Fluid inclusions in hydrothermal ore deposits

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Abstract

The principal aim of this paper is to consider some of the special problems involved in the study of fluid inclusions in ore deposits and review the methodologies and tools developed to address these issues. The general properties of fluid inclusions in hydrothermal ore-forming systems are considered and the interpretation of these data in terms of fluid evolution processes is discussed. A summary of fluid inclusion data from a variety of hydrothermal deposit types is presented to illustrate some of the methodologies described and to emphasise the important role which fluid inclusion investigations can play, both with respect to understanding deposit genesis and in mineral exploration. The paper concludes with a look to the future and addresses the question of where fluid inclusion studies of hydrothermal ore deposits may be heading in the new millenium. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The modern science of fluid inclusion geochemistry grew principally out of pioneering work on hydrothermal ore deposits more than 40 years ago (Roedder, 1958). Mineral deposits are extraordinary anomalies in the Earth that provide us with perhaps the clearest evidence for the past flow of solutions through faults, fractures and porous rocks that, in the process, dissolved, transported and concentrated elements of economic interest. Looking at fluid inclusions trapped within hydrothermal veins was recog-

nised as a direct way of saying much more than had previously been possible about the nature of these mineralizing fluids and the processes by which mineral deposits were formed. In this, nature was kind by providing ideal sample material for investigation: often coarse-grained, transparent minerals with large fluid inclusions, perfectly suited to the fledgling techniques of microthermometry and bulk chemical analysis.

The credit for the recognition of these possibilities goes back another 100 years, however, to the founding father of fluid inclusion research, Henry Clifton Sorby. In his classic paper (Sorby, 1858) he specifically described samples from ore deposits containing fluid inclusions and drew conclusions concerning ore formation that remained scientifically unfashionable for many years. We now recognise the importance of

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the ideas developed by Sorby and they form the basis for most current fluid inclusion research.

At present, the number of general reviews of fluid inclusion studies in ore deposit studies are few, providing a stark contrast to the huge number of scientific papers now being published in this field. Perhaps it is because any attempt to summarise such work presents an extremely daunting task, and cannot comfortably encompass the breadth of the subject matter. The most comprehensive review remains that of Roedder (1984), with other contributions by Roedder (1967a), Spooner (1981), Lattanzi (1991, 1994), Bodnar et al. (1985) and Roedder and Bodnar (1997).

The principal aim of this paper is to consider some of the special problems involved in the study of fluid inclusions in ore deposits and describe the methodologies and tools developed to address these issues. This involves both a consideration of the general properties of fluid inclusions in a range of different deposit types and what these data can tell us about fluid evolution processes. A discussion of fluid inclusion data from individual deposit types is presented in an attempt to illustrate the methodologies utilised in studies of ore deposit genesis and to emphasise the important role which fluid inclusion investigations can play. The paper concludes with a look to the future and addresses the question of where fluid inclusion studies of hydrothermal ore deposits may be heading in the new millenium.

2. Fluid inclusion paragenesis in hydrothermal ore deposits

As with any fluid inclusion study, determining the time relationships of the different inclusions encountered is the most important stage, yet this is beset by difficulty and is often inconclusive. Application of standard criteria for the recognition of primary, pseudosecondary and secondary inclusions (Roedder, 1984; Van den Kerkhof and Hein, 2001) is essential; however, in hydrothermal veins where reactivation and multiple phases of fluid flow are common, this can prove to be inadequate. Furthermore, as stated by Roedder and Bodnar (1997), most inclusions in most samples can be presumed to be secondary, unless proved otherwise. So how can different stages

of fluid flow be resolved and their temporal relationships determined, especially when the majority of the inclusions may be secondary in origin? Furthermore, how can the relationship between these fluids and ore formation be constrained?

2.1. Defining the relationship between inclusions and ore formation

The relationship of the inclusions being studied to the process of interest is one of the most important criteria in fluid inclusion studies of ore deposits yet often receives inadequate attention (e.g. see discussion in Roedder and Bodnar, 1997, p. 662). It is commonly assumed that primary or pseudosecondary inclusions hosted by transparent gangue minerals which show a purely spatial association with ore minerals are representative of the ore-forming fluid. However, the textural evidence for co-precipitation is often not satisfactorily documented. Even apparent equilibrium grain boundary relationships and mineral intergrowths are not proof of simultaneous deposition. A good example is provided by the work of Campbell and Panter (1990) who showed, using infra-red microscopy (see below), that inclusions in quartz intergrown with cassiterite and wolframite had different microthermometric properties to those hosted by the ore minerals themselves.

Supporting evidence for co-precipitation can sometimes be provided, such as by tests for isotopic equilibrium between two apparently co-genetic phases, for example, oxygen isotope equilibrium fractionation between quartz and magnetite. Although not a proof, this can support textural evidence for co-precipitation; however, a lack of isotopic equilibrium does not negate co-precipitation, just that full isotopic equilibrium was not attained, as is commonly the case in hydrothermal environments. Furthermore, the test pre-supposes a knowledge of the temperature of precipitation — this unknown was probably one of the reasons for studying the fluid inclusions in the first place!

Perhaps the best evidence for a temporal genetic relationship between ore and gangue minerals is the occurrence of fine-grained ore mineral inclusions within the gangue mineral itself (Fig. 1), or where fluid inclusions contain daughter ore minerals
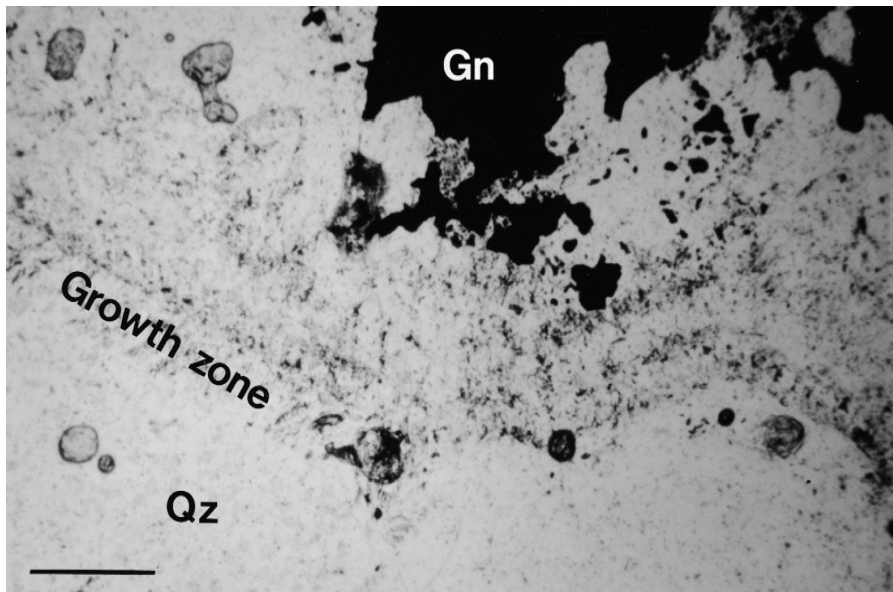
Fig. 1. Photomicrograph showing galena (Gn) precipitated in growth zones in quartz (Qz), defined by bands of primary fluid inclusions. Crosscourse Pb–Zn mineralized vein, Porthleven, Southwest England. Plane polarised light, scale bar 2 mm.

(Fig. 2). Where such relationships are not observed, any inference of co-precipitation remains inconclusive and this uncertainty must be borne in mind when using the inclusion data to constrain the geological environment or processes of ore formation. It cannot be emphasised enough that inclusion data must always be considered within the context of the full spectrum of available geochemical and geological data and inappropriate significance should not be placed upon fluid inclusion data alone.

In order to minimise such uncertainties, the ideal case is to measure inclusions hosted by the ore minerals themselves. Of the common ore minerals, sphalerite is by far the most frequently studied. Not only is it a relatively hard mineral that makes it ideal for maintaining inclusion integrity, it is also commonly translucent to white light and is therefore amenable to conventional microthermometric analysis. Pale, or honeyblende, low-iron sphalerite is the easiest to work with but, as a result of improvements in microscope optics and illumination power, it is now possible to analyse inclusions even in dark brown sphalerite. One of the principal problems with sphalerite is the high refractive index contrast between the fluid inclusions and the host mineral which renders the walls of the inclusion very dark and into

which, by the operation of Murphy's Law, the vapour bubble or ice crystals invariably move during mi-
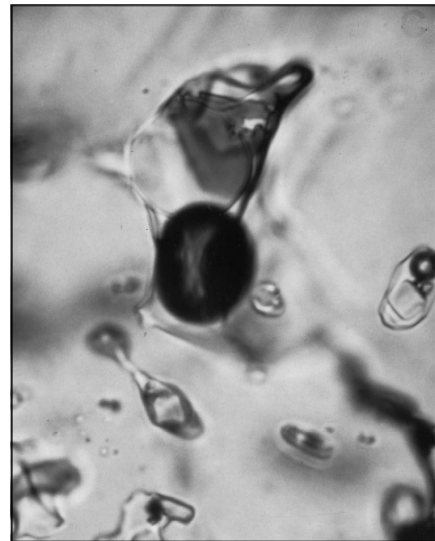

Fig. 2. Photomicrograph of large, multiphase fluid inclusion containing a number of daughter minerals including a hexagonal, red haematite plate. Th–U–REE mineralized Capitan pluton, New Mexico. Plane polarised light, width of image, 250 μm. Photo courtesy of S. Mulshaw.

crothermometry. This limitation can be partly overcome by well set-up optical (Kohler) illumination, but will always prove to be a limitation of standard transmitted light methods. A useful tip regarding homogenization is that by closing down the field diaphragm and moving the focussed light source off-centre using the centring screws, the vapour bubble can sometimes be 'moved' out into the centre of the inclusion where it is visible. The reason for this behaviour is unclear, but it works!

An alternative approach which has engendered variable enthusiasm is the use of infra-red microscopy (Campbell et al., 1984; Campbell and Robinson-Cook, 1987; Campbell and Panter, 1990; Richards and Kerrich, 1993; Luders et al., 1999). A number of ore minerals, principally sphalerite, pyrargyrite, wolframite, cinnabar, stibnite, chalcocite, enargite, molybdenite, tetrahedrite–tennantite, haematite, and even non-arsenian pyrite, are transparent to infra-red radiation. Specially designed infra-red transmitting microscopes in conjunction with video cameras sensitive, ideally, into the far infra-red (~ 2 μm) can be used to observe inclusions in such minerals. Problems encountered are the inherently limited optical resolution at long wavelengths, dark inclusion walls due to the refractive index contrast described above, and image degradation during heating. In addition, certain sulphides, such as pyrite, often do not seem to contain fluid inclusions. So, although in theory the method provides an ideal way of accessing the properties of ore-forming solutions directly, to date it has been limited to studies of large inclusions in a limited number of phases.

2.2. From mineral paragenesis to inclusion paragenesis

If the key question regarding the temporal relationship between inclusion-hosting gangue phases and the ore minerals of interest can be satisfactorily answered, a second major problem, that concerning the relative timing of different inclusion generations within the gangue phase, must be addressed. One of the advantages bestowed on workers in hydrothermal ore deposits is that veins commonly record a series of stages of mineral growth, the sequence of which, or *paragenesis*, can be resolved utilising careful

microscope petrography. This provides a time framework within which the relative ages of inclusions — even when secondary in origin — can be constrained. This is perhaps best illustrated with an example. Consider a composite vein consisting of several growth stages: quartz I, quartz II + galena, calcite I, quartz III, calcite II + sphalerite (Fig. 3). We may find that a certain inclusion type A, defined either by optical appearance at room temperature *or* by microthermometric properties, occurs as secondary inclusions in all paragenetic stages. This limits the timing of the inclusion type A to syn- to post-calcite II. If type A also occurs, even only rarely, as primary inclusions within calcite II or sphalerite, then it is probable that this inclusion type reflects the fluid present during the final paragenetic stage. Alternatively, if another inclusion type B occurs as secondary inclusions only in quartz I, II and calcite I, then it probably represents the fluid present during the precipitation of calcite I. Its absence in later phases implies it predates them since, although theoretically possible, it is highly unlikely that no secondary inclusions of type B would be observed in
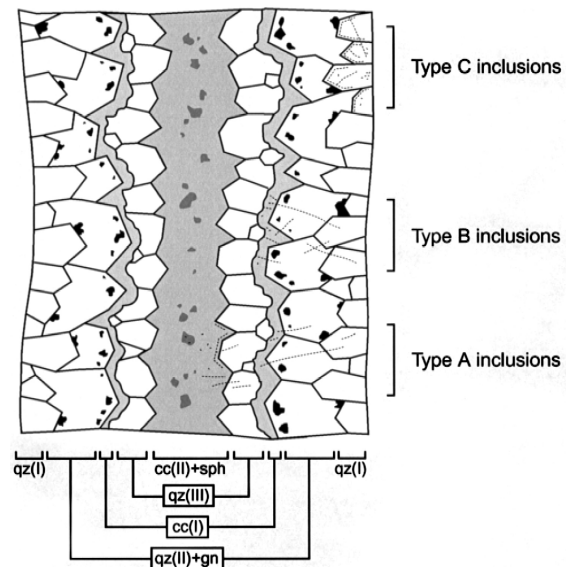

Fig. 3. Schematic representation of symmetrical crustified vein, illustrating multiple phases of mineral deposition and microfracturing events, each with related fluid inclusion assemblages. Qz — quartz, cc — calcite, gn — galena; sph — sphalerite. See text for discussion.

the later phases if they were already present within the vein at the time of fracturing and the introduction of fluid type B. The occurrence of Type C inclusions, either primary or secondary, only in quartz I, means they are likely to represent the initial vein-forming fluid. The occurrence of unequivocal primary inclusions, albeit rarely, can be used to 'fix' the inclusion type characteristic of a particular stage of evolution of the system, and can also be used to help constrain the relative timing of secondary inclusions. By this iterative process, a relatively detailed fluid inclusion chronology can be established. Almost inevitably, gaps or areas of uncertainty will remain; nonetheless, the use of a mineral paragenetic sequence to help constrain fluid inclusion chronology provides a useful approach to help avoid misinterpretation of fluid inclusion timing.

2.3. Monomineralic systems and the use of cathodoluminescence petrography

Although the approach outlined above can often provide a successful way of unravelling the complexity of hydrothermal vein systems, some deposits, particularly higher temperature systems and/or those with high fluid fluxes, tend toward a limited number of phases and are not amenable to the method. A good example is provided by mesothermal quartz–gold veins which are complex, multistage deposits but in which one phase (quartz) dominates the vein assemblage with the relatively minor occurrence of carbonates, sulphides and other phases such as tourmaline or scheelite. How can the multiple episodes of quartz growth be resolved into a paragenesis of sufficient detail to carry out the type of inclusion petrographic analysis described above?

Whilst careful transmitted light microscopy may go some way toward this goal, a powerful tool which is gradually gaining increasing recognition is that of cathodoluminescence (CL) petrography. Although this has gained wide acceptance in studies of diagenesis and carbonate cementation in, for instance, Mississippi Valley-type deposits (e.g. Montañez, 1996), its potential in wider studies of mineral deposits has not been fully realised. Apart from a number of conference abstracts, the main publications on the use of CL in quartz vein systems are those by Boiron

et al. (1992), Wilkinson and Johnston (1996), Milodowski et al. (1998) and Wilkinson et al. (1999). A more detailed treatment of instrumentation and theory is beyond the scope of this paper; for further information the reader is referred to Van den Kerkhof and Hein (2001), Marshall (1988) and Barker and Kopp (1991).

CL petrography works as a tool for resolving multiple stages of vein growth because of the changes in fluid chemistry, temperature and mineral structure that may characterise different episodes of mineral precipitation. Because of its ubiquity within the Earth's crust, quartz is the most common vein-forming mineral, yet it can be precipitated from fluids of widely varying composition and temperature. Whilst no textural differences in the quartz precipitated by these fluids may be observed in hand specimen, or even using transmitted light microscopy, the differences in precipitation conditions may be reflected by marked variation in its luminescence characteristics. This is illustrated in a recent study in which overprinting of a quartz vein gold deposit by later fluids which resulted in the remobilisation of gold was recognised by a quartz paragenesis and fluid inclusion study utilising SEM-CL (Wilkinson et al., 1999). The late phase of gold, principally occurring in fractures within pyrite grains, was clearly shown to be related to a late phase of quartz precipitation which formed angular microfracture networks crosscutting all precursor quartz stages and was characterised by a distinctive bright luminescence (Fig. 4). Analysis of fluid inclusions hosted by these microfractures showed that the fluid responsible was a low T_h, high salinity $CaCl_2$–$NaCl$ brine considered to be of probable basinal origin. This study demonstrates the power of combined CL and fluid inclusion studies for unravelling the complexities of these types of hydrothermal system and also for throwing up some unexpected results which merit further investigation.

