

Conference Report

Mineralizing fluids

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Report of a meeting held jointly by the Mineral Deposits Studies Group and the Applied Mineralogy Group of the Mineralogical Society, at Burlington House on 14 May, 1981.

This joint meeting adopted as its theme the central topic of fluids involved in mineralization, and 15 papers were presented. The emphasis was on aqueous mineralizing fluids in settings varying from granite-related tin-tungsten deposition to groundwaters involved in syn-sedimentary mineralization. Several speakers reported on studies involving or centred about fluid inclusions. Other subjects included hydrothermal experimental investigations, mineralogy and wallrock geochemistry. For the most part, the speakers took a practical approach to specific fluid/rock systems, though not neglecting discussion of the broader concepts involved. In the case of fluid inclusion work, continuing advance in analytical procedure is bringing out ever greater detail of fluid chemistry, thus allowing a more direct examination of the problems of metal transport in aqueous systems.

Rankin & Alderton reviewed their study of fluid inclusions in quartz from SW England granites, emphasizing the relationship between the variety of inclusion types encountered and the thermal and mineralization history of the area. Improved identification of daughter minerals including unusual chloride phases by SEM and of minor elements in the fluids such as boron and tin by ICP analysis is now an important part of this work. Bull described the complex mineral paragenesis in veins related to minor granite bodies in the Gunnislake area of Cornwall, and related it to three generations of fluid inclusions seen in quartz, cassiterite and fluorite. Though a history of general fluid cooling is present, his results indicate broad fluctuations of homogenization temperature within each fluid generation. A three-stage pattern of fluid evolution is also apparent in the Aberfoyle Sn-W deposit in Tasmania (Wilkins & Ewald). In addition to overall cooling, there are marked decreases in CO₂ content and salinity, together with successive changes in mineral deposition, which may reflect a diminishing ratio of granite-derived fluid to meteoric fluid in the convecting water circulation. Study of zinc-tin mineralization in the Nigerian ring complexes (Kinaird, Bowden & Leterrier) also employs fluid inclusion techniques. Evidence of fluid-rock reaction is

given by mineralogy and Rb-Sr studies, which show that significant interaction occurred in part before the main mineralization. This early stage is marked by dispersed niobium deposition. Fluid inclusion study of the Tyndrum lead-zinc deposit in Scotland (Patrick) demonstrates that boiling took place during mineralization and that fluid temperature increased with time. Formation of K-feldspar is related to the low Na/K ratio of the mineralizing fluid, a feature related to the potassic nature of the probable source rocks rather than to factors such as high fluid boron-content (see below). Shepherd & Darbyshire described preliminary Rb-Sr radiometric dating of inclusion fluid. An impressive isochron for the Carrock Fell tungsten deposit illustrates the considerable potential of this technique.

Results from experimental study of fluorine-bearing granite systems (Manning) suggest that high-F hydrothermal fluids are related to breakdown of F-rich aluminosilicates formed from late melts which may in the presence of fluorine persist to below 600°C. Formation of F-rich magmatic vapours is not favoured. Tin-tungsten mineralization is often associated with fluids enriched in boron as well as fluorine. Pichavant described lowering of the K/Na equilibrium constant of aqueous fluids in the presence of boron. Reaction of B-bearing fluid with granite wallrock can lead to quartz solution and formation of selvages enriched in tourmaline and K-feldspar.

Study of remanent magnetism in mineral deposits (Beales & Jackson), with reference to polar wandering curves, is benefiting from cryogenic magnetometry. In addition to yielding useful dates, this can help resolve some of the syngenetic *v.* epigenetic controversies which surround some mineral deposits. The importance of weathering and mineralization processes related to groundwater movement was described (Clemmey) with particular attention to copper deposition in Chile, uranium in Namibia and gold in the Witwatersrand. This impressive inventory underlines the significance of groundwaters in terms of creation of metal reserves. The speaker restricted his talk to processes involving metals transported in solution, but had he chosen to include residual deposits and placers his case could have been taken further. Hydrothermal exhalative mineralization is perhaps somewhat intermediate with respect to the high temperature, often stanniferous deposits and wholly groundwater-related deposits. Russell & Samson described the total mechanism of

deep convective flow of seawater through the crust in tenuous environments. Differences of deep source rock lead to major differences between non-volcanogenic exhalative deposits. Application of a variety of techniques is allowing reasonable quantification of such processes.

