

THE CHEMISTRY OF CRUSTAL BRINES: TRACKING THEIR ORIGINS

¹Bruce W.D. Yardley, ¹David A. Banks and ²Andrew C. Barnicoat

¹*School of Earth Sciences, University of Leeds, Leeds, UK*

²*Rock Deformation Research, School of Earth Sciences, University of Leeds, Leeds, UK*

Abstract - Brines may be generated in sedimentary, magmatic or metamorphic settings, and they change chemistry extensively as they move through rocks and interact with them. The primary constraint on their metal carrying capacity is their salinity, but they may carry very variable amounts of S in solution, depending on their source and the rocks that they have encountered. Sulphur availability and oxidation state are also major controls on which metals will be transported and which precipitated. Availability of fluid inclusion brine analyses is making possible the characterisation of a much wider range of brine types than was hitherto possible, and providing information about metal contents in a wide range of settings, as well as tracer analyses. Iron contents of brines are broadly temperature dependent, and are much higher in magmatic brines than in sedimentary ones, but basinal fluids may still carry sufficient Fe in solution to precipitate iron oxides at an oxidation front, and may be much more voluminous. Brines of different origins can often be distinguished on the basis of conservative halogen tracers unaffected by wall rock interactions: Br/Cl ratios used in conjunction with I/Cl ratios or $\delta^{37}\text{Cl}$ values separate residual bittern fluids from re-dissolved evaporites, with igneous brines forming an intermediate, but somewhat distinct, grouping.

Introduction

The significance of brines and evaporites in the genesis of ore deposits has been recognised increasingly in recent years (Warren, 1999), and they have been implicated in the formation of a wide range of deposits from base metals to emeralds. In general terms this is not surprising; many metals are complexed in aqueous solution by chloride, and so relatively small amounts of brine can transport relatively large masses of metal. However chloride is extremely soluble in aqueous solution, only entering into rock-forming minerals under exceptional conditions, and as a result its behaviour in the Earth is not well understood. Until recently, brine research has concentrated almost exclusively on oil field waters (e.g. Carpenter *et al.* 1974, Rittenhouse 1967, Hanor 1994, Land 1995), however the advent of new analytical techniques for fluid inclusions have enabled many of the geochemical techniques for interpreting oil field brine origins, to be applied to ore deposit brines (Bohlke and Irwin 1992, Kessler *et al.* 1995, Campbell *et al.* 1995). In the process, it has become apparent that comparable mechanisms to those that generate brines in the near-surface, may operate at greater depths and at elevated temperatures, in addition to derivation from magma. New models for the genesis of brine-related deposits require both an understanding of how brines can develop and interact with rocks, and the development of tracer techniques for distinguishing brines of different origins.

Highly saline fluids can evolve in four distinct geological settings, the first three of which are of potential economic significance:

- i) Exsolution from crystallising magma.
- ii) Evaporation of seawater, leading to the formation of bittern brines, enriched in Br, once halite begins to precipitate.
- iii) Re-dissolution of halite deposits.
- iv) Removal of water from chloride-bearing solutions during metamorphic hydration reactions within the crust.

This contribution is concerned with two aspects of crustal brines: the ways in which their chemical composition may be modified as a result of reactions with the rocks through which they pass, and the application of tracers to determine the origins of particular brines.

Primary Controls on Brine Chemistry

The initial chemical and isotopic composition of a brine generated by magmatic or sedimentary processes may be changed rapidly by interaction with rocks along its flow path. As a result, common chemical characteristics can appear in brines of very different origins. The fundamental distinction to be made is between *conservative* components, i.e. those that are partitioned strongly into the fluid phase and are therefore little affected by interactions with rocks, and *non-conservative* components that are

readily exchanged with wall rocks and therefore lose any distinctive signature of brine source. The best known of the conservative components, that retain the longest memory of the origins of the brine, are Cl and Br, while δD and $\delta^{37}Cl$ are conservative isotopic tracers. Cations, many anions, and most isotopic tracers such as $\delta^{18}O$ or Sr isotope ratios are less conservative; some retain a memory of the immediate environment through which a brine was finally emplaced, while others may give an intermediate memory of features along the flow path. We can also distinguish between brine components that occur in solution in a manner that is coupled to the availability of Cl⁻, and those whose solubility is, to a first approximation, independent of salinity. Many metals occur in solution predominantly as either individual ions, whose abundance is limited by the availability of anions, or as ion pairs with one or more Cl⁻ ions, some may be significantly complexed by other ligands such as fluoride, sulphate or bisulphide, if present, while others, most notably silica, form hydrated species approximately equivalent to an un-dissociated weak acid molecule. Clearly, the distinctive role of brine in ore genesis results largely from the major role that chloride plays in the solubility of many elements. Examples of a range of natural brine compositions are listed in Table 1; the way in which the compositions of these brines reflects their origin will be returned to below. Note that many of the analyses listed in Table 1 have been obtained by analyses of fluid inclusions. These analyses have been selected because they appear to be of high quality, with good charge balance and with no evidence for contamination by solid phases (for example Mn/Fe is generally much higher than in coexisting Fe-bearing minerals). Details of the analytical methods and their validation is given in the original references cited with the Table.

Brines of sedimentary origin differ subtly in their composition according to whether they are bittern brines or are produced by re-dissolution of halite (Rittenhouse 1967, Fontes and Matray 1993). While bittern brines concentrate a range of soluble elements, notably Br, relative to Na and Cl as halite precipitates, re-dissolution of halite produces brines dominated by NaCl itself. Thus the differences between them are in the concentrations of a wide range of elements initially, with bittern brines enriched in a range of components relative to seawater, while brines produced by dissolution of halite exhibit complementary depletion in many trace elements. Seawater itself has a distinctive chemistry resulting from its highly oxidised character; hence sulphate levels are high, as is Mg, whereas Fe is present only at very low levels.

