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# Determination of fluid/melt partition coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions: Controls on element partitioning

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## Abstract

Analyses of co-existing silicate melt and fluid inclusions, entrapped in quartz crystals in volatile saturated magmatic systems, allowed direct quantitative determination of fluid/melt partition coefficients. Investigations of various granitic systems (peralkaline to peraluminous in composition, $\log fO_2 = \mathrm{NNO}-1.7$ to $\mathrm{NNO}+4.5$) exsolving fluids with various chlorinities (1–14 mol/kg) allowed us to assess the effect of these variables on the fluid/melt partition coefficients ($D$). Partition coefficients for Pb, Zn, Ag and Fe show a nearly linear increase with the chlorinity of thse fluid ($D_{\mathrm{Pb}} \sim 6 * m_{\mathrm{Cl}}$, $D_{\mathrm{Zn}} \sim 8 * m_{\mathrm{Cl}}$, $D_{\mathrm{Ag}} \sim 4 * m_{\mathrm{Cl}}$, $D_{\mathrm{Fe}} \sim 1.4 * m_{\mathrm{Cl}}$, where $m_{\mathrm{Cl}}$ is the molinity of Cl). This suggests that these metals are dissolved primarily as Cl-complexes and neither oxygen fugacity nor the composition of the melt affects significantly their fluid/melt partitioning. By contrast, partition coefficients for Mo, B, As, Sb and Bi are highest in low salinity (1–2 mol/kg Cl) fluids with maximum values of $D_{\mathrm{Mo}} \sim 20$, $D_{\mathrm{B}} \sim 15$, $D_{\mathrm{As}} \sim 13$, $D_{\mathrm{Sb}} \sim 8$, $D_{\mathrm{Bi}} \sim 15$ indicating dissolution as non-chloride (e.g., hydroxy) complexes. Fluid/melt partition coefficients of copper are highly variable, but highest between vapor like fluids and silicate melt ($D_{\mathrm{Cu}} \leqslant 2700$), indicating an important role for ligands other than Cl. Partition coefficients for W generally increase with increasing chlorinity, but are exceptionally low in some of the studied brines which may indicate an effect of other parameters. Fluid/melt partition coefficients of Sn show a high variability but likely increase with the chlorinity of the fluid ($D_{\mathrm{Sn}} = 0.3$–42, $D_{\mathrm{W}} = 0.8$–60), and decrease with decreasing oxygen fugacity or melt peraluminosity.

## 1. INTRODUCTION

Exsolution of a volatile phase is of major importance in sequestering elements from crystallizing silicate melts. Due to their lower density and low viscosity the exsolved volatiles may leave their parental magma and migrate to different parts of the magmatic reservoirs or into the surrounding rocks. As physical and chemical conditions change, volatiles continuously react with the magmas or rocks in their new environment and enrich or deplete them in different chemical components. This may eventually lead to the formation of ore deposits. Alternatively, they may be degassed into the atmosphere exerting a significant impact on the atmospheric budget of numerous elements. Thus, volatiles play a crucial role in the transport of chemical components between active magmatic and other geologic environments. Metal ratios in the magmatic volatile phase are determined upon volatile exsolution and are important in determining the type of ore deposits formed. So far most of our knowledge of fluid/melt partitioning has been based on experimental work, which attempted to reproduce nature under controlled laboratory conditions (e.g., Holland, 1972; Urabe, 1987; Shinohara et al., 1989; Keppler and Wyllie, 1991; Simon et al., 2006). Experimental data show that

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the distribution of different elements between the melt and the exsolved volatile phase is strongly dependent on the chemical composition of the system and pressure and temperature (Candela and Piccoli, 1995). However, experimentalists are challenged by numerous technical difficulties, including the attainment of equilibrium and closed system behavior with respect to the investigated elements. Numerous experimental studies investigated partitioning of some economically important metals such as Cu, Pb, Zn, Au, W and Mo; however, only little or no experimental data exist on partitioning of other, economically important elements such as Sn, Ag, Bi, Sb, As, Th and U.

Data from Heinrich et al. (1992) and Audétat and Pettke (2003) indicate the potential power of the use of natural fluid and melt inclusion compositions to determine empirical fluid/melt partition coefficients in natural systems. However, no systematic investigation has been carried out with this method comparing data collected from various samples.