Returning to epigenetic deposition within the crust, the paper by Pearce & Baldwin described a survey of trace element and other parameters within the El Salvador copper porphyry deposit. Attention was drawn to late magmatic build-up and migration of vapours, showing how petrography among other things can be used to trace these phenomena. The mineralogy and geochemistry of the mineralization itself gives evidence of the subsequent fluid movements, and their results indicate an episodic pattern of fluid expulsion. The Carrock Fell tungsten deposit in Great Britain resembles the Aberfoyle deposit (see above) in some respects. Pervasive greisenitic alteration of granite wallrock (Ball, Fortey & Shepherd) is marked by loss of sodium, with feldspar breakdown and silicification. Zones of intense alteration correspond with high concentrations of fluid inclusions with high mean H_2O/CO_2 ratios, together with sulphide enrichment and high As-contents in the heavy mineral fraction. Formation of pyrrhotite and pentlandite in greenschist-facies Dalradian slate (Hall) took place in what may be pseudomorphs after gypsum. Later-formed pyrite-dominated porphyroblastic sulphides accompany the earlier sulphides on a micro-scale. Metamorphic fluids had an important function in bringing about mineral deposition in this environment. The final paper, by Larter, Boyce & Russell, described pyrite 'chimneys' from the Ballynoe baryte deposit at Silvermines. They strongly resemble features of ocean-floor exhalative vents, and their presence is indicative of truly syn-sedimentary deposition. Their apparent rarity in ancient shallow water continental settings may result in part from a low likelihood of preservation of such delicate structures.

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Fluid inclusion evidence for the evolution of hydrothermal fluids in SW England A. H. Rankin & D. H. M. Alderton

Quartz from the granites of SW England contain a complex and varied assemblage of fluid inclusions. Several generations, each recording a particular hydrothermal event, are usually present, though it is difficult to establish an unequivocal paragenesis. Vapour-rich inclusions are common and homogenization temperatures range from less than 70°C up to about 600°C with salinities varying from 0 to greater than 50 equiv. wt% NaCl. Periodic boiling and influx of more dilute fluids of meteoric origin are invoked to explain these variations.

Marked differences in the distribution and abundance of

different inclusion types occur on a regional scale. In particular, the Dartmoor granite contains a dominance of highly saline fluids characterized by high levels of Na, K, Ca and Fe chlorides (from SEM studies). Minor elements in these fluids (from ICP analysis of decrepitated) include B, S and traces of Sn, Cu, Pb, An and W. These inclusions are believed to represent the earliest fluids evolved from the cooling granite magma. The paucity of low salinity fluids indicate that later influx of meteoric fluids was restricted in this pluton. In other plutons, particularly in those parts where Sn-W-Cu mineralization is intense (e.g. N Carnmenellis), the inclusion population is often characterized by abundant low to moderate salinity fluids ($T_H \sim 150-450^\circ C$) believed to be dominantly meteoric in origin. The final phase of hydrothermal activity is represented in the granites of SW England by low temperature inclusions (less than about 150°C) which cross-cut all other generations. These fluids are particularly abundant in the kaolinized granites of St Austell.

Mineralization of the area around Gunnislake, E Cornwall: a fluid inclusion and paragenetic study B. W. Bull

The minor granitic intrusions of Kit Hill, Gunnislake and Hingston Down lie between Dartmoor and Bodmin Moor. A number of E-W striking mineral veins traverse the area, and are in spatial and probable genetic association with the intrusions.

The veins carry cassiterite, wolframite and a number of sulphide minerals. There is little evidence for a spatial zonation of the vein deposits. Examination of polished sections reveals a sequence of mineral deposition which is similar for all the E-W striking veins. Replacement phenomena are common, and it is likely that dissolution of specific minerals has played an important role in vein development.