Magmatic brines are best known from porphyry-Cu deposits, where they may have been modified by boiling, but data also exists for deeper, supercritical brines (Table 1). They are likewise dominated by NaCl, but a wide range of elements may be enriched. In particular, levels of K and a range of transition metals, including Fe, are often higher than in sedimentary brines, while Ca is generally lower. Whereas the total salinity of sedimentary brines is generally close to halite saturation at surface temperatures, magmatic brines show a much wider range of salinities. Many are of distinctly lower salinity (c. 15 eq. wt. % NaCl), but others

range up to wet salt melts; salinity variations in evolving magmatic fluids may be a complex function of the depth of crystallisation (Cline and Bodnar 1991). A key feature of brines released at magmatic temperatures is that they have a relatively high proportion of HCl available for acid leaching of cations from wall rocks: according to pressure this may occur as HCl ion pairs (shallow levels) or as dissociated ions. Although dominated by chloride, magmatic brines may contain significant concentrations of other ligands that are themselves effective at transporting certain metals, for example fluoride and borate.

Evolution of Brine Chemistry in the Crust

In the course of fluid-rock interaction, a series of factors may influence the final brine chemistry, but in most settings the Cl-content remains relatively constant, so that the load of dissolved metals must satisfy charge balance. The principal factors controlling the final brine chemistry attained due to fluid-rock interaction will have the same effects irrespective of the original source of the brine:

- i) temperature (to a lesser extent pressure, except at very shallow levels)
- ii) salinity
- iii) wall rock lithology and mineralogy, *especially*
 - redox environment
 - presence or absence of evaporite minerals

Temperature

The exchange of cations between minerals and solution is strongly temperature dependent, and this provides a basis for the use of mineral geothermometers in geothermal exploration. Most conspicuously, K/Na ratios increase rapidly with temperature relative to the very low values in seawater. In addition to ion exchange, other aspects of mineral solubility are temperature dependent. For example heating of seawater leads to precipitation of anhydrite, while quartz becomes more soluble with increased temperature. In the case of Fe in particular, there is good evidence from the analyses presented in Table 1 to suggest that its concentration in rock-buffered brines is also temperature dependent. Concentrations are generally low in oilfield brines, while in low-T shield brines it is present only at trace levels (Fritz and Frape 1987). Magmatic brines typically have much higher concentrations of Fe, although it is clear from the different examples, discussed below, that other factors also exert important controls on Fe-levels in solution. In general however, it is worth emphasising that many metals are very soluble as chlorides over a very wide range of geological conditions, and temperature is not directly a constraint on their solution and transport. This is clearly seen from the formation of ores of a wide range of metals at temperatures of just a few hundred degrees.

Salinity

Understanding how salinity influences the metal contents of brines is central to understanding their role in ore formation. There are two types of effects to be taken into consideration: firstly the proportion of mono-valent to divalent (or trivalent) cations in a fluid in equilibrium with a

fixed mineral assemblage is influenced by the total chloride content; secondly, for certain metals, complexing by chloride can become much more effective with increasing chloride activity.

The first effect has been discussed in some detail by Eugster and Gunter (1981) and can be illustrated very simply with reference to plagioclase ion exchange in saline solution:

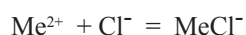


for which at quartz saturation:

$$\log K = \log \left(\frac{a_{\text{CaAl}_2\text{Si}_2\text{O}_8}}{a_{2\text{NaAlSi}_3\text{O}_8}} \right) + \log \left(\frac{a_{\text{Na}^+}^2}{a_{\text{Ca}^{2+}}} \right)$$

It follows that, for fluids in equilibrium with quartz and a given composition of plagioclase at a fixed P and T, it is the ratio of the activity of Na^+ squared to Ca^{2+} , not the Na^+ to Ca^{2+} ratio, that is buffered. As the salinity of a fluid increases, so too does the concentration, and hence activity, of Na^+ and Ca^{2+} . This means that at progressively higher salinities the Ca^{2+} activity must increase with the square of the Na^+ activity, leading to a considerable increase in the concentration ratio of Ca/Na. This is an important factor in accounting for the very high Ca-contents of many concentrated brines.

The second way in which metal contents change with salinity is through the formation of a range of chloride complexes. In sufficiently dilute solution, metals occur as free ions, with chloride complexes developing as the availability of chloride ions is increased:



and so on. The larger complexes are only likely to become significant at high salinities, where their abundance increases as a power of the chloride activity, leading to rapid increases in metal levels in solution. This effect is documented for Pb, for example, a metal which is known to be able to reach exceptional levels in chloride-rich solutions in the right circumstances (e.g. Svensen *et al.* 1999).

Wall Rock Lithology and Mineralogy

The influence of wall rocks on the composition of crustal fluid cannot be underestimated in all but the most open environments of rapid fluid flow. For example, Banks *et al.* (1991) found that many aspects of the chemistry of brine inclusions in quartz veins around the Pic de Port Vieux thrust, central Pyrenees, reflected equilibrium with local wall rocks hosting the vein in a lithologically varied sequence, whereas the chloride and bromide contents of the inclusions showed that in each case the vein fluids came from a common reservoir. In both deep diagenesis and active geothermal fields, fluids in rock-dominated systems equilibrate with their hosts, and in particular with new-formed minerals grown from the fluid (Hanor 1994, Land 1995). A common consequence of this is the removal of SO_4 and Mg from brines in the crust (below), and their enrichment in Ca. While salinity plays a role in

determining the Ca content of brines, as outlined above, an additional factor is the instability of plagioclase at low temperatures. Few plagioclase compositions are stable below about 500°C , and albitisation is a common feature of hydrothermal alteration. Anorthite component recrystallises into relatively soluble phases such as epidote. Hence while at high temperatures solutions in equilibrium with plagioclase may be rich in Na (Orville 1972), at low temperatures even low salinity fluids have significantly enhanced Ca contents, often limited by precipitation of calcite.

The most dramatic effects of wall rock reaction take place where evaporite minerals are present, and lead to enhancement of the dissolved load of the fluid by simple dissolution. While this is a process that is best known at shallow levels in sedimentary basins, it can also occur at higher temperatures, giving rise to correspondingly more saline brines. Columbian emerald fluids reach salinities corresponding to halite saturation at temperatures close to their peak metamorphic conditions.

