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A new model for the prediction of sulfide melt–silicate melt partitioning of chalcophile elements

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Abstract — Partitioning of chalcophile elements between sulfide and silicate melts is important to understand the formation of magmatic ore deposits and especially metal enrichment in sulfides. Temperature (T), pressure (P), oxygen fugacity ($f\text{O}_2$), sulfur fugacity ($f\text{S}_2$) and the chemistry of both phases are the parameters which impact this partitioning. New experiments and a large database is used to parameterize the partitioning of chalcophile elements in magmatic systems. This model is essential for the prediction of metal enrichment in sulfides.

I. INTRODUCTION

PARTITIONING OF CHALCOPHILE ELEMENTS between sulfide and silicate melts ($D^{\text{sul/sil}}$) has been largely investigated, mainly through experiments at mantle conditions and under reduced conditions, i.e. low oxygen fugacities ($f\text{O}_2 < \text{FMQ}-1$). However, natural magmas show higher oxygen fugacities ($< \text{FMQ}+2$, [1]), and the formation of magmatic sulfide deposits, in crustal conditions, may also occur under higher oxygen fugacities. New experiments and a new model covering this large range of oxygen fugacity are needed. With the oxygen fugacity, other parameters can impact the partitioning of chalcophile elements such as temperature, pressure, sulfur fugacity and composition of the different phases.

II. METHODOLOGY

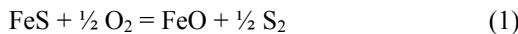
We performed experiments in internally heated pressure vessels equipped with a rapid quench device at 1200 °C and 700 MPa, under variable $f\text{O}_2$ (between FMQ-2 and FMQ+2).

The starting material consisted in a volatile-free glass of the Noril'sk-I picrite in addition with 5 wt.% of native S and 2 wt.% of distilled H₂O, together placed in Pt-capsules. The specificity of this study is that (i) a metal-undoped composition was used, and (ii) the sulfide melt segregated directly from the silicate melt during the experiment, due to S addition. Magmatic textures were generally preserved owing to the rapid quench.

All samples show equilibrium between a silicate glass, sulfide liquid droplets, olivines and a fluid phase. Silicate and sulfide melts are analyzed for major elements by EMPA (ISTO) and for minor elements by LA-ICP-MS (IRAMAT).

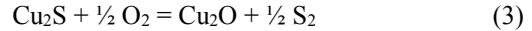
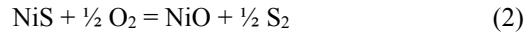
Experimental and literature data were compiled in a thermodynamic model based on exchange reactions. This new model was constructed with different parts.

We first found that the oxygen concentration in sulfide liquid, based on the exchange reaction (1), is critical.



The O concentration in sulfide liquid is strongly associate with T , P , $f\text{O}_2$, $f\text{S}_2$ and sulfide composition [2], [3].

Secondly, we used experimental data to determine the calculation of Ni and Cu partitioning with variable parameters. These parts are based on exchange reactions (2,3) between sulfide and silicate melts.



III. RESULTS & DISCUSSION

1- Oxygen content in sulfide liquid

The oxygen content in sulfide liquid was calibrated using 430 experimental data from variable sulfide liquid compositions: Fe-rich, Ni-rich, and Cu-rich. xFeO in sulfide liquid is calculated using the constant of reaction (1), interaction parameters W_{i-j} (to consider activity coefficients), $f\text{O}_2$ and $f\text{S}_2$. Even if the reaction equation (1) predict a 0.5 slope with $f\text{O}_2$ and $f\text{S}_2$, this model seems more accurate with a 0.15 slope. The resulting model is a linear regression considering T , P , $f\text{O}_2$, $f\text{S}_2$ and the composition of the sulfide liquid. Interaction parameters (W_{i-j}) in a five-component system for sulfide liquids (FeO, FeS, NiS, Cu₂S, S_{xs}) can be used to calculate the activity coefficients of these species. xFeO in sulfide liquids is positively correlated with P and $f\text{O}_2$ and negatively correlated with T and $f\text{S}_2$. The quantity of FeO dissolved in sulfide liquid is also dependent of the composition, the more Fe-rich is the sulfide liquid, the more FeO can be dissolved.

2- Partitioning of Ni and Cu

The same treatment is applied to the partitioning of Ni and Cu. Thermodynamic constants of reactions (2) and (3) [4] are calculated together with their dependences on T and P , and the interaction parameters (W_{i-j}). The interaction parameters used are simultaneously solved with the ‘oxygen content’ part of the model. Ni and Cu partition coefficients between sulfide and silicate melts are positively correlated with T and $f\text{S}_2$, and negatively correlated with P and $f\text{O}_2$.

IV. CONCLUSION

New experimental data done in conditions relevant to magmatic sulfides ore deposits are combined with the literature data to create a global model for oxygen content in sulfide liquid and partitioning of chalcophile elements between sulfide and silicate melts. The model allows to predict xFeO in sulfide liquids, $\text{DNi}^{\text{sul/sil}}$ and $\text{DCu}^{\text{sul/sil}}$ knowing intensive parameters such as temperature, pressure, oxygen and sulfur fugacities. This model can be used to predict the optimum conditions leading to the formation of mafic-ultramafic magmatic sulfide deposits.

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