Microanalysis of fluid inclusions in crustal hydrothermal systems using laser ablation methods

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Laser-ablation microanalysis of fluid inclusions in crustal hydrothermal systems

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ABSTRACT

Quantitative analysis of microscopic fluid inclusions has greatly improved our understanding of fluid–rock interaction and ore deposit formation. Spatially resolved analyses track the chemical evolution of distinct fluids, within texturally complex veins and along extensive fluid pathways. Chemical (e.g., Br/Cl) and isotopic tracers (e.g., Pb) identify sources of fluids and timescales of transient fluid flow. Selectively metal-enriched fluids, compared to normal rock-buffered fluids, control the formation of major magmatic-hydrothermal and sediment-hosted ore deposits. Besides chloride as dominant anion of crustal fluids, sulfur decisively influences the partitioning, transport and precipitation of ore metals by single-phase and two-phase fluids of sedimentary, metamorphic and magmatic origin.

KEYWORDS: Fluid inclusions, metamorphic fluids, ore fluids, fluid-rock equilibria, ore metals, sulfur

INTRODUCTION

Aqueous fluids play a key role in mass transfer processes in the Earth, including the generation of magmas in the Earth’s mantle above subduction zones, the release of fluids from crystallizing magmas, the production and migration of fluids during mountain building, the formation of hydrothermal metal ore deposits and the interaction of fluids released from the deep Earth with the hydrosphere and atmosphere. As only the topmost part of the Earth’s crust is accessible to direct sampling of fluids, e.g., discharge from geothermal systems and deep drillholes, most of the information we have about the compositions of deep Earth fluids comes from studies of paleofluids that are preserved as fluid inclusions in minerals.

Chemical analysis of the solute content (dissolved cations, anions and volatiles) of fluid inclusions historically involved bulk extraction of numerous fluid inclusions followed by analysis of leachates by ion chromatography and conventional solution chemistry. Such

27 averaged data from potentially different inclusion generations in one sample provide little
28 information about the time–space evolution of fluid–rock systems. Therefore, methods were
29 developed for performing quantitative multi-element analysis of single fluid inclusions in
30 textural context. Laser-ablation inductively-coupled plasma-mass spectrometry (LA-ICP-MS)
31 has become the most widely used method for multi-element analysis, because of its
32 efficiency, its high sensitivity and the possibilities for multi-element quantification (Heinrich
33 et al. 2003; Pettke et al. 2012 and references therein).

34

35 **FLUID INCLUSION MICROANALYSIS BY LA-ICP-MS**

36 Fluid inclusion microanalysis using LA-ICP-MS has developed from early work that targeted
37 ore metal concentrations in hydrothermal mineral deposits (Audétat et al. 1998; Ulrich et al.
38 1999) to multi-elemental analysis of a wide range of crustal fluids that include igneous,
39 metamorphic and sedimentary environments (Scambelluri et al. 2004; Samson et al. 2008;
40 Wilkinson et al. 2009; Kouzmanov and Pokrovski 2012; Marsala et al. 2013; Sirbescu et al.
41 2013). LA-ICP-MS analysis is comparatively fast and inexpensive, once dedicated
42 instrumentation is established, thus allowing compositional reconstruction of the time
43 sequence of fluid inclusion assemblages from texturally well-constrained samples (growth-
44 zoned crystals, sets of crosscutting veins and fractures). Highly sensitive mass spectrometers
45 now enable multi-element analysis of moderate sized fluid inclusions (20 to 50 μm ,
46 depending on elemental concentration and salinity), comprising major rock-forming elements,
47 ore metals, S, B and the halogens (Seo et al. 2011). Controlled ablation of diverse host
48 minerals including quartz or infrared-light transparent pyrite requires short UV wavelengths,
49 and 193 nm Excimer lasers are used in most successful fluid inclusion labs today
50 (Kouzmanov and Pokrovski 2012; Pettke et al. 2012). Recent progress has included the
51 analysis of anions such as S, Cl and Br (Seo et al. 2011; Hammerli et al. 2013), and precise
52 quantification of Pb and Sr isotope compositions from single fluid inclusions using multi-

53 collector ICP-MS (Pettke et al. 2010, 2012). The combination of different mass spectrometers
54 opens up exciting possibilities for simultaneously tracing the source of metals and the source
55 of fluid salinity in crustal fluid systems and to quantitatively address processes of fluid-rock
56 reaction.

