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Journal Article

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Publication date:

2000-12

Permanent link:

<https://doi.org/10.3929/ethz-b-000118850>

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Originally published in:

Economic Geology 95(8), <https://doi.org/10.2113/gsecongeo.95.8.1563>

Causes for large-scale metal zonation around mineralized plutons: Fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia.

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Abstract

Detailed reconstruction of the fluid evolution in several ore deposits associated with the Sn-, W- and base metal mineralized Mole Granite shows that multiple factors contributed to the zonal metal distribution around this intrusion. Information about the mechanism of ore formation was obtained from field relationships, detailed petrographic studies, and LA-ICP-MS microanalysis of single fluid inclusions. Pre-mineralization fluid inclusions in Sn-deposits are characterized by high Sn/W-ratios, whereas early fluid inclusions from W-deposits contain higher W-concentrations and comparatively low Sn/W-ratios. This indicates that the metal ratio in these deposits already was pre-defined by the composition of the magmatic input fluid. However, in both types of deposits the input fluid actually contained much higher concentrations of base metals (Pb, Zn, Cu etc.) than Sn and W, demonstrating that metal precipitation was highly selective. The metal zonation around the Mole Granite therefore reflects both a compositional variation of the source fluid, as well as sequential metal precipitation from it.

An additional process contributing to metal fractionation occurred by phase separation of the hydrothermal fluid into saline brine and low-density vapor, whereby Cu, B, Li, As ($\pm$ S, Ag, La) preferentially partitioned into the vapor phase. Analyses on six assemblages of unambiguously coexisting vapor and brine inclusions allowed direct determination of vapor/brine distribution coefficients for 24 elements.

Introduction

Mineralized granites commonly show a zonal distribution of the related ore deposits, with Sn, W, Mo $\pm$ As-dominated deposits occurring proximal to the intrusion, and Cu, Zn, Pb, Sb $\pm$ Ag-dominated deposits occurring distally (Lehmann, 1990; Pirajno, 1992). There are two basic principles that may lead to such metal zonation: (1) *sequential* metal precipitation from one parental fluid (most likely due to progressive cooling and/or fluid mixing during outward migration; Heinrich and Ryan, 1992), or (2) *bulk* precipitation from compositionally different source fluids. In the latter case, compositional differences may result either from magmatic fractionation of one parental magma (Cline and Bodnar, 1991; Candela and Piccoli, 1995), or from an origin from diverse source magmas (Burnham and

Ohmoto, 1980; Candela, 1992). A distinction between processes (1) and (2) is only possible if we know how the melts and exsolving fluids evolved geochemically through time, and how this is related to ore deposition. The Sn-, W- and base metal mineralized Mole Granite is one of the best examples to study this general question, as it displays a well-developed metal zonation across more than 1200 deposits (Eadington, 1977, 1983; Heinrich and Ryan, 1992; Kleeman et al., 1997; Audétat, 1999; Henley et al., 1999).

Methods

The magmatic-hydrothermal evolution of the Mole Granite was reconstructed on the basis of a large number of field relationships, mineralogical

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constraints, and detailed fluid inclusion studies on single quartz crystals. Fluid inclusions occurring along former crystal surfaces were classified as "primary inclusions", whereas inclusions trapped within cracks were classified as "pseudosecondary" or "secondary", depending on whether the cracks originate from an earlier or the present crystal surface (Roedder, 1984). Euhedral quartz crystals in mineralized vein systems of the Mole Granite commonly record a complex history of hydrothermal fluid evolution, which is expressed in strong color zonation, the entrapment of different generations of fluids, and the precipitation of other minerals onto the quartz surface. Thick-sections prepared from such crystals were studied with a normal petrographic microscope. Special attention was paid to primary fluid inclusions, crosscutting relationships, and pseudosecondary trails with defined starting points, as they allow the reconstruction of chronological entrapment sequences. On the basis of microthermometric study and LA-ICP-MS analysis of different generations of fluid inclusions it thus was possible to reconstruct the evolution of pressure, temperature and fluid composition in several vein systems.

Microthermometry

Microthermometric measurements were made on a Linkam stage THMSG 600, except for rare measurements above 600 °C, which were performed on a high-temperature Linkam stage TS 1500. The THMSG 600 stage was calibrated to an accuracy of ± 0.2 °C in the range -60 °C to +60 °C, and to ± 2 °C at temperatures outside this range. The α - β transition of quartz at 573 °C was used as a calibration reference at high temperatures. The apparent salinity of the inclusions (expressed in wt% NaCl_{equiv}) was determined from the final melting temperature of ice or halite ($T_{m_{ice}}$ and $T_{m_{halite}}$, respectively), using equations published in Bodnar and Vityk (1994). Clathrates were observed in some low-density fluid inclusions in topaz, where they do not seem to coexist with liquid CO₂ because fluid salinities calculated on the basis of clathrate melting temperatures are higher than those calculated from ice melting temperatures (Diamond, 1992).

LA-ICP-MS analysis of fluid inclusions

Laser-ablation inductively-coupled-plasma mass-spectrometry was the key analytical technique used for this study, with approximately 500 analyses performed in total. This technique allows individual inclusions to be ablated directly through the host

mineral, which in most cases was either quartz or topaz. Our LA-ICP-MS system consists of an Elan 6000 ICP-MS instrument (Perkin Elmer, Canada) combined with a 193 nm excimer laser (Compex 110 I, ArF, Lambda Physik, Germany; Günther et al., 1997). The use of a short transportation tube (30 cm), and a Plexiglas sample chamber with a total volume of less than 1 cm³ leads to sharp signals with a high signal-to-background ratio. Detection limits were lowered by using both Ar and He as carrier gas instead of Ar alone (Günther and Heinrich, 1999).

Special homogenization optics lead to a homogeneous energy distribution across the laser beam, which is necessary to reduce fractionation effects during ablation, and results in perfect flat-bottomed holes. The design as an optical imaging system permits the use of different pit sizes at a constant energy-density on the sample, by adjusting an aperture in the laser beam path. We used pits of 4, 10, 20, 40, 60, 80 and 100 μ m in diameter. The switch between different pit sizes can be made during the measurement, which, together with the possibility to observe the sample during ablation, is essential for successful fluid inclusion analysis (Günther et al., 1998). Fluid inclusions hosted by quartz tend to decrepitate if one tries to ablate them directly with a large beam size, resulting in partial loss of daughter minerals, and therefore in poorly reproducible results. This can be avoided by opening the inclusions in several steps, starting with a pit size much smaller than the size of the inclusion. As soon as the inclusion is breached and the first signal appears on the screen, the beam size is increased in several steps until the whole of the inclusions is ablated (Fig. 1). The risk of losing daughter minerals during ablation can be reduced even further by using a relatively high laser pulse frequency (15-30 Hz), which also improves the detection limits by a factor of 2-3 relative to analyses performed with 10 Hz.