Heating and freezing studies have been made on the vein minerals. A broad range of homogenization temperatures has been obtained, and are summarized as follows:

- (1) Quartz-cassiterite-wolframite veins:
 T_H approximately 200-400°C for quartz and cassiterite;
- (2) Sulphide veins with cassiterite and wolframite:
 - (a) T_H approximately 200-300°C for quartz,
 - (b) T_H approximately 100-200°C for fluorite.

Salinities are variable, and results range from 0 to 42.2 eq. wt % NaCl. The majority lie between 0 and 25 eq. wt % NaCl.

N-S striking veins also traverse the area, and are not restricted to the vicinity of the granite outcrops. In contrast to the E-W veins, they bear only a more limited sulphide assemblage. Homogenization temperatures from fluorite lie between 110 and 140°C. Salinities are between 20 and 25 eq. wt % NaCl.

Ore-forming fluids of the Aberfoyle tin-tungsten deposit, Tasmania R. W. T. Wilkins & A. Ewald

Aberfoyle is the largest mine within a small but significant tin and tungsten mineral field associated with the Ben Lomond Granite in NE Tasmania. The veins developed within a hydrothermal system in fractured quartzites and shales of the Mathinna Group, above a cupola of the granite. The paragenetic sequence of minerals in the veins can be broadly summarized in three major overlapping stages. In the early stage, within which most ore deposition occurred, cassiterite and wolframite were accompanied by halide-bearing minerals such as fluorite, apatite, topaz and triplite. In the

intermediate stage sulphides, chiefly arsenopyrite, pyrite, pyrrhotite, chalcopyrite, sphalerite and stannite were accompanied by quartz. In a late stage of alteration and secondary remobilization of earlier-formed minerals, minor sulphides, chiefly galena, were deposited with scheelite, carbonates and some fluorite.

A preliminary study of fluid inclusions in cassiterite and transparent gangue minerals enables the evolution of the hydrothermal system to be loosely reconstructed. Three types of fluid can be distinguished: (a) CO₂-rich, (b) H₂O-rich with high salinity, and (c) H₂O-rich with low salinity. All three fluid types were present from time to time during the primary depositional stages. Only the low salinity aqueous fluid pervaded the system during the late stage.

Fluid inclusion data indicates that cassiterite-wolframite deposition took place at c. 500–530°C and 700–750 bars total pressure. Late stage alteration of primary ore minerals took place between 150 and 225°C. Lithostatic pressure conditions appear to have prevailed from the earliest stage of ore deposition. However, the presence of naturally decrepitated inclusions in quartz shows that significant fluctuations occurred in P-T conditions.

It is postulated that the CO₂-rich and high salinity aqueous fluids, derived from crystallization of the granite, carried metals, sulphur and carbon into the fracture system. These magmatic fluids became entrained in a meteoric water-dominated convection cell and deposited their metals as the fluids cooled and mixed. The existence of such a system at depth may be inferred from the characteristic fluid inclusions even in barren veins well above the level of economic mineralization.

Mineralization of the biotite granite of the Ririwai Complex, Nigeria Judith A. Kinnaird, P. Bowden & J. Leterrier

The centrally situated biotite granite of the Ririwai ring complex varies considerably in texture and mineralogy. Related to the biotite granite are two phases of mineralization. The first, a dispersed niobium-rich phase in which the granite is texturally modified, is followed by an economically more important vein-controlled zinc-tin phase of mineralization with associated wallrock alteration. Variable mica compositions and feldspar structural states probably reflect changes in the composition of the mineralizing fluids. Rb-Sr isotopic studies on the granite and the late-stage cross-cutting lode system suggest that isotopic homogenization continued to low temperatures. Available fluid inclusion data from the mineralized lode indicates a range of depositional temperatures of 250–400°C

Mineralizing fluids at Tyndrum, Scotland R. A. D. Patrick

The Tyndrum lead-zinc deposits occur as veins and vein breccias in Moinian quartzites. The veins occupy fractures associated with the Tyndrum–Glen Fyne fault. Fluid inclusion studies revealed the mineralizing fluids carried 18 wt % equivalent NaCl, had a Na/K ratio of 3:1 and entered the veins at c. 300°C. The inclusions also revealed evidence for 'boiling', and secondary inclusions containing fresh water and displaying homogenization temperatures of ~125°C may represent trapping of the resulting condensate. Electron microscope studies of the sphalerite revealed that the secondary inclusions developed along deformation twins, zones of intense dislocation, as well as fractures.