Redox environment plays a crucial role in the solubility of many metals in brines through both its control of sulphur speciation and its direct influence on the solubility of metals with variable valency. The transition from sulphate- to sulphide-dominated solutions takes place around the hematite-magnetite buffer, in terms of oxygen fugacity, and a range of metals change solubility markedly near this boundary in S-bearing systems. Conventionally, metal solubility is often contoured onto $\log f\text{O}_2$ - pH plots drawn up for a total S concentration specified irrespective of its speciation. While this may be appropriate for fluid systems with an external control on S-level, such as volcanic gasses, it is not obviously applicable to a rock-buffered brine for which redox state and pH may be limited by oxide and silicate equilibria and the amount of S entering solution is dictated by saturation with pyrite or another S-mineral in the rock.

Fig. 1 is a $\log f\text{O}_2$ - pH plot contoured to show the concentration of S in solution in equilibrium with pyrite and an iron oxide phase (hematite or magnetite, according to the value of $f\text{O}_2$). The calculations were constructed using the EQ3 code (Wolery *et al.* 1983), for a temperature of 300°C and a pressure of 0.1 GPa, and demonstrate that, far from being constant, total S in solution varies over 2 orders of magnitude within the range of $\log f\text{O}_2$ and pH that is likely to represent reasonable upper crustal conditions. These variations have significant implications for transport and precipitation of Fe and Au.

Dissolution of iron is strongly dependent on redox state, because Fe^{2+} is much more soluble than Fe^{3+} . For example, it was noted by Bottrell and Yardley (1991) that the Mn/Fe ratio of fluids in equilibrium with vein chlorite from a hematite-bearing host rock was much greater (and in excess of 1) than the value obtained for fluids in equilibrium with a similar composition chlorite from a graphitic host. This effect is illustrated in Table 1 by the examples of brines from Alpine structures in the Pyrenees with contrasting

Table 1: Compilation of analyses of crustal brines sampled by drilling or as fluid inclusions.

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
Approx. Temp. (°C)	22	129	143	250	260	280	310	320	320	550	600	600	600
Na	18 900	61 100	63 000	61 462	32 700	29 135	62 213	130 946	54 590	78 000	39 520	182 438	178 632
K	430	854	6 150	3048	65 400	1218	14 564	5795	11 622	37 000	13 960	61 409	74 868
Ca	63 800	28 800	44 600	19 354	4346	39 004	47 637	6746	44 027	3200	9620	30 723	42 336
Mg	78	1830	2770	891	347	1133	1207	1062	639		120	343	268
Fe	2.07	338	320	1727	347	2372	2868	4300	23 791	60 000	11 950	16 310	13 915
Mn	4.57	65	60	780	<10	224	1773	420	3308	18 000	3240	21 564	17 417
Li	0.81		52	295	2780	215	1879	944	2031		215	128	54
Sr	1580	1820	1770	750	114	1145	3421	144	1605	30	175	784	1822
Ba		56	89	25	268	370	1157	118	1064		137	345	982
Pb	3.03	44	3	178	14			30	131	3300		803	536
Zn	0.52	217	18	80	307	76	392	196	573	5200	1569	2207	1340
Cu	0.33			25	1383		348	393	115	900		<10	<10
As				86				78	17	480	59		
B	6.2			160	6233	203	156				3975	438	214
F	7				4503	203					817	1770	357
Cl	162 700	150 700	200 400	138 401	20 853	124 875	187 405	230 082	211 091	266 000	106 360	398 937	429 504
Br	1250	1070	2340	529	251	800	2793	36.7	100.6	420	150	146	250
I	7			1.9		32.7	2.2	0.3	0.2		4.8	0.91	0.54
SO ₄	223	80	128	1457	153 258		2184	463	1189		6075	24 210	21 472

1. Shield brine, Sudbury, Canada. Fritz & Frape (1987), sample N3646A
2. Oilfield brine, C. Mississippi, USA. Carpenter et al. (1974), sample 39
3. Oilfield brine, C. Mississippi, USA. Carpenter et al. (1974), sample 3
4. Variscan low grade metamorphic brine, Allihies, SW Ireland. Meere & Banks (1997), vein 7
5. Quartz-hematite vein acid sulphate fluid, Ouro Fino, Brazil. Boiron et al. (1999)
6. Low grade metamorphic brine from Alpine vein, Pic de Port Vieux, central Pyrenees. Banks et al. (1991), sample 50177 (reduced wall rocks)
7. Low grade metamorphic brine from Alpine vein, Neouville massif, central Pyrenees. McCaig et al. (2000), sample 55141 (oxidised wall rocks)
8. Brine inclusions in emerald, Coscuez, Columbia. Banks et al. (2000b), sample GG-6
9. Brine inclusion in gangue quartz, Coscuez emerald deposit, Columbia. Banks et al. (2000b), sample GG-5
10. Granite-derived brine, quartz-cassiterite vein fluid, Mole granite, Australia. Heinrich et al. (1992)
11. Granite-derived brine, quartz-tourmaline-topaz rock, Cornwall, U.K. Bottrell & Yardley (1988)
12. Granite-derived hypersaline brine, quartz-fluorite vein, Capitan pluton, New Mexico. Campbell et al. (1995), sample CPU-2 (also 1290 ppm REE)
13. Granite-derived hypersaline brine, quartz-fluorite vein, Capitan pluton, New Mexico. Campbell et al. (1995), sample MTE (also 193 ppm REE)

wall rocks (analyses 6 and 7). Iron solubility may also be enhanced by decreasing pH. However iron solubility in S-bearing rocks is limited by the availability of reduced sulphur; as this increases so pyrite saturation limits Fe-levels in solution. The effect of variation in the S-content of the fluid, as shown in Fig. 1, is to modify the pattern of conditions favouring precipitation or dissolution of elements such as Fe. For example, the increase in total S to low fO_2 values will limit the increase in iron solubility below the hematite-magnetite buffer; similarly the decrease in iron solubility towards higher pH values will be exaggerated by an increase in S.