The resulting transient signals are integrated and compared with signal intensities from reference materials (Nist 610 and Nist 612 standard glasses, or standard solutions), allowing calculation of *relative* element abundances in the inclusion:

$$\frac{c_{x,incl}}{c_{y,incl}} = \frac{c_{x,std} \cdot I_{y,std} \cdot I_{x,incl}}{c_{y,std} \cdot I_{x,std} \cdot I_{y,incl}} \quad (1)$$

where c = concentration, and I = intensity (in cps) of the elements x and y in the standard (std) and inclusion (incl), respectively. To transform these relative abundances into *absolute* concentrations, the absolute concentration of one element has to be determined by an independent method. Usually, we took the microthermometrically determined NaCl_{equiv}-value,

and corrected it for other major cations (X) present in the inclusion, by using the equation of Heinrich et al. (1992):

$$\text{NaCl} = \text{NaCl}_{\text{equiv}} - 0.5 \cdot \sum \text{XCl}_n \quad (2)$$

This empirical formula is based on the observation that isotherms in the ternary systems H_2O - NaCl - KCl and H_2O - NaCl - CaCl_2 are approximately perpendicular to the H_2O - NaCl -join, implying that the other salts contribute by about 50% of their concentration to the true NaCl value. This seems to be valid also for the system H_2O - NaCl - FeCl_2 (Chou and Phan, 1985, 1986). Transformation of the elemental concentration ratios into chloride salt ratios

$$\frac{\text{X}}{\text{Na}} \cdot k_j = \frac{\text{XCl}_n}{\text{NaCl}}, \text{ where}$$

$$k_j = \frac{0.3935 \cdot (\text{M}_x + n \cdot \text{M}_{\text{Cl}})}{\text{M}_x} \quad (3)$$

(M = molar weight) allows equation (2) to be expressed as:

$$\text{NaCl} = \text{NaCl}_{\text{equiv}} - 0.5 \cdot \left[\text{NaCl} \cdot \sum \left(\frac{\text{X}}{\text{Na}} \cdot k_j \right) \right] \quad (4)$$

which can be solved for the true NaCl concentration:

$$\text{NaCl} = \frac{\text{NaCl}_{\text{equiv}}}{\left[1 + 0.5 \cdot \sum \left(\frac{\text{X}}{\text{Na}} \cdot k_j \right) \right]} \quad (5)$$

Figure 1. Typical LA-ICP-MS signal of a single fluid inclusion (40 μm in diameter) ablated through quartz. To reduce the risk of uncontrolled decrepitation and associated loss of daughter minerals we opened the inclusion with a small beam diameter, which then was increased in several steps until the whole of the inclusion was removed. The resulting signal was integrated from 35 s to 95 s.

Calculation of absolute element concentrations within a fluid inclusion therefore requires the following procedure:

- 1) Estimation of the equivalent salinity ($\text{NaCl}_{\text{equiv}}$) in the inclusion by microthermometry.
- 2) Analysis of the inclusion by LA-ICP-MS to calculate *relative* element abundances in the inclusion (equation 1).
- 3) Correction of the $\text{NaCl}_{\text{equiv}}$ -value on the basis of the relative element abundances (equation 5)
- 4) Calculation of the absolute concentration of Na in the inclusion from the corrected $\text{NaCl}_{\text{equiv}}$ value.
- 5) Transformation of the relative element abundances into absolute concentrations, based on Na as internal standard.

The main source of (potentially systematic) uncertainty in this procedure is introduced by the correction formula (equation 2), because it is not known whether the effect of several cations is additive, nor whether the phase diagram geometry of other salt systems is similar to those including K, Ca and Fe. Furthermore, it often is difficult to decide which elements should be considered for correction, as only dissolved components will have an effect on final ice-melting and halite-melting temperatures (e.g., Fe bound in a hematite daughter crystal does not affect the ice melting temperature).

In fluid inclusions dominated by cations other than Na (which is not often the case) the overall uncertainty associated with absolute element

concentrations is estimated to be 50% at most. This may appear very high at first glance, but it is acceptable because (i) elemental abundances in natural fluids commonly vary over several orders of magnitude, hence are easily resolved, and (ii) measured elemental ratios are accurate within much better analytical uncertainty (~20% RSD). Finally, the concentration of many elements reported in this study has not been known even at the level of orders of magnitude.

The whole procedure of LA-ICP-MS analysis and internal standardization was tested successfully on a set of synthetic fluid inclusions containing 7.9 wt% Na, 2.6 wt% K, 14.5 wt% Cl, and 200 ppm of each of Cs, Rb, Sr, Tl and Zn (Günther et al., 1998; Frischknecht 1999). Absolute element concentrations calculated on the basis of a K-corrected $\text{NaCl}_{\text{equiv}}$ -value perfectly match the concentrations of the starting solution (<1% deviation), whereas without correction they would be 12% too high. Other evidence for the validity of the correction formula was found in the freezing/melting-behavior of standard solutions immersed in paraffin oil (Audétat, 1999). Final ice melting in a solution with 8.0 wt% KCl, 4.4 wt% NaCl and 3.6 wt% BaCl_2 occurred at -8.2 °C, corresponding to an equivalent salinity of 12.1 wt% $\text{NaCl}_{\text{equiv}}$. If Na were calculated directly from this value, the result would be wrong by a factor of 2.75 (!). However, by applying the correction formula a value of 5.2 wt% NaCl results, which is only 18% higher than the true value.

Theoretically, one could base the internal standardization also on Cl instead of Na, which would be associated with exactly the same amount of uncertainty as the approach via Na. However, because our analytical system is much more sensitive to Na than to Cl we always used Na as internal standard. Cl was measured mainly for charge balance calculations, which depend only on *relative* element concentrations (i.e., are independent of the correction formula as long as the same internal standard is used for all elements). Most charge balances calculated from the data in Table 1 show an excess of cations, implying that Cl was not the only anion present in the solution. This is particularly likely for vapor inclusions, which seem to contain about twice as much sulfur as chlorine (Table 1). In the case of strongly anion-deficient brine inclusion analyses, F- and possibly HCO_3^- are potential candidates, but an unknown analytical problem with Cl cannot be excluded reliably at this stage.

Distribution of ore deposits associated with the Mole Granite

Of the more than 1200 ore deposits recorded in the Mole Granite district (Henley et al., 1999), most were mined either for Sn or W+Bi, whereas a smaller number was mined for Cu, Pb, Zn, As and Ag (Fig. 2). Except for some large, mineralized fault systems, all these deposits are confined to within a 100-200 m vertical distance from the upper granite margin (Lonergan, 1971; Kleeman et al., 1997). More deeply eroded parts of the Mole Granite (e.g., the areas N and NW of the large sedimentary roof pendant) are not mineralized. Ore deposits within the granite comprise mineralized quartz veins, and disseminations within massive quartz±topaz greisens ("silexites"; Eadington and Nashar, 1978). Ore deposits outside the granite include pegmatites, sheeted veins (above ridges or cupolas in the roof), and mineralized faults and shear zones.