The use of SEM-CL also provides us with an opportunity to eliminate one of the critical problems of inclusion classification: how to resolve the relative time of formation of different secondary inclusion generations. Whilst this may be possible utilising the mineral paragenetic approach described above, it is not generally possible to do this in monomineralic systems except in the rare cases where
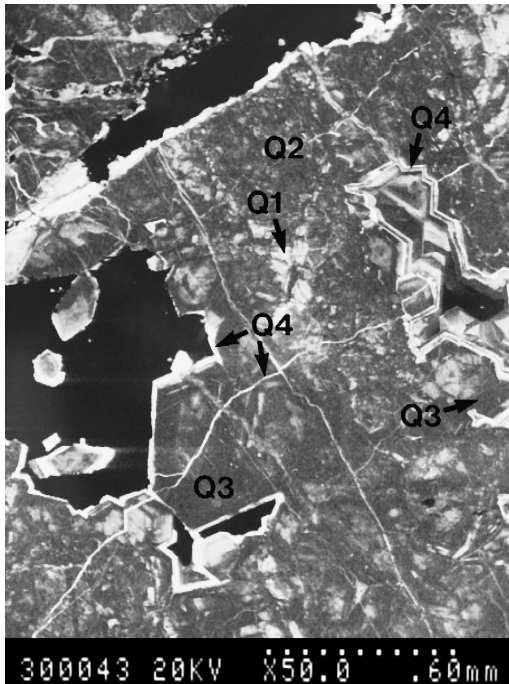
Fig. 4. SEM-CL photomicrograph of multiple stages of quartz precipitation in veins from the Curraghinalt gold deposit, Northern Ireland. Q1: pre-mineralization, brecciated quartz (moderate luminescence); Q2: main gold–sulphide stage breccia cement (dull luminescence); Q3: post-mineralization, sector zoned euhedral quartz overgrowths (variable luminescence); Q4: Late overprint causing gold remobilization (bright luminescence).

clear crosscutting relationships between different microfractures are visible (e.g. Lattanzi, 1991, p. 693). SEM-CL potentially allows the resolution of even individual microfractures and to enable the relative timing of different microfracture generations to be established. As long as the not insignificant practical difficulties of relocating the CL-resolved microfractures can be overcome, the fluid inclusions within these microfractures can be analysed by microthermometry or other single inclusion analytical methods. These inclusions thus become primary with respect to the microfracture-annealing phase. In the gold deposit case described above, Wilkinson et al. (1999) showed how inclusions which would normally be classified as secondary could be related to a specific quartz generation. Unfortunately, with purely imaging SEM-CL systems, this can only be achieved where a distinctive difference in luminescence inten-

sity happens to be developed. Optical systems are not restricted to monochromatic light so that the additional dimension of luminescence colour can be used to resolve different growth stages. This is particularly useful for recognition of multiple phases of carbonate precipitation in veins or carbonate cements in sediment-hosted mineral deposits (e.g. Montañez, 1996). Quantitative spectroscopic systems are now available and should enable individual mineral generations to be 'fingerprinted' in terms of characteristic emission wavelength patterns, thereby allowing even similarly luminescent but separate stages of growth to be resolved.

2.4. Problems of post-entrapment modification

General aspects of post-entrapment modification of fluid inclusions have been dealt with by Van den Kerkhof and Hein (2001). However, there are a number of specific problems of post-entrapment modification of fluid inclusions that are particularly relevant to hydrothermal mineral deposits. As these are intrinsically related to interpretation of fluid inclusion data from mineralized systems, they will be briefly discussed below.

2.4.1. Diffusion

Diffusion of components into or out of inclusions has long been recognised as a possible problem in fluid inclusion studies (Roedder and Skinner, 1968). Diffusion may either occur through the bulk mineral lattice or, more commonly, via grain boundaries and crystal defects. Components prone to suffer this problem will be those with small molecular or ionic radii such as H_2 or He, and diffusion will be more likely to occur in minerals with open structures and high ionic diffusivity. For example, gold has been shown to be an excellent host for volatile species (Eugster et al., 1995); conversely, quartz is a poor host for helium which can diffuse rapidly out of inclusions (Stuart et al., 1995). Different rates of diffusion for different isotopes (e.g. ^{3}He vs. ^{4}He) limits the suitability of many minerals for studies of noble gas isotope ratios.

One well-documented example that illustrates the problem of hydrogen diffusion comes from fluid inclusion studies of porphyry–copper deposits. The

occurrence of chalcopyrite as well as other apparent daughter minerals has been widely reported from quartz-hosted inclusions in porphyry systems. However, these apparent chalcopyrite daughter minerals, although displaying consistent solid/liquid volumetric ratios, do not dissolve on heating to inferred trapping temperatures and this is one of the criteria for such solid phases being truly precipitated within inclusions during cooling. This apparent paradox was resolved by Mavrogenes and Bodnar (1994) who showed that post-entrapment hydrogen diffusion had occurred so that the redox state of the inclusions at the present day no longer reflects that of the environment in which they formed. By subjecting the samples to elevated partial pressures of H_2 gas in an experimental vessel, they were able to diffuse hydrogen back into the inclusions. Subsequent microthermometric runs showed that the chalcopyrite daughter minerals did indeed dissolve. Such changes in oxidation state may be the norm in many fluid inclusions and any species with redox-sensitive equilibria (such as carbon-bearing volatile species) could be affected. However, most hydrothermal deposits are not maintained at elevated temperatures for extended time periods (unlike metamorphic environments for instance), or are not characterised by strong chemical potential gradients, so that hydrogen diffusion is not thought to be a general problem. Even so, it would not affect many of the parameters on which we rely for interpretation of microthermometric data, such as the volumetric properties and low temperature phase equilibria of salt–water systems.

2.4.2. Isotopic exchange

Determining the isotopic composition of inclusion fluids, particularly the oxygen and hydrogen isotopic composition of inclusion water, has become commonplace in studies of hydrothermal mineralization. This is because the isotopic composition of the water can place useful constraints on the source of the water and interactions along the flow path, and can therefore be used to test alternative geological models for ore deposit genesis.

The hydrogen isotopic composition of inclusion water is often analysed directly, after fluid extraction, usually by decrepitation at high temperature (Jenkin et al., 1994). Potential problems do exist arising from isotopic exchange between fluid inclu-

sions, the host mineral, and water bound in different structural sites (such as defects) within minerals like quartz (Simon, 1997). However, these are not thought to be generally significant, principally due to the small volumes of fluid trapped in such sites in most samples (Gleeson et al., 1999b).

The oxygen isotope composition of inclusion fluids cannot be determined directly for inclusions hosted by many gangue phases for the simple reason that oxygen is commonly a major constituent of the host mineral. Subsequent to inclusion trapping, a certain amount of retrograde isotopic exchange will occur between the inclusion fluid and the host, the extent of this being controlled by isotope exchange kinetics, time and temperature. Given that fluid inclusions generally form a relatively small proportion of the total mass of a sample (typically around 10^{-3}), the effect of such exchange on the isotopic composition of the inclusions may be large. Conversely, the net effect on the bulk composition of the host mineral will be negligible. This can be illustrated by a simple example. If quartz precipitated with a $\delta^{18}O$ composition of $+18.0‰$ from a fluid of $+11.1‰$ at 300°C and contained a mass proportion of water of 10^{-3}, complete isotopic re-equilibration at 25°C would result in the quartz having a value of $+18.05‰$, within analytical error of the initial composition. However, the inclusion water would have a composition of $-16.25‰$!

As a result of this, oxygen compositions of inclusion waters are usually calculated from the measured oxygen isotope composition of the host mineral and an experimentally determined temperature-dependent mineral–fluid fractionation factor. This procedure requires that the temperature of precipitation is known; often this information is derived from fluid inclusion homogenization temperature measurements.

3. Interpretation of fluid inclusion data in hydrothermal ore deposits

3.1. General characteristics

3.1.1. Homogenization temperatures and salinity

Although it is difficult to generalise about the properties of fluid inclusions that occur in different

types of ore deposit, a number of parameters are consistent enough to be worth summarising. The most obvious and simplest way of characterising the fluid inclusions present in mineralized systems is in terms of homogenization temperature and NaCl equivalent salinity. Whilst these properties are not direct functions of fluid temperature and fluid salinity, the general relationship which exists and the natural variability of these two parameters in hydrothermal systems make them useful for comparative purposes.

Fig. 5 represents a compilation of T_h and salinity information from different deposit types, drawing significantly on the summaries of Roedder (1984) together with a wide range of published data. The main classes of ore deposits occupy broad fields in T_h–salinity space which reflect the basic properties of the fluids involved in their formation and are broadly constrained between the halite saturation curve and the critical curve for pure NaCl solutions. For instance, epithermal deposits are primarily formed from modified, surface-derived fluids that have circulated to a range of depths within the brittle regime of the crust, often in areas of elevated crustal permeability and heat flow. They are therefore typified by low salinity fluids and a range of homogenization temperatures that, because of the generally

low trapping pressures involved, serve as an approximation of trapping temperatures, spanning the typical epithermal range of $< 100°C$ to $\sim 300°C$. It should be emphasised that such fields are not sharply delimited and that examples exist which do not fall into the defined ranges; such information should solely be used as a guide and provides for the inexperienced worker a feel for the type of data characteristic of different mineralizing systems.

3.1.2. Fluid density

Homogenisation temperature information when coupled with fluid salinity data defines the density of the fluid, irrespective of fluid trapping conditions. Variations in fluid density are particularly important with respect to mechanisms of fluid flow and evaluation of spatial variations in fluid density in a system can provide constraints on the flow process. A particularly useful diagram in this respect is a conventional T_h–salinity plot but contoured with lines of constant fluid density (Fig. 6; e.g. Bodnar, 1983). Fluid inclusion data can be plotted on such a diagram and density variations considered. For example, fluid inclusion data from 'feeder' vein systems hosted by basement rocks in Ireland are plotted in Fig. 7 in comparison with the typical range observed for fluids observed within the overlying Zn–Pb–Ag–
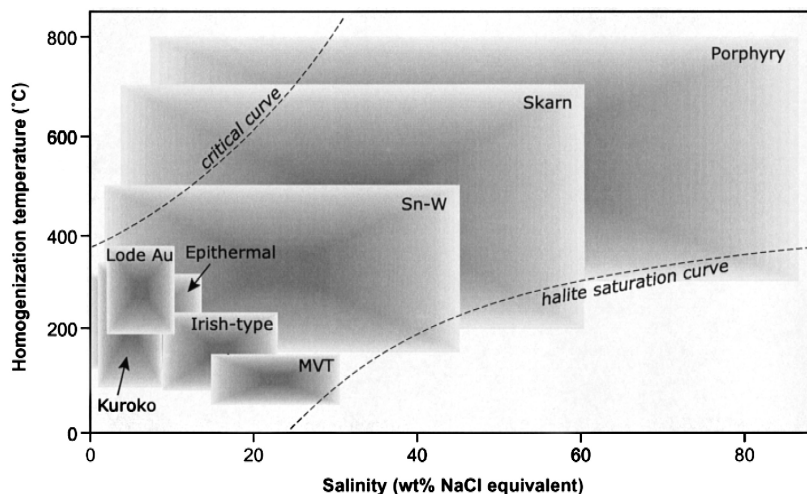

Fig. 5. Summary homogenization temperature–salinity diagram illustrating typical ranges for inclusions from different deposit types. Note that fields should not be considered definitive and compositions exist outside the ranges shown.
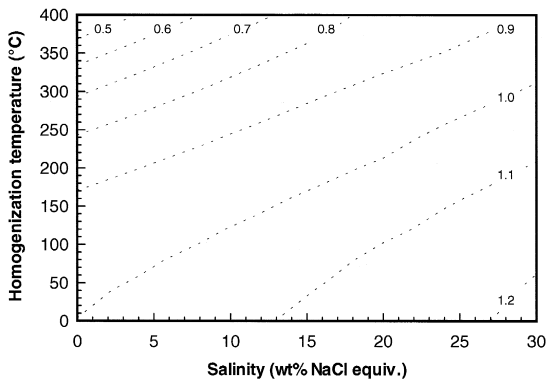
Fig. 6. Temperature–salinity plot showing densities (g cm^{-3}) of vapour-saturated NaCl–H$_2$O solutions. Contours regressed from data generated by the equation-of-state of Zhang and Frantz (1987) using the FLINCOR computer program (Brown, 1989).

Ba deposits. The data show that the lowest density fluids are observed within and proximal to the deposits, consistent with a density driven flow mechanism with low density hydrothermal plumes being responsible for the location of mineralization.

3.1.3. Volatile content

Another approach to subdividing different classes of mineralizing fluids is on the basis of their non-aqueous volatile or gas content. Notwithstanding the problems involved in analysing the gas content of inclusions and the common requirement for the analysis of bulk samples, the gas composition of inclusion fluids can provide a useful indicator of fluid provenance. In particular, N$_2$, Ar and He are conservative tracers that provide a means for discriminating between fluids from magmatic, sedimentary and deep- or shallow-circulated meteoric sources (Norman and Sawkins, 1987; Landis and Rye, 1989; Norman and Musgrave, 1994; see Fig. 8). Together with CO$_2$ and CH$_4$ contents, these compositional parameters have been determined in porphyry–Cu, porphyry–Mo and other magmatic-related systems (Graney and Kesler, 1995), epithermal and sediment-hosted base metal deposits (Norman et al., 1985; Jones and Kesler, 1992; Norman and Musgrave, 1994).

3.1.4. Solute composition

A huge number of analyses of solute compositions have been made on fluid inclusions from hy-

drothermal ore deposits using a wide range of analytical methods and it is difficult to generalise about mineralizing fluid compositions. However, in common with most crustal fluids, the dominant cations found are Na, K and Ca followed by Fe and Mg, and the dominant anion is almost always Cl$^-$ with lesser amounts of SO$_4^{2-}$, HCO$_3^-$ and NO$_3^-$. The abundance of Cl$^-$ is critical for many ore-forming solutions since it is the principal complexing ligand for many metals, especially base metals.

Of perhaps more direct concern are data pertaining to ore metal contents in inclusion fluids. Some of the earliest work reported Cu and Zn concentrations of up to several weight percent from porphyry–copper and MVT deposits using a variety of techniques such as instrumental neutron activation analysis (Czamanske et al., 1963) or more conventional crush-leach analysis (Roedder, 1967a). More recent work using synchrotron-XRF (Rankin et al., 1992; Mavrogenes et al., 1995a,b), proton-induced excitation (e.g. Heinrich et al., 1992; Zaw et al., 1996) and laser ablation methods (Wilkinson et al., 1994; Shepherd and Chenery, 1995; Audetat et al., 1998) have determined an ever increasing range of metals with gradually improving precision. In particular, Audetat et al. (1998) have shown how the metal content in tin mineralizing fluids from the Mole Granite, Australia, decreased in response to dilution by a second fluid and as a result of ore mineral precipitation (Fig. 9).
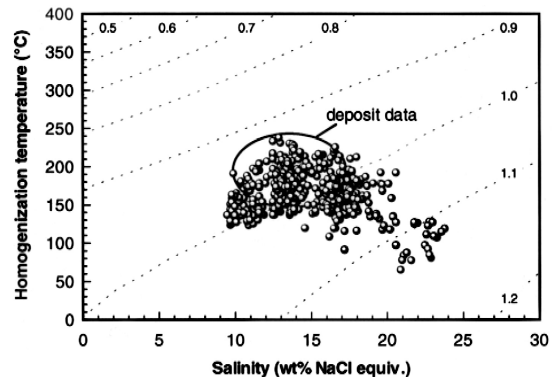

Fig. 7. Fluid inclusion data from feeder veins (round symbols) and mineral deposits (shaded field) in the Irish base metal orefield. Deposits, located in upflow zones, are associated with minimum fluid densities. Data from Everett et al. (1999a) and Wilkinson (unpublished).
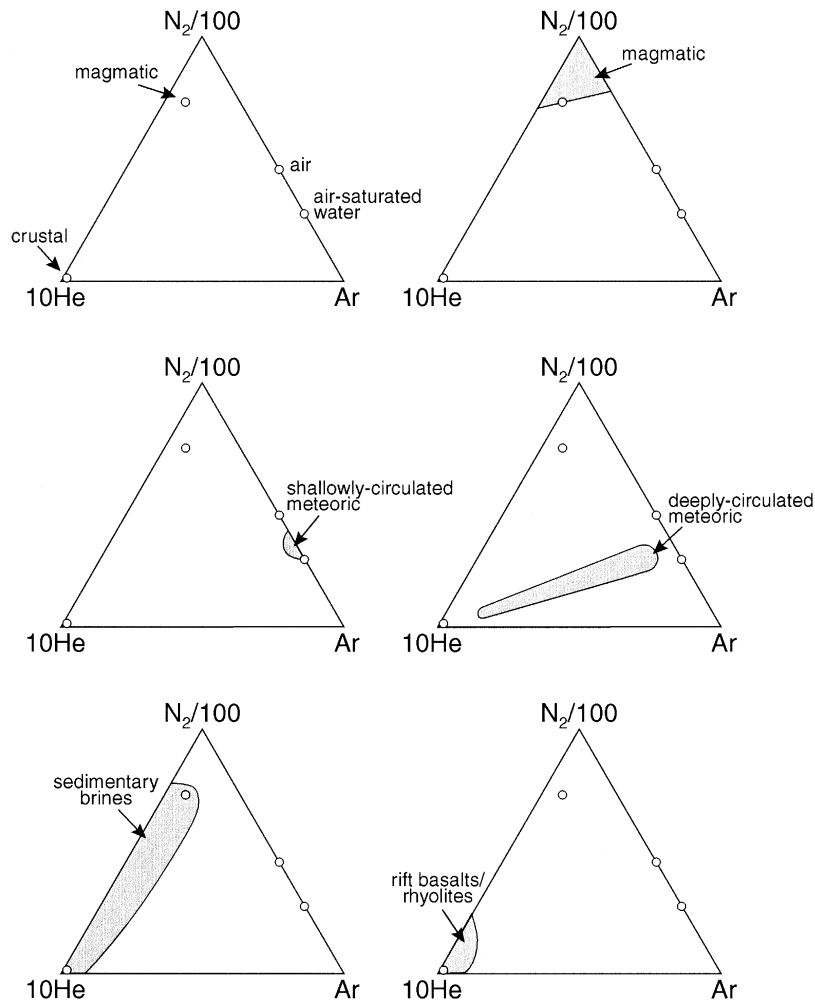
Fig. 8. Ternary diagrams illustrating typical gas compositions of fluids from various sources. (a) Ideal end-member fluid compositions; (b)–(f) typical compositional ranges for fluid inclusion gases from a range of environments. Redrawn from Norman and Musgrave (1994).