The case for gold is more complex because it forms a range of species with reduced S (Seward 1973) and diagrams calculated for constant S show a solubility maximum just to the acid side of the $H_2S^0 - HS^-$ boundary and below the hematite-magnetite boundary. Hence there is a gold solubility maximum located in an optimum position in terms of both fO_2 and pH. The effect of allowing for variable, rock-buffered, sulphur levels will be that, while the marked decrease in solubility into the sulphate field remains, Au will remain relatively soluble under progressively more reducing conditions because of the increase in dissolved S. Likewise, the increase in S towards higher pH under reducing conditions will enhance Au solubility also, so that the solubility maximum will not be so tightly constrained with respect to either increase in pH or decrease in fO_2 .

Synthesis: The Major Chemical Features of Brines

The foregoing section summarises both the original chemical characteristics of brines of different origins, and the ways in which they are likely to change as they migrate through the crust (excluding boiling events in the epithermal environment). While these changes mean that brines can end up with rather similar chemistries, irrespective of origin, it also remains true that the chemical changes that they induce in wall rocks as they equilibrate, may be very different.

The examples of low temperature, sedimentary brines listed here are typified by high, but variable contents of Ca relative to Na, low levels of elements such as K, Mg, Fe and Mn, and variable concentrations of the alkaline earth elements, close to saturation with sulphate minerals. Bromide levels relative to chloride are often elevated by comparison with seawater, but some very Br-depleted brines also occur.

Medium temperature brines that have evolved continuously into a metamorphic environment (Yardley 1997) retain many similar characteristics to oilfield brines, and may likewise be enriched in Ca. Some elements, such as K, Fe and Mn, appear to be distinctly enriched relative to the lower temperature brines, but many metals show no enrichment relative to oilfield brines. It is notably that the Columbian emerald brines range between Br-depleted, NaCl-rich fluids with very low concentrations of trace metals and brines that are richer in Br and depleted in NaCl, carrying much higher levels of a wide variety of elements.

The NaCl-rich brines have not equilibrated with wall rocks since being derived by dissolution of local halite beds.

The magmatic brines listed in Table 1 have several high-T characteristics: elevated K/Na ratios and high levels of Fe and Mn for example. They are also significantly poorer in Ca relative to Na than the sedimentary and metamorphic fluids, but are enriched in B and F and tend to have high sulphate levels. The relative proportions of K, Na and Ca have changed primarily to reflect derivation from a feldspar-bearing source. At elevated temperatures the stability of albite-rich plagioclase in granite means that there is no Ca-rich phase present, and so the Na/Ca ratio of the fluid increases accordingly while K/Na continues to increase to higher temperatures for feldspar-equilibrated fluid. Of the examples given, the Capitan Mountain brines are clearly distinctive, both in terms of their very high salinity (they are effectively wet salt melts) and their composition. Campbell *et al.* (1995) interpreted these brines, which are from fluorite-quartz veins with associated REE mineralisation, as resulting from the melting and assimilation of country rock evaporite beds into the ascending magma as it was finally emplaced through them. This explains their very distinctive halogen signatures which are similar to redissolved evaporite brines in sedimentary rocks (below). In agreement with such an origin, Fe is relatively low for this group of brines, while the Mn/Fe ratio is very high, consistent with oxidation by assimilation of red beds associated with the evaporites. Banks *et al.* (1994) reported exceptional REE contents for some of these brines, and showed that this arose as a result of chloride complexing; F and other ligands that may preferentially complex the REE were simply at too low a level relative to Cl to have a significant impact.

Tracers of Brine Origins

In the first part of this paper, we have concentrated on the general chemical features of brines, but have shown that these are often readily modified by interaction with rocks along the flow path. As a result, it is apparent that there are few chemical characteristics that can be employed to address the issue of the source of a brine. The first point to establish therefore is that there is no simple, single source for any crustal fluid. A fluid moving through the crust has continuity as an event as long as the solvent is continuously present, but the individual atoms in the solvent molecules may continuously exchange with wall rocks, as may atoms in solution. Depending on how conservatively different components behave, they may retain memories of different points along the flow path. Thus oxygen isotopes are readily reset and indicate the ultimate fluid source only in high flux settings, while hydrogen isotopes are much more conservative because of the very different ratio of atoms in the fluid to atoms in the rock. For many elements the situation is more complex because their solubility can be changed dramatically by changes in chemical environment. Pb can be transported long distances in chloride fluid with only modest interaction with wall rocks, retaining a source isotope signature, but will be quantitatively removed from solution by addition of reduced sulphur.

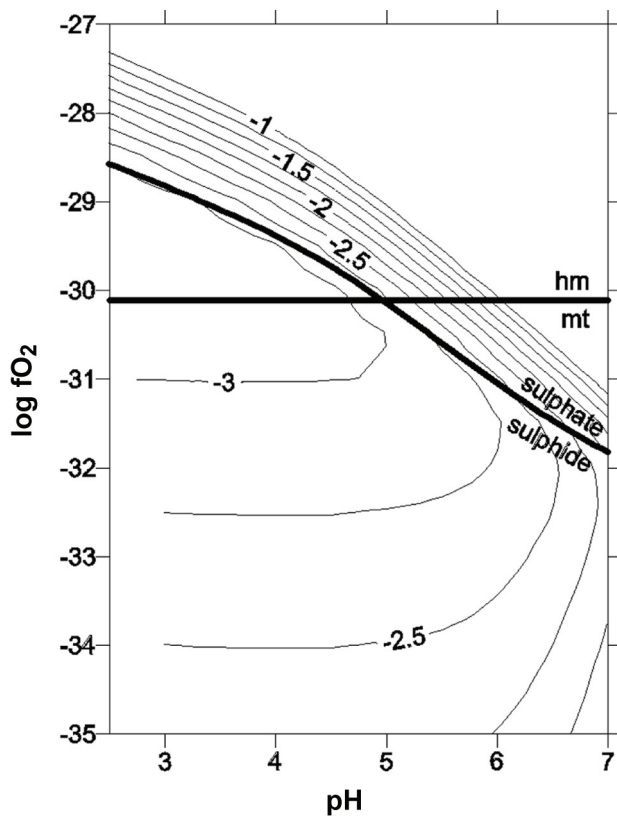


Figure 1: $\log fO_2$ - pH plot contoured to show the log molality of total S in a 1m NaCl solution equilibrated with pyrite and either hematite or magnetite (according to which is stable) at 300°C and 0.1GPa. Also shown is the species predominance boundary between oxidised and reduced sulphur species.