There is a prominent zonation from Sn-dominated deposits (± B, Cu, Pb, Zn) in the granite interior, to W-dominated deposits (± F, Be, Bi, As, Mo) at the granite margin, and base metal deposits (As, Pb, Zn, Cu, Sb, Ag) in the surrounding sediments (Fig. 2; see also Henley et al., 1999). Well documented examples of multistage deposits ("telescoping") are rare, and their interpretation complicated by the presence of two varieties of wolframite. Nevertheless, a general sequence from high-temperature Fe-rich wolframite (± native bismuth, arsenopyrite, beryl) to later cassiterite (± chalcopyrite, tourmaline, galena, sphalerite and low-temperature Mn-rich wolframite) can be recognized in some deposits (e.g. *Taronga*, *Paradise Lode* and *Butler Mine*).

The Mole Granite hosts some of the world's largest quartz-topaz greisens, which are characterized by an average content of 20-30 vol% topaz, 0.1-0.3 wt% WO_3 , and 0.05 wt% Bi (McClatchie, 1981; Creech, 1992). Based on analyses of supposed melt inclusions in topaz, Eadington and Nashar (1978) proposed a magmatic origin of these rocks. However, the "glassy melt inclusions" described by these authors are in fact remains of minerals that were replaced during greisenization, whereas true melt inclusions are completely crystallized (Audétat et al., 2000). Further evidence for a dominantly metasomatic origin of the quartz-topaz greisens is given by field relations discussed in Kleeman (1985), Kleeman et al. (1997), and our own observations at Fielders Hill (see below). Descriptions of individual ore deposits can be found in Mulholland (1943), Lonergan (1971), Weber (1974), Stegman (1983), Brodie (1983), Cozens (1984) and Eadington (1977), whereas summaries are given by Eadington (1983), Plimer et al. (1985), Kleeman et al. (1997) and Henley et al. (1999). For the present work, a total of 29 sites and deposits were studied (Audétat, 1999), of which 11 yielded critical

information. These latter occurrences are described in the following sections.

Figure 2. Overview of ore deposits associated with the Mole Granite, based on a recent compilation of the Geological Survey of New South Wales (see also Henley et al., 1999). Exposed parts of the granite are shown in white, whereas gray represents sedimentary and volcanic country rocks. Included are locations mentioned in the text.

Miarolitic cavities

Miarolitic cavities are present in all textural variants of the Mole Granite, indicating that fluid saturation was reached at a relatively early stage of crystallization (Candela and Blevin, 1995). They are relatively common in porphyritic granite and microgranite, whereas only few have been observed in seriate granite. Most of them are less than 10 cm in diameter, but one cavity near the homestead Lenore measured 30x20x10 cm. Evidence for the early coexistence of melt and magmatic vapor was found in a quartz crystal from a miarolitic cavity near the Gulf Fluorite Mine. The 2-mm-sized crystal contains crystallized melt inclusions and low-density fluid inclusions arranged on a former crystal surface.

The miarolitic cavity from Lenore ("Leno")

Macroscopically, this cavity contained only quartz and potassic feldspar. Quartz crystals of up to 4 cm length host numerous trails of pseudosecondary fluid inclusions (Figs. 3a and 3c), some of them showing signs of post-entrapment modifications (Audétat and Günther, 1999). Based on their relative starting position on former crystal

surfaces, and limited crosscutting relationships (trail 3 cutting trails 1 and 2), it was possible to put at least 8 of these trails into a well-defined time sequence. Together with LA-ICP-MS analyses of 32 single fluid inclusions, this allowed a detailed reconstruction of the compositional evolution of the fluid in the cavity (Fig. 3b). During the first 6 stages recorded in Figure 3b the concentration of most major and minor elements shows a parallel decrease, suggesting that the magmatic fluid was diluted by an aqueous fluid. At first sight, this interpretation seems to be contradicted by the fact that the concentration of B and Li *increases* during the same time interval. However, as will be shown later, this is readily explained by the addition of these elements via a Li, B and Cu-rich vapor phase. The large drop in elemental concentrations after stage 6 (trail 12) reflects further dilution with aqueous fluid (note the decrease in fluid salinity), as well as precipitation of muscovite. The smallest negative change sets an upper limit for the dilution factor, whereas all larger negative changes can be explained by mineral precipitation. The total dilution factor recorded in the sequence shown in Fig. 3 is therefore on the order of 40 (based on Na as the least diminishing element).

Figure 3. (a) Petrography of quartz sample *Leno 1* from a miarolitic cavity. At least 8 of the labeled fluid inclusion trails can be put into a relative time sequence. (b) Chemical and physical evolution of the fluid in the miarolitic cavity, reconstructed from LA-ICP-MS analysis and microthermometric study of 8 successive generations of fluid inclusions. (c) Brine inclusion on trail 2 (37 wt% NaCl_{equiv}), containing a large halite daughter crystal and several birefringent other daughter minerals.

Tungsten-deposits

Balmains and Rumsby's Lodes

The Balmains and Rumsby's Lodes ("Uppw"/"Loww"/"Adit"; coordinates 350.2E/6759.9N) belong to a group of tungsten deposits located at the south-western rim of the Mole Granite (Figs. 2 and 4). According to Weber (1974) a total of ~27 t wolframite and ~1 t scheelite was produced from this vein system. The majority of the ore was found at the main vein intersections named "Uppw" and "Loww" in Figure 4, of which the latter produced 4.5 t wolframite within the first 4 meters of development (Carne, 1911). A large cavity (~10 m³ volume) was hit further down in the shaft, containing

massive wolframite intergrown with green fluorite (pers. comm. Terry Clifford, Emmaville).

In more recent times, an adit of 148 m length has been developed at the southwestern end of the Balmains Lode. This adit is easily accessible, providing good exposure to different styles of mineralization and host rocks along the vein system. A sudden change from seriate granite to porphyritic granite at 103 m distance from the adit entrance is accompanied by a major change in vein morphology. Veins hosted by porphyritic granite are characterized by open-space mineralization and only minor wallrock alteration, whereas veins hosted by seriate granite are dominated by wallrock alteration. Successive replacement of feldspars and micas by quartz resulted in an essentially monomineralic rock,

in which former Kfsp-phenocrysts are recognizable as small, crystal-lined cavities. The width of the

alteration zone seems to be independent of the vein width or ore grade.

Figure 4. (a) Geology of the southwestern margin of the Mole Granite, showing several W-deposits associated with porphyritic granite, and Sn-deposits associated with seriate granite. (b) Enlargement of the area around the Balmain and Rumsby's Lodes. Isolated masses of porphyritic granite occur at major vein intersections, suggesting that vein formation and development of porphyritic granite texture are related to each other.