Although analysis of inclusion fluids, particularly with regard to determining metal contents, has been seen as a goal in its own right, the emphasis is now shifting more towards utilising the data that can be obtained. The most obvious directly addresses one of the main aims of any ore deposit study — to understand the complex interplay of processes that have resulted in ore deposition. This is often difficult to achieve from observations alone and one of the ways of helping to understand these processes (but not to identify them!) is to carry out chemical–thermodynamic modelling, usually involving reactive-trans-

port codes (e.g. Reed, 1997). However, this requires as much information as possible concerning the chemistry, temperature and other properties of the fluid to be known, hence the need for accurate and extensive chemical data. Such modelling allows sensitivity analysis to be carried out to identify the key parameters controlling the system, to provide constraints for mass balance estimates and to make predictions of mineral distributions and textural inter-relationships that can be compared with field observations (e.g. Plumlee et al., 1994). Such prediction-test cycles enable the model to be validated and
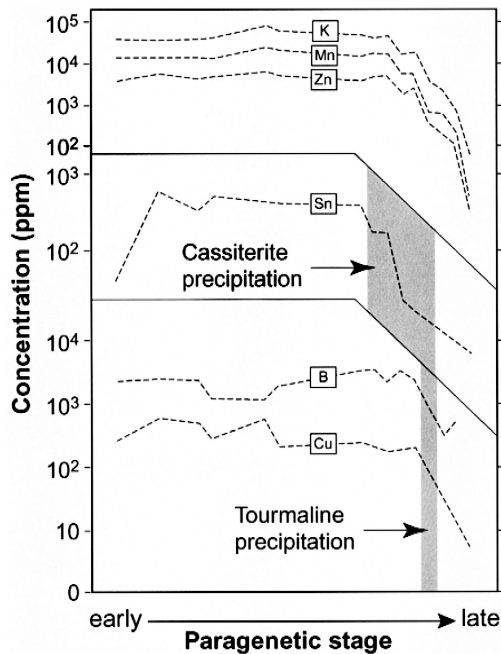
Fig. 9. Fluid dilution during progressive precipitation of quartz and ore minerals. Modified after Audetat et al. (1998).

refined. Although a powerful approach, it must always be remembered that modelling is really a thought experiment and that the truth is in the rocks, not in the computer!

3.2. Recognition of physical processes of fluid modification

In many ore deposits, physical processes — principally phase separation and fluid mixing — are arguably the most important mechanisms that ultimately result in the deposition of economic concentrations of ore minerals (e.g. see Skinner, 1997). The reasons for this can be summarised by a number of simple observations.

(1) Cooling is rarely sufficient to result in significant mineral precipitation in a limited volume of rock due to the lack of extreme temperature gradients in most crustal environments. There are, of course, exceptions to this, particularly in the shallow crust, as illustrated by the importance of conductive cooling in controlling precipitation in high tempera-

ture submarine hydrothermal vent chimneys (e.g. Bowers et al., 1985). However, even here, the probability of forming economic concentrations of ore minerals is likely to be dependent on other processes such as mixing with shallowly circulating seawater.

(2) For most sulphides, it has been shown theoretically and experimentally that it is difficult to transport significant concentrations of sulphur and metals within a single fluid (Sverjensky, 1984). The exception is where sulphur is transported in an oxidised form, most commonly as sulphate. The result of this is that sulphur and metals are often transported by separate fluids and ore formation can only occur where mixing of these two fluids occurs.

(3) In some instances, fluid–rock reactions are invoked as possible controls on ore deposition. An example is the inferred importance of sulphidation of iron-rich silicate wall-rocks on gold deposition in basalt-hosted mesothermal lode gold deposits. Fixing of reduced sulphur by pyrite formation can reduce the activity of bisulphide in the hydrothermal fluid resulting in destabilisation of gold–bisulphide complexes. Two prime factors limit the efficiency of this process: first, the vein or fluid conduit may become armoured by reaction (alteration) products so that the hydrothermal fluid is unable to effectively interact with the wall-rocks after an initial period of reaction (Cathles, 1991; Woitsekhowskaya and Hemley, 1995); second, the sluggish kinetics of mineral–fluid reactions may not provide a rapid mechanism for destabilisation of metal complexes in solution. Thus, unless flow rates or durations are very large, economically significant concentrations of ore minerals cannot be produced. Exceptions may be where the wallrocks are particularly reactive to acidic hydrothermal solutions (e.g. carbonates) or where wallrock alteration produces a net volume decrease (e.g. dolomitization). The latter process can lead to a positive feedback mechanism with alteration increasing the permeability of the wallrock, thereby allowing greater fluid ingress and further reaction.

The two processes that commonly do provide the necessary conditions for effective ore mineral precipitation in a limited rock volume are *boiling*, or *effervescence* in volatile-rich systems, and *fluid mixing*. One or both of these processes are very often cited as one of the major, or sole causes of ore deposition in hydrothermal ore deposits. Both these

processes can deliver the key condition for efficient ore formation, namely, rapid supersaturation of hydrothermal fluid(s) in a restricted rock volume.

Here it is appropriate to digress briefly into the use of the term 'boiling' with respect to mineralizing systems. Although widespread in the literature, the term is imprecise and is not appropriate for systems containing volatiles in addition to water. Reference to a simple phase diagram shows that for pure water or water–salt systems, production of a vapour phase can occur as a result of temperature increase, pressure decrease, or a combination of these (e.g. Roedder, 1984). These are the typical changes assumed to cause separation of a vapour phase in most shallow hydrothermal systems and where the term 'boiling' is appropriate. However, for systems containing additional volatiles such as CO_2, the situation is more complicated; for example, it is inappropriate to use the term 'boiling' for the vapour separation that occurs on opening a bottle of beer. In this case, the term 'effervescence' is more suitable. Consideration of a phase diagram for the H_2O–CO_2–NaCl system (e.g. Gehrig et al., 1979) shows that separation of a vapour phase from an initially homogeneous 'liquid-like' fluid can occur as a result of temperature *decrease* or pressure decrease, unlike the first case described above. In such instances, the terms 'effervescence' or 'phase separation' are preferred. These are examples where a 'liquid-like' homogeneous supercritical fluid, with a density above the critical density, evolves a lower density vapour phase by crossing the *bubble-point curve* of the system. This is commonly recognised as an important process in mesothermal gold deposits (see below). However, it is possible for a low density 'vapour-like' supercritical fluid, with a density less than the critical density, to cross into the two-phase field via the *dew-point curve*. This would result in production of a relatively high-density liquid phase; such a process could also be referred to as phase separation, but more specific would be use of the term 'condensation'. This process is important in environments where high temperatures, high thermal gradients and low pressures are developed such as in porphyry–copper deposits (see below). In porphyry systems, confusion can occur in the supercritical region where the term 'condensation' has also been applied to fluids crossing the critical isochore (by

cooling) to change from a 'vapour-like' supercritical fluid to a 'liquid-like' supercritical fluid (Fig. 22a). This change would result in a shift from the production of vapour-homogenizing to liquid-homogenizing inclusions. Since no change in state has occurred, the term 'condensation' is not really appropriate.

So, how can fluid inclusion data be used to identify and constrain such processes? In terms of basic T_h and salinity properties, both processes may be expected to produce a spread of data on a T_h–salinity bivariate plot (Fig. 10). Boiling, or effervescence, results in the production of vapour and, in open systems, loss of H_2O (and other volatile species) occurs. As a result of the strong partitioning of salts into the liquid-like phase, the residual liquid becomes more saline. In addition, as a result of adiabatic expansion, the liquid phase may also undergo cooling. Salinity variations can therefore be produced by boiling or effervescence, but significant salinity increases will only occur by continuous boiling in restricted fractures (Fig. 11). Significant salinity variations, in fact, are most likely to be controlled by fluid mixing, except where dissolution of evaporites can be demonstrated. This is where the conservative nature of fluid salinity is extremely useful since it can only be easily modified by adding or removing water (or by mixing with a more or less saline solution). Salinity measurements are therefore very useful for inferring the presence of two fluids and estimating the extent of mixing between them.

An additional point worthy of note is the possibility that salinity estimates determined from ice melt-
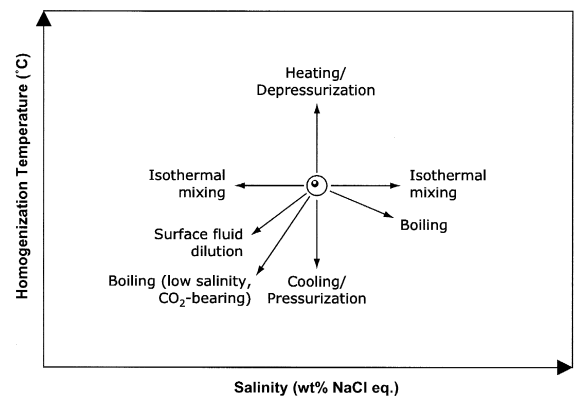

Fig. 10. Schematic diagram showing typical trends in T_h–salinity space due to various fluid evolution processes.
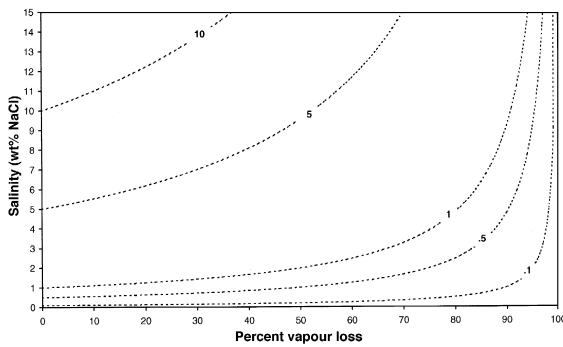
Fig. 11. Effect of open system boiling on the salinity of the liquid phase in epithermal systems. Curves labelled for initial salinities of 0.1, 0.5, 1, 5 and 10 wt.% NaCl. Note that at low initial salinity, extensive vapour loss has to occur for a significant increase in salinity of the residual liquid.

ing temperatures in dilute fluids can be significantly in error where even small amounts of CO_2 or other volatiles are present (Hedenquist and Henley, 1985). Thus, the presence of such gases will affect the distribution of T_h–salinity data and the trends produced by mixing and boiling processes. In low salinity fluids containing moderate amounts of CO_2 (of the order of several weight percent), the contribution to freezing point depression by CO_2 can dominate. Preferential loss of CO_2 to the gas phase on effervescence can result in an *increase* in the ice melting temperature for the residual liquid, i.e. an apparent salinity *decrease* (Fig. 10).

4. Further interpretation of fluid inclusion data in hydrothermal ore deposits

The basic properties derived from fluid inclusion microthermometry and more sophisticated chemical and isotopic analyses may be used to make a range of geological deductions concerning ore formation. A number of additional methods that have specifically been applied to mineralizing and geothermal systems are summarised here since they can provide further insights and constraints on ore-forming processes.

4.1. CO_2 content and effervescence–depth curves

Many hydrothermal fluids involved in the transport and deposition of ore minerals contain other volatiles in addition to H_2O, particularly CO_2. The

importance of elevated concentrations of CO_2 lies in its marked effect on raising the pressure along the liquid–vapour curve and the expansion of the liquid–vapour curve into a divariant field in pressure–temperature space (e.g. Shepherd et al., 1985). The consequence of these effects is that phase separation can occur at higher pressures and therefore greater depths than in simple salt–water solutions and there are a wider range of *P–T* conditions in the crust under which phase separation can occur. Both of these have direct significance with regard to ore formation. In mesothermal gold deposits, CO_2 contents are generally high and liquid CO_2 is commonly observed in inclusions. As a result of their particular properties, these inclusions are considered in the section on mesothermal gold deposits below. However, many ore deposits, particularly those forming in epithermal and magmatic–hydrothermal environments, are associated with fluids containing low concentrations of CO_2 (typically < 3 mol%, see Bodnar et al., 1985).

Despite the fact that constraints on the depth of formation and the potential for phase separation are useful pieces of information, the possible effects of CO_2 are rarely considered. Good examples of the construction of boiling point–depth relationships for epithermal precious metal deposits based solely on NaCl–H_2O solutions are discussed by Vikre (1985) and Arribas et al. (1995); however, any interpretation of depth of mineralization may be underestimated by several hundred percent if low CO_2 concentrations are ignored. An additional point worthy of note is the effect low concentrations of CO_2 have on lowering ice melting temperatures in fluid inclusions. Failure to take this into account may result in a significant overestimate of the salinity, especially in low salinity fluids (Hedenquist and Henley, 1985).

Effervescence curves for fluids containing low concentrations of CO_2 can be constructed assuming a model involving a fluid rising adiabatically (that is without losing heat energy to the surrounding rocks) through the shallow crust. As it rises, the confining hydrostatic pressure[1] decreases until phase separa-

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[1] In fact, in flowing systems pressure is *hydrodynamic*; data from geothermal fields suggest that fluid pressure gradients are often up to 10% above hydrostatic resulting in slightly higher temperatures at a given depth on the boiling point curve.
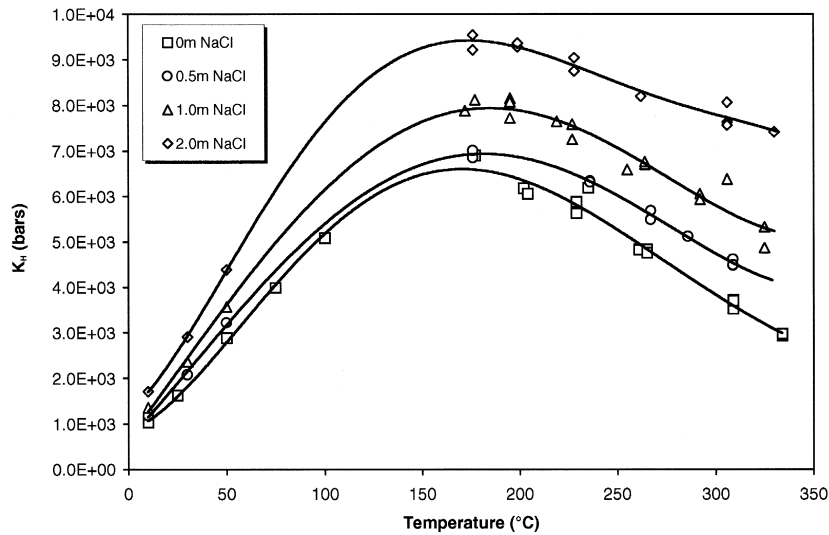
Fig. 12. Variation in Henry's Law constant for CO_2 as a function of fluid temperature and salinity. Data from Ellis and Golding (1963) and references therein were fitted using a least-squares polynomial expression (see text for details).

tion occurs. In a closed system, the amount of vapour produced and its composition can be calculated, in addition to the partial pressure of the CO_2 and the total pressure when phase separation commences. This process is carried out at a series of temperatures T_n, starting from an initial temperature, T_0.

The calculations utilise Henry's Law constant (K_H) which relates the partial pressure of a gas (P) to its mole fraction in aqueous solution (X) according to:

$$P\alpha = K_H X$$

where α is the fugacity coefficient. In solutions with low gas concentrations, the fugacity coefficient will be close to unity so that it can safely be ignored. K_H data from the studies of Ellis and Golding (1963) and references therein were regressed (Fig. 12) to

generate an expression for $K_H(CO_2)$ over the temperature range 0–350°C:

$$K_H = at^5 + bt^4 + ct^3 + dt^2 + et + f$$

where t is the temperature (°C) and a–f are salinity-dependent empirical fit coefficients (Table 1).

The partitioning of CO_2 between liquid and vapour is described by the distribution coefficient, B, which is defined as the gas concentration in the vapour divided by the gas concentration in the liquid.

It can be expressed in the form:

$$B = \frac{\overline{V}K_H}{nRT}$$

where $\overline{V}$ is the molal volume of steam which can be obtained from standard steam tables (e.g. Keenan et

Table 1
Regression parameters for the temperature dependence of $K_H(CO_2)$

Salinity	a	b	c	d	e	f	Regression fit (r^2)
0 m NaCl	0	3.2765×10^{-6}	-0.0020811	0.23442	39.167	574.60	0.9863
0.5 m NaCl	0	2.6410×10^{-6}	-0.0016409	0.14491	46.452	675.42	0.9985
1.0 m NaCl	0	2.7635×10^{-6}	-0.0016786	0.12526	55.881	703.25	0.9846
2.0 m NaCl	-2.3385×10^{-8}	2.3310×10^{-5}	-0.0078775	0.84713	36.643	1262.9	0.9967

al., 1969); n, the number of moles of gas can be set to unity; R is the gas constant and T is the absolute temperature (Kelvins). It is also necessary to know the mass fraction of vapour phase (y) that would be formed in a closed system as the result of effervescence. This can be calculated from:

$$y = \frac{H_{L,T_n} - H_{L,T_0}}{H_{L,T_n} - H_{V,T_n}}$$

Where H_L and H_V are the enthalpies of the liquid and vapour phases, respectively (Haas, 1976) at the initial temperature (T_0) and temperature of interest (T_n). At each temperature, the mole fraction of gas remaining in the liquid after vapour separation C_L is given by:

$$C_L = C_0 \frac{1}{1 + y(B - 1)}$$

where C_0 is the initial mole fraction of CO_2 in the fluid. The partial pressure (bars) of CO_2 (P_{CO_2}) is then given by:

$$P_{CO_2} = K_H C_L$$

and the total pressure (P_T) on the two-phase curve by:

$$P_T = P_{CO_2} + P_{H_2O}$$

To simplify the estimation of depth from the calculated fluid pressure, an empirical relationship can be used (Henley, 1984):

$$\text{Depth} = 7.9697 \, P_T^{1.1031}$$

A series of curves calculated using this approach are illustrated in Fig. 13 as a function of both increasing CO_2 content, which increases the effervescence depth, and increasing salinity, which has the opposite effect. As can be seen, the effect of dissolved CO_2 is more significant than elevated salinities. Although subject to a number of simplifying assumptions (see Henley, 1984, for a fuller discussion), the method is practical and accurate enough for the purposes of most geological investigations.