The mineralogy of the deposits indicates the temperature

of the solutions increased with time. K-feldspar is a wall rock alteration product and its formation was the result of boiling, a high SiO₂ concentration and the low Na/K ratio of the mineralizing solutions. This low Na/K ratio is explained by the fluids reacting with the K-rich metamorphic source rocks. Sulphur isotope studies indicate a different source of sulphur for the baryte and the sulphides.

Fluid inclusion Rb-Sr geochronometers T. J. Shepherd & D. P. F. Darbyshire

The precise dating of mineral deposits has important implications for understanding the lifetime of ore-forming systems and their temporal relationship to magmatism and other geological events. However, not all deposits provide material suitable for conventional radiometric dating, or data which are amenable to unequivocal interpretation. Nor is it always easy to verify that such samples have remained isotopically 'closed' since their formation. Fluid inclusions provide an alternative closed system approach. By analysing the isotopic composition of Rb and Sr in inclusions within quartz from the Carrock Fell tungsten vein deposits, Cumbria, we are able to demonstrate the feasibility of obtaining Rb-Sr fluid inclusion isochrons. The age for the mineralization, 392 ± 5 Ma, is in good agreement with the mean K-Ar age, 387 ± 6 Ma for the vein micas. Preliminary data was also presented for the North Pennine orefield.

The behaviour of fluorine at the late-magmatic and early post-magmatic stages in the development of the Cornish granites: the application of experimental studies D. A. C. Manning

Experimental studies of the system Qz-Ab-Or at P_{H₂O} = 1 kb have shown that fluorine partitions predominantly into the melt rather than the vapour phase, and that F-rich melts may exist down to 550°C or less. In Cornish F-rich granites, a proportion of the fluorine content of the magma has been fixed prior to complete consolidation in primary topaz and lithium-mica. Alteration of these F-rich aluminosilicate phases (F/(F+OH) ≈ 0.8) leads to F-poor muscovite (F/(F+OH) ≈ 0.05) and fluorite of hydrothermal origin. The hydrothermal fluid is thus enriched in fluorine by post-magmatic reactions with F-rich aluminosilicate phases. Experimental and petrographic data suggest that whereas fluorine may aid concentration of metals such as Sn and W by magmatic processes, the affinity of magmatic fluorine for aluminosilicate phases does not favour the formation of residual F-rich ore-forming fluids. Such fluids may be produced by post-magmatic reaction between aqueous solutions of many possible origins and F-rich granitic rocks, independent of their crystallization.

Potash metasomatism induced by circulation of boron-bearing fluids: experimental evidence M. Pichavant

The effect of the percolation of boron-bearing hydrothermal fluids upon alkali partitioning between rock and fluid was experimentally studied. The results obtained in the Or-Ab-Na₂B₄O₇-K₂B₄O₇-H₂O system between 400 and 600°C, at P = 1 kb, show that the equilibrium constant K/Na of boron bearing fluids in equilibrium with two alkali feldspars is lowered with respect to that of chlorine-bearing fluids which can be taken as a reference. Thus, percolation of

fluids containing borate anions leads to a potash metasomatism of the wall-rocks with the fluid becoming more sodic. This result can be applied particularly to many Hercynian granites in which evidence exists for the circulation of boron-bearing hydrothermal fluids.

