



Metal (copper) segregation in magmas

Jean-Louis Vigneresse^{a,*}, Laurent Truche^a, Pratim K. Chattaraj^b

^a GéoRessources, UMR 7539, BP 23, 54501 Vandoeuvre Cédex, France

^b Department of Chemistry and Center for Theoretical Studies, Indian Institute of Technology – Kharagpur, Kharagpur 721302, India



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ABSTRACT

Before precipitating to form porphyry-type deposits, metals are transported and concentrated into magmas. Ultimately, they can enter crystalline phases or segregate into the volatile phase. In both cases, partition coefficients determine the partitioning according to the ambient physico-chemical conditions. Metal partitioning between the melt and the magmatic volatile phase (MVP) is driven by their solubility. In this study, Cu has been selected as a test for metal segregation. We evaluate qualitatively the metal's behavior with respect to the melt or to the MVP by comparing the difference in chemical potential and polarizability between the fluid phase and dissolved copper compound. Maps of polarizability are drawn after computing the chemical reactivity parameters (electrophilicity, hardness, and polarizability) for various silicate melts; a synthetic fluid phase with water, CO₂, S₁₈ compounds and halogens; and Cu-compounds as a test metal. Cu-compounds show a better affinity with the fluid phase, enhanced by the presence of S in its reduced form. It explains how Cu could segregate into the fluid phase at the magmatic stage before being enriched by diffusion or melt/vapor partitioning, leading to late hydrothermal precipitation. The method should therefore be considered as a model for understanding the behavior of other metals and their segregation during the magmatic stage.

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1. Introduction

Porphyry-type deposits represent some of the richest concentrations in base metals (Cu, Au, Ag, Mo, W, Sn) in the Earth's crust (Robb, 2004). They form huge deposits linked to granitic intrusions, and/or volcanic settings (Sillitoe, 2010). Examples are Chuquicamata, El Teniente or La Escondida, all in Chile, or Henderson, Butte and Bingham, in the USA. A silicic magma chamber of several tens to hundreds of km³ typically underlies those deposits (Dilles, 1987; Sillitoe, 2010). Its composition commonly ranges from calc-alkaline to alkali-calcic, typical of subduction zones. The magma consists of a silicate melt, already formed crystals and a magmatic volatile phase (MVP). Their whole proportions progressively evolve with time and magma chamber composition. The magma chamber grows incrementally by additions from below of multiple recharges, either mafic or felsic, (Annen, 2009; Miller et al., 2007; Vigneresse, 2008). The composition of the exsolved volatile phase mainly consists of water, with variable proportion of CO₂, sulfur compounds and halogens (Wallace, 2005), but it also varies with time depending on magma composition pressure, temperature and crystallinity. Owing to the depth (3–5 km) to which magma chambers form, i.e. corresponding to a pressure of about 100–200 MPa, the volatile phase is supercritical (Aranovich and Newton, 1996; Roedder, 1971). The late separation into a vapor

phase (low density fluid) and a brine occurs at a much shallower depth (Williams-Jones and Heinrich, 2005), after leaving the magma chamber. This later aspect will not be considered here, though it controls metal precipitation.

Metal partitioning between melt and minerals ($K^{\text{mineral/melt}}$) represents the usual way for trace elements and metals to enter into common minerals during crystallization. The value of the partition coefficients determines how much one element is present in both the viscous melt and the solidified crystal. Such values are commonly measured experimentally (f.i. Li and Audétat, 2012). Their theoretical prediction can be apprehended either from crystallography (Blundy and Wood, 2003; Nagasawa, 1966) or from thermodynamics (Vigneresse, 2007).

Element partitioning between the silicate melt and the MVP ($K^{\text{fluid/melt}}$) is the other fate for metals during magma cooling and depressurization in magmatic hydrothermal ore forming system typical of porphyry Cu deposits. Volatile phase exsolution from the magmatic melt is known to be highly effective at scavenging and transporting copper and other ore components, from the silicate melt into the overlying porphyry environment. The high concentration in metals at high temperature and the ability of a degassing melt to supply significant quantities of Cu to the superjacent magmatic-hydrothermal environment via a MVP can be inferred from:

- i) The high concentrations of Cu in fumaroles from active volcanoes assumed to be present day analogs of porphyry–Cu system (Nadeau et al., 2013; Simon and Ripley, 2011; Streck and Dilles, 1998; Taran et al., 1995, 2000; Zelenski and Bortnikova, 2005).