Open-space mineralization is dominated by quartz, which occurs as euhedral crystals of up to 30 cm length. These crystals usually contain a dark, smoky colored core that is overgrown by one or several generations of colorless to milky quartz. Wolframite is present as ferberite (the high-temperature, Fe-rich end-member), and commonly is intergrown with native bismuth, fluorite, arsenopyrite, ilmenite and monazite. Tourmaline appears to have been precipitated later, together with chalcopyrite, pyrite and chlorite (Fig. 5).

Early brine inclusions in smoky quartz and beryl have salinities of 31-45 wt% $\text{NaCl}_{\text{equiv}}$ and homogenize at 420-460 °C, whereas brine inclusions of similar salinity in fluorite homogenize at temperatures of 470-560 °C. Some trails show unambiguous evidence for fluid boiling, as demonstrated by the occurrence of vapor and brine inclusions ($\pm$ intermediate members) on the same fracture plane.

Eastern Flagstone Lodes

The Eastern Flagstone Lodes ("EFlag"; coordinates 364.5E/6763.2N) comprise a small

number of workings located close to the northwestern end of the sedimentary roof pendant. Despite their proximity to the granite margin they seem to be hosted by seriate granite rather than by porphyritic granite. The lodes, which are up to 30 cm wide, consist of smoky quartz, wolframite, beryl and monazite, and are bordered by quartz-muscovite-topaz alteration. Euhedral quartz crystals in open spaces record a complex history of fluid evolution and mineral precipitation, involving one stage of quartz dissolution. The following history can be reconstructed for sample *EFlag 2* (Fig. 6a): (1) growth of dark, smoky quartz, (2) growth of beryl crystals on the quartz surface, (3) corrosion of both quartz and beryl, (4) growth of colorless quartz over the corroded relicts, (5) precipitation of muscovite, potassic feldspar and tourmaline (forming a first growth zone) and (6) precipitation of potassic feldspar, ilmenite, tourmaline, muscovite, zircon, allanite and helvite (a sulfur- and Mn/Fe/Zn-containing beryllium-silicate), forming a second growth zone.

Balmains / Rumsby's	stage 1	stage 2	replacements
quartz	(smoky)	(colorless)	
arsenopyrite	=====		
wolframite	=====		-> scheelite
native bismuth	=====		
monazite	=====		
fluorite	=====		
beryl	=====		
Fe-Cu-S s.s.*	=====		-> chpy+po +cubanite
Li-biotite (?)	=====		-> chlorite
ilmenite	=====		-> hematite +rutile
adularia	=====		
muscovite	=====	-----	
tourmaline	-----	=====	-> chlorite
chlorite		=====	
chalcopyrite		=====	-> covellite
pyrite		=====	

* Solid inclusions within quartz, composed of constant proportions of pyrrhotite, chalcopyrite and cubanite. This indicates that they were trapped as a single-phase solid solution above ~300°C (Vaughan and Craig, 1997).

Figure 5. Mineral precipitation sequence in the Balmains and Rumsby's Lodes

Even if the precipitation of wolframite, monazite and bismuth is not directly recorded in the quartz crystal, it is clear from petrographic relations in the other samples that these minerals precipitated at the same time as the beryl. Trails 1 and 2 are the only ones that formed demonstrably earlier than the precipitation of beryl, and therefore may be the only representative of the pre-mineralization fluid. The strong decrease in the concentration of W, Bi, and Ce between stages 1 and 2 (Fig. 6c), with all other concentrations remaining more or less constant (Fig 6b), suggests that this is indeed the case. After the formation of trail 5 there is a marked decrease in the concentration of K, Mn, Zn, Pb, Sr and B, whereas that of Bi and Ce diminishes much less. This is readily explained by the precipitation of muscovite, potassic feldspar, helvite and tourmaline onto the second growth zone. The trend of Cu and B is similar to that of Li and B reconstructed for the miarolitic cavity (Fig. 3), showing steady or even increasing values at times where all other concentrations decrease. Again, we like to explain this by the addition of these elements by a Cu, B and Li-rich vapor phase (see below).

Figure 6. (a) Petrography of quartz crystal *EFlag 2* from the Eastern Flagstone Lodes. Corroded relicts of smoky quartz and beryl are overgrown by a younger generation of colorless quartz. (b-e) Fluid evolution based on 7 generations of fluid inclusions ordered by decreasing salinity. Trails 1 and 2 clearly formed before the corrosion event, whereas trails 8, 9 and 10 formed afterwards.

Most fluid inclusions of *EFlag 2* were subject to post-entrapment modifications, as is indicated by their distorted shape and the fact that the salinities of unambiguously coexisting vapor- and brine inclusions do not fit onto the two-phase curves in the H₂O-NaCl system (Audétat and Günther, 1999). However, the latter could also be a consequence of the complex fluid chemistry, for which the phase diagram topology may differ significantly from that of the binary H₂O-NaCl system (Bodnar and Vityk, 1994).

Fielders Hill

The Fielders Hill open cut ("*Fiel*"; coordinates 367.0E/6762.8N) provides excellent exposure of the geology at the upper contact of the Mole Granite. It produced approximately 75,000 t of ore grading at 0.5-1.6 wt% WO₃ (Griffin and Weber, 1972). The main ore mineral was Fe-rich wolframite (WO₃ 74.9 wt%; FeO 20.4 wt%, MnO 3.3 wt%; Creech, 1992) that occurred together with native bismuth in vugs and fractures within the quartz-topaz greisen. The granite contact is particularly well exposed on the western wall of the pit, where a 10-m-thick sill of microgranite cuts through the hornfelsed sediments. This sill branches out from the main feeder dike located in the now water-filled center of the pit (Griffin and Weber, 1972; Creech 1992). Petrographic relationships imply the following sequence of events (Fig. 7a):

- 1) Intrusion of highly differentiated melt along a horizontal zone of structural weakness.
- 2) Detachment of large blocks of already sheeted-veined sediments from the roof, which later accumulate at the sill's base. The fact that the average veining direction varies from one block to another suggests that the veins formed *before* the detachment of the blocks, probably even before the intrusion of the microgranite.
- 3) After crystallization was complete, parts of the microgranite were transformed into massive quartz-topaz greisen. Massive greisen bodies (like the one in the left part of Fig. 7a) display the same characteristics as thin greisen-veins in the adjacent unaltered granite.
- 4) Formation of an irregular mass of beryl + biotite within the main greisen body.

Topaz (3-5 vol%) occurring in unaltered parts of the microgranite is clearly of magmatic origin, since it hosts primary melt inclusions (Audétat et al., 2000). Massive quartz-topaz greisens, on the other hand, contain 20-30 vol% topaz on average. Most of this topaz is metasomatic, as indicated by the field relationships (Fig. 7) and the presence of abundant inclusions of resorbed feldspar, biotite and quartz.

