentrations, or formation brines that have lower metal concentrations offset by much greater volumes, provided flow can be focused to a precipitation site.

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