SPECIATION AND TRANSPORT OF METALS IN HETEROPHASE HYDROTHERMAL FLUIDS

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In the last 10 years significant progress has been made in our understanding of geological vapors and fluids of high temperature and pressure, owing both to improvement of existing hydrothermal techniques such as different kinds of chemical reactors or synthetic fluid-inclusions techniques and to the development of new tools like different kinds of spectroscopic cells coupled with synchrotron techniques, which allow to see the true molecular entities responsible for the element transport. Today these experimental tools combined with modern sensitive micro-analytical techniques like ICP-MS and molecular modeling have improved our knowledge of classical hydrothermal fluids of moderate pressures and temperatures and allowed to extend studies to vapor-like fluids operating in magmatic-hydrothermal systems at high temperatures and to liquid-like in subduction zones at very high pressures. At low to moderate pressures, the metal transport and deposition can be reasonably estimated using the thermodynamic data for chloride, sulfide or oxide gaseous species available in water-free systems that we can find in well-known thermodynamic databases such as Ivtanthermo, Janaf or NIST. However, the absolute partition coefficients between the volcanic gas and magma for many economic metals like Cu, Zn, Mo, Au. This results in absolute metal concentrations in the ppb to ppm range in the vapor phase, which is in most cases not enough to form an economic deposit directly from the volcanic vapor phase. In contrast, when we go just a few kilometers deeper into the earth, the things change dramatically in terms of vapor-phase transport. In particular, boiling and vapor-brine separation at pressures several hundreds bars is a ubiquitous phenomenon during the formation of magmatic-hydrothermal deposits. This is because the physical-chemical properties of the major fluid constituents, water and salt, allow for the existence of an extremely vast domain where vapor and brine may coexist in the T-P range typical of magmatic-hydrothermal deposits, as you can you on this water-sodium chloride phase diagram. Classical models of ore deposit formation have usually ignored the metal vapor-phase transport assuming that boiling results in the departure of volatiles from the aqueous solution into the vapor whereas all metals remain in the brine. However, fluid inclusions studies have demonstrated that vapor can transport far more metals than ever believed. Thanks to the experimental and thermodynamic studies conducted over the past 50 years, we know that in dense saline S-bearing solution metalloids like As, Sb, Si, B form predominantly neutral hydroxide species prone to be volatile, the speciation of base metals like Zn, Fe or silver is largely dominated by chloride complexes in most cases; chalcophile metals like copper, gold and platinum, in contrast, form chloride and sulfide complexes depending on the fluid acidity and ligand concentration, lithophile elements like Al or Ti form rather unsoluble hydroxide complexes, whereas the speciation of rare earth elements may be dominated by chloride, fluoride, or carbonate species depending of availabilities of these ligands in the fluid. Vapor-liquid equilibria of many elements can be described by simple relationships involving the densities of the coexisting vapor and liquid phases [1]. The partition coefficient of a metal, which is the ratio of its concentrations in the coexisting phases, is linearly proportional to the ratio between the vapor and liquid densities which are well known in the water-sodium chloride system. All lines tend to a partition coefficient of 1 by definition, at the critical point. This is in agreement with natural coexisting brine and vapor inclusions from a variety of natural magmatic-hydrothermal deposits, except for gold and copper. The partition coefficient obtained over the past fifteen years using in situ laser ablation ICP-MS on coexisting brine and vapor fluid inclusions in quartz. As and Mo partitioning is close to one on average, consistent with the volatile properties of their hydroxide species, and base metals concentrate in the brine, in almost quantitative agreement with the density model. In contrast, there are systematic enrichments of the vapor phase by copper and gold and sometimes Mo, which are not accounted for by the density model. The most plausible hypothesis of such enrichment is the formation of volatile species with sulfur, the second most important ligand after chloride in crustal fluids [2]. It is only recently that the effect of sulfur on the metal volatility could be demonstrated experimentally using batch-reactor measurements allowing controlled sampling of the vapor and liquid, and synthetic fluid inclusion techniques. The addition of 1 wt% of S to the water-salt system, Cu, Au and Pt partition coefficients increase by 1 to 2 orders of magnitude, attaining values in favor of the vapor, whereas the volatility of silver increases only slightly, and the partitioning of Zn, Fe or lead is almost unaffected. Using these new data we can evaluate the role of vapor in the formation of magmatic-hydrothermal deposits [3]. Using the typical partitioning coefficients of metals between silicate magmas and fluids and between vapor and brine, we can estimate that the degassing of a 100 cubic kilometers of andesitic magma, and subsequent vapor-brine unmixing of the metal-and sulfur-bearing fluid may produce will produce a brine phase that retains relatively small part of the total Au and almost 90% of the total Cu, which will end up by forming a porphyry deposits. The far more mobile vapor phase carrying most of Au and the rest of Cu will rise to shallower levels, cool down, interact with rock and precipitate Au and Cu in the form of an epithermal deposit. Note that despite low vapor-brine partitioning of Cu, this vapor phase will still contain large absolute amounts of Cu and other base metals to form an economic deposit. *Work was supported by RFBR project 17-05-00257.*

Keywords: Hydrothermal fluid, metal speciation, hydrothermal deposits

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