4.2. Enthalpy plots

In the geothermal literature, the use of enthalpy plots is a common and extremely useful way of evaluating fluid mixing and boiling processes in the shallow crust (Hedenquist, 1990; Hedenquist et al., 1992; Henley, 1984). However, despite their potential, they have rarely been utilised in studies of hydrothermal mineral deposits, a notable exception being an investigation of the Lepanto–Far Southeast porphyry–epithermal system in the Philippines (Hedenquist et al., 1998). Construction of such plots is simple and involves plotting the enthalpies of the fluids involved rather than temperature or homogenization temperature. Enthalpy data for vapour-saturated water or simple NaCl–H_2O solutions (the effect of salinity is very small) can be extracted from standard steam tables (e.g. Keenan et al., 1969; Haas, 1976) using the homogenization temperature. This represents the enthalpy of the fluid inclusion at the homogenization point. This information can then be evaluated as a function of fluid salinity or final ice melting temperature. The approach has the advantage that mixing lines and phase separation trends will be linear. The most useful diagram is a salinity–enthalpy plot that is an analogue of the salinity–homogenization temperature plots with which fluid inclusion workers are more familiar. An example is shown in Fig. 14, which illustrates how mixing with different types of fluids and boiling processes can be resolved and also quantified.

4.3. Halogens and the origin of brines

A useful method for distinguishing different hydrothermal fluid types is on the basis of the halogen content of inclusion fluids. Whilst only chloride can normally be detected or inferred from microthermometric measurements, bulk sample analysis, now even of very small sample masses, can be used to determine the content of the other halogens (F, Br and I) in inclusion fluids. Two main approaches have been used, the first involving neutron irradiation (Bohlke and Irwin, 1992b), the second being a more straightforward application of ion chromatographic analysis of conventional crush–leach solutions (Banks and Yardley, 1992; Channer and Spooner, 1992).

Absolute halogen concentrations and halogen ratios are probably the most useful tracers of fluid sources and fluid mixing processes since they are conservative (or 'incompatible') elements, rarely par-
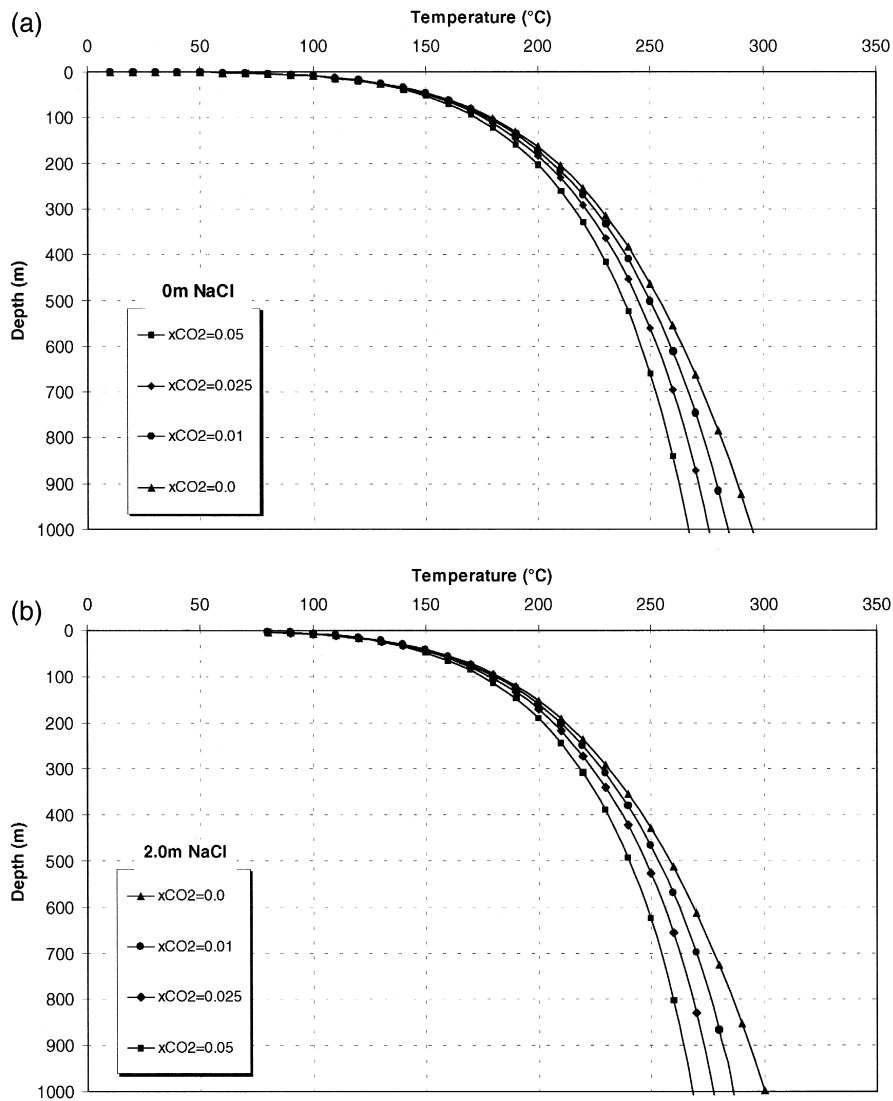
Fig. 13. Effervescence–depth curves for NaCl–H_2O solutions containing 0–5 mol% CO_2. (a) 0 m NaCl; (b) 2 m NaCl.

ticipating in fluid–mineral exchange. As a result, halogen systematics are generally not modified during flow, unlike most other potential tracers such as stable isotopes, and can therefore preserve information concerning fluid source. In addition, since evaporites and seawater provide by far the largest reservoir of halogens in the Earth's crust, halogen systematics are very sensitive to the involvement of these reservoirs in mineralizing solutions (e.g. McKibben and Hardie, 1997). Given the great importance of chloride complexing as an agent for metal trans-

port under a wide range of conditions, understanding the origin of fluid salinity is a critical, but perhaps under-studied, aspect of ore deposit formation.

Particularly useful representations for understanding halogen systematics are Cl vs. Br and Cl/Br vs. Na/Br plots (Fig. 15). These can be used to identify a range of fluid origins and interaction processes such as seawater, partially evaporated seawater, bittern brines (seawater evaporated past the point of halite precipitation), diluted examples or mixtures of the above, or fluids that have acquired their salinity
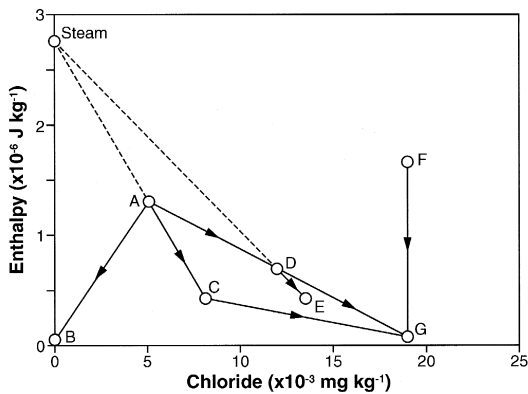
Fig. 14. Enthalpy–salinity plot illustrating a range of fluid evolution processes. A, low salinity fluid (~ 1 wt.% NaCl) at 300°C; A–B, dilution of A by low temperature groundwater B; A–C, adiabatic boiling of A and cooling to 100°C; G, higher salinity (~ 3 wt.% NaCl), low temperature fluid produced by cooling of high temperature fluid F from 350°C; D, fluid produced by 50:50 mixture of A and G. D–E, adiabatic boiling of D and cooling to 100°C; C–G, mixing of residual liquid after boiling A and fluid G.

by halite dissolution (e.g. Hanor, 1994). A number of workers have analysed the halogen systematics of a range of crustal fluid types that provide a reference with which to compare fluids of unknown origin (Bohlke and Irwin, 1992b; Yardley et al., 1992). Based on Cl, Br and I contents, these results show that wide variations exist in crustal fluid halogen chemistry (Fig. 16), enabling likely fluid sources to be pinpointed. Examples of the use of halogen compositions as fluid tracers include studies of gold vein systems (Yardley et al., 1993), magmatic fluids (Campbell et al., 1995), MVT deposits (Bohlke and Irwin, 1992c; Kesler, 1996; Viets et al., 1996) and sediment-hosted copper mineralization (Heinrich et al., 1993).

4.4. Noble gases

The analysis of noble gases (He, Ar, Kr, Xe) in fluid inclusions, and more specifically noble gas isotope ratios, has been carried out for a number of years (e.g. Kelley et al., 1986; Bohlke and Irwin, 1992a; Norman and Musgrave, 1994) and several applications to studies of ore deposits have been published (Kelley et al., 1986; Burgess et al., 1992; Turner and Bannon, 1992; Stuart et al., 1994, 1995; Shail et al., 1998; also see Villa, 2001). Perhaps one of the most useful noble gases is helium, since the

^{3}He/^{4}He isotope ratio is a sensitive discriminator of mantle (^{3}He/^{4}He $> 1.4 \times 10^{-6}$), crustal (^{3}He/^{4}He $\ll 1.4 \times 10^{-6}$) or atmospheric (^{3}He/^{4}He $= 1.4 \times 10^{-6}$) contributions to hydrothermal fluids.

There are two main problems with helium: first it has a high diffusivity through many minerals resulting in uncertainty over whether initial inclusion compositions have been preserved; and second it can be produced in situ from U- and Th-bearing minerals. Based on their analyses of a range of crustal fluids, Norman and Musgrave (1994) argued that significant diffusion does not occur in most crustal environments. However, to minimise potential problems, the analysis of U- and Th-poor, dense minerals, where the outward diffusion rate of He is low, is recommended (Stuart et al., 1995). This includes sulphides, wolframite or even gold (Eugster et al., 1995). Unfortunately, this introduces its own problems since conventional microthermometric methods are not possible and means that, without infra-red studies, the noble gas analysis must be carried out on uncharacterised inclusion assemblages. Furthermore, in some cases, the gas analysed may not even be derived from inclusions as such but may come from inter-atomic sites within the mineral itself.

Since helium is so mobile, the presence of, for instance, a mantle contribution (^{3}He/^{4}He $> 1.4 \times 10^{-6}$) in a crustal ore-forming system does not necessarily imply that the hydrothermal (i.e. aqueous) fluids were mantle derived. The occurrence of ^{3}He-rich volatiles is more a monitor of mantle heat contribution than an indicator of significant mass transfer.

Argon isotopes have also been analysed in order to constrain processes of hydrothermal mineralisation (e.g. Burgess et al., 1992). Liberation of Ar using a laser microprobe enables detemination of ^{40}Ar/^{36}Ar and Cl/^{36}Ar ratios in small bulk samples of inclusion fluids. These data can be used to constrain fluid mixing, particularly involving meteoric waters, as well as boiling, although interpretations are complicated by the possibility of derivation of excess ^{40}Ar from wallrocks.

4.5. Coupling isotope measurements and fluid inclusion data

In their own right, conventional fluid inclusion data and isotopic data have been regularly collected
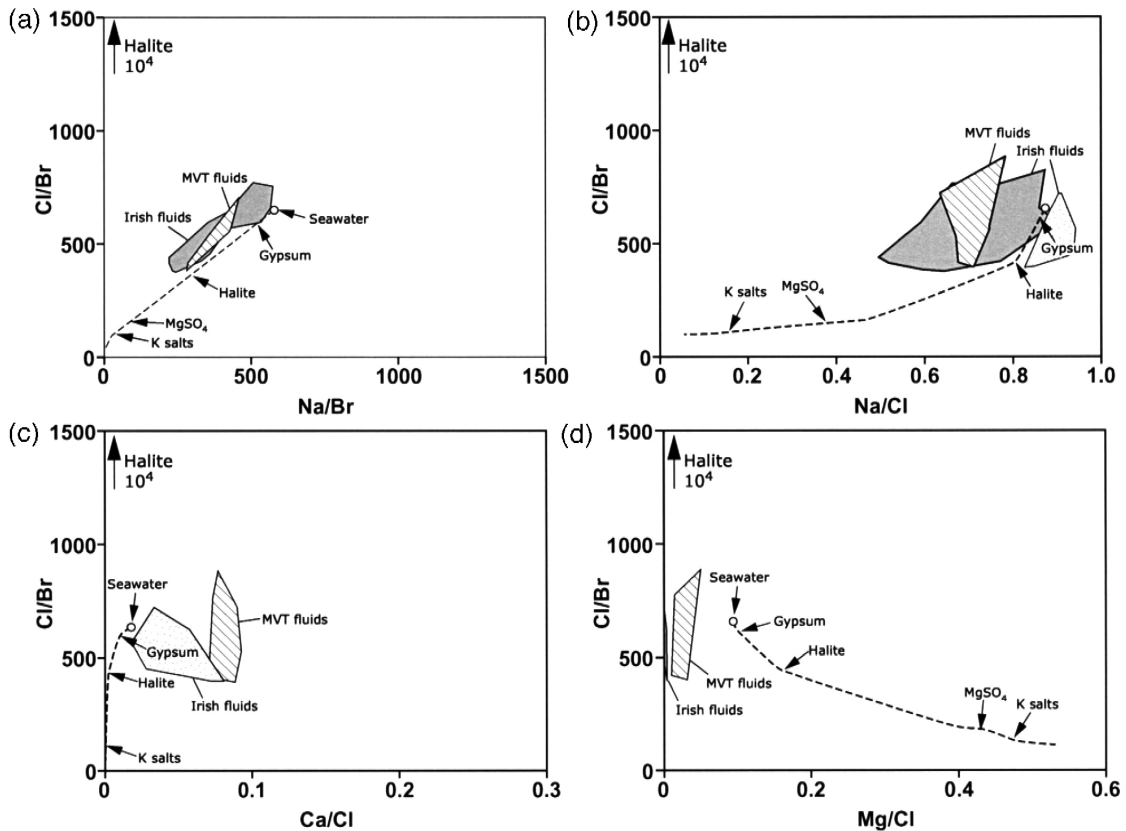
Fig. 15. Halogen discrimination diagrams (modified after Viets et al., 1996). (a) Cl/Br vs. Na/Br; dashed line shows seawater evaporation trajectory (SET) after the point of halite precipitation which results in enrichment of the residual bittern brine in Br. The arrowed points on the curve mark the first visible appearance of evaporite minerals, although saturation of these minerals actually occurs at higher Cl/Br and Na/Br ratios. (b) Cl/Br vs. Na/Cl; fields for Mississippi Valley-type brines (Upper Mississippi Valley and Viburnum Trend) and Irish fluids (data from Everett et al., 1999b; and Everett, 1999) are shown. Shaded field for Irish data with cation determined by crush–leach analysis; dotted field for cation determined by decrepitation-ICPAES. Fields plotting to the left of the SET represent fluids produced by evaporated seawater which have undergone some Na-loss, possibly by albitization of plagioclase. (c) Cl/Br vs. Ca/Cl; Analysed brines show Ca enrichment over evaporated seawater, probably due to either albitization or dolomitization. (d) Cl/Br vs. Mg/Cl; Analysed brines show strong Mg depletion from evaporated seawater, interpreted to be due to dolomitization for MVT fluids and Mg smectite or chlorite formation for the Irish fluids. Only a few of the MVT brines show evidence for involvement of halite dissolution waters in their genesis.

from hydrothermal minerals. Obviously by its very nature, fluid inclusion microthermometry is a micro technique that allows acquisition of data from distinct phases of microfracturing or mineral growth. Until relatively recently, however, isotopic analysis was largely restricted to bulk samples and could not be carried out on the same scale. Recent advances in technology now make possible the micro-sampling and isotopic analysis of mineral phases. The ability we now have to collect coupled data from the same minerals or even within specific domains of individ-

ual minerals offers significant advantages, allowing much more refined interpretations and insights into the detailed isotopic evolution of mineralizing systems than were hitherto possible.

4.5.1. Oxygen isotopes in silicates

Oxygen isotope data provide useful information concerning possible fluid sources and the degree of fluid–rock isotopic exchange during flow. Micro-sampling for oxygen in silicates can now be carried out either using the ion probe (e.g. Eiler et al., 1997)
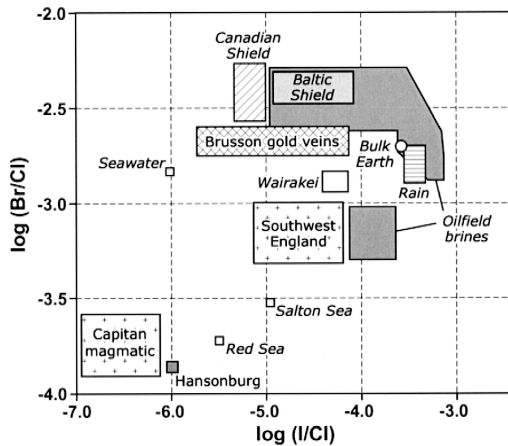
Fig. 16. Crustal fluid halogen chemistry. Small squares indicate compositions of contemporary waters; various shaded fields represent palaeofluid compositions as determined by crush–leach analysis of fluid inclusions. Modified after Yardley et al. (1992, 1993).

or laser fluorination (e.g. Sharp, 1990) of small samples separated from a mineral using a dentist-type micro-drill. In the latter case, required sample masses of only ∼ 1 mg means that individual generations of minerals such as quartz, perhaps defined by CL petrography, can be separated. Consequently, the temperature information provided by individual fluid inclusion populations can constrain variations in the oxygen isotopic composition of fluids involved at different stages of quartz vein growth (e.g. Wilkinson et al., 1999).

4.5.2. Oxygen and carbon isotopes in carbonates

Laser ablation analysis now allows the determination of carbon and oxygen isotopic compositions of carbonates in situ (Smalley et al., 1992). With a resolution down to ∼ 200 μm, the technique enables determination of isotopic variations in individual growth zones for which fluid inclusion data are available. Even the more traditional methods of micro-sampling (micro-drilling) and conventional analysis can still be effective in resolving variations in isotopic compositions of fluids during growth of veins or cements. The coupling of inclusion data with isotope data from carbonates allows powerful additional constraints to be placed on models of fluid flow and isotopic exchange in carbonate systems. In some cases, distinguishing between isotope exchange mechanisms and fluid mixing may not be possible on the basis of isotope data alone, yet with the addition of salinity information, the role of fluid mixing in controlling observed isotopic trends can be evaluated.

