

Vapor as a medium for the transport of metals: Implications for ore deposit modeling

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Despite increasing evidence to the contrary, most economic geologists still assume that hydrothermal ore deposits form exclusively from aqueous liquid. However, analyses of fluid inclusions in porphyry systems show that the vapor can contain ore-forming concentrations of metals, and that to varying degrees some metals, e.g., Cu, favor the vapor over the coexisting brine.

Although most partitioning experiments have shown that Cu, Zn, Ag, Au and Fe strongly favor the brine, recently reported experiments involving sulfur showed a preference of Cu for the vapor. The solubility of Cu, Ag, Au, and Sn in vapor has been investigated at sub-critical temperatures in the HCl-H₂O system, and that of Mo in pure water vapor. Models developed from these experiments, which assume that the dissolved species have the form, MeCl_m.nH₂O, predict metal concentrations in the vapor approaching those required by an ore fluid, but substantially lower than those measured in vapor-rich fluid inclusions from ore deposits. Metal solubility experiments in sulfur-bearing vapor are now in progress.

Considering that vapor is the dominant fluid in high level magmatic hydrothermal systems, and fluid inclusion and experimental evidence that Cu partitions preferentially into the vapor, we argue that vapor can be the principal agent of metal transport in some porphyry copper systems. We further argue that high sulfidation epithermal deposits closer to the earth's surface are also formed by this vapor. Early in the evolution of these latter systems the vapor condenses, producing acid-sulfate and vuggy silica alteration, and in some cases Cu-As-Au-Ag mineralization. In other cases, this mineralization is later, after the site of magmatic fluid exsolution has receded to greater depth. Vapor separating at this stage cools along a P-T path above the critical curve of the system, causing it to contract to a liquid from which precious metals subsequently deposit.

Transport of elements by high-temperature and highly oxidized gases from Colima Volcano

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Colima volcano is the most active volcano in Mexico. Before November 1998, when a new eruption started (it still is going on), we have succeeded to sample condensates, natural incrustations and silica tube sublimates from a 800°C fumarole and a 600°C thermal ground. Some results have already been published [1, 2]. Here we report new findings and review all the data obtained. The main difference of Colima gas vents before the 1998 eruption from other well studied volcanoes with strong high-temperature fumarolic jets (Kudryavy, Momotombo, Merapi, Satsuma-Iwojima, Showa-Shinzan) was a very diffuse emission of a hot air + magmatic gas mixture from the whole surface of the former summit dome. Therefore, the mineral set deposited on the inner wall of the silica tube was quite different from minerals of "common", reduced volcanic gases. We found V- and Te-sulfates, which have never been found inside silica tubes and in natural incrustations before. Native gold has been observed in natural incrustations at other volcanoes, but never in silica tubes. The deposited "pneumatolitic" material in silica tubes is close in chemical composition to a rich "high-sulfidation" ore body of precise metals. The observed distribution of metals along temperature gradient is in a good agreement with the modeled distribution using the SOLVGAS computer code with a modified thermodynamic data base. The redox-control of the variability of mineral phases is discussed in detail; in particular, the cause of the V- and Te- enrichment and the absence of "common" Mo and Cd phases in Colima sublimates. The REE abundances and distribution is also discussed.

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New type of rare-metal mineralization: Deposition of metals in high-temperature vapor system of Kudriavy volcano, Iturup Island, Kuriles, Russia

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Fumarolic fields of the Kudriavy volcano represent that part of modern ore-forming system where deposition of ore minerals is now taking place directly from vapor phase. Different temperature regime and rugged topography of these fields allow to study matter precipitated within wide temperature range (up to 870°C). There are four high-temperature fumarolic fields on the top of the volcano with different temperature of gases and geochemical specialization of sublimates: "Rhenium" (300-560°C), Re-Cd-Zn-In; "Molybdenum" (400-650°C), Mo-Zn; "Main" (700-870°C) Mo; "Dome" (400-730°C) Mo-Zn-Cd-In. Pb-Bi-S and pyrite mineralization is widespread excepting Molybdenum field.

