Fluid inclusion microanalysis: Advances and future challenges

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Introduction

The analysis of fluid inclusion contents is one of the main keys to predictive mineral discovery. For terrain selection it may characterize vital ingredients that lead to the formation of problematical ore types (e.g. the sources of salinity in iron oxide-copper-gold (IOCG) deposits). Within terrains it provides essential constraints for geochemical models of ore deposition in so much that in the absence of such constraints the models have no demonstrated connection to reality. Fluid inclusion analysis has therefore formed a cornerstone of research within the pmd*CRC, particularly through the enabling technologies F3 project: Micrometallogeny of Hydrothermal Fluids. Here we highlight advances in fluid inclusion microanalysis research both within the pmd*CRC and elsewhere, and we discuss some of the challenges that lie ahead in a rapidly developing research field.

Progress within pmd*CRC

Prior to the commencement of the pmd*CRC, Australian researchers led the world in economic geology applications of one relevant microanalytical technology, namely Proton Induced X-ray Emission (PIXE; Heinrich et al., 1992; Heinrich et al., 1999; Ryan et al., 2001; Ryan et al., 1993). Elsewhere, laser ablation inductively coupled mass spectrometry (LAICPMS) techniques have been developed and through the application of an internal standard and the use of a short wavelength laser now allow absolute quantification of single fluid inclusions (Günther et al., 1998; Heinrich et al., 2003).

The major achievements of F3 and other recent work in Australia outside the scope of the CRC have been (a) the development here of complementary LAICPMS methods and the first demonstrations anywhere, of reproducibility of results from these two leading technologies in a variety of datasets; and (b) the application of these datasets in CRC terrain-based projects (Fu et al., 2004; Gillen et al., 2004; Mark et al., 2004; Mustard et al., 2004). A particularly challenging outcome has been the common discovery that ostensibly homogeneous fluid inclusion populations display substantial chemical variations (Figures 1 and 2). While this complicates the application of data in modelling it also offers an unexpected insight into the geochemical processes at the time of fluid entrapment.

Limitations, challenges and opportunities

Some imperfections in the combined technology reproducibility referred to above, combined with outcomes from new PIXE imaging technology, have revealed a number of issues that require modifications to existing experimental and data-reduction procedures (Figure 2). Modified LAICPMS software also needs to be written to replace the current procedures, which are overly labour intensive, prone to human error, and non-conducive to scientific rigour. The number of samples investigated to date is small and it is evident that analytical datasets from
some systems of interest are dominated by fluids that were highly evolved prior to entrapment (i.e. “input fluids” not sampled). This represents a major challenge particularly for geochemical modelling and requires careful examination of the geological context of the fluid inclusion to constrain the suitability of the microanalytical data to the modelling issue being addressed.

Figure 1: The plot of Fe/Ca versus K/Mn illustrates the range in fluid compositions from petrographically similar brine inclusions. Both PIXE and LAICPMS techniques display this variation independently confirming that the wide compositional ranges is a real phenomenon and demonstrating the reproducibility of the techniques.

Figure 2: The plot of K/Ca versus Zn/Pb further illustrates the use of combined PIXE and LAICPMS on fluid inclusion populations. Three different inclusion types have been analysed from the Bismark skarn deposit (Baker and Lang, 2003; Baker et al., 2004) including brine inclusions (halite and sylvite bearing), low salinity vapor-rich inclusions and low to moderate salinity critical inclusions (liquid/vapor ratio approximately equal). PIXE and LAICPMS analyses of the vapor-rich inclusions have reasonably consistent K/Ca and Zn/Pb ratios whereas there are distinct differences in the K/Ca ratios in the brine inclusions. The explanation for this has yet to be fully resolved but may reflect a combination of depth estimate and X-ray absorption issues from PIXE, and/or elemental ablation (e.g. Ca in the liquid versus K in sylvite) and surface contamination issues in LAICPMS. Critical inclusions have similar K/Ca ratios between the two methods, however, Pb is below detection in all PIXE analysis (therefore no PIXE data are shown on the plot for critical inclusions). LAICPMS has lower detection limits for Pb than PIXE and has provided new insights into the Zn/Pb ratios of this key ore stage fluid (Bertelli et al., 2004).
Bertelli et al. (2004) describe the application of fluid inclusion microanalytical data to geochemical modelling. This test case study highlights several important features of the combined microanalysis and modelling approach. Firstly, the techniques were applied to a geologically well understood ore deposit that possessed a well constrained fluid inclusion history (Baker and Lang, 2003; Baker et al., 2004). Secondly, the application of LAICPMS analysis to ore stage fluids enabled accurate estimates on Pb contents of ore stage fluids that had previously been poorly constrained through PIXE (due to high detection limits; Figure 2). Finally, the salinity and P-T conditions of the ore stage fluids were well defined through microthermometry and can be constrained by known thermodynamic datasets (Bertelli et al., this volume). This represents another significant challenge in the interface between fluid inclusion microanalysis and geochemical modeling, because many of the ore systems of interest have fluid inclusion P-T-X histories that are unconstrained by current thermodynamic datasets. An excellent example of this is highlighted by Mustard et al. (2004) at the Osborne deposit that exhibits high pressure, high temperature unmixing between multi-solid brine inclusions and halite-bearing liquid CO2 inclusions.

A major deficiency at the present time is the inability of the existing technologies to determine geologically-relevant concentrations of sulphur, except in extreme circumstances such as in examples of copper and sulphur-rich magmatic vapour inclusions. This needs to be addressed though a combination of technique development and the establishment of routines to constrain sulphur abundance and speciation from independent measurements. While the determination of halogen ratios may provide the solution to several major ore genetic problems, there is currently no method for halogen ratio (e.g., Br/Cl) determination by LAICPMS in Australia, whereas PIXE has inherent limitations. Evaluation of LAICPMS data from brine inclusions at Cannington suggest that halogen analysis is achievable, provided that appropriate standards are obtained and specialized methodologies applied to generate consistent data (Figure 3). Heinrich et al. (2003) have also shown that such analysis is achievable by LAICPMS techniques.

While work is evidently needed to enhance the value of our existing data and methodologies it is equally clear that there are exciting new possibilities ahead for the next few years. These include integration of single inclusion halogen data from modified LAICMPS procedures with halogen and noble gas data from in vacuo extraction-MS analysis of irradiated fluid inclusion populations, dating of fluid inclusions using the $^{40}\text{Ar}/^{39}\text{Ar}$ method, determination of Pb isotope ratios, and the application of synchrotron techniques in areas such as the characterization of ore metal speciation in natural and synthetic fluid inclusions.
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References


Mark, G., Baker, T., Williams, P.J., Ryan, C.G. and Mernagh, T.P., 2004. The geochemistry of magmatic fluids, Cloncurry district, Australia: relations to IOCG systems. This volume.