4.5.3. Sulphur isotopes in sulphides and sulphates

Laser analysis of sulphur-bearing minerals (Kelley et al., 1992; Hall et al., 1994) now provides an analytical resolution down to ∼ 300 μm. For determination of isotopic variations across individual sulphide grains, this technique is invaluable (e.g. Anderson et al., 1998). It opens up the possibility of coupled isotopic and fluid inclusion analyses across successive growth zones in sphalerite crystals and other semi-transparent or even infra-red transparent ore minerals, as well as geothermometry on coexisting sulphides and sulphates (Alonso-Azcárate et al., 1999). Even conventional methods of sulphur isotope analysis, when coupled with inclusion data, can provide effective constraints on fluid evolution in a mineralizing hydrothermal system (e.g. Everett et al., 1999b).

5. Mineral deposit case studies

Fluid inclusion studies have, over the last 30 years, evolved into one of the fundamental tools for understanding the genesis of hydrothermal ore deposits. This is principally because inclusions provide the only direct means for accessing the properties of ore-forming solutions and, in many cases, are the most precise geothermometers and geobarometers available. A detailed review of specific deposit types is beyond the scope of this paper. However, there is a justification for considering a selection of individual deposit types with the principal aims of summarising the basic characteristics of the fluid inclusions present and illustrating how fluid inclusion studies have contributed toward the formulation of genetic models. A summary of the main properties of inclusions in these systems is given in Table 2.

5.1. Mississippi Valley-type Zn–Pb–F–Ba deposits

The processes responsible for the formation of Mississippi Valley-type (MVT) deposits have been

Table 2
Typical characteristics of fluid inclusions in hydrothermal ore deposits

Deposit type	Host minerals	T_h range (°C)	Salinity range (wt.% NaCl equiv.)	Daughter minerals	Trapped phases	Comments
Mississippi Valley-type	cc, dol, fluor, ba, qz, sph	50–180	15–30	–	Petroleum	CH_4 may be present
Irish-type	cc, dol, sph, qz, ba	150–240, 80–150	10–18, 20–25	–	Calcite, K-mica	Mixing of two fluids, high T fluid has low CO_2
Volcanic-associated massive sulphide	qz, ba	80–340	1–8	–	–	Higher T_h and S in stockwork zones
Granitoid-associated veins	qz, wolf, fluor, cc	150–500	0–45	hal, syl, chlor, bor, anh, cc, hm, mt, sulph	Tourm, ksp	CO_2 often present, common effervescence
Porphyry-copper	qz	200–700	0–70	hal, syl, chlor, cpy, hm	–	Effervescence common, CO_2 in deep systems
Epithermal	qz, cc, sph	100–300	0–12	daw	–	Sometimes low CO_2, common effervescence
Mesothermal gold	qz, cc	200–400	2–10	daw	–	High $CO_2 + CH_4$ or N_2

anh, anhydrite; ba, barite; bor, borates; cc, calcite; chlor, alkali earth and transitional metal chlorides; cpy, chalcopyrite; daw, dawsonite; dol, dolomite; fluor, fluorite; hal, halite; hm, hematite; ksp, K-feldspar; mt, magnetite; qz, quartz; sph, sphalerite; sulph, various sulphides; syl, sylvite; wolf, wolframite.

the subject of debate and controversy for many years and this brief review will inevitably be incomplete. However, a few comments are in order regarding how fluid inclusion studies have made a significant contribution toward understanding this important class of deposits. For a more detailed review, the reader is referred to Roedder (1976).

Fluid inclusions have been studied in a range of minerals from MVT deposits, principally calcite, dolomite, fluorite, barite, quartz and sphalerite. The inclusions themselves are relatively simple, generally comprising two-phase liquid–vapour aqueous inclusions (Fig. 17a) with a small vapour bubble ($< 10\%$ of the inclusion volume), sometimes accompanied by monophase aqueous or petroleum inclusions (Fig. 17b). Low temperature phase behaviour in the aqueous inclusions shows a number of common characteristics. First, metastable freezing temperatures are very low (often below $-60°C$), characteristic of high salinity inclusions. Apparent first melting temperatures are also low (values as low as $-70°C$ are commonly reported). Whilst such temperatures have been used to infer the presence of unusual cations such as Cu^{2+} or Li^+ it is unlikely that such ions would be present in sufficient quantities to have any

observable effect. Even at high concentrations in fluid inclusions, Cu only forms perhaps 5% of the total solute load (e.g. Czamanske et al., 1963). The probable explanation is either metastable first melting (e.g. Davis et al., 1990) or the observation, not of melting, but sub-solidus grain coarsening as amorphous ice and solutes recrystallise into stoichiometric salt hydrate(s). A clear 'burst' of melting often occurs around $-50°C$ to $-55°C$, corresponding to stable eutectic melting in the $NaCl$–$CaCl_2$–H_2O system. The last solid phase to melt may be either a salt hydrate, usually inferred to be hydrohalite, or ice, depending on the bulk salinity. Measurement of both phase changes allows estimation of the $NaCl/CaCl_2$ ratio (e.g. Shepherd et al., 1985) and spreadsheet algorithms are available for automatic calculation of this value (J. Naden, pers. comm.).

Fluid inclusions have helped to constrain a number of key parameters regarding the genesis of MVT deposits. Fluid density is high (> 1000 kg m^{-3}) and exceeds that of many crustal fluids which has important implications for flow mechanisms. Fluid pressures are generally thought to exceed vapour pressures, i.e. no boiling, although exceptions have been reported (e.g. Jones and Kesler, 1992). Fluid temper-
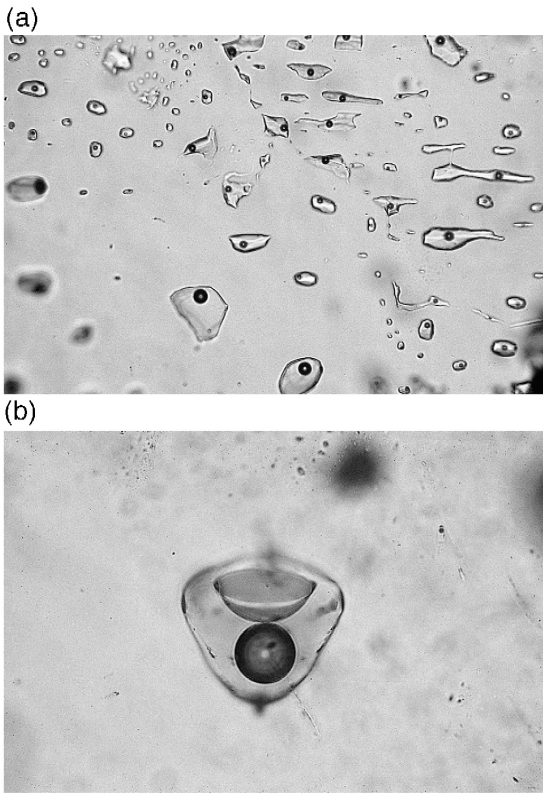
(a)

(b)

Fig. 17. (a) Photomicrograph illustrating two-phase aqueous fluid inclusions on annealed fracture plane in fluorite from the Hansonburg Mississippi Valley-type deposit, New Mexico. Width of view, 100 μm. Photo courtesy of A. Rankin. (b) Photomicrograph of pale brown oil inclusion in fluorite containing a vapour bubble, solid bitumen (out of focus in lowermost portion of inclusion) and lens of immiscible water (top of inclusion) from the Koh-I-Maran barite–fluorite deposit, Pakistan (Rankin et al., 1990). This inclusion is unusual in that it shows reverse wetting of the inclusion walls by the oil phase. Width of view, 200 μm. Photo courtesy of A. Rankin.

atures are low, generally $< 150°C$, although exceptions do exist (e.g. Shelton et al., 1992). Salinities are high (> 15 wt.% NaCl equiv., but not halite saturated) and organic compounds (petroleum inclusions) are common. Carbon gases, particularly CH_4 but also CO_2, have been recorded at concentrations up to several mole percent (Roedder, 1967b; Norman et al., 1985; Jones and Kesler, 1992). Cations in solution are in order of abundance: Na, Ca $\gg$ K, Mg, Fe, B; with characteristically high Na/K ratios of around 20 by weight.

These characteristics are remarkably consistent for MVT deposits worldwide, despite wide variations in metal ratios, mineralogy and other parameters between individual districts or deposits. This suggests that the basic fluid responsible for transport of metals is similar in most cases and it can be inferred that it is variations in the geochemistry of the flow path and processes operating at the site of ore deposition which result in the observed differences in the orebodies (e.g. Sverjensky, 1984). Based on the similarity between inclusion geochemistry and contemporary oilfield brines, particularly the high salinity, high density and $CaCl_2$-rich character, basin-derived brines have been considered to be the principal ore fluids in MVT deposits (Sverjensky, 1984; Roedder, 1984; Hanor, 1996). A link between MVT-type brines responsible for base metal mineralization in Cornwall, UK, and basinal waters in Permo-Triassic sediments offshore was documented by Gleeson et al., (2000).

Experimental data (Barrett and Anderson, 1988), thermodynamic modelling studies (e.g. Anderson, 1975; Barrett and Anderson, 1982; Sverjensky, 1981, 1984) and analyses of fluid inclusions (Roedder, 1958, 1967a; Hall and Friedman, 1963; Viets and Leach, 1990; Plumlee et al., 1994; Counter-Benison and Lowenstein, 1997) and contemporary brines (Carpenter et al., 1974) have shown that such fluids can transport at least ppm quantities of base metals, supporting the basic model. However, high metal content and high reduced sulphur content are mutually exclusive within a single fluid, which means that either large volumes of fluid are required, that metals and sulphur are derived from different sources or sulphur is transported in an oxidised form. The two most likely possibilities in the latter two cases are the transport of sulphur with metals in an oxidised form (SO_4^{2-}), with reduction occurring at the site of ore deposition, or transport of metals and sulphur in two different fluids, requiring mixing at the site of ore deposition (e.g. Beales and Jackson, 1966).

Although the basinal brine model, with flow being principally driven by topographic relief (e.g. Garven and Freeze, 1984), has been widely accepted, fundamental questions remain regarding the sources of metals, sulphur (Shelton et al., 1995) and also salinity. This last point is now starting to attract increasing attention and the complex sources of

salinity in MVT mineralizing fluids, involving both bittern brines and halite-dissolution waters is now being realised (e.g. Kesler et al., 1995; Viets et al., 1996). The key to these studies has been the application of halogen analysis of inclusion fluids as discussed earlier and there is little doubt that further studies of this type will produce significant advances in understanding in the years ahead.

5.2. Irish Zn–Pb–Ag–Ba deposits

The carbonate-hosted deposits of the Irish orefield represent one of the world's largest concentrations of base metals in the shallow crust. Since the first discoveries were made in the 1960s, these deposits have been the subject of detailed research (Andrew et al., 1986; Bowden et al., 1992; Andrew, 1993; Anderson et al., 1995a; Hitzman and Beaty, 1996). As with MVT deposits, much controversy still exists regarding their genesis. Unlike MVT mineralization, fluid inclusion data, until relatively recently, were sparse, so that information which could have provided constraints on the conflicting models has been lacking.

Fluid inclusions have been studied in a range of minerals from the Irish deposits, principally dolomite, calcite, barite, quartz and sphalerite (Fig. 18). Results have been obtained from prospects and economic deposits (see summary in Hitzman and Beaty, 1996) as well as from vein systems hosted by 'basement' rocks, underlying the carbonate sequences, considered to represent feeders to the overlying mineralization (Everett et al., 1999a,b). The only well-studied deposits are Silvermines (Samson and Russell, 1987), Tynagh (Banks and Russell, 1992) and Lisheen (Thompson et al., 1992; Eyre et al., 1996; Eyre, 1998). In addition, new data have also recently been reported from Navan and Keel (Everett et al., 1997; Everett et al., 1999a).

The inclusions are relatively simple, predominantly comprising two-phase liquid–vapour aqueous inclusions with a small vapour bubble ($< 10\%$ of the inclusion volume) although monophase aqueous inclusions have also been observed. Three broad groups of inclusions have been distinguished: (1) moderate salinity (10–15 wt.% NaCl eq.), moderate T_h (150–220°C) with first melting around -22°C indicating dominance of NaCl; (2) high salinity (20–25 wt.%
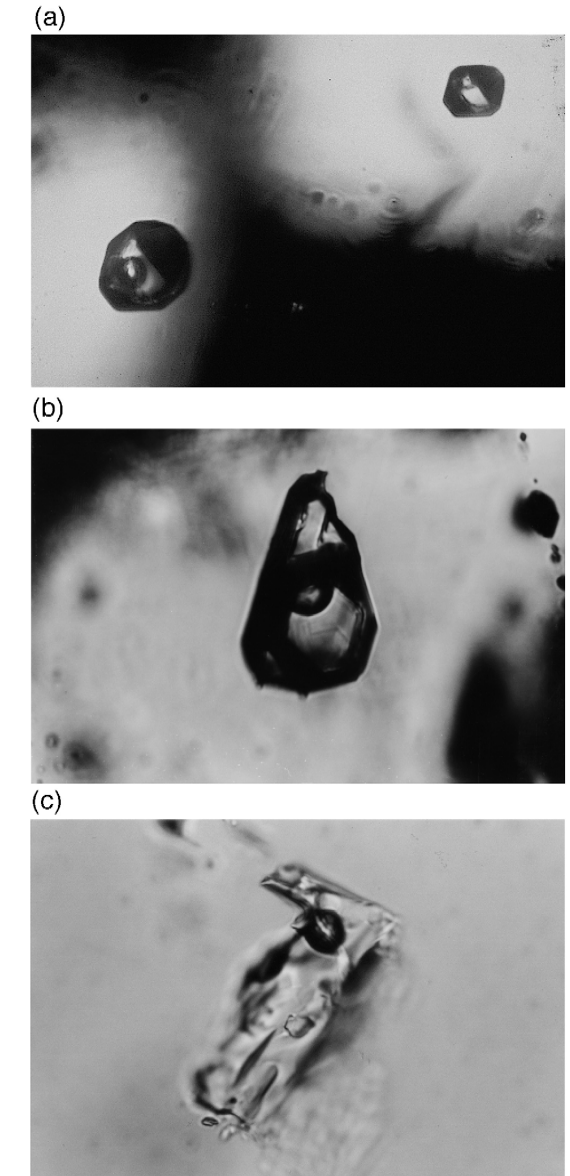

Fig. 18. Photomicrographs of primary fluid inclusions from the Irish orefield. (a) Sphalerite-hosted inclusions from the Lisheen deposit, Ireland. Width of image, 130 μm. Photo courtesy of S. Eyre; (b) Sphalerite-hosted inclusion from Lower Palaeozoic-hosted feeder vein, Fantane Quarry, Co. Tipperary. Width of image, 180 μm.; (c) Quartz-hosted inclusion from Lower Palaeozoic-hosted feeder vein containing trapped K-mica platelet (centre). Width of image, 180 μm. Photographs courtesy of C. Everett.

NaCl eq.), low T_h (< 150°C) with first melting around -55°C indicating NaCl–CaCl$_2$ composi-

tions; and (3) a subordinate population of low salinity (< 5 wt.% NaCl eq.), low to moderate T_h (120–200°C) inclusions with NaCl-dominated compositions. There is general agreement that ore deposition occurred during mixing of fluids represented by inclusion types (1) and (2) as inferred from coupled T_h–salinity variations (Fig. 19). Fluid 1 is thought to transport the metals and is now known to carry a 'hydrothermal' sulphur component into the deposits (Everett et al., 1999b), whereas Fluid 2 is inferred to have been rich in bacteriogenically produced H_2S (Wilkinson et al., 1998).

In general, daughter minerals are not observed, although an unidentified small, birefringent solid has been reported in inclusions hosted by feeder veins (Everett et al., 1999a). These are thought to be either a sulphate or a carbonate and may not represent true daughters as they do not dissolve on heating to the inferred trapping temperature. The last solid phase to melt during warming runs is usually ice, although in the most saline inclusions, hydrate melting may oc-

cur after ice. Rarely, peculiar low temperature phase behaviour has been described, with both ice and a hydrate melting above the eutectic for the NaCl–H_2O system (Banks and Russell, 1992). This was interpreted as most likely due to the dominance of sulphate or bicarbonate in one group of low salinity inclusions.