* Corresponding author. Tel.: +33 3 8368 4737; fax: +33 3 8368 4701.
E-mail addresses: jean-louis.vigneresse@univ-lorraine.fr (J.-L. Vigneresse), laurent.truche@univ-lorraine.fr (L. Truche), pkc@chem.iitkgp.ernet.in (P.K. Chattaraj).

Table 1
Fluid inclusions temperatures.

Locality	Reference	Metal	T FI (°C)
Bajo de la Alumbrera, Argentina	Ulrich and Heinrich (2001)	Cu	720–780
Zaldivar Chile	Campos et al. (2002)	Cu	750–900
La Escondida Chile	Padilla-Garza et al. (2004)	Cu	650–680
Bingham Utah	Landtwing et al. (2010)	Cu	650–725
Hudson Bay NM	Bloom (1981)	Mo	320–600
Henderson CO	Carten et al. (1988)	Mo	550–650
Nambija Ecuador	Markowski et al. (2006)	Au	400–460
South Africa	Kolb (2008)	Au	500–700
Mole Australia	Audétat et al. (2000)	Sn, W	600–460
Podlesi, Germany	Thomas et al. (2003)	Sn	550–680

- ii) The high temperature fluid inclusions (Table 1) recorded in porphyry-type intrusions (Bloom, 1981; Campos et al., 2002; Carten et al., 1988; Halter et al., 2004; Markowski et al., 2006; Padilla-Garza et al., 2004; Roedder, 1981; Ulrich and Heinrich, 2001).
- iii) The spectacular enrichment of Cu in fluid inclusions (Audétat and Pettke, 2003; Baker et al., 2006; Campos et al., 2009; Cauzid et al., 2007; Harris et al., 2003, 2005; Heinrich et al., 1999; Rusk et al., 2004; Ryan et al., 2001; Seo et al., 2009; Zajacz et al., 2008).
- iv) The experimental copper solubility measurements in magmatic hydrothermal conditions (Etschmann et al., 2010; Frank et al., 2011; Hack and Mavrogenes, 2006; Lerchbaumer and Audétat, 2012; Pokrovski et al., 2002, 2008; Rempel et al., 2009; Ripley et al., 2002; Simon et al., 2006; Zajacz et al., 2013).

Partitioning of metal from the melt into the MVP is described as a dynamical process controlled by numerous parameters including temperature, pressure, melt composition, redox condition, and the chemical composition of the MVP (sulfur activity, salinity, HCl concentration). In addition, the efficiency of the MVP to extract and transport elements up through the magma body is also dependent on physical processes such as kinetics (diffusion) and transport (advection) (Huber et al., 2012).

There has been considerable work over the last two decades toward unraveling the complex thermodynamics that control the transport efficiency of metals in the fluid phases involved at shallow depths and the factors that affect their solubility in the hydrothermal system. However, the fundamental physicochemical mechanisms that control the exsolution process, the fractionation process between the melt and the MVP and the subsequent metal transport in a deeply sourced, magmatic fluid as it ascends toward the surface, remain poorly understood. The diversity of experimental conditions precludes at present a detailed comparison and determination of which effect is predominant. The combined effect of i) solute–solvent interactions, ii) chemical speciation and iii) formation of volatile species with sulfur or chloride prevents the direct extrapolation of experimental results to the natural systems even with the most advanced thermodynamic model.

The present paper focuses on the chemical aspects under which metals, and more particularly Cu, segregate during the magmatic stage, suggesting why they incorporate into the MVP. The problem of metal partitioning between the melt and the MVP profoundly differs from the partitioning between melt and minerals. There is no mechanical strain, or physical constraint, imposed to the element for entering the fluid phase. The constraint is purely chemical depending mostly on the fluid composition.