Our data on zoning, mineral associations and phase compositions of the high-temperature fumarole products let us assume volatile chlorides (halogenides), oxychlorides and oxide compounds as predominant carriers of metals. Ppb-level amount of metals in gas (according to ICP-MS analyses of condensates) is enough to form individual mineral phases by means of vapor transport. Sublimate minerals in general occur as euhedral crystals, as well as skeletal, plate, needle crystals and their morphology reflects growth from low-dense medium.

Three new minerals of rare metals have been found among sublimates of the Kudriavy volcano to date: rheniite ReS_2 (Znamensky et al., in prep.), cadmoindite CdIn_2S_4 and kudriavite $(\text{Cd,Pb})\text{Bi}_2\text{S}_4$.

Molybdenite, earlier concerned to crystallize separately from rheniite at higher temperatures, was found as epitaxial growth on rheniite. Micron-sized particles of native gold were determined among crystals of this molybdenite.

Metallogenic specialization of the mineralization in some aspects is close to Cu-Mo porphyry and Mo-W skarn deposits of ancient vapor-hydrothermal systems.

Reference

Znamensky et. al., in preparation

Transport of metalloids by low-density hydrothermal fluids: Insights from X-ray absorption spectroscopy

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Metalloids such as As, Sb, Si, and Ge are ubiquitous components of hydrothermal systems. They often accompany precious metals and may serve as geochemical tracers of hydrothermal and volcanic processes. However, the behavior and chemical forms of these elements in low-density fluids and vapor-brine systems are still poorly known.

The present contribution summarizes our recent X-ray absorption spectroscopy studies of As, Sb and Ge speciation and solubility in supercritical aqueous fluids. Our experiments were conducted using a new X-ray cell allowing simultaneous *in situ* measurement of both metal local atomic structure (XANES and EXAFS spectra) and its total dissolved concentration to 500°C and 1 kbar. Results show that in both neutral vapors and moderately-saline solutions (< 2 mol NaCl), As(III), Sb(III) and Ge(IV) form hydroxide complexes whose structures change little in a wide range of temperature (20-500°C) and fluid density (1-0.1 g/cm³). In acid chloride-rich brines and HCl-bearing vapor (> ~0.05 mol HCl) in contrast, chloride species appear to be the dominant form of Sb at temperatures below 400°C. At higher temperatures and lower acidities corresponding to the conditions of most porphyry deposits, however, our data indicate that antimony chloride species are less important compared to the hydroxide $\text{Sb}(\text{OH})_3$. Our X-ray cell allowed, for the first time, an *in situ* measurement of Sb vapor-brine equilibrium fractionation at the two-phase boundary of the H_2O -NaCl-HCl system.

Both solubility patterns of Sb(III) and Ge(IV) oxides in low-density aqueous fluids and vapor-brine partition coefficients of As, Sb and Si are directly related to the fluid density in a wide range of conditions. This implies that water-solute interaction is a key factor controlling the metalloid transfer by vapour-like fluids in the Earth's crust. Our new findings allow quantitative prediction of the vapour-liquid distribution patterns and vapor-phase transport of metalloids in magmatic-hydrothermal environments.

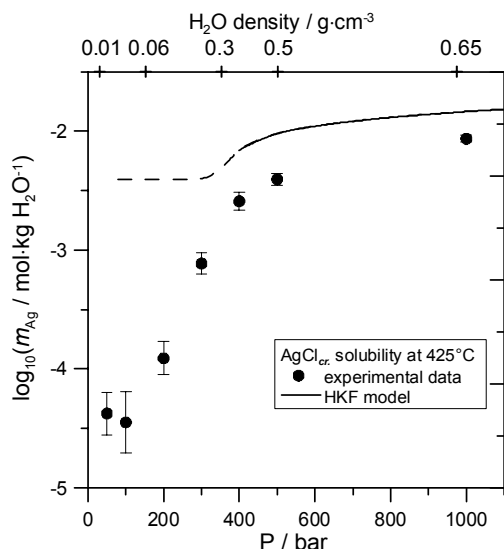
Solubility of chlorargyrite AgCl_{cr} in low density aqueous fluid at 400 - 425°C and 50 - 1000 bar

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The goal of this study is to develop an approach to thermodynamic description of neutral aqueous complexes in a wide range of fluid density. For this purpose chlorargyrite solubility has been measured in water as a function of solvent density.

