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 H_2S 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 solvatation reactions. The form of gaseous specie can be determined by $logP(H_2S)-logX(Ag)$ plot (fig.1). There are two reactions of acanthite solubility in hydrogen sulfide:

 $Ag_2S(cr)+H_2S(g)=2AgHS(g), logK=-6.36\pm0,1 and Ag_2S(cr)+5H_2S(g)=2AgHS^{*}(H_2S)_2(g), logK=-10.8\pm0,2.$

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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 latemagmatic 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, <10um to 80um long, to be trapped on the growth surface. There was no contact between melt and crystal and crystallization occurred solely from the vapour.

 $D_{v\text{-m}}$ 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.