57 Absolute quantification of elemental concentrations in fluid inclusions is based on
58 models that use Na concentration as the internal standard, which is obtained from the
59 interpretation of fluid inclusion freezing experiments in terms of binary and ternary water-salt
60 systems. The accuracy of correction methods has been tested against synthetic fluid inclusions
61 (Allan et al. 2005), but the approach requires correction for more complex natural geofluids
62 containing high concentrations of dissolved gases and salts other than NaCl.

63 Despite analytical progress, the short and highly transient signals from fluid inclusions
64 still pose major challenges for single-collector mass-spectrometric analysis and data
65 quantification. Analysis of numerous inclusions from a petrographically well-defined fluid
66 inclusion assemblage is essential to average signal fluctuations, to assess the significance of
67 element concentrations for each element, and to estimate the real chemical variability of each
68 fluid represented by one fluid inclusion assemblage (Heinrich et al. 2003). Quadrupole and
69 sector-field ICP-MS instruments (Wälle and Heinrich 2014) measure different masses
70 (elements) sequentially by rapid scanning, requiring a trade-off between accurate
71 characterization of transient signals (detection limit, representative quantification) and the
72 number of recorded elements (typically 10-25). Sequential measurement of multiple elements
73 in a short transient signal from a fluid inclusion can lead to non-representative sampling
74 (Pettke et al. 2012), which is the main cause of random errors of 10-30 % when analyzing
75 multiple inclusions in a fluid inclusion assemblage with consistent microthermometric
76 properties (Heinrich et al. 2003). Non-representative sampling of transient signals may even
77 lead to a systematic bias in concentration results (Rauchenstein-Martinek et al. 2014). Recent
78 improvements in time-of-flight (TOF) ICP-MS instrumentation may overcome this limitation,

because this detection method simultaneously records the entire mass spectrum with a repeat rate that is at least 1000 times faster than in typical quadrupole ICP-MS analysis (FIG. 1). This novel technique has great potential for the next level of fluid inclusion microanalysis (Harlaux et al. 2015), particularly if applied to small inclusions in combination with laser sampling cells with shorter wash-out times.

CHEMISTRY OF METAMORPHIC FLUIDS

The bulk compositions of metamorphic fluids in orogenic belts and subduction zones have been studied by conventional microthermometry and Raman spectroscopy, but few studies have used LA-ICP-MS analysis to determine the elemental compositions of metamorphic fluids (Scambelluri et al. 2004; Marsala et al. 2013; Rauchenstein-Martinek et al. 2014). Classical fluid inclusion studies demonstrate that the fluid composition changes in a systematic way along a prograde Barrovian sequence from subgreenschist- to amphibolite-facies, with consecutive fluid zones characterized by predominance of heavier hydrocarbons, methane, water and carbon dioxide. The fluid inclusion data support the generally accepted model of progressive devolatilization driven by increasing temperature and pressure along a prograde metamorphic sequence.