We are concerned here primarily with the use of halogens as tracers, because they are both conservative and coupled to the transport of metals. As a result, we are investigating the origins of the salinity in the fluid, not the sources of its water molecules or of any specific metals in solution.

The most widely used halogen tracer for brine origins is the ratio Br/Cl; both elements are readily analysed in bulk fluid samples or fluid inclusion leachates, and their relative proportions are linked to precipitation and dissolution of halite, which are key processes in the generation of sedimentary brines. I/Cl ratios may also be a valuable indicator, but interpretation is more ambiguous because of the role of organic matter in concentrating I from seawater, while very low concentrations make for analytical difficulties and uncertainties. Nevertheless, the pioneering work of Bohlke and Irwin (1992), who first published Cl-Br-I data for fluid inclusions, demonstrated that I/Cl is a useful adjunct to Br/Cl data, and facilitates the distinction of saline fluids from different sources. In particular, they first defined a distinct field for magmatic fluids. Fig. 2 is a $\log \text{Br/Cl}$ vs $\log \text{I/Cl}$ plot for a range of brines, all analyses of fluid inclusion in vein systems, and including some of the samples presented in Table 1. The suite of brines from Alpine veins associated with thrusting and related deformation in the Pyrenees (Banks *et al.* 1991,

McCaig *et al.* 2000) exhibit distinctive characteristics of many oilfield brines (Bohlke and Irwin 1992): enrichment in both Br/Cl and in many cases I/Cl relative to seawater. The Br-depleted brines, from the Columbian emerald veins (Banks *et al.* 2000b) and from Capitan pluton veins Campbell *et al.* 1995) likewise have halogen ratios typical of sedimentary brines derived by dissolution of halite, but cannot have a simple sedimentary origin because their very high salinities (Table 1) requires an origin by dissolution or assimilation of halite at elevated temperatures in the crust. The SW England fluids (unpublished data) are generally less saline, below salt saturation at room temperature, but most nevertheless differ significantly from seawater in both Br/Cl and I/Cl values. The high temperature fluids in particular occupy a distinctive region corresponding to the magmatic fluid field of Bohlke and Irwin (1992). Thus, while magmatic fluids do appear to be distinct on this fluid, they are within a range of values that might be achieved by mixing of sedimentary brines of different origins.

An additional conservative tracer that has been developed in recent years is the stable isotopic composition of Cl, $\delta^{37}\text{Cl}$ (Desaulniers *et al.* 1986, Kauffmann *et al.* 1984, 1988, Eastoe and Guilbert 1992). Variations in $\delta^{37}\text{Cl}$ (measured relative to seawater) are generally small, but are well outside analytical uncertainties. Banks *et al.* (2000a) have used a miniaturised technique based on TIMS analysis of Cs_2Cl^+ ions (Xiao and Zhang 1992) to measure $\delta^{37}\text{Cl}$ of fluid inclusion leachates and confirmed a distinction between results from high-T fluids associated with the SW England granites and those associated with the Capitan pluton, also apparent in Fig. 2.

Fig. 3a combines the data of Banks *et al.* (2000a) (some samples now redetermined) with the results of Eastoe *et al.* (1999) on brines of the Palo Duro Basin of Texas, closely related to the host rocks of the Capitan Pluton. The sedimentary brines range from bittern fluids to brines derived by redissolution of evaporites, and show a correspondingly large spread in Br/Cl, but at very uniform $\delta^{37}\text{Cl}$ values, between 0 and -1‰. The high-T Capitan fluids overlap the halite-dissolution brines on this plot, in agreement with the model for their origin discussed above. That they are tightly clustered at this end of the spectrum of basin fluids only, is in agreement with the proposal that salt was incorporated into the magma by melting and assimilation of halite beds, as opposed to interactions with saline groundwaters. Granite-stage fluids from SW England form a distinct population at higher $\delta^{37}\text{Cl}$ than the Palo Duro and Capitan evaporite-related fluids, just as they were separate in Fig. 2, and we take this to represent a distinct magmatic fluid field. Clearly, there is insufficient data to define this with any authority at present, but the fact that one point from Capitan is displaced towards this field is supportive of the idea that it may be of wider applicability than just the area on which it is defined at present.

The use of coupled Br/Cl and $\delta^{37}\text{Cl}$ is explored further in Fig. 3b, which shows details for a wider range of hydrothermal rocks and veins from SW England. High-T