Experiments were carried out in pure water using titanite alloy VT8 autoclaves at temperatures 400 and 425°C and pressure range of 50-1000 bar. The density of solvent thus changes within the limits of 0.015-0.7 g/cm³. Solubility of AgCl was determined by means of loss-weight and atomic adsorption methods. The results of experiment are shown in the figure as a filled symbols. It can be seen that AgCl solubility decreases sharply with lowering pressure in comparison to the HKF model (solid line in the figure).



Thermodynamic description of the experimental data is based on the new equation of state of Akinfiyev & Diamond (2003) for neutral aqueous species.

Acknowledgements

This study was supported by the projects of NSERC-CRO "Gaseous transport of metals" and RFBR 05-05-64139.

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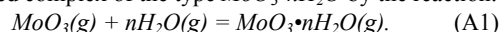
Akinfiyev N.N. and Diamond L.W. (2003) *Geochim. Cosmochim. Acta* **67**, 613-627.

Molybdenum solubility and speciation in water vapor at elevated temperatures and pressures

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Given that hydrothermal systems responsible for the formation of porphyry *Mo* deposits are commonly vapor-dominated, it is reasonable to ask if vapor could be the agent of *Mo* transport. As a first step in addressing this question, we have experimentally investigated the solubility of MoO_3 in dry water vapor at 300, 320, and 360°C and 39 to 163 bars. Results of these experiments show that the solubility of MoO_3 is between 1 and 25 ppm, which is 19-20 orders of magnitude higher than in the water-free system. Molybdenum solubility increases with increasing $f_{\text{H}_2\text{O}}$, indicating that *Mo* forms a hydrated complex of the type $\text{MoO}_3 \cdot n\text{H}_2\text{O}$ by the reaction:



The hydration number, n , is 2.3 at 300°C, 2.9 at 320°C, and 3.2 at 360°C and the corresponding values of log K are 17.5, 15.1, and 12.0. Calculations based on these data predict that the solubility of *Mo* in water vapor is ~0.06 ppm at conditions typical for the formation of a porphyry *Mo* deposit. This would be sufficient to form an economic deposit within the lifetime of typical hydrothermal systems. However, the high salinity of porphyry *Mo* systems, and evidence that *Mo* forms stable gaseous chloride species in water-free systems, suggest that the *Mo* solubility in water vapor may be enhanced by the formation of hydrated chloride species. This conclusion is strengthened by the fact that the fugacities of MoO_2Cl_2 , [1] MoCl_4 , [2] and MoCl_6 [3] in the water-free system are many log units higher than that of MoO_3 (e.g., at 300°C, the log fugacities are 2.79, 3.11, and 0.92 bars, respectively, whereas MoO_3 has a log fugacity of -28.76).

The hypothesis that *Mo* forms stable gaseous hydrated chloride complexes will be investigated experimentally in the system *Mo-Cl-H₂O* at temperatures from 300 to 600°C, at both undersaturated and saturated water vapor pressure. The latter experiments will be used to determine the partition coefficient for *Mo* between liquid and vapor, in order to evaluate the relative importance these phases in the transport of *Mo* in magmatic-hydrothermal systems.

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Experimental study of silver transport in gaseous hydrogen sulfide at 300°C

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The experimental study of the solubility of silver sulfide (acanthite) in gas hydrogen sulfide was carried out in titanium alloy autoclaves at 300°C and pressures up to 200 bar put in an air-thermostat oven SNOL-3.5M.. The purified and dried hydrogen sulfide was frozen out in the autoclave using solid carbon dioxide and acetone mixture. The autoclave was loaded with an open titanium ampoule containing a natural or synthetic crystal of acanthite. The total pressure in the system was calculated from the volume of the gas phase as well as the mass and pVT properties of hydrogen sulfide. The time required to attain equilibrium in the system studied is about 5 days. The duration of all runs was 7 days.

After the run, the autoclave was quenched to room temperature with air and the autoclave volume was washed closed with a weighted amount of 10% HNO₃ at 200°C during 1 hour in an air-thermostat oven with shaking. Silver concentrations in washing solutions were measured using atomic absorption spectroscopy.