In this paper we present a new systematic approach to determine partition coefficients between melts and exsolved fluids in natural magmatic systems. This approach is based on analyses of silicate melt and fluid inclusions entrapped in quartz, crystallized in volatile saturated magmas. Co-existence of fluid and silicate melt inclusions in the same assemblages ensures that they represent equilibrated fluid and melt phases. This method allowed simultaneous determination of fluid/melt partition coefficients of over 30 major and trace elements. The studied samples are from different locations, systems characterized by various chemical composition and crystallization conditions. Comparison of the data obtained from the various samples allows identification of the major intensive variables exerting control on the partitioning of the studied elements. This is the first comprehensive fluid/melt partition coefficient dataset reported based on natural samples.

## 2. SAMPLE LOCATIONS

The investigated samples have been collected from miarolitic cavities of various granitic intrusions. The main objective was to find samples providing good textural evidence for the co-existence of fluid and silicate melt inclusions. To facilitate investigation of the effect of P, T, $fO_2$, fluid and melt composition on the fluid/melt partition coefficients we investigated samples from various intrusions characterized by significant differences in these physicochemical variables. Below, we describe separately the major characteristics of the studied samples.

### 2.1. Mt. Malosa

Mt. Malosa is the northern part of the Zomba-Malosa intrusion in the Chilwa alkaline province in Malawi. The intrusion is related to Cretaceous magmatic activity in the earliest stage of the East-African Rift (Woolley, 1987; Woolley and Jones, 1992). Mt. Malosa is composed of alkali pyroxene and alkali amphibole bearing syenites, Q-syenites and alkali granites and contains abundant miarolitic cavities and pegmatitic veins (Bloomfield, 1965; Woolley and Jones, 1985; Woolley and Jones, 1992). The pegmatites contain freegrown quartz, alkali feldspar, aegirine, alkali amphiboles, zircons and numerous other high field strength element (HFSE) and rare earth element (REE) minerals. The samples containing assemblages of co-existing fluid and melt inclusions are mainly specimens where a continuous transition can be observed from graphic intergrowth of alkali feldspar and quartz towards large (up to a few cm) freegrown quartz and feldspar crystals (Fig. 1a, b, k and l). Co-existent fluid and melt inclusions were found in both the quartz of the graphic intergrowths (mal03a,b, mal25as2, mal02i) and in the root zone of the freegrown quartz crystals (mal40, mal41, mal25as1). The assemblages typically contain silicate melt, brine and vapor inclusions (Table 1).

### 2.2. Baveno and Cuasso al Monte intrusions

Both intrusions are granitic and are part of the Hercynian gabbro-granite series of the “Serie dei Laghi” in the Southern Alps, Italy. Both granites are slightly peraluminous with aluminum saturation indexes (ASI) ranging between 1.06 and 1.17 (Boriani et al., 1990; Boriani et al., 1995). Miarolitic cavities are abundant in both intrusions and characterized by a very similar high temperature mineral paragenesis with quartz, feldspar and fayalite in the magmatic-hydrothermal transition stage, and abundant HFSE, REE-, Sc-, Be-silicates and phosphates and fluorite in the high temperature hydrothermal stage (Pezzotta et al., 1999; Pezzotta et al., 2005). Miarolitic cavities in Baveno evolved as isolated systems, while in Cuasso al Monte they formed an interconnected network (Pezzotta et al., 1999). The investigated samples from Cuasso al Monte and Baveno are both composed of a microgranitic part containing alkali feldspar, quartz and minor biotite, showing a continuous transition towards the free grown quartz and feldspar crystals in the cavity (Fig. 1c and e). The transition zone contains co-existent intermediate density aqueous fluid and silicate melt inclusions in Baveno (Fig. 1d) and co-existent vapor, brine and silicate melt inclusions in the sample from Cuasso al Monte.

### 2.3. Ehrenfriedersdorf pegmatite

The pegmatite is associated with a Variscan granite in the Erzgebirge which belongs to the peraluminous high F, high $P_2O_5$, Li-mica granite group described in Forster et al. (1999). The pegmatite is composed of quartz, alkali feldspar, muscovite, Li-micas, minor topaz, cassiterite, beryl, fluorapatite and other phosphates. The investigated sample is the one described by Thomas et al. (2000). The sample is a large quartz crystal containing silicate melt and numerous generations of intermediate to low-density fluid inclusions (Fig. 1g). The studied inclusion assemblages are short (up to a few 100 μm long) pseudosecondary trails containing silicate melt and vapor inclusions (Fig. 1h).

### 2.4. Rito del Medio

The Rito del Medio pluton is part of the Tertiary Latir volcanic field in northern Mexico. Formation of the pluton