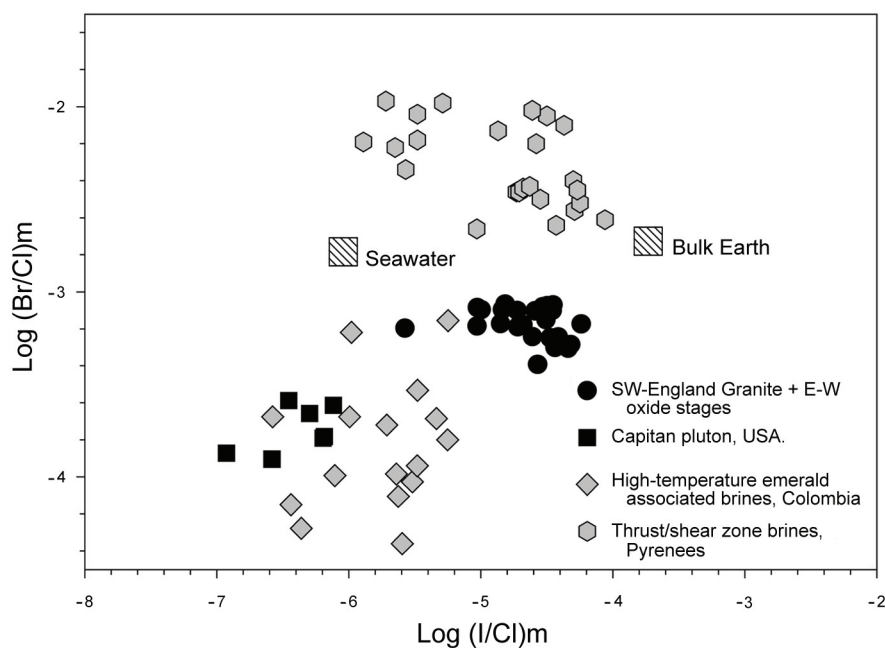


Figure 2. Log plot of Br/Cl versus I/Cl compositions (molar ratios) of a range of hydrothermal fluids (see text). The Pyrenees fluids are from a low grade metamorphic setting and are sedimentary bittern brines that have evolved within more or less the same sedimentary sequence from deposition to Alpine deformation (McCaig *et al.* 2000). Fluids from veins in Columbian emerald deposits have been derived by interaction with halite beds, but at metamorphic rather than sedimentary temperatures. Solid symbols are high-T veins related to granite emplacement, but whereas the SW England examples appear to be genuine magmatic brines, the wet salt melts from the Capitan pluton mostly plot in the same field as the emerald fluids, and evidently arise by assimilation of halite beds through which the magma was emplaced.

oxide veins plot close to the granite stage fluids, but different generations of lower-temperature veins (Gleeson *et al.* 2000) are more widely scattered. Late N-S veins appear to be the result of the involvement of partially evaporated seawater in granite-driven hydrothermal processes. All this data is combined in Fig. 3c with analyses from a range of settings. The Norwegian eclogite samples are salt-bearing inclusions from omphacite with, in some case, exceptionally evolved compositions resulting from removal of water during the formation of hydrous minerals, leading ultimately to Cl-bearing amphibole and a residual fluid enriched in extreme incompatible elements such as Br and Pb (Svensen *et al.* 1999). It is salutary that these plot so close to examples of vein fluids from low grade Variscan rocks from Belgium. The Tunisian fluid is an example of a near-surface water draining halite beds, and rightly plots at the very low Br/Cl ratio of the halite itself; the fact that the $\delta^{37}\text{Cl}$ value is within error of 0 attests to the very limited fractionation during development of halite. Also shown on this figure is a suite of analyses of volcanic gas samples from a range of locations around the Pacific rim (Pitcairn 2000). This data is salutary, as it spreads from the magmatic field defined by the SW England granites all the way across the field of sedimentary brines. It is certainly possible that this is a damning indictment of this approach as a means of distinguishing magmatic brines from those of sedimentary origin, but it is also possible that it is simply a consequence of boiling near the surface. Chlorine isotope fractionation is possible at this stage, with the light isotope, ^{35}Cl , being preferentially fractionated into HCl in vapour given off at high temperatures. It is therefore

very possible that the large spread in $\delta^{37}\text{Cl}$ for these samples reflects fractionation during the process of magmatic degassing, and they do not correspond to primary magmatic compositions.

Summary

Halogens provide valuable tracers of the origins of fluid salinity, and can be used to identify the sources of many brines. Br/Cl, I/Cl and $\delta^{37}\text{Cl}$ measurements when used in combination can clearly distinguish brines derived by halite dissolution, and are also able to characterise residual brines from which Cl has been removed, although in crustal settings the total salinity must be examined in order to clarify whether or not these were near-surface processes. Magmatic brines appear to occupy a compositional space that is intermediate in terms of Br/Cl, but is somewhat distinct in terms of I/Cl and $\delta^{37}\text{Cl}$. Their relatively narrow compositional range in terms of ratios, but more variable salinities, may also be distinctive.

Conclusions: Applications to Ore Deposits

Brines may develop as a result of sedimentary, metamorphic or igneous processes, and have considerable potential for formation of a wide range of ores. However, in general they are linked to the large scale concentration of salt in the crust through sedimentary processes at particular times in Earth history (Warren 1999), or to emplacement of certain acid magmas. Brines, like salt emplaced into the crust,

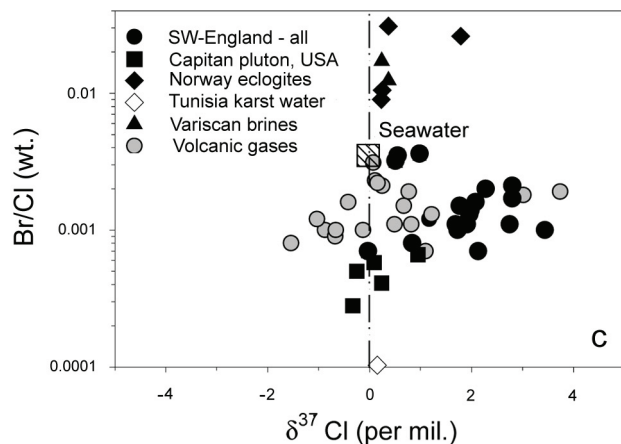
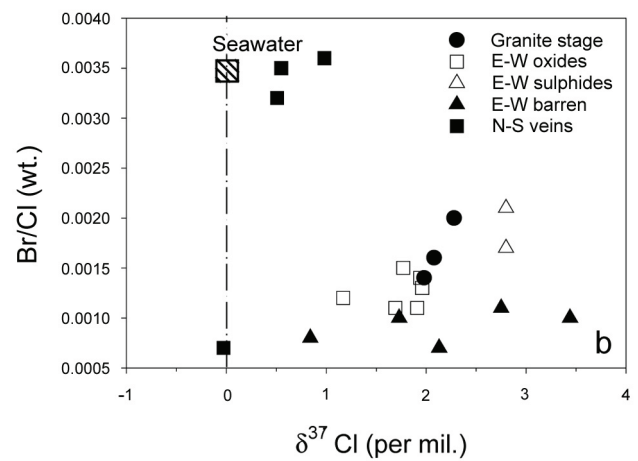
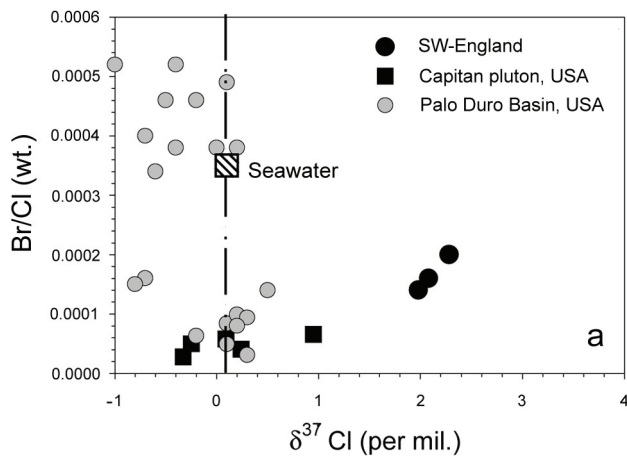