Recent studies from the Alpine and Hercynian orogenic belts (Marsala et al. 2013; Rauchenstein-Martinek et al. 2014) showed that in rock-buffered low- to moderate-salinity (1 to 10 wt.% NaCl equivalent) aqueous to aqueous-carbonic fluids, Na, K and Ca are the dominant cations, whereas the concentrations of other alkali and alkaline-earth metals (Li, Rb, Cs, Mg, Sr and Ba) are much lower, typically on the order of a few ppm. The concentrations of the alkali and alkaline-earth metals correlate with bulk salinity, consistent with the general trend of rock-buffering in a wide range of geological environments (Yardley 2005). B, As and Sb are characteristic elements of metamorphic fluids (Scambelluri et al. 2004; Marsala et al. 2013). The concentrations of boron vary in a rather narrow range between 200 and 1500 ppm

(FIG. 2), suggesting that B is rock-buffered by minerals such as tourmaline or B-bearing muscovite. The concentrations of the base metals Cu, Zn and Pb are on the order of 1-10 ppm, which contrasts with the much higher concentrations (several 100 to 1000 ppm) in basin- and basement-hosted fluid systems that are linked to sediment-hosted Pb-Zn and Cu ore deposits (Wilkinson et al. 2009). Typical low-salinity metamorphic fluids are therefore unlikely candidates for forming major base metal ore deposits.

Sulfur concentrations increase systematically along a prograde sequence through the Central Alps, from 100-300 ppm in veins hosted by subgreenschist- and lower greenschist-grade rocks, up to 3500 ppm in veins in amphibolite-grade rocks. This increase reflects progressive desulfidation of the host rocks along with prograde dehydration and decarbonation, producing S-rich aqueous-carbonic fluids at amphibolite-grade conditions (Rauchenstein-Martinek et al. 2014). Thermodynamic modeling of fluid–mineral equilibria demonstrates that the measured S concentrations are in agreement with saturation of pyrite (FIG. 3A). The measured Au concentrations are very low, on the order of 3 to 30 ppb, and are one to three orders of magnitude lower than the Au solubility calculated assuming saturation of metallic Au (FIG. 3B). These results suggest that metamorphic fluids produced by devolatilization along a prograde sequence are normally undersaturated in Au, and their Au-transporting potential is not limited by solubility but rather by Au availability in the source rocks. Typical metamorphic fluids produced from devolatilization of metasediments, metagranitoids and mafic schists have therefore only moderate potential for forming major orogenic gold deposits, unless extreme degrees of fluid focusing and highly efficient precipitation are invoked. World-class orogenic gold deposits more likely form when metamorphic fluids are produced from specialized source rocks that are pre-enriched in gold, or when metamorphic fluid systems experience an input of Au-rich magmatic fluids. This conclusion is consistent with the first experimental study that combined synthetic fluid

inclusions with LA-ICP-MS microanalysis, to demonstrate very high Au solubility at high-temperature metamorphic conditions (Loucks and Mavrogenes 1999).

MAGMATIC-HYDROTHERMAL FLUIDS

Magmatic-hydrothermal ore fluids were the first target of research after successful development of LA-ICP-MS for microanalysis of fluid inclusions. LA-ICP-MS analysis has been particularly influential in elucidating magmatic-hydrothermal processes because of the textural complexities of natural samples, which commonly record a time sequence of multiple fluid pulses with variable fluid compositions and fluid phase states. In particular, the evolution of single-phase ‘supercritical’ fluids in magma chambers separating into two phases of coexisting saline liquid and lower-density vapor on ascent to hydrothermal ore deposits can lead to large variations in elemental composition of magmatic fluids. Careful petrography of successively trapped inclusion assemblages followed by LA-ICP-MS analysis identified fluid mixing as a major factor driving ore mineral precipitation in cassiterite-tourmaline veins (Audétat et al. 1998). A rapid decrease in Cu concentrations in brine inclusions has shown that Cu is deposited from vapor-dominated two-phase fluids in porphyry Cu-Au deposits over a small temperature interval. In combination with cathodoluminescence imaging of vein textures, similar results from several porphyry deposits showed that economic mineralization occurred at rather low temperature, after the precipitation of quartz in the prominent stockwork veins in such deposits.