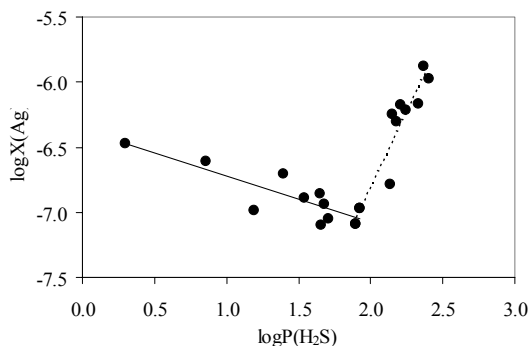
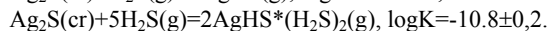


Figure 1. Log of Ag mole fraction in the gas phase versus log of total H₂S pressure.

Results have shown that the addition of hydrogen sulfide in a system increases the solubility of silver sulfide. High values of solubility permit to assume the solvation reactions. The form of gaseous specie can be determined by logP(H₂S)-logX(Ag) plot (fig.1). There are two reactions of acanthite solubility in hydrogen sulfide:



Acknowledgement

This research was supported by RFBR 03-05-64696.

Partitioning and vapour transport of Pt at magmatic conditions

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Knowledge of element distribution between melts and fluids is fundamental to understanding their transport in late-magmatic stages. Vapour-melt partitioning experiments are limited by the formation of quench products and the reactivity of trapping materials at high temperatures. To overcome these problems we have developed a method to trap fluid inclusions, in equilibrium with a basaltic melt, within overgrowths on seed crystals at naturally relevant conditions. Vapour-melt partition coefficients (D_{v-m}) are determined through analysis of the inclusions by laser-ablation ICPMS and of the quenched melt by isotope dilution ICPMS.

An₄₂Di₅₈ glass, water and a diopside seed crystal were sealed in a Pt capsule, avoiding contact between the diopside and glass. Capsules were heated to 1498K at 200 MPa in an internally heated pressure vessel with an intrinsic fO₂ that lies along the MnO-Mn₃O₄ buffer curve. At the initial P-T-X conditions of the experiment H₂O is a vapour, with a molar volume of 65 cm³/mol, that coexists with melt and diopside. After equilibration times of 6-12 hours, the temperature was dropped by 50 degrees, promoting growth on the seed crystal. Crystals grew for 18-36 hours via transport of silicate components through the vapour phase, allowing inclusions, <10µm to 80µm long, to be trapped on the growth surface. There was no contact between melt and crystal and crystallization occurred solely from the vapour.

D_{v-m} of Ba, Sr, Cs, and Rb are being determined for use as internal standards to quantify Pt concentrations in the inclusions, the focus of this study. Though semi-quantitative, preliminary results suggest ppm levels of Pt in the vapour, in contrast to a few hundred ppb in the melt.

The capacity of the vapour to transport Pt supports magmatic/hydrothermal models of Pt enrichment and shows that vapour saturation is an important consideration in any model of deposit formation. This method also shows promise for determining D_{v-m} of a variety of elements between high temperature melts and fluids.

Distribution of solutes between coexisting steam and water: Test of the new equation of state

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Boiling of hydrothermal fluid that brings to appearance of coexisting dense (liquid) and vapour phases is usually considered as a typical reason of ore deposition during natural fluids evolution. Thus the theoretical modelling of such processes is of great geochemical interest. Nevertheless it is to state that while description of equilibria in the dense fluids is rather reliable (Tanger and Helgeson, 1988), the low density fluids are bereft of an approach that takes into account the hydration of solute in the vapour phase.

The goal of this study is to apply the recently proposed equation of state (Akinfiiev and Diamond, 2003) for the description of liquid-vapour partitioning of various solutes to the critical temperature of water.

The master equation for the partitioning constant between vapour and liquid $K \equiv m_{\text{vap}}/m_{\text{liq}}$ at given temperature T yields

$$\ln K = - \left[\xi \ln \frac{\rho_{\text{vap}}}{\rho_{\text{liq}}} + \left(a + b \left(\frac{10^3}{T} \right)^{0.5} \right) \right] (\rho_{\text{vap}} - \rho_{\text{liq}})$$

and uses only three empirical parameters ξ , a and b that can be estimated from the low temperature data. Here ρ_{vap} and ρ_{liq} stand for density of pure solvent (H_2O) in coexisting vapour and liquid phases respectively.