Their glassy appearance and rounded, irregular shape has repeatedly lead to the erroneous conclusion that these inclusions represent glassy melt inclusions (Eadington and Nashar, 1978; Creech, 1992). However, this interpretation is clearly disproved by the fact that they are birefringent, many of them even showing optical continuity with other inclusions nearby. True melt inclusions that occur in rare magmatic cores within dominantly metasomatic topaz are always crystallized, and are indistinguishable (optically and chemically) from those occurring in the magmatic topaz of the unaltered microgranite. Large (>50 µm) fluid inclusions occurring in metasomatic topaz have been analyzed with LA-ICP-MS by Rankin et al. (1992).

The alteration of granite into quartz-topaz greisen can be expressed by the following mineral reaction, which is balanced with respect to relative mineral abundances in the starting rock and the resulting greisen (Fig. 7b, c). The volume of the minerals was calculated on the basis of their oxygen-content, assuming that this element dominates the volume proportions (Thompson, 1982).

siderophyllite (3 vol%) + potassic feldspar (36 vol%)
 + albite-rich plagioclase (26 vol%) + quartz (35 vol%)
 = Li biotite (3.7 vol%) + fluorite (0.6 vol%)
 + topaz (22.3 vol%) + quartz (73.4 vol%)

This reaction implies that the greisenizing fluid was acid (note the input of HF and HCl) and contained fluorine.

Early brine inclusions in hydrothermal (?) quartz-topaz veins show salinities of 30-35 wt% NaCl_{equiv}, and homogenization temperatures of 500-550 °C, whereas unambiguously coexisting vapor inclusions have salinities between 3 and 7 wt% NaCl_{equiv}. The presence of large, primary brine inclusions in fluorite allowed direct determination of Si and Al-concentrations in the fluid, which normally was not possible because Si and Al are contained in the host minerals quartz and topaz. Calculated concentrations for Al and Si are 1.2 and 0.8 wt%, respectively, which is not unreasonable in view of the ubiquitous presence of fluorine in the Mole Granite. London et al. (1988) showed that an aqueous fluid equilibrated with Macusani-glass (a rhyolitic glass containing 1.3 wt% F) at 600-775 °C and 2 kbar carries 9-15 wt% dissolved silicates. This agrees well with experiments conducted by Webster (1990), revealing that a fluorine-rich fluid (4 wt% F) equilibrated with

rhyolitic melt at 2 kbar, 800 °C contains 16 wt% dissolved silicates.

Figure 7. (a) Geological view of the western wall of the Fielders Hill open cut, showing a 10 m thick sill of microgranite capped by sheeted-veined sediments. Large, sedimentary xenoliths accumulated at the sill's base, which is 1-2 m below the exposed wall-section. Parts of the microgranite were transformed after its solidification into massive quartz-topaz greisen. **(b)** Zoned greisen vein bordered by unaltered microgranite. The lettering corresponds to the zones shown in c. **(c)** Change in volumetric mineral abundances (in %) across the same greisen vein.

Other Tungsten Deposits

The New Hope Mine ("Wolf"; coordinates GR 367.7E/6762.8N) was established on a series of quartz-veins and quartz-topaz greisens occurring along the contact of the Mole Granite with the sedimentary roof pendant (Audétat, 1999). These veins and greisens produced a total of approximately 270 t of wolframite concentrate from ore grading at 0.5 wt% W in average (pers. comm. of Bill Sherratt, Torrington). Mineralized veins cut through both the greisens and the adjacent sediments, and are characterized by the presence of quartz $\pm$ topaz $\pm$ wolframite $\pm$ native bismuth. The ore grade is locally very high, as demonstrated by a single mass of 70 t of wolframite won from the 'Bung Line' (Creech, 1992). Disseminated wolframite within quartz-topaz greisen is always interstitial, and is concentrated along ill-defined planes that show no evidence for open-space mineralization. This suggests that the wolframite precipitated after the main stage of greisenization.

Bismuth ("Bism"; coordinates 367.1E/6760.9N). The exact origin of sample *Bism* 3 (cf. Fig. 12; table 1) is not known because it was collected on a large block of quartz-topaz greisen found near the old ore treating plant, in which material from several ore deposits in the roof pendant area was processed. Fluid inclusion analyses reported from this samples refer to primary brine inclusions in metasomatic topaz, which are characterized by a salinity of 30-40 wt% NaCl_{equiv} and homogenization temperatures of 500-570 °C.

Unnamed Au-Bi-deposit ("Gol"; coordinates GR 367.3E/6760.4N) At the southwestern rim of the sedimentary roof pendant a small number of quartz-topaz-greisens has been mined for Au and Bi (Fig. 2). The ore grade in these deposits is locally very high, with concentrations of 30-120 g/t Au and 3 wt% Bi reported in an old record of unknown provenance. Mineralization seems to be related to bismuth-rich quartz-veins that are difficult to distinguish from the surrounding quartz-topaz greisen. Rare open spaces in these veins contain light blue topaz and smoky quartz crystals of up to 2 cm length. Fluid inclusions in the latter mineral typically show evidence for simultaneous entrapment of both vapor and brine.

Tin-deposits

The Yankee Lode

The Yankee Lodes ("Yank"; coordinates 351.5E/6759.9N) comprise a set of at least 14 tin-mineralized lodes that are located about 1 km east of the homestead Kathida/Amaroo at the southwestern

margin of the Mole Granite (Fig. 4). Most of them are hosted by seriate granite, but some extend into the porphyritic carapace, which is very thin (<10 m) in this area. Individual veins are up to several hundred meters long and have been worked underground to a maximum depth of 75 m. Open-space mineralization is dominated by quartz and cassiterite, with only minor feldspar present. Molybdenite has been reported once in one lode (New South Wales Geological Survey report GS 1982/589). Some of the veins show almost no wallrock alteration, whereas others are bordered by chlorite alteration. One lode contained quartz + cassiterite in its upper part (without alteration), and potassic feldspar + cassiterite associated with Kfsp-alteration at greater depth (pers. comm. of a local miner). Cassiterite occurs both within the quartz veins and in the adjacent chlorite alteration, and is enriched in steeply pitching ore-shoots (1.5-4.0 m length, 0.2-0.4 m width and 15-25 m depth) with typical ore grades of 10-25 wt% cassiterite (New South Wales Geological Survey Report GS 1982/589). Massive ore (so-called "bungs") is commonly found at the intersection of the main vein with smaller horizontal veins. Total production recorded from the Yankee Lodes is at least 99 t of cassiterite. In the following text, the name "Yankee Lode" (in singular) refers to the Kathida Mine, which presently is worked by R.W. Clifford for collector's cassiterite specimens. Some quartz crystals from this lode contain exceptionally large and well-preserved fluid inclusions (Fig. 8), making them very suitable for microthermometric and analytical investigations (Eadington, 1983; Heinrich et al., 1992). A detailed fluid inclusion study on two of these crystals is summarized in Audétat et al. (1998). Both crystals show identical histories of hydrothermal growth and precipitation of other minerals, recorded by the occurrence of zircon, thorite, feldspar, cassiterite, ilmenite, tourmaline and muscovite on 4 successive growth zones (Fig. 8b).