The discovery of high concentrations of selected elements in magmatic-hydrothermal vapor inclusions (e.g., Cu, Au, As, B; Audétat et al. 1998) triggered experimental research into metal solubility in low-density fluids at high temperature (Migdisov et al. 1999; Pokrovski et al. 2008; Zajacz et al. 2010). It also motivated instrumental improvements for the analysis of anions by LA-ICP-MS (Seo et al. 2011). The detection of high S concentrations in magmatic vapor inclusions support the interpretation that sulfide is the

dominant complexing agent driving the selective transfer of Au from saline brine to low-salinity vapor, but it also identified S as the chemical driver for selective ingress of Cu into S-rich vapor inclusions after fluid entrapment in quartz (Lerchbaumer and Audétat 2012).

Physical separation of vapor from brine in the proximal magmatic-hydrothermal domain of miarolitic cavities and porphyry deposits leads to a chemical divide between different evolution paths taken by fluids during cooling from magmatic to normal upper-crustal temperatures. Magmatic vapor expansion leads to wholesale co-precipitation of metals in high-grade porphyry-Cu-Mo-Au deposits, probably accompanied by saturation of solid halite. Alternatively, the vapor phase can cool at depth and contract in the single-phase stability field towards a S-, As- and Au-enriched, but Fe- and base-metal depleted low-salinity aqueous liquid (Heinrich et al. 2004). Such fluids are the optimal transport medium for Au from a hydrous magma to high-grade epithermal ore deposits, where Au is precipitated either in reduced sedimentary host rocks (Carlin-type deposits) or in high- to intermediate-sulfidation precious-metal veins (Márquez-Zavalía and Heinrich 2016; FIG. 4). The Fe-rich magmatic-hydrothermal brine, on the other hand, becomes progressively depleted in sulfide by precipitation of pyrite during cooling, leading to residual brines with anomalously high Pb, Zn and possibly Cu concentrations (FIG. 5). Such brines may be mobilized by later fluid convection, e.g., if evaporitic brines of sufficient density displace and mix with deep-seated post-magmatic brine, potentially generating sulfide-depleted ore fluids for efficient formation of sediment-hosted base metal deposits.

BASIN-BASEMENT INTERACTION IN ORE FORMATION

Chloride-rich metal-bearing aqueous fluids are responsible for the formation of a wide range of hydrothermal ore deposit types, including sediment-hosted low-temperature Pb-Zn, Cu and U deposits (Wilkinson et al. 2009; Richard et al. 2012). Unconformities between sedimentary basins and the underlying basement and crustal-scale fault zones extending into the basement

182 exert first-order structural controls on mineralization. They are the locations where deep-
183 sourced S-depleted and metal-rich saline fluids derived from the basement are injected into
184 the sedimentary units. Mixing of these metal-loaded fluids with formation waters that are rich
185 in reduced S then drives efficient ore precipitation (Wilkinson et al. 2009). Combined LA-
186 ICP-MS analysis of metal concentrations and halogen ratios (Br/Cl) in fluid inclusions
187 provides new insight into the dynamics of fluid mixing processes, by revealing evidence for
188 mixing at the scale of individual quartz growth zones from unconformity-related Pb-Zn veins.
189 Accounting for fault hydrology and likely timescales required for fluid mixing, this feature
190 can only be explained by fast upward flow of chemically distinct fluids drained from different
191 levels of the crystalline basement (Bons et al. 2014). This process model provides a distinct
192 alternative to classical scenarios where interaction of different fluid systems takes place at the
193 basement-cover interface.

194 Further insight into the ultimate source of ore fluids in sediment-hosted Pb-Zn, Cu and
195 U deposits can be gained from comparing their ore metal concentrations with those of typical
196 rock-buffered crustal fluids (FIG. 5). The concentrations of Pb and Zn in rock-buffered fluids
197 from geothermal systems and sedimentary formations define a broad trend that correlates
198 positively with temperature and fluid salinity (Yardley 2005). By contrast, the ore stage fluids
199 of unconformity related deposits plot distinctively above this trend, and their metal
200 concentrations have been described as anomalously high (Wilkinson et al. 2009). These data
201 include the exceptionally high Pb (and reconstructed Zn) concentrations of sphalerite-hosted
202 fluid inclusions from the Pb-Zn deposits of the Irish Midlands Basin (Wilkinson et al. 2009).
203 Even more extreme base metal concentrations have been found in fluid inclusions from
204 unconformity-related U deposits (Richard et al. 2012), probably reflecting their highly
205 oxidized and low pH character sustaining high base metal solubility. The most metal-poor
206 fluids from subeconomic basement-hosted Pb-Zn veins in the Schwarzwald area, with low
207 Br/Cl ratios fingerprinting them as sedimentary formation waters derived from halite