Palaeomagnetic imprints of fluid migrations in sedimentary basins F. Beales & Charlotte (Claesson) Jackson

Some sedimentary rocks and stratabound ores carry measurable detrital, diagenetic and/or epigenetic magnetic remanence. The Newfoundland Zinc Mines epigenetic sphalerite ore is probably early Middle Ordovician in age, not much younger than the host dolostones. In contrast, the Viburnum trend of SE Missouri galena/sphalerite ores are probably late Pennsylvanian in age hosted by late Cambrian dolostones. At Nanisivik Mines on northern Baffin Island, only the epigenetic sphaleritic ores were measurable and indicate a late Proterozoic age significantly younger than the early Helikian dolostone host. In general, palaeomagnetic measurements on sediments and their diagenetic/epigenetic cements may provide crude but geologically and economically useful dates.

Sedimentary gold, uranium and copper deposits, and the role of groundwater in their genesis H. Clemmey

Weathering, diagenetic breakdown of unstable silicates, desorption from detrital clays and oxidation of metalliferous minerals may all contribute metal to groundwaters. Such fluids may produce orebodies depending on the degree of hydraulic isolation, flow rates, aquifer/aquiclude geometry, bedrock/cover relationships, and metal concentration (effected by local 'hot spot' sources, groundwater ponding, evaporation). Groundwater fluids also produce important 'protore' concentrations in palaeosols and sediments.

Exploration implications are important. Location of flow-paths by a combination of sedimentary facies analysis and certain geochemical and mineralogical pathfinders can lead to 'primary' basement ore or 'secondary' sedimentary ore. The contention that groundwater fluids were involved in sedimentary ore formation affects genetic theory and hence exploration models.

Solutions feeding Irish Zn+Pb (+Ba) and other 'non-volcanogenic' exhalative deposits M. J. Russell & I. M. Samson

The properties of the hydrothermal solutions that fed the Irish exhalative Zn+Pb ore deposits have been estimated from fluid inclusion studies, geological and geochemical modelling [Russell *et al.*, *Mineral Deposita* (in press)] and experimental rock/water interactions at elevated temperatures and pressures [Bischoff *et al.*, *Econ. Geol.* (in press)]. Salinities ranged from 10 to 25 equiv. NaCl wt % and the solutions are considered to represent some ground water but the dominant fraction is probably modified highly saline early Carboniferous seawater. Metals mainly occurred in solution as chloride complexes. K/Na ratios were about 0.2. H₂S concentration was X0 ppm.

Saline seawater modification was by reaction with hot Lower Palaeozoic greywackes. The process was probably downward penetrating convection. Solutions were 1 pH unit on the acid side of neutral and were saturated with pyrite. Temperatures of the (boiling) solutions feeding Silvermines

rose to at least 265°C and at Tynagh temperatures are assumed to have increased with time to perhaps >300°C to account for the late copper. Increase in temperature with time possibly reflects deepening of convection cells as the upper crust is cooled (Russell *et al.*, op. cit.).

Non-volcanogenic exhalative deposits which formed in tensional environments elsewhere in the world (e.g. Mount Isa, Sullivan) probably had similar origins. Variations between deposits may be explained in terms of differences in fluid and source rock chemistry. Where source rock allows a modified seawater mineralizer of normal salinity (~3 wt % NaCl), this may give rise to exhalative antimony deposits. Convection of solutions in a pile of mafic and felsic volcanics may result in some P₂O₃ and F accompanying Pb+Zn ore (e.g. Broken Hill, Australia). Where the upper crust contains anomalous B and Sn, exhalative tin deposits may occur.

The main causes of precipitation of sulphides in these deposits is boiling in the feeder zones (Finlow-Bates, T. & Large, D. E. 1978, *Geol. Jb.* **D30**, 27–39) and mixing with seawater just below and on exhalation onto the seafloor. Boiling in the feeder zones causes a rise in pH and a sudden drop in temperature which results in the precipitation of very fine-grained sulphide which may be carried in the rising solutions to be rained onto the seafloor from the bottom-hugging fraction of a double diffusive plume.