A recent, and potentially significant, observation is the reported occurrence of clathrate formation in Type (1) sphalerite-hosted inclusions from the Navan deposit and in sphalerite- and quartz-hosted inclusions from basement-hosted feeder veins. Clathrate melting temperatures are in the range -4°C to $+5$°C (Everett et al., 1999a). Based on the observation of apparent melting around the vapour bubble in several large inclusions at approximately -58°C, this was inferred to be a CO_2-rich clathrate. The occurrence of low levels of CO_2 is of particular genetic significance: its presence had been predicted for a relatively high temperature orefluid originating in the basement rocks underlying the deposits (Andrew,
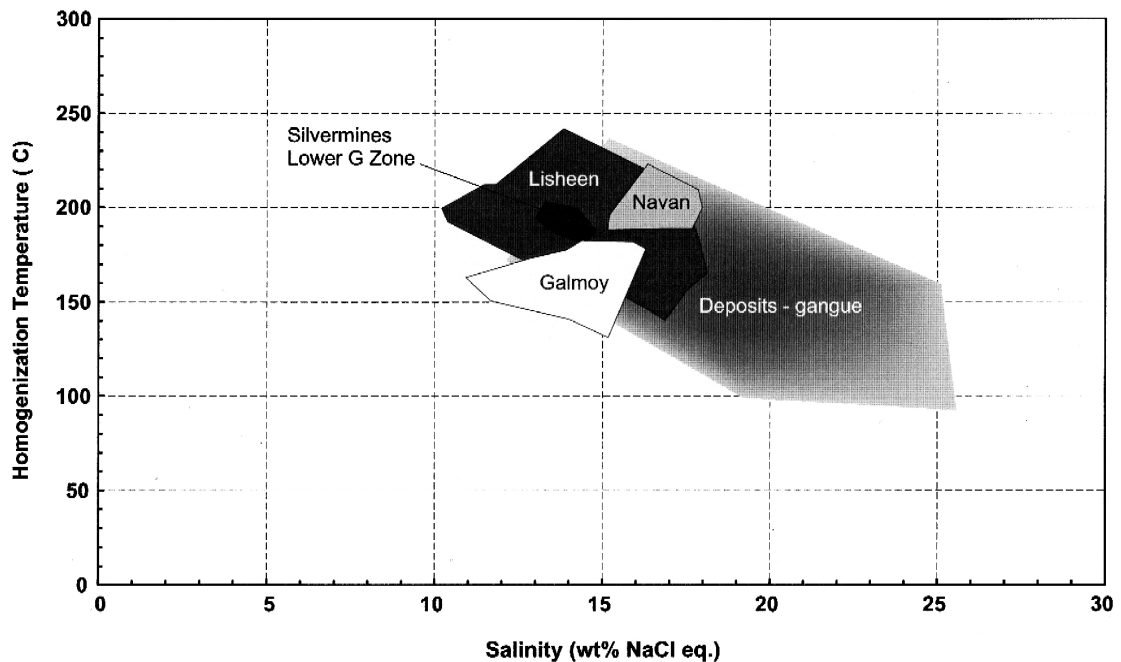

Fig. 19. Summary T_h–salinity diagram for data from the Irish orefield showing main fluid types. Data derived from Samson and Russell (1987), Banks and Russell (1992), Eyre (1998), Everett et al. (1999a,b) and Wilkinson (unpublished).

1986) and it may have played an important role by generating acidity in the mineralizing fluid through hydrolysis on cooling and ascent. Carbonate dissolution and replacement is of fundamental importance in the genesis of the Irish deposits and CO_2 hydrolysis provides a mechanism whereby such acid fluids could have been generated. In addition, the presence of CO_2 would have raised the pressure at which effervescence could have occurred, raising the possibility that phase separation could have been important at the shallow depths of formation inferred for the Irish deposits (Large, 1981). Although some evidence for phase separation, in the form of vapour-rich inclusions, has been reported (Samson and Russell, 1987), it is not thought to have been a common phenomenon. Consideration of an effervescence–depth curve for an H_2O–CO_2–NaCl solution constructed using $X_{CO_2} = 0.05$, 2 m NaCl (Fig. 13) shows that at 200°C, the two-phase curve would have been intersected at a hydrostatic depth of 190 m. Given that seawater depths of > 200 m are likely to have existed over the deposits at the time of formation and that mineralization may have occurred up to several hundred metres below the seafloor, effervescence is not likely to have occurred. Nonetheless, the fluids are likely to have been very close to the two-phase curve making pressure correction of homogenization temperature data unnecessary. Alkali geothermometry results reported by Everett et al. (1999a) indeed show that fluid temperatures appear to have spanned the same range as homogenization temperatures, supporting this inference.

The existing fluid inclusion data provide some constraints with regard to genetic models for the Irish deposits. Average fluid temperatures are around 180°C and (reliably) extending up as high as 240°C. Such temperatures are considerably higher than observed for MVT mineralization and low temperature basinal brine flow models are clearly inappropriate. To attain such high temperatures, either deep circulation (> 7 km) under normal crustal geothermal gradients, moderately deep circulation under elevated geothermal gradients (∼ 5 km), such as may have been developed in an extensional tectonic regime, or a shallow heat source are required. Given that it is known that the Irish Midlands basin was actively extending during mineralization and that there is no evidence for significant volcanic activity or intrusions at the time of mineralization, the second alternative seems most likely (Everett et al., 1999b).

The origin(s) of the hydrothermal fluids involved in mineralization has also been the subject of considerable debate. Deep convection models (Russell, 1978) invoked circulation of contemporaneous seawater, compaction models appealed to connate waters (Lydon, 1986) and MVT models implicate lateral, topographically driven flow of basinal brines (Hitzman and Beaty, 1996). Recent stable isotope and halogen data (Everett et al., 1999b) have for the first time shown that the principal, high temperature orefluid (Fluid 1) was ultimately derived from seawater which had equilibrated with basement rocks during moderately deep circulation. Additional data from the deposits (Gleeson et al., 1999a) have highlighted the complex origins of the low temperature brines also involved in mineralization (Fluid 2).

Whilst many questions remain unanswered, the picture is beginning to emerge in Ireland of a class of deposits which are in many ways transitional between MVT deposits and the sedimentary-exhalative (SEDEX) class. It seems likely that a spectrum of deposits spanning these categories exists and fluid inclusion studies may play an important future role in rationalising our understanding of base metal mineralization in such environments.

5.3. Volcanic-associated massive sulphide deposits

Perhaps somewhat surprisingly, given the recent upsurge in interest in contemporary submarine hydrothermal analogues to many of the ancient ore deposits in this group, fluid inclusion data from these deposits are comparatively limited. Roedder (1984) summarised results from the Kuroko deposits of Japan, which show that inclusions are dominantly aqueous, two-phase liquid–vapour with fairly low salinity (1–8.4 wt.% NaCl equiv.) and low to moderate homogenization temperatures (80–340°C). In general, a difference is observed in T_h and salinity values between the lower stockwork zones, where they tend to be higher, and the upper parts of the ore system where they tend to be lower. By analogy with modern systems, the wide spread in temperatures overall may be in part due to overprinting of earlier higher temperature stages by cooler fluids as the

hydrothermal systems waned and collapsed inward in response to decreased local volcanic activity. Application of some of the detailed textural analytical techniques described earlier may be necessary to confirm the operation of such processes in fossil systems.

Early interpretation of the source of fluids in these systems was largely driven by stable isotope studies (Ohmoto and Rye, 1974; Sheppard, 1977). Using the oxygen and hydrogen isotopic composition of fluids trapped in sulphides, Ohmoto and Rye (1974) suggested that the solutions originated as mixtures of seawater and meteoric water which had undergone modification via exchange with the host volcanic sequence, with a possible contribution from magmatic water. This study, however, nicely illustrates many of the ambiguities which exist in interpreting stable isotope data from hydrothermal fluids which have clearly (as evidenced by the extensive alteration developed in these deposits) undergone significant fluid–rock interaction. The simplest conclusion that can be drawn from the data in this case is that the analysed ore-fluids are essentially rock-buffered and are close to isotopic equilibrium with the host rocks at around 200°C. This means that the water could have originated from *any* source, or mixtures of sources, and, in the absence of additional information, cannot be constrained. Here, the application of fluid inclusion halogen analyses may have enabled this problem to be resolved.

As a result of the discovery of active submarine hydrothermal vents in 1977, we now have a much better understanding of how ancient seafloor ore-forming systems may have evolved. Evidence from the mid-ocean ridges clearly shows that the venting fluids are modified seawater (e.g. Bowers et al., 1985) as might be anticipated from their setting. An interesting observation from analyses of the vent fluids is that they display a range of salinity, as observed in the Kuroko deposits, extending both above and below seawater values (Von Damm, 1990). Possible explanations include the involvement of vapour condensates in boiling systems, mixing of seawater with residual, more saline, liquids produced by boiling (e.g. Cathles, 1993), water loss/gain during rock hydration/dehydration reactions and buffering by a soluble Cl-bearing phase (e.g. Campbell and Edmond, 1989). Thus, salinity variations appear to be an inherent aspect of submarine seawater-dominated hydrothermal systems and further study of contemporary vents, particularly using tracers such as halogen ratios, will no doubt increase our understanding of the ancient ore-forming processes.

5.4. Granitoid-associated vein systems

Sn–W–Cu-bearing vein systems and pegmatitic deposits associated with granitoids have received a great deal of attention. Inclusions have been predominantly studied in quartz, although data have also been obtained from topaz (Rankin et al., 1992; Fig. 20) wolframite (Campbell and Panter, 1990), fluorite and carbonates. A summary of microthermometric results from a range of deposits is presented by Roedder (1984). Homogenization temperatures are predominantly between 150°C and 500°C and estimated salinities show a wide range from 0–45 wt.% NaCl equiv., with a few examples of higher salinity. Multiple daughter phases are present in the higher salinity inclusions, including halite, sylvite, Ca–Mg–Fe–Mn chlorides, borate minerals, anhydrite, carbonates, haematite, magnetite and sulphides.

Evidence for effervescence is commonly reported, as is the presence of CO_2, with the occasional occurrence of liquid CO_2-bearing inclusions. In a number of cases, elevated CO_2 contents are associated with W-rich mineralization (e.g. Higgins, 1980). Effervescence of CO_2 has been invoked as an important control on deposition of cassiterite and the formation of high grade zones (e.g. Kelly and Turneaure,
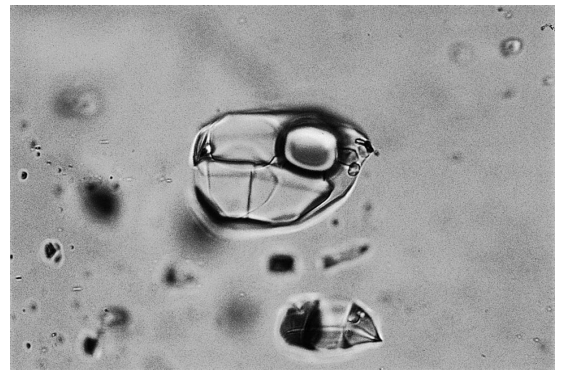

Fig. 20. Photomicrograph of a primary multiphase fluid inclusion hosted by topaz from Fielders Hill W-deposit, New South Wales, Australia. Contains several large Na–K–Fe chloride daughter minerals as well as an opaque (probably chalcopyrite). Width of view, 180 μm. Photo courtesy of A. Rankin.

1970), with later stage shifts to lower salinity fluids often being attributed to an influx of meteoric water (Kelly and Turneaure, 1970; Jackson et al., 1989).

Perhaps one of the most comprehensive studies of any hydrothermal ore deposit is that of the Panasqueira W–Sn deposit in Portugal (Kelly and Rye, 1979). This showed that the mineralizing fluids were dominantly low salinity (5–10 wt.%) in the temperature range 360–230°C and that early CO_2 effervescence occurred (with CO_2 contents up to 9 mol%) but that the fluids were in the one-phase region for most of the mineralizing history. This contrasts with the high salinity fluids often observed in Sn–W deposits and can be attributed to relatively high fluid pressures being maintained, thereby preventing extensive phase separation. This is consistent with the thick, subhorizontal veins that characterise the orebody and occurrence of coarse, bunchy clusters of ore minerals such as wolframite, suggesting vertical dilation and infiltration by lithostatically pressurised magmatic fluids, with slow, diffusion-controlled growth of vein-forming phases.

One peculiarity observed in this study and subsequently shown to be a more general phenomenon (Gleeson et al., 1999b) was the measurement of unusually low δD values in inclusion fluids from the early paragenetic stage (down to −124‰). Although high latitude meteoric waters could yield such values, the near-equatorial position of Western Europe at the time precludes such a source. The origin of these waters remains uncertain but, in both studies cited above, anomalous δD waters appear to have precipitated minerals in apparent textural equilibrium with phases containing 'normal' δD waters.

5.5. Porphyry–Cu deposits

Many fluid inclusion studies of porphyry–copper systems have been carried out (see Roedder, 1984) although, perhaps surprisingly, relatively few detailed studies have been published (e.g. Roedder, 1971; Eastoe, 1978; Beane, 1983; Bowman et al., 1987). This work has played an important role in the debate regarding the source of fluids and metals in porphyry systems, particularly regarding the relative importance and timing of magmatic and externally derived (meteoric, formation etc.) waters. Although many complexities in individual systems exist, it is

now generally accepted that the fluids and probably most of the metals required to form porphyry deposits were derived from an intrusion hosting, or occurring immediately beneath, the deposits themselves (e.g. Bodnar, 1995). The importance of infiltration of lower temperature external fluids into the system appears to be primarily as a trigger for ore deposition, principally by cooling and dilution of the magmatic fluids.

A wide range in inclusion properties and homogenization styles have been reported from porphyry–copper deposits, with homogenization temperatures generally in the range 200–700°C and salinities mainly in the range 0–70 wt.% NaCl equivalent. Perhaps the most distinguishing feature is the common occurrence of highly saline inclusions containing multiple daughter minerals including halite (Fig. 21), in addition to sylvite and commonly chalcopyrite. These often appear to coexist with low density vapour inclusions, hence the assemblages have commonly been interpreted as the product of liquid–vapour phase separation, a process considered to be an intrinsic part of the magmatic–hydrothermal evolution of such systems (Henley and McNabb, 1978). However, it is equally possible, under particular conditions, for separate liquid and vapour phases to exsolve directly from the source magma (Bodnar, 1995). Climax-type porphyry–Mo systems appear to be somewhat different in that salinities are lower and may be controlled by pressure variations in fluids exsolved directly from the crystallizing melt (Cline and Vanko, 1995).
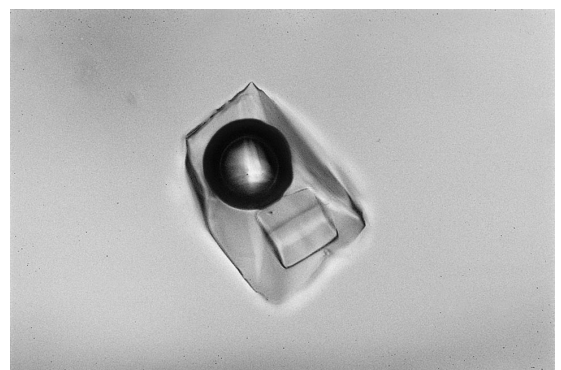

Fig. 21. Photomicrograph of a primary halite-saturated fluid inclusion hosted by quartz from the San Pedro porphyry deposit, New Mexico (see Wilkinson et al., 1994). Width of view, 90 μm. Photo courtesy of A. Rankin.

The interpretation of inclusion data from porphyry systems is greatly facilitated by the use of *P–X* and *P–T* phase diagrams for the model NaCl–H$_2$O system (Fig. 22). This illustrates the nature of fluid inclusions formed under the range of *PT* conditions typical of porphyry deposits as observed at room temperature. Inclusions can be broadly divided into five groups:

1. halite undersaturated inclusions homogenizing to the liquid;
2. halite undersaturated inclusions homogenizing to the vapour;
3. halite saturated inclusions showing liquid–vapour homogenization to the liquid and total homogenization by halite dissolution;
4. halite saturated inclusions showing liquid–vapour homogenization to the liquid and total homogenization by vapour disappearance;
5. halite saturated inclusions showing liquid–vapour homogenization to the vapour.

Types 1 and 2 may be related by phase separation of an aqueous fluid or by direct separation from a crystallizing melt. The occurrence of opaque daughter minerals in type 2 inclusions would support the latter process since vapour inclusions produced by immiscibility are less likely to contain such phases (Bodnar et al., 1993). Inclusion types 3 and 4 could be the product of phase separation of an aqueous phase or direct exsolution from a melt at low pressure (Cline and Bodnar, 1991). The mode of homogenization depends on the *PT* trapping conditions relative to the isochore which originates at the L + V + H triple point (Fig. 22). A special class of inclusions (type 5) are those which are trapped on the high temperature side of the critical isochore but within the one-phase field. These will homogenize by vapour disappearance but this does not imply that they must have coexisted with a separate liquid-rich population.

The common occurrence of chalcopyrite and haematite as daughter minerals in magmatic-related inclusions (Fig. 2) testifies to the high levels of dissolved Fe in such fluids. Recent data indicate that Fe is a major component of such solutions, together with K, Na and lesser amounts of Ca (Rankin et al., 1992; Wilkinson et al., 1994; Ulrich et al., 1999; see Fig. 23). Mn and Zn can also be present at the weight percent level. Although the brine component is commonly assumed to be the dominant phase responsible for metal transport, new data are beginning to show that transport of certain species in low-density fluids is possible. Ulrich et al. (1999) using a laser ablation ICP-MS system have shown how Au, Cu and also As appear to be preferentially partitioned into the vapour phase in two-phase systems. This has important implications for the transport and deposition of these metals in the porphyry environment and is a mechanism whereby these metals can be fractionated and preferentially transported into the overlying epithermal regime.

### 5.6. The porphyry–epithermal transition

The Lepanto–Far Southeast Cu–Au deposits in the Philippines provide one of the best examples of genetically linked porphyry and epithermal systems (Hedenquist et al., 1998). As such, they enable a rare opportunity to investigate changes in fluid inclusion properties between the typical porphyry and epithermal regimes and also to relate these changes to the palaeohydrology during mineralization.

High salinity inclusions are closely associated with the porphyry itself and are restricted to a zone generally less than 300 m above the top of the intrusive body (Fig. 24). Maximum homogenization temperatures (294–196°C) and salinities ($\sim$ 3–1.5 wt.% NaCl equiv.) gradually decrease above and laterally away from the porphyry body within the high sulfidation enargite–Au epithermal orebody (Mancano and Campbell, 1995). These changes provide evidence for the flow of fluids away from the porphyry centre, with focusing at the intersection of a major fault and an unconformity surface, and progressive mixing with cool (< 50°C) ground water of negligible salinity (Fig. 25). The parent solution ($T \sim 350$°C, 5 wt.% NaCl) is considered to represent a magmatic fluid which had not intersected the solvus to separate into saline liquid and vapour phases, and was linked to the late sericitic alteration stage in the porphyry system (Hedenquist et al., 1998).