dissolution, mostly plot on the rock-buffered trend (FIG. 5). By contrast, the most metal-rich fluids with the highest Br/Cl ratios are above the rock-buffered trend. Despite the large and systematic variation in absolute base-metal concentrations and in Br/Cl, the ratio of Pb/Zn of fluids from a wide range of geological environments are remarkably constant (FIG. 6). This suggests that base metal ratios and their concentrations are largely solubility-controlled through temperature-dependent equilibria between fluid and sulfide minerals (Yardley 2005), but with different factors controlling redox conditions and S speciation. Therefore, the metal-transporting ore fluids of sediment-hosted Pb-Zn, Cu and U deposits are only anomalous for the inferred temperatures of fluid entrapment and ore deposition (FIG. 5). Their metal concentrations and Pb/Zn ratios are consistent with rock-buffered fluids derived from reservoirs at greater depths and higher temperatures. Tectonically controlled, highly transient episodes of focused fluid flow are able to transfer large volumes of such hot metal-rich fluids from deep reservoirs to the basement-cover interface and drive the formation of major unconformity-related ore deposits.

FUTURE WORK

Despite major progress in our ability to analyze fluid inclusions with LA-ICP-MS during the past decade, there still remains much work to be done to fill the large gaps in our knowledge of the composition of paleofluids in a wide range of geological environments. A major challenge is the analysis of small fluid inclusions (below 10 μm) with low total dissolved solute content, which are ubiquitous in many igneous, metamorphic and sedimentary rocks and important types of world-class hydrothermal ore deposits. More sensitive ICP-MS instruments that facilitate better time resolution and simultaneous analysis of many elements (Harlaux et al. 2015) have great potential to overcome the current analytical limitations. Then it may become possible to obtain multi-element fluid inclusion data from eclogite- and

granulite-facies metamorphic rocks, as well as from poorly understood but globally important ore deposits such as iron-oxide–copper–gold deposits and Carlin-type gold deposits.

Another major challenge concerns the reliable and accurate quantification of LA-ICP-MS fluid inclusion data. Progress in quantification of complex geofluids requires a combination of LA-ICP-MS analysis with additional microthermometric, Raman (Sirbescu et al. 2013) or FTIR spectroscopic measurements, and integration with better thermodynamic models for interpreting microthermometric data (Leisen et al. 2012) based on accurate experimental studies of phase equilibria.

Finally, trapping synthetic inclusions of fluids and melts during experiments at high pressures and temperatures offers new and still expanding methods in experimental geochemistry. With different inert trapping phases including quartz, corundum or diamond, studies of fluid–melt partitioning and mineral solubility (e.g., Loucks and Mavrogenes 1999; Zajacz et al. 2010; Zhang et al. 2012) can be extended from crustal conditions to those of the upper mantle (Spandler et al. 2007). LA-ICP-MS microanalysis thus provides access to understanding the trace element geochemistry of unquenchable phases at extreme conditions of the Earth's interior.

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FIGURE CAPTIONS

FIGURE FOR ICON ON THE TITLE PAGE An aqueous fluid inclusion from an orogenic gold deposit observed in the crosshairs of the GeoLas 193 nm laser-ablation system at the University of Helsinki.