Figure 3: Plot of Br/Cl (by weight, note different scale in part c) against $\delta^{37}\text{Cl}$ for a range of sedimentary, metamorphic and magmatic fluids. See text.

It is clearly possible to generate brines in a range of settings, and for Fe mineralisation to result from a variety of brines encountering appropriate conditions. The behaviour of Cu and Au is much harder to predict from the data presently available. Nevertheless, their patterns of solubility are sufficiently distinctive to hold out some hope that they will allow models for hydrothermal iron oxide-Cu-Au deposits to be much more closely constrained than is presently possible.

Acknowledgements

This work has been supported through NERC grant GR3/1108 and earlier NERC projects. We are grateful to James Cleverley for assistance with the EQ3/6 modelling and to Sarah Gleeson for helpful discussions and provision of samples from SW England.

References

- Banks, D.A., Davies, G.R., Yardley, B.W.D., McCaig, A.M., and Grant, N.T., 1991 - The chemistry of brines from an Alpine thrust system in the Central Pyrenees: An application of fluid inclusion analysis to the study of fluid behaviour in orogenesis; *Geochimica et Cosmochimica Acta*, v. 55, pp. 1021-1030.
- Banks, D.A., Yardley, B.W.D., Campbell, A.R., and Jarvis, K.E., 1994 - REE composition of an aqueous magmatic fluid: A fluid inclusion study from the Capitan Pluton, New Mexico, U.S.A; *Chemical Geology*, v. 113, pp. 259-274.
- Banks, D.A., Green, R., Cliff, R.A., and Yardley, B.W.D., 2000a - Chlorine isotopes in fluid inclusions: Determination of the origins of salinity in magmatic fluids; *Geochimica et Cosmochimica Acta*, v. 64, pp. 1785-1789.
- Banks, D.A., Giuliani, G., Yardley, B.W.D., and Cheillett, A. 2000b - Emerald mineralisation in Colombia: Fluid chemistry and the role of brine mixing; *Mineralium Deposita*, v. 35, pp. 699-713.

appear to be capable of long residence times in a particular basin (Eastoe *et al.* 1999, McCaig *et al.* 2000) and so they can be involved in ore formation long after their original development. Likewise, igneous activity can remobilise halite deposits.

While metal concentrations in igneous brines are sometimes extreme, sedimentary brines are also capable of significant metal transport, and variations in redox environment can then lead to rapid precipitation. This means that there may be examples of Fe-oxide deposits of both magmatic and sedimentary origins, and their distinction merits careful evaluation. As an example, the SW England magmatic brines discussed here have very high contents of Fe (Bottrell and Yardley 1988, see Table 1), but the region has only rather minor hematite deposits. In contrast, historically more significant iron ores in the north west of England (Shepherd and Goldring 1993) appear to be related to sedimentary brines, being localised in Carboniferous limestones immediately beneath the Permo-Triassic unconformity. Fe is actually very insoluble in a red-bed environment, so while a simplistic interpretation would be that Fe was somehow leached down into the limestones from the overlying deserts, it is actually more reasonable to suppose that the deposits represent a redox front where Carboniferous basin brines, rising up as a result of basin inversion, encountered local oxidised groundwaters, causing hematite to precipitate.