This study shows how inclusion data can help in investigations of the interface between the magmatic-dominated and meteoric-dominated fluid flow

systems characteristic of intrusion-centred hydrother-mal ore deposits. The relationship between these

flow systems, their evolution through time and con-tribution to the alteration patterns and metal budget
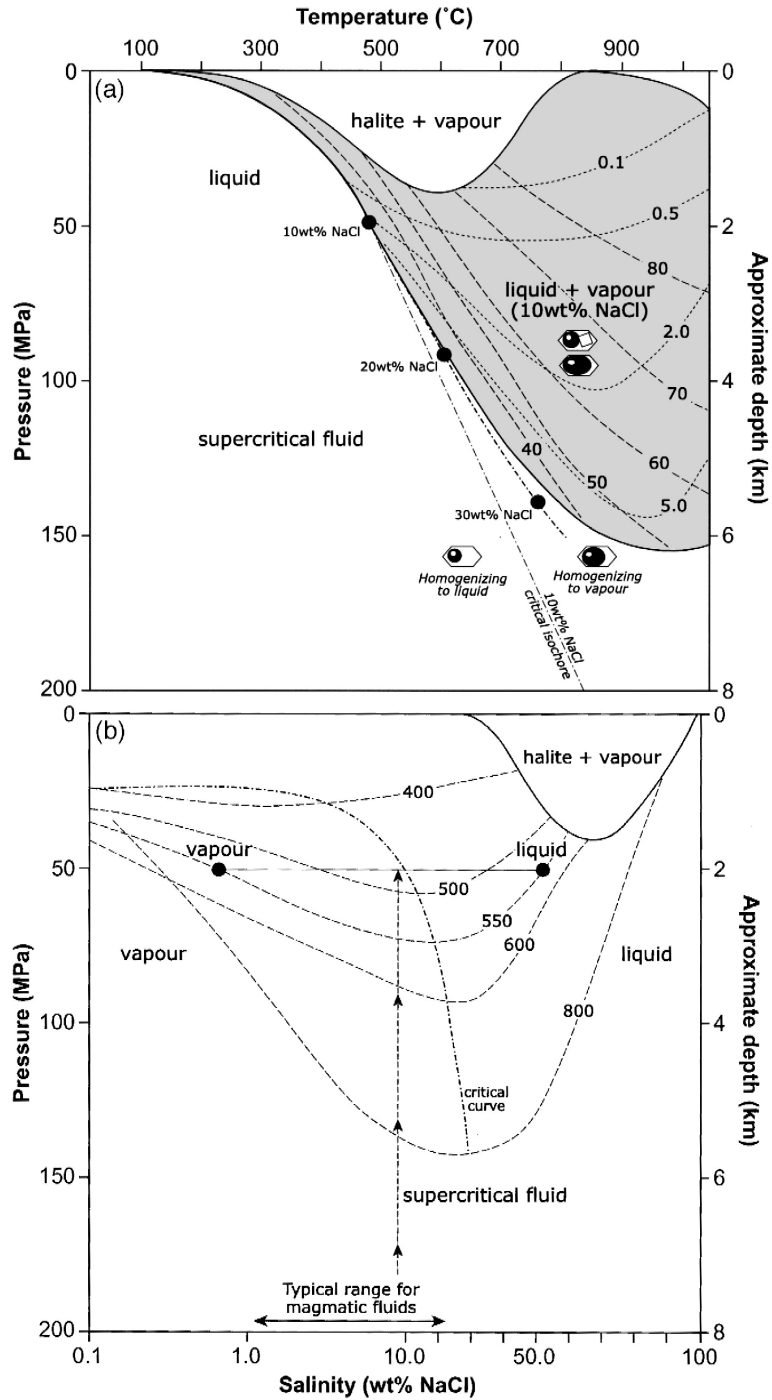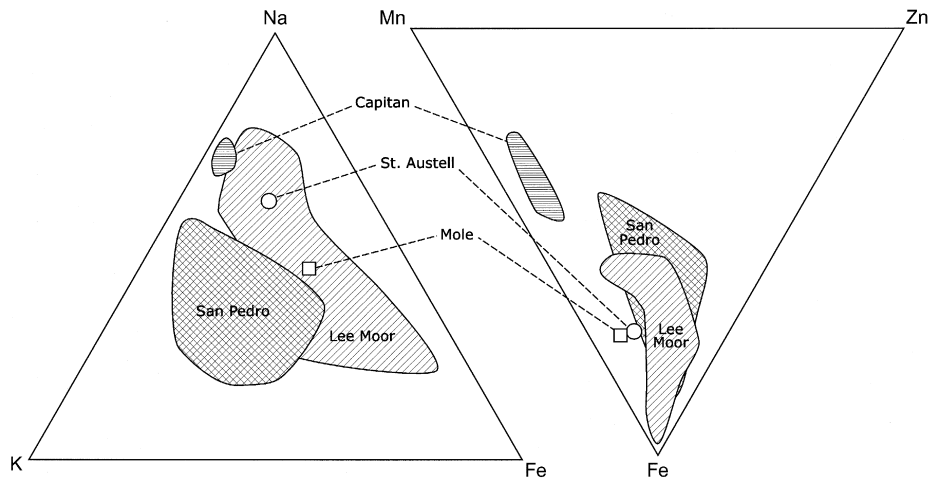
Fig. 23. Fe–K–Na and Fe–Mn–Zn ternary diagrams (by weight) showing typical compositions of magmatic–hydrothermal fluids. Sn–W–Cu mineralization, Lee Moor, Devon, and Cu–Au porphyry mineralization, San Pedro, New Mexico — fields for single fluid inclusion analyses by laser ablation–ICP-AES (both from Wilkinson et al., 1994); St. Austell, Cornwall — crush–leach analysis (Bottrell and Yardley, 1988); Th–U–REE mineralization, Capitan Mountains, New Mexico — crush–leach analysis (Campbell et al., 1995).

of these systems are important questions worthy of further research.

5.7. Epithermal deposits

Epithermal mineral deposits, defined as those forming in the near-surface environment (< 1 km; Hedenquist, 1987) at temperatures < 300°C, have been perhaps the most studied deposits in terms of fluid inclusions (e.g. see Roedder, 1984). This is primarily due to the often coarsely crystalline nature of the mineral phases (at least at the higher temperature end of the spectrum) and resulting large (sometimes up to mm in size), and/or optically clear inclusions. Due to their geological setting, many different types of fluids may be involved in the formation of epithermal deposits; as a result, fluid inclusion studies have played a very important role in understanding ore genesis (see Evans, 1993, for a general summary). For a detailed review of the specific methodology that can be applied in studies of epithermal systems, the reader is referred to Bodnar et al. (1985).

One special characteristic of epithermal systems is that fluid inclusion homogenization temperatures are a good proxy for true trapping temperatures since the trapping pressure is generally low. Furthermore, evidence for effervescence is commonly observed in

Fig. 22. Binary phase diagrams relevant to interpretation of microthermometric data from porphyry systems. (a) Isocompositional $P–T$ diagram illustrating phase relationships in the NaCl–H_2O system. The shaded field represents the two-phase field for a solution bulk salinity of 10 wt.% NaCl and is countoured with isopleths of vapour phase salinity (short dashes) and liquid phase salinity (long dashes). Heavy dash–dot line represents the critical curve labelled with critical points for salinities of 10, 20 and 30 wt.% NaCl. The critical isochore for a 10 wt.% solution is shown. Schematic inclusion images show the type of inclusions formed in different fields. Note that fluids exsolved directly from a magma at ∼ 700°C at depths of ∼ 6 km may be in the single-phase region but have densities below critical and will therefore homogenize to the vapour phase. Such fluids may cross the critical isochore during cooling and depressurization to produce liquid-homogenizing inclusions. Modified after Fournier (1987) and Bodnar (1995). (b) Isothermal $P–X$ diagram illustrating phase relationships in the NaCl–H_2O system showing evolution path for an ascending magmatic fluid of 8.4 wt.% NaCl (note log–linear scale change on x-axis at 10 wt.% NaCl). On cooling to 550°C at ∼ 2 km depth, the fluid will separate into a liquid with a salinity of ∼ 50 wt.% NaCl (comprising ∼ 8 wt.% of the bulk fluid) and a dominant vapour phase with a salinity of ∼ 0.7 wt.% NaCl (comprising ∼ 92 wt.%). Modified after Shinohara and Hedenquist (1997) and Hedenquist et al. (1998).
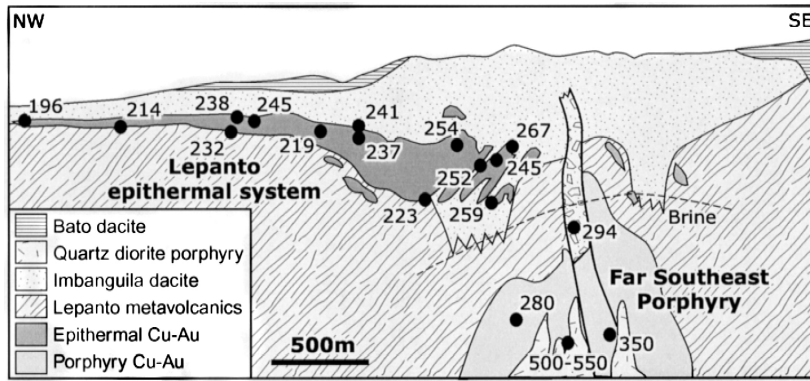
Fig. 24. Variation in maximum fluid inclusion homogenization temperatures between the Far Southeast porphyry copper system and Lepanto high sulphidation epithermal deposit (modified after Hedenquist et al., 1998).

which case no correction to homogenization temperature values is necessary. To illustrate this point, consider a non-boiling, low salinity NaCl solution trapped at 1 km depth, with inclusions homogenizing at 200°C. At depths of less than approximately 3 km in the crust, fluid pressures are generally close to hydrostatic so that, using the relation $P = \rho g z$, where ρ is fluid density, g is gravitational acceleration and

z is depth, a trapping pressure of ~ 100 bars can be estimated. Given that the dP/dT of such a solution is approximately 20 bar °C^{-1} and the homogenization pressure for such an inclusion about 16 bars, the pressure correction would be ~ 4°C. This is within the range observed for most individual inclusion populations and would also be equally applicable to different groups of inclusions formed at about the same time. The correction is negligible with regard to any geological interpretation, and can therefore be safely ignored. In cases where non-condensible gases are suspected or analysed, pressure correction is even less significant since their presence tends to raise the vapour pressure curve to higher pressures, thereby reducing any required correction (e.g. see section on CO_2-bearing fluids above).

The Creede deposit in Colorado provides a classic case study of an entire epithermal system (Berger and Henley, 1989) in which detailed paragenetic, geochemical and isotopic studies have been carried out. The deposit consists of relatively simple, crustiform veins containing a variety of mineral phases, principally, sphalerite, galena, chalcopyrite, pyrite, haematite, chlorite, quartz, adularia and sericite. Five paragenetic stages have been defined, four of which have yielded fluid inclusion data. The sphalerite is particularly useful since it contains multiple growth zones that can be correlated throughout the deposit, thereby providing an excellent temporal framework for the analysis of primary inclusions.

Inclusions are predominantly liquid-rich, although coexisting vapour-rich inclusions are observed in the
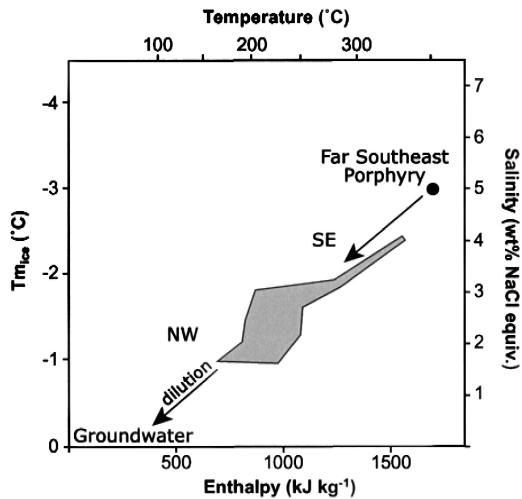

Fig. 25. Enthalpy–salinity plot for fluid inclusion data from the Far Southeast–Lepanto porphyry–epithermal system (shaded field) showing inferred mixing relationship between higher temperature more saline fluids of magmatic derivation in the SE with low temperature groundwaters dominating in the NW (modified after Hedenquist et al., 1998).

upper part of the system indicating that effervescence occurred. Crushing tests (Roedder, 1970) did not reveal the presence of significant additional volatiles in the vapour-rich inclusions, possibly because any present were rapidly lost during vapour separation. Homogenization temperatures are typical for epithermal deposits, ranging from 200–270°C, whereas salinities are slightly higher than the norm, ranging from 4.9–11.7 wt.% NaCl equivalent. There is a progressive shift through the paragenesis toward lower homgenization temperatures and salinities (as was discussed above in the porphyry–epithermal environment) although, in detail, the evolution is complex with many reversals (Roedder, 1977b; Woods et al., 1982).

Isotopic studies of the Creede system (Bethke and Rye, 1979) showed that the sources of fluids in the system was difficult to resolve, with the possible involvement of two meteoric sources and a magmatic contribution. Some of the problems of interpretation may have resulted from the analysis of bulk inclusion samples for δD with mixing of more than one of the inclusion stages described above. This highlights one of the problems of conventional methods of isotopic analysis and why the development of single inclusion analytical methods is very important. Where microthermometry can define a complex and detailed evolution in temperature and salinity, techniques which can determine additional compositional parameters at least down to the single zone scale are not just desirable but are a fundamental requirement.

Zone-by-zone analysis of base metal mineralized quartz veins from Cornwall (Gleeson, 1997) showed a different type of evolution with fairly consistent homogenization and salinity characteristics, but non-systematic variations in fluid and isotope geochemistry. This illustrates the complex evolution of many epithermal systems for which adequate explanations are currently lacking, although local disequilibrium precipitation is one likely possibility.

General cooling and dilution trends are often observed in epithermal deposits (e.g. Rossetti and Colombo, 1999), probably reflecting the general retrograde evolution of these systems, with an initial high temperature phase (probably related to a specific intrusive or volcanic event) followed by progressive cooling and collapse of cold surface waters into the system resulting in dilution and enhancing

the temperature decline. This would also lead to the characteristic telescoping of the ores, with mineral assemblages (and their associated inclusions) formed at lower temperatures overprinting higher temperature stages. Related to this would be the development of late secondary inclusions with lower homogenization temperatures and salinities.

5.8. Mesothermal lode gold deposits

A vast literature exists on the geological characteristics and processes governing the formation of mesothermal shear-zone or lode gold deposits of Archaean and Phanerozoic age and it would be impossible to provide anything approaching a comprehensive review here. For more detailed information the reader is referred to the reviews of Colvine (1989), Groves and Foster (1993), Nesbitt (1993) and Kerrich and Cassidy (1994). However, these systems are worthy of mention since not only have fluid inclusions played a pivotal role in understanding ore-forming processes in these deposits, but they have also provided important more general insights into the inter-relationships between fault activity and fluid flow in the crust.

Inclusions in mesothermal quartz veins are predominantly of small size (typically $\sim 5~\mu m$) and of secondary origin. In fact, it is rare for unequivocal primary inclusions, according to the detailed criteria of Roedder (1984), to be observed. However, given the multistage development of such vein systems, it is probable that many of the secondary inclusions present will represent the primary vein-forming fluids. Furthermore, gold is commonly paragenetically late in many deposits, often occurring in fractures in early sulfides and accompanied by late quartz, carbonates, galena, sphalerite, and tellurides (Nesbitt, 1993). Obviously, a key question which must be addressed in any study is how do the inclusions observed relate to the gold depositing event? The likelihood of overprinting by later, unrelated fluids is high in these systems (Guha and Kanwar, 1987; Robert and Kelly, 1987; Claoué-Long et al., 1990; Kerrich and Cassidy, 1994; Boullier et al., 1998) since they are usually associated with major transcrustal structures which are repeatedly reactivated (e.g. Wilkinson et al., 1999). The use of careful petrography and also CL studies (see above) are critical in this respect.

The small size of inclusions can pose a problem; however, with recent improvements in optics and the use of high resolution video cameras and monitors, inclusions down to the sub-2 μm range can now be analysed. This, in fact, provides some advantages in that it is the large, and commonly more irregular inclusions which may have been the only workable inclusions in the past, yet these inclusions are those that are most likely to have suffered post-entrapment modification. The ability to collect precise microthermometric measurements from small inclusions may make studies more representative and also, perhaps, more accurate.

CO_2 is virtually ubiquitous in these systems and 3-phase H_2O–CO_2 rich inclusions at room temperature are the norm (Fig. 26). The content of other volatiles in addition to CO_2 and H_2O is variable, resulting in depressed CO_2 melting temperatures, typically above $-60°C$, but in some cases, particularly where graphitic or carbonaceous lithologies occur, much lower values may be observed (e.g. Cole et al., in press). A particular feature of these fluids is that they commonly contain predominantly CO_2–N_2 mixtures or CO_2–CH_4 mixtures; intermediate compositions are rare. Salinity, generally estimated from clathrate melting temperatures, is typically low (< 5 wt.% NaCl equiv.) and this is one of the characteristic features of fluids associated with these deposits. Homogenization temperatures generally range from 200–350°C, although values up to and even above 400°C have been recorded (Roedder, 1984). Lower T_h inclusions are commonly paragenetically late. In some systems, notably those apparently forming at lower temperatures and with a mineral association including phases such as stibnite and carbonates, aqueous inclusions, sometimes of moderate to high salinity, can be important (Hagemann et al., 1994). Daughter minerals are not usually present although dawsonite ($NaAlCO_3(OH)_2$) has been recorded in a number of cases (e.g. Coveney and Kelley, 1971).