This equation was successfully employed to describe partitioning of both volatile nonreactive solutes (H_2 , O_2 , N_2 , CH_4 etc), and reactive solutes which undergo protolytic equilibria in water (CO_2 , NH_3 , H_2S , $\text{B}(\text{OH})_3$, and even HCl) in the temperature range from 0 to 370°C . Some preliminary estimation for description of vapour-liquid partitioning of NaCl as a characteristic example of strong electrolyte was also implemented. The study was supported by grants RFBR 05-05-64139 and NSERC CRO.

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Akinfiiev N.N. and Diamond L.W. (2003) *Geochim. Cosmochim. Acta* **67**, 613-627.

Fluid inclusion evidence for extreme element partitioning during subcritical phase separation

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Fluid phase separation (boiling) can be the primary cause of major variations in fluid composition in many land-based and marine hydrothermal systems. Such major variations commonly lead to extreme enrichments of important metals and to ore deposits. Subcritical boiling produces a vapour phase and a brine that can be chemically very different from each other and from their parent fluid. Under the best circumstances, fluid inclusions trapped in hydrothermal minerals can provide a direct link to the fluids that formed them. Therefore the study of fluid inclusions in minerals from boiling systems using Laser-ablation ICP-MS (LA ICP-MS) and Synchrotron radiation X-ray fluorescence (SR XRF) have revealed new insights on the partitioning of elements between the liquid and vapour phase.

SR XRF has the advantage of being non-destructive but is limited to higher Z elements ($Z > 16$). LA-ICP-MS can detect all elements but is destructive and limited to 10 or less elements per ablation to achieve optimal results.

The fluids studied here are trapped as inclusions in quartz from cavities hosted by granitic rocks of the Torres del Paine complex, Chile. Primary boiling assemblages of vapour-rich and highly-saline (>30 eq. wt% NaCl) inclusions have been analyzed by LA-ICP-MS and SR XRF.

Qualitative results from SR XRF analysis reveal extreme element partitioning between the vapour and liquid phase. The brines are typically enriched in Mn, Fe, Ni, Zn, As, Br, Rb, Mo, Cd, Sn, Sb, Cs, Pb, W, Ce, Pr, Nd, and minor amounts of Ag, but Cu could not be detected. In contrast, most of the vapour-rich inclusions show strong signals for Cu and Fe, Zn, As, Sn, Pb, \pm Mn, Rb, and Br.

LA-ICP-MS analysis shows that Cu and La are preferentially enriched in the vapour, Mn, Zn, Fe, Pb, Na and K are enriched in the high salinity brine, while Ca, Mg, Ni Li and Ti do not show clear partitioning into either phase. For example Cu concentrations in the vapour phase are c. 1000 ppm and c. 80 ppm in the brine. Zn concentrations in the vapour phase are c. 1200 ppm and c. 7500 ppm in the brine.

Ore metal transport by hydrocarbon vapour in the footwall of the Sudbury Igneous Complex, Canada

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We report hydrocarbon vapour inclusions occurring in quartz-epidote-sulfide alteration veins associated with footwall Cu-Ni-PGE (platinum-group element)-Au sulfide deposits at the Fraser Mine (Sudbury Igneous Complex). Primary inclusions comprised of immiscible CH₄ vapour + brine were trapped during quartz growth at relatively low T (~ 145–315°C) and P < 0.6 kbar, prior to the crystallization of sulfide minerals in the veins. Secondary inclusions contain solid halite and a mixture of light aliphatic hydrocarbons and nitrogen (~ 55 mol% CH₄, 35% C₂H₆, 5% C₃H₈, 5% N₂; by gas chromatography). The secondary inclusions may represent immiscible hydrocarbon vapour + halite melt (minimum trapping T ~ 710°C) that exsolved from crystallizing sulfide melt postdating early alteration quartz hosting the primary brine-CH₄ assemblage. Alternately, halite may have been precipitated from a halite-saturated hydrocarbon fluid phase at lower T (< 500°C).