For that purpose, we introduce chemical hard–soft acid–base (HSAB) concepts (Pearson, 1993) applied to the MVP, the melt and Cu-compounds as a case study for metal partitioning. Metal integration depends on the metal's chemical reactivity with respect to the silicate melt (Vigneresse, 2012), or the volatile phase (Vigneresse, 2009). Copper is selected as an example of metal through its possible S- and Cl-complexes, or oxides (Duley et al., 2012). The considered volatile phase

is essentially S-bearing in the case of Cu ore formation, but we also examine the behavior of halogens through modeling. Finally the selected chemical descriptors (electrophilicity, hardness and polarizability) for the melt, the MVP and the Cu-compounds are plotted in similar diagrams that take into account the three major principles ruling HASB concepts (Chattaraj et al., 2012a). Identifying the correlation between the S-bearing fluids and Cu compounds and determining the trends for different volatile phase compositions provide new insights to the processes leading to metal segregation into the MVP in the magmatic stage.

2. Chemical reactivity parameters

Chemical reactions can be described either as chemical interactions between elements, or better as electronic exchanges in a global electronic cloud. There, attraction between elements rules their chemical reactivity. It assumes that elements will react together to adjust their chemical potential according to a minimum energy effort. This is the basis of the hard–soft acid–base (HSAB) concepts that presently determine how chemical reaction should evolve (Parr and Pearson, 1983; Pearson, 1968). Quantification of chemical descriptors ruling reactivity is done through density functional theory (DFT) (Parr and Yang, 1989). The quantification of the HSAB concepts led us to determine which chemical descriptors and principles rule chemical reactions (Chermette, 1999; Geerlings et al., 2003).

2.1. HSAB and DFT basics

Two major parameters determine the potential reactivity of an element, i.e. the electronegativity and the hardness (Parr et al., 1978). Electronegativity (χ) is the negative of the chemical potential. It corresponds to the first derivative of the energy when an electron is added or removed to the element, whereas other variables (P, T) are kept constant. Electronegativity determines the power to attract an electron. Hardness (η) is the second derivative of the energy in the same conditions (Parr and Pearson, 1983). It indicates the resistance to a charge transfer. A third parameter, electrophilicity ($\omega = 0.5 \chi^2/\eta$) has been introduced (Chattaraj et al., 2006; Parr et al., 1999) that combines the two preceding parameters. It indicates the deficiency in electrons of an element. A fourth quantity, polarizability (α) indicates the tendency of an electron cloud to be distorted from its normal shape when in presence of an external electronic charge. It links with electronegativity (Nagle, 1990). Negative ions have excess electrons and a large ionic radius, which make them highly polarizable. Small highly charged cations, such as most common metals, can easily distort under the influence of an external field. Units are usually in eV for the three first parameters, whereas atomic unit (a.u.) is used for polarizability, with 1 a.u. = 0.529 Å.

Simple principles rule chemical reactions, stating that reactions should evolve toward maximum hardness (MHP) (Chattaraj, 1996; Parr and Chattaraj, 1991), toward minimum electrophilicity (mEP) (Chamorro et al., 2003) or toward minimum polarizability (mPP) (see review in Chattaraj et al., 2012b). However, the principle of minimum electrophilicity has been questioned (Noorizadeh, 2007) and reaffirmed (Morell et al., 2009; Pan et al., 2013).

They are used to draw fitness landscape diagrams [η – ω], that are two dimensional diagrams with hardness and electrophilicity as abscissa and ordinate, respectively. However, those diagrams are not simply bi-dimensional since their coordinates can be used to map a third parameter, such as polarizability or charge exchange. They should indicate the paths of the reactions toward a pole of higher stability, i.e. conform to the HSAB principles (Duley et al., 2012).

When elements are solvated in an ionic medium, the former introduce a supplementary electric field. It deforms the surrounding electronic cloud, affecting their polarizability. Equilibrium requires the compensation of the local electric field, hence implying depolarization. Local equilibria are places of minimum polarizability.

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