

## Introduction

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Fluid inclusion gas analysis has lurked just beyond the horizon of mineral exploration methods for several decades. The papers in this volume suggest that the technique will soon come into clearer view and wider application in exploration. Inclusion gas analysis is an attractive method for modern exploration for several reasons. First, gas analyses can provide useful insights into the chemistry of hydrothermal fluid and possible mechanisms of ore deposition. Ultimately, we should be able to use fluid inclusion gas analyses to rank a group of similar geologic environments in terms of their chemical favorability for a specific ore-forming mechanism. Second, although there is a problem of secondary inclusions, fluid inclusion gases are probably more widespread and homogeneous than most other types of samples used in exploration. This is particularly true of precious-metal deposits, which suffer from a strong nugget effect, and it alleviates some of the concern about sampling variability that is part of most exploration programs. Finally, fluid inclusion gases appear to be relatively sensitive indicators of their overall geologic environment and fluid history. In other words, when fluids pass through different country rocks, they react with these rocks to take on characteristic gas compositions. Since travel distance correlates roughly with degree of reaction, gas analyses should delineate the extent and geometry of ore-forming hydrothermal systems and, hopefully, provide vectors toward the center or more intensely mineralized part of a hydrothermal system. In areas of reactive country rock, wall-rock–fluid reaction might even add enough gas to trigger ore deposition.

The potential for application of gas analyses in exploration appears to be greatest in the search for gold (Kesler, 1987). Recent studies have demonstrated that gold is probably carried in solution as bisulfide complexes (Seward, 1973; Shenberger and Barnes, 1989) and that it can be deposited from hydrothermal solutions by boiling or phase separation (Drummond and Ohmoto, 1985). (“Phase separation” refers to separation of a vapor containing significant proportions of more volatile gases such as CO<sub>2</sub>, CH<sub>4</sub>, or N<sub>2</sub>. Since these gases are present in most natural hydrothermal fluids and their separation has profound effects on liquid chemistry (Drummond and Ohmoto, 1985), boiling in most natural settings is best regarded as phase separation.) Thus, fluids that contain high levels of reduced sulfur and that

appear to have undergone phase separation will have the greatest potential for depositing gold. Unfortunately, conventional geologic and mineralogical observations are not particularly effective in recognizing high sulfur fluids and considerably less cost effective in recognizing boiling or phase separation. High reduced sulfur contents are not indicated by ore-alteration studies because most minerals more accurately reflect the ratio of reduced to oxidized sulfur. Conversion of iron silicates, carbonates and oxides to iron sulfides is a relatively good indicator of high reduced sulfur content (Kettler, 1990), but its application is limited by mineralogy to iron-bearing wall rocks. Boiling or phase separation can be recognized by optical study of fluid inclusions, although this process is time consuming and expensive and it provides limited information on the composition of the gas phase.

In contrast, fluid inclusion gas analyses provide direct information on both of these diagnostic characteristics. Elevated reduced sulfur levels are most easily indicated by the  $H_2S$  content of the sample. In strict practice, this method provides information on total reduced sulfur content only in fluids with pH lower than the  $\log K$  value for the first dissociation of  $H_2S$ :



This restriction is not important in most cases, however, because the  $\log K$  for this reaction is between  $-7$  and  $-8$  for temperatures up to about  $300^\circ C$  and most hydrothermal solutions are slightly acid. (The same reasoning applies to  $CO_2$  analyses of inclusion fluids because  $\log K$  for the first dissociation of  $H_2CO_3$  is in the same range.) The papers by Landis and Hofstra, and Graney and others in this volume provide examples of the correlation between high  $H_2S$  values and gold mineralization, and the paper by Norman and others shows that this correlation carries over to silver-rich base metal ores. These studies also demonstrate that fluid inclusion gas analyses can be used to constrain geochemical calculations that test the effectiveness of suspected depositional mechanisms.

Boiling or phase separation is commonly recognized in inclusion gas analyses by the presence of unusually high gas values. If an estimate of the pressure of the mineralizing environment is available, it is possible to calculate the amount of gas that could have been dissolved in the hydrothermal fluid using Henry's Law coefficients or gas solubility data (Drummond, 1985; Spycher and Reed, 1989). Comparison of such calculated values to gas analyses from a specific location can be used to recognize samples that almost certainly contain vapor-rich inclusions. The papers in this volume by Wilkins and Jenatton, Shepherd and others, and Takenouchi all take this approach in recognizing environments that have undergone phase separation. Since phase separation is pressure dependent, it could produce vertical compositional gradients in hydrothermal systems. Gradients that probably reflect this effect are described here by Bray and others for  $CH_4$ , by Norman and others for  $H_2S$  and

by Letnikov and Narseev for  $H_2$ , CO and  $CH_4$ . As indicated by these authors, an understanding of these gradients can be used with gas analyses of exploration samples to determine the probable paleodepth that currently outcropping samples might have had in buried hydrothermal systems, a parameter that could help judge the depth potential for grassroots discoveries. Graney and others (this volume) describe how it is possible to use mixing trends between  $H_2O$  and the more volatile gases to estimate the composition of the gas phase in systems that have undergone boiling or phase separation. This approach might help rank favorability of "boiling" hydrothermal systems on the basis of the type of vapor that they form, although no such effort has been published.

The use of fluid inclusion gas analyses in exploration for other metals and commodities has received less attention, although there are glimmers of hope. For instance, phase separation has been suggested as a general depositional mechanism for base metals (Drummond and Ohmoto, 1985). Haynes and others (1989) have used gas analyses to suggest that this process caused deposition of some Mississippi Valley-type ores, and Landis and Hofstra show in this volume that it could have been important in the mid-continent Mississippi Valley-type ores. Zoning of inclusion gas compositions will probably be useful in exploration for both precious and base metal deposits. The papers by Shepherd and others, Wilkins and Jenatton, Takenouchi, and Letnikov and Narseev illustrate variations of this sort. The first two of these papers show how barren and mineralized veins in the same area can be distinguished on the basis of their composition. Shepherd and others also demonstrate the very important fact that reaction between the vein fluid and wall rock can increase the  $CH_4$  content of the fluid, possibly leading to phase separation and ore deposition. Thus, fluids that would otherwise form barren veins might deposit ore where they intersect rocks that increase the gas content of the fluid. Landis and Hofstra show how an understanding of wall-rock–fluid interaction resulted in a revised genetic model and exploration philosophy for the Coeur d'Alene district.

As geochemical research provides further information on ore-forming processes, and these processes are more completely integrated into exploration models, it is likely that inclusion gas chemistry will be more widely applied to exploration. As this takes place, an emphasis must be placed on better efforts to calibrate results by the use of similar analytical techniques and interlaboratory standards, neither of which are in use at present. The small size of fluid inclusions makes the problem of standardization particularly difficult (Norman and Sawkins, 1987) and almost certainly requires that future calibration efforts use synthetic fluid inclusions (Sterner and Bodnar, 1984) with compositions similar to natural environments. In parallel with these efforts to improve analytical quality, we must also undertake better studies coordinat-

ing optical and chemical study of fluid inclusions to determine the most cost-effective type of fluid inclusion sample and analytical process for regional- and deposit-scale studies. These are not small jobs and there will be some disappointments along the way, but the potential of fluid inclusion analysis in the search for blind ore deposits is sufficiently strong to merit the effort.

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