Laser ablation ICP-MS microanalysis shows that hydrocarbon vapour, brine and halite melt inclusions contain significant concentrations of Cu (100 µg/g to 1 wt% range), Au, Bi, Ag and Pt (all 0.1-10 µg/g range). Cu:Pt and Cu:Au ratios in the primary hydrocarbon inclusions are up to 4 orders of magnitude lower than in the host alteration veins and adjacent parent massive sulfide ore veins, suggesting either (i) early Cu loss by chalcopyrite precipitation during cooling of the vapour phase or (ii) enhanced Au and Pt solubility relative to Cu at the low temperature of entrapment. Concentration ratios between coexisting primary hydrocarbon vapour and brine inclusions [$C_{\text{hydrocarb}}/C_{\text{brine}}$] are higher for Cu (0.1 to 100; avg.=10), Au, Bi and Ag (0.1 to 10; avg.=2) than for other elements (Na, Ca, Fe, Mn, Zn, Pb; all < 0.1) indicating that during interaction with the brine, the hydrocarbon vapour was selectively enriched in specific ore metals.

Our study reports the first direct measurements of precious metal concentrations in fluid inclusions from a magmatic Ni-Cu-PGE environment (the Sudbury district) and demonstrates the importance of non-polar solvents for vapour phase transport of ore metals in magmatic Ni-Cu-PGE systems.

Carbonic vapor-dominated fluid systems in orogenic-type Au deposits

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The ore-forming fluids of the majority of orogenic-type gold deposits have compositions in the H₂O-CO₂-NaCl system, with generally low salinities and CO₂/H₂O molar ratios <0.5. In some cases, including the giant Ashanti deposit, Ghana and the Campbell-Red Lake deposit, Canada, the predominant fluid inclusions are carbonic (without detectable H₂O), while aqueous or aqueous + carbonic inclusions are rare. Whether the carbonic inclusions represent the ore-forming fluids or result from post-trapping leakage of water is still a matter of considerable debate.

Microthermometric, Laser-Raman spectroscopic, and gas chromatographic measurements indicate that fluid inclusions from Campbell-Red Lake are predominantly carbonic, composed mainly of CO₂, with minor CH₄ and N₂, and trace amounts of H₂S. Homogenization temperatures of these fluid inclusions vary considerably but in individual fluid inclusion assemblages the range of T_h is relatively narrow, indicating that H₂O depletion in the carbonic inclusions was not due to post-trapping modifications and host mineral deformation.

Fluid phase modeling supports a hypothesis in which the Campbell-Red Lake gold deposit formed from an H₂O-depleted carbonic vapor derived from phase separation of an originally carbonic-enriched hydrothermal fluid. We propose that the gold was preferentially partitioned into the vapor phase during phase separation and transported as H₂S- or hydrocarbon-solvated species to the site of ore-deposition. If correct, this hypothesis will require a re-evaluation of existing models for the formation of orogenic-type gold deposits.

Bingham: A mesothermal Cu-Au deposit dominated by vapor transport of metals?

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Bingham (Utah) is one of the largest and richest porphyry Cu-Mo-Au deposits, formed in intimate association with stockwork veining and potassic alteration centered on a quartz monzonite porphyry stock. Geological mapping, cathodoluminescence (CL) petrography and fluid inclusion study including LA-ICPMS analyses of metal ratios in successively trapped inclusion assemblages have led to somewhat surprising results (Redmond et al., 2004; Landtwing et al., 2005).

While the conditions of quartz deposition in the veins span the large range of pressures and temperatures (>550°C/600bar to 200°C/150bar) observed in many other porphyry systems, the precipitation of bornite and chalcopyrite occurs in a narrow P-T interval, at relatively low temperatures between 425°C and 350°C. CL-textural evidence for vein reactivation and quartz dissolution indicates that Cu-Fe-sulfides precipitate where copper solubility decreases with cooling (Hezarkhani et al., 1999), while silica solubility is reverse (Fournier, 1999).

Even though Cu-depletion with falling temperature is best recorded by inclusions of hypersaline liquid, a coexisting low-salinity vapor must have been the dominant metal-introducing phase at Bingham. This fluid is trapped by numerous lower-density inclusions, whose Cu/Na ratio is even higher than that of the brine inclusion and varies over a similar range. Retrograde quartz solubility is confined to a small P-T-X(NaCl) window on the low-salinity vapor side of the salt-water fluid-phase stability field, at temperatures just above the critical point of water. Precise mass-balance estimation of the phase proportion of liquid/vapor is difficult, because of the poorly defined chloride concentration in the low- to intermediate-density inclusions, but the vapor probably predominated over the hypersaline liquid by a factor of at least five by mass (or fifty by volume).

