

The effect of Cl on the solubility of Au and Pd in andesitic melts

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Chlorine is considered as an important agent responsible for the mobilization and transport of metals in magmatic systems associated with porphyry ore mineralization and with late-stage metal-rich horizons of large igneous intrusions. In the former case, the considerable role of Cl is confirmed by the observation that fluid inclusions associated with porphyry ores are often composed of low-salinity aqueous vapor and high-salinity brines, whereas in the later case it is believed that the mobility of metals in different horizons of layered intrusions might have been controlled by the general process of chromatographic separation of metals during migration and evolution of Cl-enriched fluids. Since at given magmatic conditions the mobility and transport of metals by exsolving Cl-bearing fluid phase(s) is presumably dependent on chemical potential of metal components complexing with Cl in silicate melt, quantitative experimental data on metal solubility in melts and melt-fluid partitioning are required.

Here we report the results of experiments on the solubility of Au and Pd in andesitic melts equilibrated with Au₈₀Pd₂₀ capsule material at 1200°C, oxidizing conditions (FMQ+3) and pressures in the range from 50 to 500 MPa as a function of Cl content in the system. Due to non-ideality of mixing in Cl-bearing fluids, the investigated systems are characterized by coexistence of andesitic melts with vapor, vapor+brine, brine, or supercritical single-phase fluid, depending on the bulk Cl content and P. The obtained data show that an addition of Cl to the system increases significantly the solubility of both metals in the silicate melt at all investigated pressures, in particular in melts coexisting with brine or supercritical fluid. The concentration of Au increases from 1-2 upto 40-50 µg/g, whereas the concentration of Pd increases from 0.1 to 20 µg/g with increasing Cl content of the melt from 0 to 2.5 wt%. Since the calculated activity coefficients of Au and Pd in the Au₈₀Pd₂₀ capsule are both close to 0.7, the solubility values of pure metals should be slightly higher. The results clearly show that Cl can indeed control on the mobility of Au and Pd in natural magmas.

The transformation of ACC to vaterite; An *in situ* SAXS/WAXS study

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Vaterite ($\mu\text{-CaCO}_3$) is rarely observed in natural systems, as it is thermodynamically unstable with respect to calcite and aragonite [1]. However, some organisms produce and stabilize vaterite as biominerals [2]. At high supersaturation vaterite forms via a nanoparticulate, poorly-ordered and metastable precursor, amorphous calcium carbonate (ACC). In the pure system, ACC transforms to vaterite within minutes, and subsequently to calcite [3]. The detailed mechanisms of the ACC to vaterite transformation are however still lacking due to the fast kinetics of this first step of crystallization. In this study we demonstrate the use of *in situ* time-resolved synchrotron-based Small- and Wide-angle X-ray Scattering (SAXS/WAXS) combined with off-line characterization to quantify the kinetics and crystallization mechanisms of vaterite at fast time scales.

The SAXS/WAXS data collected at 1 second / frame for up to 32 minutes, revealed that the ACC to vaterite transformation occurs in 3 stages. The initial stage (0-2 min) was governed by ACC precipitation and growth (to $\bar{\phi} \sim 38$ nm). During this stage ~ 70 % of the total vaterite ($\bar{\phi} \sim 10$ nm) formed via spherulitic growth at the expense of the metastable ACC [4]. The end of the spherulitic growth (at 2 min) was concomitant with a drop in supersaturation below the limit for spherulitic growth of vaterite ($SI \approx 1.4$ [4]). During the 2nd stage (2-7 min), remnant ACC lead to a further increase of the amount of vaterite (~ 30 %) due to ACC dissolution and vaterite nanocrystal reprecipitation. During this stage the vaterite crystallite size increased from ~ 10 to ~ 35 nm. Finally during the 3rd stage (> 7 min), no *de novo* precipitation of vaterite occurred, however the vaterite crystallite size continued to increase reaching ~ 60 nm at the end of the experiment (32 min). This increase in crystallite size was solely governed by Ostwald Ripening.

- [1] Plummer L.N. and Busenberg E. (1982) *GCA* **46**, 1011-1040. [2] Lowenstam (1981), *Science* **211**, 1126-1131, [3] Rodriguez-Blanco, J.D. *et al* (2011) *Nanoscale* **3**, 265-271, [4] Andreassen, J.P. (2005) *J. Cryst. Growth* **274**, 256-264.