Of the numerous fluid inclusion trails measured in these crystals, about 16 could be placed in an unambiguous time sequence, permitting a detailed reconstruction of the chemical and physical evolution of the hydrothermal fluid (Fig. 9). In the first 7 stages (indicated at the bottom of the figure) the concentration of most elements remains basically unchanged, despite huge variations in pressure and temperature (Fig. 9a). This can be explained by repeated build-up of overpressure in the vein system, each followed by a fracturing event and a pressure drop to near-hydrostatic conditions. Of these P/T-cycles there might be only the pressure drop recorded in the quartz crystals, as it is not likely that quartz precipitated during periods of pressure increase. The

Figure 8. (a) Photograph of a doubly polished thick section of quartz crystal *Yank 20* from the Yankee Lode. (b) Drawing of an immediately adjacent section prepared from the same quartz crystal, showing four distinct growth zones marked by solid inclusions of zircon, feldspar, cassiterite, ilmenite, tourmaline and muscovite. (c) Two vapor inclusions on trail 39 (9 wt% NaCl_{equiv}), which were trapped together with brine inclusions homogenizing at 595 °C. (d) Early brine inclusion on trail 26 ($T_{\text{tot}} = 528$ °C; salinity = 27.7 wt% NaCl_{equiv}). (e) Later brine inclusions on trail 36 ($T_{\text{tot}} = 490$ °C; 28.9 wt% NaCl_{equiv}). (f) Late fluid inclusion consisting of nearly pure water, showing final homogenization at 198 °C.

decrease in temperature would be caused by the exsolution of vapor (boiling), for which there is clear evidence in all stages of the evolution.

Figure 9. Evolution of pressure, temperature and chemical composition in the Yankee Lode fluid. (a) Variation in temperature and pressure, calculated from microthermometric data. (b) Concentration of non-precipitating elements in the brine phase, based on LA-ICP-MS analysis of 16 subsequent generations of fluid inclusions. The parallel drop of these elements is interpreted to reflect progressive mixing with groundwater. (c) The sharp drop in Sn-concentrations at the beginning of cycle 3 is caused by precipitation of cassiterite (d) Condensation of magmatic vapor into the fluid mixture leads to elevated B, Cu and As-concentrations even after the beginning of dilution (see text for further explanations).

After stage 7 the concentrations of all non-precipitating elements (i.e., elements that are not

incorporated in the vein minerals) show a parallel decrease (Fig. 9b), whereas that of Sn drops significantly faster due to the precipitation of cassiterite (Fig. 9c). The fact that the non-precipitating elements maintain constant concentration ratios throughout this decrease suggests that it was caused by mixing with a very dilute fluid, which probably was of meteoric origin (Sun and Eadington, 1987). The concentration of Cu, B and As, on the other hand, decreases less markedly than that of the non-precipitating elements, implying that the diluting fluid was enriched in these three elements (Fig. 9d). As will be shown later, this is readily explained by the addition of a Cu, B and As-rich magmatic vapor phase to the fluid mixture.

The fact that only minor wallrock alteration is present, and that the magmatic fluid underwent two cycles of pressure and temperature decrease before cassiterite started to precipitate at the onset of the dilution, clearly shows that the Sn-ore formation in the Yankee Lode was caused by fluid mixing (Audétat et al., 1998).

Other Sn-deposits

The Breakfast Mine (also called *Specimen Hill* or *Mt. Garth*; coordinates 356.0E/6760.3N) was developed on a series of cassiterite-bearing veins that are characterized by extensive quartz $\pm$ tourmaline $\pm$ muscovite alteration and only minor open-space mineralization. Quartz crystals from this locality contain hydrothermal xenotime and moderately saline brine inclusions.

The Paradise Lode (also called *Gayden's Lode* or *Garth's Lode*; coordinates 358.8E/6758.9N) consists of a vein of 700 m length that produced a total of 77 t of cassiterite concentrate (Weber, 1974). The vein mineralogy is rather complex, comprising members of the typical "wolframite paragenesis" as well as the "cassiterite paragenesis". Textural relationships indicate that an early stage of wolframite-mineralization was overprinted by a later stage of cassiterite deposition.

An *unnamed Sn-deposit* in the Carpet Snake area ("vnl", coordinates 360.9E/6765.9N) was developed on small, chlorite-greisen bordered veins containing cassiterite intergrown with magnetite and potassic feldspar. Pre-mineralization brine inclusions show salinities of 43 wt% NaCl_{equiv} and a homogenization temperatures of 390 °C, whereas later brine inclusions contain only 18 wt% NaCl_{equiv}, but still homogenize at 370 °C. This means that, if ore precipitation was caused also here by fluid mixing, the diluting fluid was relatively hot.

Sheeted veins and stockwork systems

Sheeted vein systems typically form above ridges or cupolas in the underlying granite. They are defined by numerous sub-parallel veins of usually less than 3 cm width, originating at an approximately right angle from the granite margin. Sheeted vein systems related to the Mole Granite were described from Taronga, Big Plant Creek, Emerald County and Poverty Point (Stegman, 1983). All these occurrences lie within a 3-4 km wide and 10 km long corridor southwest of the exposed part of the Mole Granite. Economically less important sheeted vein systems occur at the Mosman Prospect and Sam's Mountain Prospect northeast of the Mole Granite (Brodie, 1983), and in the sediments above the quartz-topaz greisens in the Fielders Hill open cut. A stockwork-like occurrence of quartz-biotite-topaz-loellingite-veins within porphyritic granite was observed near the Poppy Adit in the Carpet Snake area.

Taronga

The Taronga prospect ("Taro"; coordinates 367.3E/6742.7N) is probably the best studied sheeted vein system of the Mole Granite, having been explored until the 1980's. Newmont Holdings Pty. Ltd. defined two ore-bodies with an estimated minable reserve of 31 million tons of ore grading at 0.165 wt% Sn (Stegman, 1983). However, the deposit never went into production because the ore was too complex to be treated by traditional methods, and because of the decline of the Sn price in the late 1980's.

Several kilometers of drill cores stored in a shed near Taronga have recently been vandalized, so that the information about their exact provenance has been lost. Crosscutting relationships observed on 56 drill-core samples suggest that an early assemblage of quartz, potassic feldspar, fluorite, wolframite, molybdenite and bismuth was overprinted by a later assemblage of quartz, topaz, arsenopyrite, beryl, tourmaline, cassiterite, chalcopyrite and pyrite (Fig. 10). This sequence stands in marked contrast to that proposed by Stegman (1983), who states that the cassiterite- and sulfide-bearing sheeted veins are overprinted by a later stockwork of molybdenum-bearing veins. However, crosscutting relationships observed in our samples are in clear favor for early development of the molybdenum-bearing veins.