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Coupled heat and salt transport around cooling magmatic intrusions

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We present the results of numerical simulations of coupled heat and salt transport around a cooling magmatic intrusion exsolving a saline fluid. The 800°C magma chamber is emplaced 5 kilometers below the surface at lithostatic pressure conditions. For the crust, we consider both uniform and depth-dependent permeability distributions and allow the permeability to change transiently as a function of pressure and temperature.

Using a new equation of state for the NaCl-H₂O system, we investigate the impact of a model magmatic fluid that is geologically more realistic than pure H₂O. In particular, we study the effects of phase separation of a saline single-phase fluid into a high-density, high-salinity brine and low-density, low-salinity vapor phase well above the critical pressure and temperature of pure H₂O. This allows us to identify transient flow patterns of vapor and brine and their likely effects on the formation of porphyry-style Cu-Mo-Au deposits.

At lithostatic conditions, the magmatic fluid is initially exsolved as a single-phase fluid. It separates into a vapor and brine phase at the transition from lithostatic to hydrostatic conditions, which is accompanied by a steep drop in temperature from magmatic (~800°C) to hydrothermal (~400°C) conditions.

The vapor rises quickly in the crust and recondenses at shallow depths into meteoric waters. The brine is largely immobile because its volume fraction is very low. The brine contains the majority of the magmatic salt and is progressively diluted by entrained meteoric water. Low permeabilities around the magma chamber cause slower cooling of the intrusion and less movement and dilution of the exsolved magmatic fluid. Fluid pressures are close to lithostatic and can be above lithostatic, leading to hydrofracturing. High permeabilities around the magma chamber, however, cause convection dominated fluid flow, faster dilution of the magmatic fluid and rapid diffusion of the lithostatic fluid pressure in the vicinity of the magma chamber, but are probably less favorable for the formation of economic porphyry-style ore deposits.

Transport of Au, platinum-group elements, Ni and Cu in a S-vapor

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There are a number of experiments demonstrating that platinum-group elements (PGE), Au, Ni and Cu have high partition coefficients between silicate melt and base metal sulfide liquid and between silicate melt and alloys. Thus in igneous systems the distribution of PGE is thought to largely be controlled by a combination of sulfides and alloys. The role of vapors in controlling PGE is much less understood and yet some volcanic vapors do contain PGE. Furthermore, transport of PGE, S, Cu and Ni by vapor have been suggested for some ore deposits such as Noril'sk and Duluth. The purpose of our study was to investigate whether: Au, PGE, Ni and Cu could be transported by a S-vapor, whether there was a preferential transport of some elements; and as which species the elements were transported

Twenty-three runs using the tube-in-tube technique were carried out. A S-rich (FeNiCu)_{1-x}S donor doped with 2000 ppm of Au and PGE's was placed in the outer tube and S-poor FeS receiver in the inner tube. The tubes were then evacuated and heated to 1000 °C or 1100 °C for 2 days, after which they were quenched and the run products mounted and polished. The compositions of the phases were determined by microprobe and ICP-MS laser ablation.

Copper Ni, Au, Pd and Pt were found to be present in the receiver and thus were transported by the S-vapor. Iridium, Rh and Ru concentrations in the receiver were close to detection level (20 ppb) and thus transport by a S-vapor seems unlikely for these elements. The order of mobility for the precious metals appears to be Au>Pd~Pt>>Ru~Rh~Ir. In most runs Ni was more mobile than Cu. These observations suggests that deposits from S-vapor should be enriched in Ni, Cu, Au, Pt and Pd and depleted in Rh, Ru and Ir. Neither Cu nor Au showed a positive correlation with fS_2 suggesting that these elements were transported as metals in the S vapor. Platinum, Pd and Ni concentrations correlated with fS_2 suggesting that these elements were transported as S-species. In those runs where Rh, Ru and Ir concentrations were > detection limit there is a positive correlation with fS_2 suggesting that these elements were transported as S-species, but as there are only a few data points this conclusion is tentative.