FIGURE 1 Time-resolved transient LA-ICP-MS signals of a single fluid inclusion, comparing (A) selected data collected simultaneously for all masses between ^{23}Na and ^{238}U using the new Time-of-Flight ICP-MS of TOFWERK GmbH (Thun) with (B) a synthetic signal simulating the acquisition of all 24 elements detected in this fluid inclusion by TOF, but using the typical time resolution of sequential scanning by Quadrupole ICP-MS. To achieve quantifiable signals by Laser-Ablation Quadrupole ICP-MS, inclusion analysts are forced to restrict acquisition to fewer elements, typically 6 to 12 elements only.

FIGURE 2 Range of B concentrations in different types of crustal fluids, including granite-hosted hydrothermal veins and pegmatites, porphyry-copper deposits, metamorphic fluids and unconformity-related Pb-Zn, Cu and U deposits. References of data sources are available online at elementsmagazine.org/supplements.

FIGURE 3 Comparison between calculated and measured concentrations of (A) S and (B) Au in rock-buffered metamorphic fluid inclusions in barren fissure veins from the Central Alpine metamorphic dome. Analyzed S concentrations are consistent with the predicted increase with temperature, assuming iron sulfide excess in the local host rock. Analyzed Au concentrations, however, are orders of magnitude lower than the predicted solubility of the metal, showing that these prograde metamorphic fluids

are highly Au-undersaturated (Rauchenstein-Martinek et al. 2014). The difference between the rock-buffered solubility curves for greenschist- and amphibolite-facies fluids is the result of different whole-rock compositions for both metamorphic units.

FIGURE 4 High Au concentrations ranging from 10 to 0.1 ppm can be sustained in low-salinity (2-4 wt.% NaCl equivalent) aqueous liquids of magmatic origin down to epithermal temperatures of about 250°C, provided that high sulfide concentrations (1000-10000 ppm) act as the complexing agent for Au. Most fluid inclusions with reliably detected Au from the Alto de la Blenda vein deposit in the Farallón Negro Volcanic Complex show an excess of S relative to Fe (Márquez-Zavalía and Heinrich 2016), as predicted from thermodynamic modeling of Au solubility in low-salinity aqueous fluids derived from magmatic vapor. Complementary Fe, Pb and Zn-enriched brines, likely depleted in sulfide, are preserved as residual fluids in porphyry copper deposits, including the Bajo de la Alumbrera deposit that occurs nearby in the same volcanic complex, as shown in FIG. 5.

FIGURE 5 Plots of the (A) $m(\text{Zn})/m(\text{Cl})$ and (B) $m(\text{Pb})/m(\text{Cl})$ ratios as a function of temperature for different types of crustal fluids, including granite-hosted hydrothermal veins and pegmatites, porphyry-copper deposits, metamorphic fluids and unconformity-related Pb-Zn, Cu and U deposits. Data from various sources are compared to the temperature trend (grey shaded field) of Yardley (2005). References of data sources are available online at elementsmagazine.org/supplements.

FIGURE 6 Correlation plot of the Pb and Zn concentrations for different types of crustal fluids. All data fall approximately on a linear trend of constant Pb/Zn ratio, suggesting that metal concentrations are largely controlled by the solubility of accessory galena and

402 sphalerite in the host rocks. References of data sources are available online at
403 elementsmagazine.org/supplements.
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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Magmatic Fluids

- ◆ Bingham Canyon Cu-Au stage
- ◆ Bingham Canyon late Cu-Fe stage
- ◇ Bingham Canyon Cu-Au stage
- ◇ Bingham Canyon Mo stage
- △ El Teniente Porphyry Cu-Mo
- ★ Bajo de Alumbrera Porphyry Cu-Au
- ▽ Mole Granite

Basement-basin interaction fluids

- Athabasca basin U deposits
- Schwarzwald Pb-Zn vein
- Sailauf Fe-Mn veins
- ▲ Irish Midlands Pb-Zn deposits (quartz)
- △ Irish Midlands Pb-Zn deposits (sphalerite) (Zn concentration extrapolated)

Figure 6