Fluid inclusions found at this locality are generally very small and deformed, except for one quartz crystal in which solid inclusions of muscovite, cassiterite and fluorite occur along a former crystal surface. Primary fluid inclusions within the fluorite have a filling ratio of $F = 0.5$, a salinity of 1.4 wt% NaCl_{equiv}, and homogenize at a temperature of 385 °C

by fading of the meniscus (critical homogenization behavior).

Figure 10. Mineral precipitation sequence in the Taronga sheeted vein deposit, reconstructed from 14 crosscutting relationships observed in 56 drill-core samples.

Base metal deposits

Collison's Silver Mine (also "Webb's Silver Mine")

This mine ("Coll"; coordinates 358.8E/6757.9N) was one of the most important producers of silver in the New England area during the early 1880's to 1900. It produced a total of 50,000 t of ore from which 2,000 t of concentrate was extracted, averaging at 0.34 wt% Ag, 7 wt% Pb, 4 wt% Cu, 13 wt% Zn, 9.5 wt% As and 7.5 wt% Sb (Weber, 1974). The mineralization extends for almost 1.5 km along the intersection of a large fault with a steeply dipping bed of Permo-Carboniferous dolomite. The surface mineralization at Collison's Silver Mine is restricted to a number of outcrops of strongly silicified mudstone. Mineralized veins contain high-grade ore with only a small proportion of gangue minerals. The ore consists of sphalerite (47%), arsenopyrite (17%), tetrahedrite (14%), chalcopyrite (11%) and galena (10%), with minor amounts of stannite, cubanite, covellite, bournonite, cassiterite and chalcocite (Clark, 1963). Fluorite and minor quartz were precipitated together with the ore in open spaces within intensely fractured and brecciated siltstone. Pseudosecondary fluid inclusions in fluorite are of low salinity (1 wt% NaCl_{equiv}), and homogenize at 230-260 °C into the liquid phase ($F = 0.8-0.9$).

Reid's Copper Mine

The Reid's Copper Mine ("Reids"; coordinates 360.4E/6748.8N) is a small working located next to the road to the Collison's Silver Mine. The ore is composed principally of chalcopyrite, bornite and chalcopyrite, and occurs as fine disseminations and veinlets within altered conglomerate host rock (Godden, 1982). The same author reports that a leucocratic granitoid (probably an apophysis of the Mole Granite) was exposed at the bottom of the shaft. No information is available about ore grades or tonnages. Other minerals found at this locality include fluorite, arsenopyrite, pyrite, cassiterite, beryl(?), ilmenite(?), chlorite and galena, of which fluorite was the first to crystallize. Fluid inclusions occurring on pseudosecondary and secondary trails within fluorite are aqueous. Of the two populations measured, one is characterized by filling ratios of $F = 0.95-0.98$, a salinity of 6.5 wt% NaCl_{equiv}, and homogenization temperatures between 220 °C and 240 °C, whereas the other population revealed a similar filling ratios ($F = 0.95-0.98$), but a salinity of 2 wt% NaCl_{equiv} and even lower homogenization temperatures (180-210°C).

Discussion and Conclusion

Element partitioning between coexisting brine and vapor

Vapor/brine distribution coefficients determined by LA-ICP-MS analysis of 8 pairs of coexisting vapor and brine inclusions are presented in Fig. 11.

Most plots show two more-or-less distinct groups of element behavior, with Mn, K, Ba, Rb, Sr, Cs, Zn, Pb, Sn, Fe, Bi, Tl and Sb fractionating into the liquid phase, and Cu, B ($\pm$ La, S) fractionating into the vapor phase. Distribution coefficients of As, Ag, and Li are less uniform, showing both fractionation behaviors. Evidence for a preferential fractionation of Cu into the magmatic vapor phase was presented in Sawkins and Scherckenbach (1981), Heinrich et al. (1992), Bodnar (1995) and Damman et al. (1996). However, all these studies are associated with some degree of ambiguity, because the two types of fluid inclusions could not be proved to be truly coexisting. Similar sets of distribution coefficients (including Au) have recently been reported from clear-cut boiling assemblages from three Cu-Au-(Mo-)-porphyries, a mesothermal base metal deposit, and another Sn-granite (Heinrich et al., 1999).

It has been argued that the preferential enrichment of Cu, Au, Ag and possibly As in the vapor phase may be due to complexation with sulfur (Heinrich et al., 1992), which reduced form is highly volatile (Drummond and Ohmoto, 1985). This seems

to be supported by the high sulfur distribution coefficients determined for sample Loww9 (Fig. 11), even if the two types of inclusions were not unambiguously coexisting in this sample. Another potentially vapor-fractionating element is silver, showing a vapor/brine-distribution coefficient of ≥ 1 in three of the six cases. In view of the close association of Cu, Au and Ag in many epithermal ore deposits (Arribas, 1995) and the high stability of Ag-hydrosulfide complexes (Seward and Barnes, 1997), this is not surprising.

Causes of the metal zonation around the Mole Granite

Regional metal zonations around mineralized intrusions may reflect either selective metal-precipitation from one parental fluid, or bulk metal-precipitation from fluids with different ore-metal contents. Ore precipitation may have been caused by (i) mixing with external fluids (without considering the effect of cooling), (ii) fluid cooling, (iii) changes in fluid pressure (leading to boiling), or (iv) fluid/rock-interaction (Heinrich, 1990).

In the Mole Granite, at least part of the metal zonation was caused by sequential precipitation from one parental fluid, because the pre-mineralization fluid in pure Sn-deposits (Yankee Lode) and pure W-deposits (Eastern Flagstone Lodes, Bismuth) contained much higher amounts of base metals than Sn and W (see Table 1). Ore precipitation probably was driven by fluid mixing in both types of deposits, as indicated by the local occurrence of extremely rich ore grades at the intersection of two vein systems (Mulholland, 1943, Weber, 1974), and the general lack of correlation between the degree of wallrock alteration and ore grade.

Figure 11. Vapor/brine distribution coefficients determined by LA-ICP-MS analysis of unambiguously coexisting vapor and brine inclusions (in sample *Loww*)

the coexistence is less clear). Columns represent the value calculated from the average composition of each fluid population, whereas error bars indicate the maximum variation defined by the 1σ standard deviation associated with these averages. Distribution coefficients displayed by only one bracket (e.g., Cu and Zn in *EFlag 2*) are minimum values based on detection limits determined for one of the two inclusion types. Consistently vapor-fractionating elements include Cu, B, La and probably S, whereas As, Ag, and Li show both fractionation behaviors. All other elements clearly fractionate into the liquid phase.