One of the key processes which has now been documented in many mesothermal gold vein systems is phase separation (e.g. Robert and Kelly, 1987; Herrington et al., 1993; Wilkinson and Johnston, 1996; Parry, 1998). The environment of formation of many of these deposits, typically at greenschist facies metamorphic conditions and within the brittle–ductile transitional regime in the crust, is such that the typical fluid compositions summarised above are close to the two-phase region. Thus, as a result of either temperature decrease, and/or pressure decrease the fluid may intersect its solvus and separate into a CO_2-rich ($\pm N_2$ or CH_4) fluid and a H_2O-rich ($\pm CO_2$), more saline fluid. Depending on the conditions and bulk fluid composition, these two fluids could be of similar density, which may result in both fluids being retained within the system, or strongly contrasting density, where the CO_2-rich phase forms a low density vapour that can physically separate and escape from the immediate environment. A potential consequence of the latter process, and exacerbated by the tendency of the H_2O-rich fluid to wet growing mineral surfaces, is that CO_2-rich, vapour-like fluids may be under-represented or even absent from the resulting inclusion assemblage. Ideally, however, both types of fluid would be represented in the inclusion assemblage produced, with CO_2-rich inclusions homogenizing to the carbonic phase and H_2O-rich inclusions homogenizing to the aqueous phase over the same temperature range. Unfortunately, due to the common mechanical trapping of a small amount of H_2O-rich fluid within CO_2-rich inclusions when they form (heterogeneous trapping), the carbonic inclusions are not representative of the end-member fluid composition. As a result, they yield anomalous T_h values, commonly 50°C or even more above cogenetic aqueous inclusions. Consequently, it
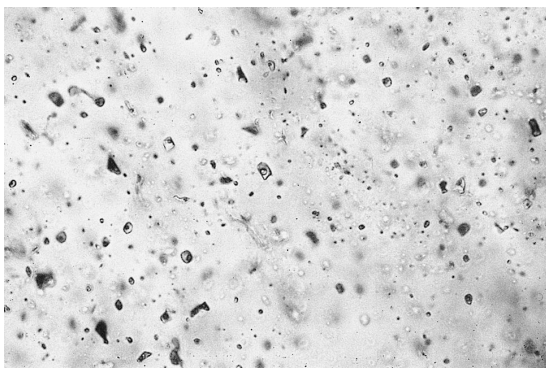

Fig. 26. Photomicrograph of a typical quartz-hosted fluid inclusion assemblage from the Patchway mesothermal gold deposit, Zimbabwe. A slightly larger than average, three-phase H_2O–CO_2–NaCl inclusion can be seen in the centre. Plane polarised light, width of image, 200 μm (photo courtesy of R. Herrington).

is the H_2O-rich inclusions in such assemblages that generally provide the most reliable information. A detailed treatment of the necessary criteria to confirm trapping of two immiscible fluids is beyond the scope of this paper; for more information the reader is referred to Ramboz et al. (1982). Finally, it is possible to observe apparently coexisting inclusions of contrasting composition that represent partial mechanical mixtures of two fluids, rather than one fluid that underwent separation (e.g. Anderson et al., 1992). Recognition of this possibility is not necessarily a trivial matter.

A common aim in studies of mesothermal gold deposits is to constrain the pressure–temperature conditions during gold deposition (Hagemann and Brown, 1996). In cases where phase separation can be confirmed, then pressure correction of homogenization temperature data is not necessary and trapping pressures (equivalent to the homogenization pressure, P_h) can be calculated based on microthermometric measurements. In the absence of evidence for trapping on the solvus, such estimates provide a minimum constraint on trapping pressure so that construction of isochores, together with an independent temperature or pressure constraint, are needed for estimation of trapping conditions.

There are a number of approaches which can be used to estimate P_h which require measurements of either the volumetric proportion of the carbonic phase, clathrate melting and CO_2 homogenization temperatures, or clathrate melting, CO_2 homogenization and total homogenization temperatures (Bodnar et al., 1985; Parry, 1986; Schwartz, 1989). The latter approach, although more complicated, avoids the need for estimation of volumetric proportions which is subject to large errors and uncertainty. Some of these calculations are simplified by the use of the data reduction computer programs FLINCOR (Brown, 1989) and MacFlincor.

Constraints on fluid temperature and pressure variations in natural systems derived from fluid inclusion studies have gone far toward confirming seismic valving (Sibson et al., 1988; Sibson, 1994; Parry, 1998) as an important regulator of fluid flow in the mid-crust. This process, whereby rising fluid pressure in a deep, overpressured fluid reservoir triggers failure in a fault zone resulting in draining of fluid into the fault zone and rapid fluid pressure

decrease, has been invoked as an important control of gold deposition in mesothermal quartz–gold veins (e.g. Robert and Kelly, 1987; Herrington et al., 1993). Wilkinson and Johnston (1996) showed how phase separation of a low salinity H_2O–CO_2 fluid, caused by fluid pressure decrease, was responsible for gold deposition in a gold deposit in Ireland and that these linked processes were localised to specific parts of the vein network.

Trapping pressure constraints from fluid inclusions is one of the critical pieces of evidence which has led to the hypothesis that mesothermal gold systems can form over a wide range of depths in the crust — the so-called crustal continuum (Nesbitt, 1988; Colvine, 1989; Groves et al., 1992). Surface water influx has been inferred in a number of Archaean deposits such as in the Norseman–Wiluna belt in the Yilgarn craton of Australia (e.g. Hagemann et al., 1994). These examples appear to have formed at low temperatures and pressures at relatively shallow depth (< 5 km) and contain atypical mineral assemblages including silver sulphosalts, stibnite and abundant carbonate. In contrast, some deposits are thought to have formed at high metamorphic grades (e.g. Colvine, 1989), but the interpretation of these is controversial.

Despite the wealth of fluid inclusion data from mesothermal gold deposits, fundamental questions remain unanswered, particularly regarding the source(s) of the fluids involved in mineralization. Further careful geological studies and the use of effective fluid tracers will be required to solve some of these remaining gaps in our knowledge.

6. Fluid inclusions and mineral exploration

The use of fluid inclusions in mineral exploration has received varying degrees of attention over the years with the bulk of applications reported in the Soviet literature (see Roedder, 1984). Whether any major breakthroughs can be ascribed to fluid inclusion data alone seems highly unlikely, but this probably holds true for any geochemical technique. Nonetheless, it is probable that if carried out carefully and with clearly defined objectives, fluid inclu-

sions can provide very useful information as part of a target selection process and, as one dataset amongst several, can be used to justify drilling that last hole. However, the most significant impact of fluid inclusions is perhaps less obvious and is best summed up by the oft quoted and still valid comment of W.C. Kelly in a letter to Ed Roedder: 'the greatest contribution of fluid inclusions lies in the subtle but pervasive impact they have had on the basic philosophy of explorationists' (Roedder, 1984, p. 468). The importance of feedback of fluid inclusion data into empirical and conceptual exploration models should not be underestimated, and it is here where fluid inclusion studies still have much to contribute.

The more direct uses of fluid inclusions in exploration mainly rely on defining an empirical relationship between some inclusion characteristic and mineralization. Methods for using fluid inclusions to assist target selection on a regional scale or for more localised definition of likely zones of focussed fluid flow or ore shoots can be subdivided into three categories:

1. the occurrence or relative abundance of a specific inclusion type
2. systematic variations in microthermometric properties
3. systematic variations in other properties (e.g. decrepitation behaviour, inclusion chemistry)

6.1. Using the occurrence of specific inclusion types

In terms of ease of application, solely identifying inclusions of a given type is the simplest procedure as it only requires observation and perhaps point-counting of inclusions in thin-section, polished wafer or even grains under immersion oil and can therefore be carried out rapidly with a minimum of sample preparation. With a practised eye, it is easy to recognise different inclusion types from the phases present at room temperature, and even the likely range of homogenization temperature.

Rankin and Alderton (1983) used this type of approach to correlate the relative abundance of specific inclusion types in granite samples with the

distribution of Sn–W–Cu mineralization in the Cornish orefield. It was found that there was an empirical relationship between inclusion abundance in granite samples and mineralized areas. A similar approach has been used in porphyry–copper systems, where the occurrence of hypersaline fluid inclusions containing several daughter minerals and/or vapour-rich inclusions has been linked to ore (Roedder, 1971; Nash, 1976; Bodnar, 1981). Another example is in epithermal precious metal systems, where the occurrence of cogenetic vapour- and liquid-rich inclusions may be used to identify zones of boiling and, therefore, ore mineral precipitation (Kamilli and Ohmoto, 1977).

The occurrence of CO_2-bearing inclusions has also been suggested as a favourable characteristic for exploration of vein–gold deposits (e.g. Ho, 1987). Either optical identification, or even a more simple crushing test (Diamond and Marshall, 1990), can be used to determine whether quartz vein material contains abundant CO_2-bearing inclusions. In a detailed study of the Croagh Patrick prospect in Ireland, Wilkinson and Johnston (1996) showed that high gold grades were correlated with the occurrence of inclusion assemblages indicating that phase separation had occurred. Their study of the whole vein system showed this process was restricted to a particular stage of vein formation and to certain vein orientations.

6.2. Using systematic variations in microthermometric properties

Utilising microthermometric data is obviously more involved and will, for an adequate characterisation of a given system or area, require a significant number of measurements on a large number of samples. This has obvious implications regarding increased cost; even so, in relation to an overall exploration budget, such costs would only form a very small proportion.

Spooner (1981) described T_h data from a Au–Ag district in Arizona in which specific ranges of T_h were associated with mineralization. A similar observation was made by Vikre (1989) on a study of the Comstock lode in Nevada. Earls et al. (1996) re-

ported data from a regional study of gold-bearing veins in Northern Ireland which showed that clathrate melting temperatures of CO_2-bearing inclusions in the Curraghinalt deposit were lower than in uneconomic (but related) veins on a regional scale (Fig. 27). A remarkably similar observation was made by Lattanzi et al. (1989) from gold-bearing veins in north-west Italy (Fig. 27). Roedder (1977a) and Mavrogenes et al. (1995b) also described differences in fluid properties between gold-bearing and barren veins in a number of mineralized districts.

Perhaps one of the most obvious uses of inclusion data is the use of inclusion homogenization measurements to map out thermal zonations, an approach of direct relevance to exploration in epithermal and intrusion-centred hydrothermal mineralization (e.g. see Fig. 24).

Utilising coupled salinity and homogenization measurements can also provide important informa-

tion concerning the anatomy of a hydrothermal system, with exploration implications. Everett et al. (1999a) showed how inclusion homogenization temperatures declined and fluid salinity decreased within the Silvermines fault zone with increasing distance from the Silvermines Zn–Pb–Ba deposits in Ireland. Interestingly, homogenization temperatures also decreased but fluid salinities generally *increased* on moving into the footwall of the same fault zone.

6.3. Using other inclusion properties

In general, the use of data from more complex methods of inclusion analysis for exploration will be limited by the additional time and cost restrictions such methods often require. The probability of being able to analyse a large enough number of samples will be a problem, and limits potential techniques to relatively simple bulk methods. Nonetheless, several studies have pointed out uses for such analyses.

Alderton et al. (1992) analysed bulk quartz samples from stream sediments on the margin of the Dartmoor granite in the Cornubian orefield using the decrepitation-ICP technique (Rankin et al., 1993). The chemistry of fluids related to mineralization show a distinct chemical signature, with systematic variations in relative abundances of Na, Ca, S, Ba, Sr and Rb being correlatable with mineralized and unmineralized areas. Another empirical relationship between inclusion chemistry and mineralization was demonstrated by Haynes and Kesler (1987) in a study of MVT mineralization in east Tennessee. They showed that the Ca/Na ratios of inclusion decrepitates as measured by SEM-EDS analysis were higher in ore-related dolomites than in barren dolomites.

An alternative method involves the use of decrepitometry which involves measuring, using an acoustic device, the temperature distribution of inclusion decrepitation during heating. Roedder (1984) reviewed a number of applications from the Soviet literature, and Burlinson (1988) described its application to a number of deposit types. The problem with this method lies not only in the fact that it is a bulk technique (also a limitation of the methods described above), but that the control of inclusion decrepitation is a complex function of a number of parameters,
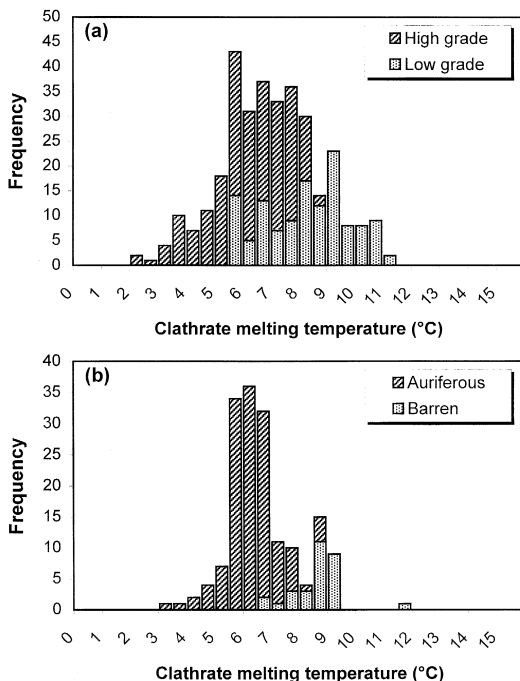

Fig. 27. Comparison of clathrate melting data from barren and mineralised veins. (a) Curraghinalt, Northern Ireland (data from Earls et al., 1996); (b) Northwest Italy (data from Lattanzi et al., 1989).

including inclusion size, shape, density and textural or mineralogical characteristics of the host mineral. Some of these may be unrelated to specific inclusion types or 'favourable' inclusion properties and the data obtained are therefore difficult to interpret. As a result, the technique has not gained routine acceptance although some detailed studies have been carried out (e.g. Mavrogenes et al., 1995b).

In summary, fluid inclusion analysis is gradually gaining acceptance as a useful tool in mineral exploration. It is likely that the careful collection and assessment of inclusion data will play a small but constructive role in the search for hydrothermal mineral deposits in the years to come.

7. The future

There is no doubt that the next millenium holds much in store for studies of fluid inclusions in ore deposits. It is likely that many advances will be due to a continuing rapid pace of technological development, generating new possibilities for sophisticated chemical and isotopic analysis. Already the application of laser-ablation ICP-MS to studies of ore metal transport is providing new insights into the evolution of ore-forming systems (Audetat et al., 1998; Ulrich et al., 1999). It is inevitable that a wider availability and application of these techniques will result in significant advances in understanding mineralizing processes. The application of multiple-collector ICP-MS analysis will push the limits of detection back and improve precision of analyses even further, such that isotope ratios of even trace elements in inclusion fluids may be determined. The analysis of rare earth elements (REE) in fluid inclusions using laser ablation ICP-MS techniques, as well as conventional bulk analyses of suitable samples will, together with analyses of host minerals, allow quantification of the partitioning of these elements between hydrothermal fluids and minerals. As sensitive indicators of source and/or flow paths, the REE may play an increasing role in the hydrothermal geochemists' toolkit.

Advances in ICP-MS technology and laser microprobe efficiency may also enable the determination of isotope ratios from individual inclusions. The ability to measure different isotopes of Pb, Zn, Cu, Fe, Ag, Sn, W and many other metals may be of use

in tracing metal sources and understanding depositional processes. The degree of fractionation of such isotopes in nature, presently largely unknown, may be a limiting factor, although it would be anticipated that elements which display variable oxidation states (such as Fe or Mn) or are involved in biogenic processes would show marked isotopic variation. Determination of isotope ratios of Sr, Mg, Ca in non-carbonate host minerals and possibly Si in carbonate-hosted inclusions may be of use in monitoring fluid–rock interactions in mineralizing systems.

The ability to date inclusions will be an important goal, not only because it will ultimately resolve the ambiguities which often exist regarding inclusion timing, but because of the constraints that can be placed on *rates* of hydrothermal processes. How long do mineral deposits take to form? This is a critical but largely unanswered question (although see Stein and Cathles, 1997) that has direct impact on interpretations of mass fluxes and fluid flow mechanisms.

One fundamental uncertainty regarding fluid inclusion studies which, although very important, also remains unresolved is the question of whether inclusions hosted by an ore-associated phase trap the orefluid 'before', 'during' or 'after' precipitation of the ore mineral of interest. The question is pertinent, since from analyses of ore metal contents we want to be able to make estimates of the fluid flux required to form a given quantity or ore. Are we looking at the spent ore-fluid in most systems? Should we be looking to analyse inclusions from the feeder zones beneath ore deposits to gain a true picture of the fertile ore-fluid? For major elements which are relatively incompatible (i.e. are not strongly partitioned into precipitating phases), this is not a problem. However, for trace metals that have much higher concentrations in an ore mineral than in solution, the question is paramount. Perhaps the first data to really start to address such a key issue was recently reported (Audetat et al., 1998). Many further studies of this type can be anticipated.

Improvements in analytical techniques such as laser Raman spectroscopy will also enable better determination of anions in inclusion fluids. Since these species are the main ligands responsible for metal transport, it is important to be able to identify and quantify them. Further, identification of specific

metal complexes in inclusion fluids by laser Raman (e.g. see Murphy and LaGrange, 1998) or by high energy X-ray absorption fine structure (XAFS) methods (e.g. Anderson et al., 1995b) will be important for understanding metal transport processes. The ability to measure low concentrations of sulphur species would be particularly useful; if we can precisely determine SO_4^{2-} and HS^- or H_2S in solution then we have a means of estimating the redox potential of palaeo-orefluids. Further work on the halogen chemistry of crustal fluids will help us to better understand their behaviour and use as fluid tracers. Although the halogens are largely incompatible, the possibility of their incorporation and fractionation by rock-forming minerals needs to be addressed (e.g. Martin, 1999).

Fluid inclusions have become, and will remain, one of the most important sources of geochemical information regarding ore-forming processes in hydrothermal systems. Improvements in analytical technology mean that the difficulties intrinsically associated with the analysis of such small volumes of fluid are gradually being solved. Nonetheless, it should always be borne in mind that the ability to measure metal concentrations to the parts per billion level is pointless without careful sample characterisation beforehand. Fieldwork and the collection of carefully located samples, together with detailed mineralogical, textural and fluid inclusion petrography, will always remain fundamental requirements for effective studies of hydrothermal ore deposits.

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