- Bohlke, J.K. and Irwin, J.J., 1992 - Laser microprobe analyses of Cl, Br, I and K in fluid inclusions: Implications for sources of salinity in some ancient hydrothermal fluid; *Geochimica et Cosmochimica Acta*, v. 56, pp. 203-225.
- Boiron, M.C., Moissette, A., Cathelineau, M., Banks, D.A., Monnin, C. and Dubessy, J., 1999 - Detailed determination of paleofluid chemistry: An integrated study of atypical sulphate-volatile rich brines and aquo-carbonic fluids in quartz veins from Ouro Fino syncline (Brazil); *Chemical Geology*, v. 154, pp. 179-192.
- Bottrell, S.H., and Yardley, B.W.D., 1988 - The composition of a primary, granite-derived ore fluid from S.W. England, determined by fluid inclusion analysis; *Geochimica et Cosmochimica Acta*, v. 52, pp. 1509-1518.
- Bottrell, S.H., and Yardley, B.W.D., 1991 - The distribution of Fe and Mn between chlorite and fluid: Evidence from fluid inclusions; *Geochimica et Cosmochimica Acta*, v. 55, pp. 241-244.
- Campbell, A.R., Banks, D.A., Phillips R.S., and Yardley, B.W.D., 1995 - Geochemistry of Th-U-REE mineralizing magmatic fluids, Capitan Mountains, New Mexico; *Economic Geology*, v. 90, pp. 1271-1287.
- Carpenter, A.B., Trout, M.L., and Pickett, E.E., 1974 - Preliminary report on the origin and chemical evolution of lead-and-zinc-rich oilfield brines in Central Mississippi; *Economic Geology*, v. 69, pp. 1191-1206.
- Cline, J.S., and Bodnar, R.J., 1991 - Can economic porphyry copper mineralisation be generated by a typical calc-alkaline melt?; *Journal of Geophysical Research*, v. 96, pp. 8113 - 8126.
- Desaulniers, D.E., Kaufmann, R.S., Cherry, J.A., and Bentley, H.W., 1986 - ^{37}Cl - ^{35}Cl variations in a diffusion-controlled groundwater system; *Geochimica et Cosmochimica Acta*, v. 50, pp. 1757-1764.
- Eastoe, C.J., and Guilbert, J.M., 1992 - Stable chlorine isotopes in hydrothermal processes; *Geochimica et Cosmochimica Acta*, v. 56, pp. 4247-4255.
- Eastoe, C.J., Long, A., and Knauth, L.P., 1999 - Stable chlorine isotopes in the Palo Duro Basin, Texas: Evidence for preservation of Permian evaporite brines; *Geochimica et Cosmochimica Acta*, v. 63, pp. 1357-1382.
- Eugster, H.P. and Gunter, W.D., 1981 - The compositions of supercritical metamorphic fluids; *Bulletin de Mineralogie*, v. 104, pp. 817-826.
- Fontes, J.Ch., and Matray, J.M., 1993 - Geochemistry and origin of formation brines from the Paris Basin, France 1. Brines associated with Triassic salts; *Chemical Geology*, v. 109, pp. 149-175.
- Fritz, P., and Frape, S.K., (eds.), 1987 - Saline Water and Gases in Crystalline Rocks; *Geological Association of Canada*, Special Paper 33, 259p.
- Gleeson, S.A., Wilkinson, J.J., Shaw, H.F., and Herrington, R.J., 2000 - Post-magmatic hydrothermal circulation and the origin of base metal mineralisation, Cornwall, U.K.; *Journal of the Geological Society of London*, v. 157, pp. 589-600.
- Hanor, J.S., 1994 - Origin of saline fluids in sedimentary basins; in Parnell, J., (ed.) *Geofluids: origin, migration and evolution of fluids in sedimentary basins*, *Geological Society of London*, Special Publication 78, pp. 151-174.
- Heinrich, C.A., Ryan, G.C., Mernagh, T.P. and Eadington, P.J., 1992 - Segregation of ore metals between magmatic brine and vapour: a fluid inclusion study using PIXE microanalysis; *Economic Geology*, v. 87, pp. 1566-1583.
- Kaufmann, R.S., Long, A., Bentley H., and Davis, S., 1984 - Natural chlorine isotope variations; *Nature*, v. 309, pp. 338-340.
- Kaufmann, R.S., Long, A., and Campbell, D.J. 1988 - Chlorine isotope distribution in formation waters, Texas and Louisiana; *American Association of Petroleum Geologists Bulletin*, v. 72, pp. 839-844.
- Kesler, S.E., Appold, M.S., Martini, A.M., Walther, L.M., Huston, T.J., and Kyle, J.R., 1995 - Na-Cl-Br systematics of mineralising brines in Mississippi Valley-type deposits; *Geology*, v. 23, pp. 641-644.
- Land, L.S., 1995 - Na-Ca-Cl formation waters, Frio formation (Oligocene), south Texas, USA: products of diagenesis; *Geochimica et Cosmochimica Acta*, v. 59, pp. 2163-2174.
- McCaig, A.M., Tritlla, J., and Banks, D.A., 2000 - Fluid mixing and recycling during Pyrenean thrusting: evidence from fluid inclusion halogen ratios; *Geochimica et Cosmochimica Acta*, v. 64, pp. 3395-3412.
- Meere, P.A., and Banks, D.A., 1997 - Upper crustal fluid migration during an orogenic cycle: An example from the Variscides of South West Ireland; *Journal of the Geological Society of London*, v. 154, pp. 975-985.
- Orville, P.M., 1972 - Plagioclase cation exchange equilibria with aqueous chloride solution: results at 700°C and 2000 bars in the presence of quartz; *American Journal of Science*, v. 272, pp. 234-272.
- Pitcairn, I. (2000) - $\delta^{37}\text{Cl}$ and Cl/Br systematics in volcanic gases. Unpublished M.Sc. thesis, *University of Leeds*, UK.
- Rittenhouse, G., 1967 - Bromine in oil-field waters and its use in determining the possibilities of origins of these waters; *American Association of Petroleum Geologists*, Bulletin 51, pp. 2430-2440.

- Seward, T.M., 1973 - Thio complexes of gold and the transport of gold in hydrothermal solutions; *Geochimica et Cosmochimica Acta*, v. 37, pp. 379-399.
- Shepherd, T.J., and Goldring, D.C., 1993 - Cumbrian hematite deposits, North-west England; in Patrick, R.A. and Polya, D.A. (eds.), Mineralization in the British Isles, *Chapman and Hall, London*, pp. 415-445.
- Svensen, H., Jamtveit, B., Yardley, B.W.D., Engvik, A.K., Austrheim, H. and Broman, C., 1999 - Lead and bromine enrichment in eclogite-facies fluids: Extreme fractionation during lower-crustal hydration; *Geology*, v. 27, pp. 467-470.
- Warren, J., 1999 - Evaporites; *Blackwell Science, Oxford*, 438p.
- Wolery, T.J., 1983 - EQ3NR: a computer program for geochemical aqueous speciation-solubility calculations, user guide and documentation; UCRL-53414, *Lawrence Livermore National Laboratory, University of California*.
- Xiao, Y.K., and Zhang, C.G., 1992 - High-precision isotopic measurement of chlorine by thermal ionisation mass spectrometry of the Cs_2Cl^+ ion. *International Journal of Mass Spectrometry Ion Processes*, v. 116, pp. 183-192.
- Yardley, B.W.D., 1997 - The evolution of fluids through the metamorphic cycle; in Jamtveit, B. and Yardley, B.W.D., (eds.), Fluid flow and transport in rocks, *Chapman and Hall, London*, pp. 99-122.