But why do most Sn and W-deposits contain only the oxide stage of mineralization, although a full "dilution sequence" is recorded in the quartz crystals? Why were the base metal sulfides mostly precipitated in the surrounding sediments? Fluid-rock interaction with different host rocks cannot be the reason because late-stage base metal mineralization occurs also in some *granite*-hosted ore deposits (e.g., *Butler Lode*, *Poppy Adit*, *Wallaroo Lode*, *Silent Grove*). Cooling alone can be discarded as well, because effective precipitation of base metal requires an adequate source of sulfur. Brine inclusions from the Balmain Lode, for example, contain 14,000 ppm Zn but less than 1,000 ppm sulfur, which means that at most 15% of the Zn could be bound in sphalerite by direct precipitation from this magmatic fluid. The observations can be explained by a two-step fluid evolution, with a first stage of fluid mixing that leads to the precipitation of Sn and W at the mixing site, and a second stage of fluid cooling that leads to base metal precipitation after leaching of additional sulfur from the surrounding sediments (Heinrich and Ryan, 1992). The observation of "full dilution sequences" in zoned quartz crystals is only apparent, as late generations of fluid inclusions may not be representative of the fluid that was admixed at earlier stages.

The mechanism of sequential metal-precipitation from one parental fluid explains well the segregation between base metal deposits and Sn/W-deposits, but gives no explanation for the spatial separation between the latter two types of deposits. Comparing the composition of pre-mineralization brine inclusions in W-deposits (*Bism 3.4*, *Bism 3.3*, *EFlag 2*) with that of early brine inclusions in the Yankee Lode Sn-deposit, it is evident that the former contained much more W, Bi and Ce (Fig. 12, Table 1). W, Bi and Ce are the most characteristic elements of W-deposits, because they are hosted by the typical ore assemblage wolframite + native bismuth + monazite. By comparison, the Sn-mineralizing fluids contained smaller W/Sn-ratios ($W/Sn \approx 1$, as opposed to $W/Sn \approx 10$ in the W-deposits), although the absolute Sn-concentration is similar to that of the W-mineralizing fluids. This indicates that the Sn/W-ratio

in the high-temperature ore deposits was pre-defined by the metal-content of the source fluid, and therefore is the result of processes at earlier stages in the magmatic-hydrothermal evolution.

The hydrothermal evolution of the Mole Granite System

A model of the hydrothermal fluid evolution in the Mole Granite should explain: (1) the formation of pure Sn or W-deposits from fluids that actually contain higher amounts of base metals, (2) the fact that most Sn or W-deposits occur within the granite, whereas base metal deposits typically occur in the overlying sediments, (3) the presence of late-stage base metal mineralization in *some* Sn or W-deposits, and (4) the observation of full "dilution sequences" in quartz crystals from pure Sn or W-deposits.

Figure 12. Composition of the pre-mineralization ore fluid in three W-deposits, compared to the pre-mineralization ore fluid in the Yankee Lode Sn-deposit. To eliminate the effect of different bulk salinities we normalized the concentrations to an equal Na-value. The highest relative enrichment is found in W, Bi and Ce, which are contained in the main ore-forming minerals of W-deposits (i.e., wolframite, native bismuth, and monazite). It suggests that the Sn/W-ratio of the ore mainly reflects the Sn/W-ratio in the source fluid.

Based on the findings in the previous section we propose the following model (Fig. 13). Shortly after the formation of the porphyritic carapace, fractures start to develop in the more or less solid rock portions (Fig. 13a). Fracturing and development of porphyritic granite seem to be closely related to each other, as indicated by the occurrence of circular bodies of

porphyritic granite at the intersection of large vein systems (e.g., at Balmains and Rumsby's Lodes, Fig. 4). Brine and vapor exsolving from the crystallizing melt rise up along these cracks, and mix with pre-heated meteoric water circulating in the upper parts of the granite. The relatively high temperature of the meteoric fluid (probably $>300^{\circ}\text{C}$) explains why only Sn and W but little or no base metals are precipitated at the site of fluid mixing (Heinrich and Ryan, 1992). Further ascent of the fluid mixture into colder country rocks leads to a significant amount of cooling, which results in the precipitation of base metals in the upper part of the vein systems. The sulfur required for sulfide precipitation may in part be H_2S from magmatic vapor that condensed into low-salinity meteoric water, but probably includes $\delta^{34}\text{S}$ -depleted sulfur from the metasediments (Heinrich and Ryan, 1992).

In a later stage (Fig. 13b), magmatic fluid still ascends through the right vein system, whereas the left vein system is sealed with respect to further input of magmatic fluid. Quartz crystals growing at the site of W-mineralization in the left vein system will therefore record a full "dilution sequence" without ever seeing a stage of base metal mineralization, whereas the vein system on the right will develop typical characteristics of "telescoped" deposits, i.e., low-temperature base metal sulfides overprinting an earlier stage of Sn/W-oxide mineralization.

Throughout this process, brine – vapor separation caused selective enrichment of Cu, B, Li, As ($\pm$ S, Ag, La) in the magmatic vapor phase, which condensed into low-salinity meteoric fluid circulating in the upper parts of the granite. This must have involved significant amounts of copper being transferred to the low-salinity fluid environment overlying and surrounding the Mole Granite, but no vapor-phase dominated deposit could be identified in the Mole Granite system, perhaps due to erosion of the apical part of the intrusion. However, similar fractionation processes may be critical to the formation of epithermal Cu – Au – As deposits in calcalkaline-related magmatic-hydrothermal systems (Heinrich et al., 1999).

Figure 13. Model of the fluid evolution in the Mole Granite. **(a)** Mixing of magmatic fluid with pre-heated meteoric water circulating in the upper parts of the granite leads to the precipitation of W, Bi, and Ce at the site of fluid mixing, whereas base metals like Pb, Zn, Ag, Cu, Sb are precipitated further up in the vein system as a result of fluid cooling. **(b)** Quartz crystals growing at the site of W-deposition in the left vein system (which now is sealed with respect to further input of magmatic fluid) will record a full history of fluid dilution and cooling without ever seeing a stage of base metal precipitation. Mixing of later, Sn and base metal rich magmatic fluid in the right vein system leads to the deposition of base metals at the former site of W-mineralization, and to Sn-deposition at deeper levels in the pluton.

Acknowledgments

We would like to thank Paul Ashley (University of New England, Armidale), Jim Stroud, Harvey Henley and Bob Barnes (all at the Geological Survey of New South Wales, Armidale) for their great support during the first author's extended visit during 1996/1997. We are also grateful to Rolf Frischknecht and Urs Menet (ETH Zürich), who both contributed

significantly to the development of the LA-ICP-MS System at ETH Zürich. Critical comments by *Economic Geology* reviewers A. E. Williams-Jones and Jacob Lowenstern, as well as by Thomas Pettke and Werner Halter helped to improve the manuscript. This project was generously supported by ETH Zürich (grant 0-20-041-95) and by the Swiss National Science Foundation (grants 21-455548.95 and 20-52265.97).

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