Experimental study of boron transport in vapor phase to 200°C

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Dissolution experiments of boric acid in under-saturated water vapor at 100, 120, 155 and 171°C were performed in 40 cm³ titanium-alloy (VT-8) reactors put in an air-thermostated oven SNOL-3.5M. Open titanium ampoule containing 0.5 to 1 g of dry solid was placed into the autoclave. Weighted amount of de-ionized and degassed water was introduced at the bottom of the reactor outside the ampoule. Pressure was estimated from the reactor free volume and loaded amount of water according to PVT properties of pure water vapor. At the end of the run, the reactor was quenched in cold water for 15 min., the ampoule was weighted, and the solid and water condensed on the reactor walls and bottom were washed with de-ionized water. Boron concentrations aqueous solutions were measured using colorimetry with the ash-rezorcine complex.

The results obtained shows that at low water pressures boron concentration decrease with H₂O pressure. This can be interpreted by the formation in the vapor of dehydrated boron species: $H_3BO_3(s) = HBO_2(g) + H_2O(g)$. But at H₂O pressures close to the saturation, we find other dependence - increasing of boron concentration with H₂O pressure, that is likely to be interpreted by the formation of hydrated species. The quantification of species stoichiometry was estimated by $\lg P(H_2O) - \lg X(B)$ plot as hydrated polymer $H_8B_2O_7$. The reaction of boric acid solubility in this condition is $2H_3BO_3(s) + H_2O(g) = H_8B_2O_7(g)$.

Vapor-aqueous solution partition coefficients were determined at 100 and 155°C at the saturated vapor pressure of the system using a special titanium reactor which allows sampling of the vapor phase through a capillary tubing during the run. The values of partition coefficients for boron between water vapor and aqueous solution of boric acid were found to be independent of boron solution concentrations up to 2 mol B/kg H₂O. In more concentrated solutions we find the dependence of partition coefficients. This result has a good agreement with solubility of boric acid in non-saturated vapor and other data.

The results of this study imply that hydrolysis and hydration could be also important for other elements in H₂O vapor phase. These processes should be taken into account to accurately model element fractionation and chemical equilibria during both magma degassing and fluid boiling.

Acknowledgement

This research was supported by RFBR 03-05-64696.

Extreme fractionation of REE and some transition metals in the natural high-temperature vapor systems

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Principal peculiarities of mineral precipitation from high-temperature gas fluids are considered on the example of the Kudryavy volcano (Kuril Islands, Russia). Unusual association of Gd and Y titanates, Ce-aluminosilicate, ferberite, scheelite, povellite, various chlorides and oxychlorides was found in sublimates precipitated at about 650°C in the Dome fumarolic field. Mineral phases contain up to 45 wt.% Gd and 34 wt. % Y and correspond to formulas $Gd_3Ti_4O_{12}$ and $YTiO_4$, respectively. Numerous fine grains (less than 50 mkm in size) of Gd-Zr oxide in association with Ce-monazite, ZrO_2 , molybdates, tungstates and oxychlorides occur at about 500°C in the Molybdenic fumarolic field. Plate crystals of $Cu_3(Au,Ag)_2$ alloy crystallized also in this temperature zone. The surface of Gd-rich phases is covered with the smallest spherical particles of native molybdenum, the interior of grains was established in polished sections also contains round inclusions and finest impregnation of native molybdenum. Morphology of HREE phases and their intergrowths with native molybdenum and others minerals indicates that they were precipitated in situ by means of crystallization from vapor. The results of ICP-MS analyses of high-temperature gas condensates as well as INA analyses of precipitations from serial zones in silica tubes also revealed selective fractionation and HREE enrichment.

Formation of native Mo in sublimates, as well as native modes of other transition metals, is explained by passing of the gas transport disproportionation reactions with coeval deposition of the zero-valent modes and formation of volatile compounds. As a result nonequilibrium association of native Mo, MoS_2 and Ca-molybdates occurs among the sublimates. Selective brine-vapor fractionation and HREE enrichment of gas phases confirmed also by experiments (Shmulovich et al., 2002) can play important role in formation of similar mineral associations with REE phases and native elements (including PGE and Au) in the real ore deposits at supercritical conditions of mineralization (Waterberg, Sukhoi Log etc.).

Reference

Shmulovich et al., (2002), *Contr. Min. Petr.*, 144, 257-273.