Geochemical tracers for identifying the pathlines of mineralizing fluids: examples from the El Salvador porphyry copper deposit, Chile J. A. Pearce & J. A. Baldwin

The aim of this work was to trace the origin and evolution of magmatic mineralizing fluids during the formation of the El Salvador porphyry copper deposit in Chile. The subject can be treated in two parts: the concentration of magmatic fluids within the magma chamber and expulsion of these fluids; and the passage of the fluids through the surrounding rocks.

The concentration and expulsion of fluids can be traced by means of whole-rock chemistry, mineralogy and textures. The parts of the magma chamber through which volatiles have passed in significant quantity may be indicated by negative Mn anomalies in the intrusive rocks; areas of volatile build-up are indicated by the presence of magmatic biotite and biotite after hornblende; areas where rapid loss of volatiles has occurred are delineated by the presence of an aplitic groundmass. The distribution of these features points to an episodic loss of volatiles from a cupola developed on a high-level intrusive stock.

The passage of fluids away from the cupola can be monitored by the compositions of vein sulphides, hydrothermal and hornblende replacement biotites and altered wall-rock. Closest to the fluid source, the sulphide mineralogy has a high Cu/Fe ratio, hydrothermal biotites have high Mg/Fe and Si/Al ratios and the K-silicate alteration zone has high K/Rb and Ba/Rb ratios. The distribution of these parameters within the El Salvador mine area indicates that spatial geochemical variations must be explained by the superimposition of at least three significant episodes of fluid expulsion.

Wallrock alteration profiles around the Harding and Smith veins, Carrock Fell Mine, Cumbria T. K. Ball, H. J. Fortey & T. J. Shepherd

Studies of the detailed geochemistry and petrography of the granitic host rock surrounding the Smith and Harding

Veins were presented. Two related processes affecting the geochemical distribution were noted. One is related to the greisenizing of the wallrock, resulting in the breakdown of feldspar, the other to the introduction of ore mineral forming elements. These processes are related in turn to the fluids present or introduced into the wallrock at the time of emplacement of the lodes.

Fluid-dominated metamorphic processes of sulphide re-precipitation in the Ballachulish slate A. J. Hall

A detailed mineralogical study of a sample of greenschist facies, Lower Dalradian, graphitic, Ballachulish slate has revealed that two different equilibrium-assemblages of sulphides within the slate were precipitated in distinct stages. Early quartz + pyrrhotite (with exsolved pentlandite) \pm pentlandite discoid lenses (typically 1000 μm diameter and 500 μm thick) are interpreted as precipitating from low F_{S_2} aqueous solutions perhaps indicative of migrating metamorphic fluids. Late pyrite porphyroblasts (10 mm³) with co-precipitated inclusions (<100 μm) of pyrrhotite, chalcopyrite, galena and sphalerite are interpreted as growing in higher F_{S_2} conditions at the expense of disseminated sulphides perhaps in a closed aqueous-fluid system. Chemical redistribution of sulphides and silicates has therefore resulted

in the two sulphide assemblages existing together, on the micro-scale, in the same rock.

It may be inferred that, in general, fluid-dominated metamorphic processes, rather than simply the imposed pressure and temperature, may control the behaviour of sulphides in regional metamorphism.

Hydrothermal pyrite chimneys: feeders to the syn-sedimentary Ballynoe baryte deposit R. C. L. Larter, A. J. Boyce & M. J. Russell

The discovery of pyrite tubes, 0.1–20 mm in diameter, in the Ballynoe sedimentary baryte deposit was reported. Well developed tubes comprise concentric layers of contrasting crystal sizes 0.05–1 mm thick. The central canals contain myriad pyrite framboids, where these are not weathered out.

These tubes are strikingly similar to the ephemeral chimney spires found on the East Pacific Rise at 21°N, from which metal-bearing solutions issue at temperatures of up to 380 \pm 30°C. (Spiess *et al.* 1980; Hekinian *et al.* 1980).

The ancient chimneys are presumed to have formed in a similar fashion, but at a lower temperature and in a shallow sea 20–100 m deep. The discovery of these structures precludes the hypothesis that the Ballynoe baryte deposit was merely a distal, shallow water, high Eh facies equivalent to the 'proximal' pyritic lead + zinc ores at Silvermines.