Modeling Sulphide Solubility in MORB Glasses and Ol Cumulate Piles: The Opposite Effect of NiO vs FeO in the Melt

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ABSTRACT. We present a new SCSS model which accounts for the effects of temperature, major components, and NiO content in the melt. Despite relatively low concentrations, nickel is shown to have a pronounced effect on S solubility, causing significant variations in the onset of sulphide immiscibility in melts with similar major element compositions. The SCSS model was tested on sulphide-saturated MORBs followed with incorporation into the COMAGMAT program (ver. 5.2, 2010) allowing one to simulate various sulphide-silicate assemblages, including changes in bulk sulphide-silicate ratios and sulphide compositions. An important feature of the sulphide version of COMAGMAT is its ability to define onset of sulphide saturation during late-stage solidification of Ol cumulate piles. These calculations led us to the realization of the importance of an earlier stabilization of Ni-rich sulphide liquid in high-Ni olivine-enriched cumulate piles. Examples of such calculations for solidification of chilled picritic rocks and dunites from the Dovyren intrusion are given below.

1 CALIBRATION AND TESTING OF THE SCSS MODEL

In 2008, we presented a sulphide-solubility model allowing for calculations of SCSS in basaltic melts at low fO_2 and 1100-1400ºC (Ariskin et al. 2008). The model is based on a premise of the existence of complex sulphide species $(Fe_nS)^{2(n-1)+}$ (n=2,3,4…) in the melt, so that precipitation of liquid FeS could be described by a combined reaction of decomposition of the iron-sulphur complexes in the melt. The proposed mechanism of sulphide solubility was applied to a dataset of 182 anhydrous 1 atm experimental glasses and 53 natural sulphide-saturated MORB to calibrate an empiric SCSS equation which reproduced the calibration database within 10% (Figure 1a). Additional testing of this model has been carried out on independent sulphide-saturated tholeiitic glasses with Ol-liquidus temperatures in the range ~1080-1250ºC (Ford et al. 1983), Figure 1b. These calculations (performed under reducing and anhydrous conditions) fitted well a strong positive correlation between FeO and S contents observed in MORB glasses. However, this model required further development if it was to be applied successfully to a range of natural mafic to ultramafic systems. This is because the results of thermodynamic modelling of sulphides in silicate slags have demonstrated that, due to a high non-ideality of the Cu-Ni-Fe sulphide solutions (Hsieh and Chang 1987; Kongoli and Pelton 1999), even small amounts of Ni and Cu may have a strong effect on S capacity in the metallurgical systems. In an attempt to account for the effect of “minor” elements, we have updated the proposed SCSS model, incorporating NiS as the second principal component of the modelled sulphide solution (Bychkov et al. 2010).

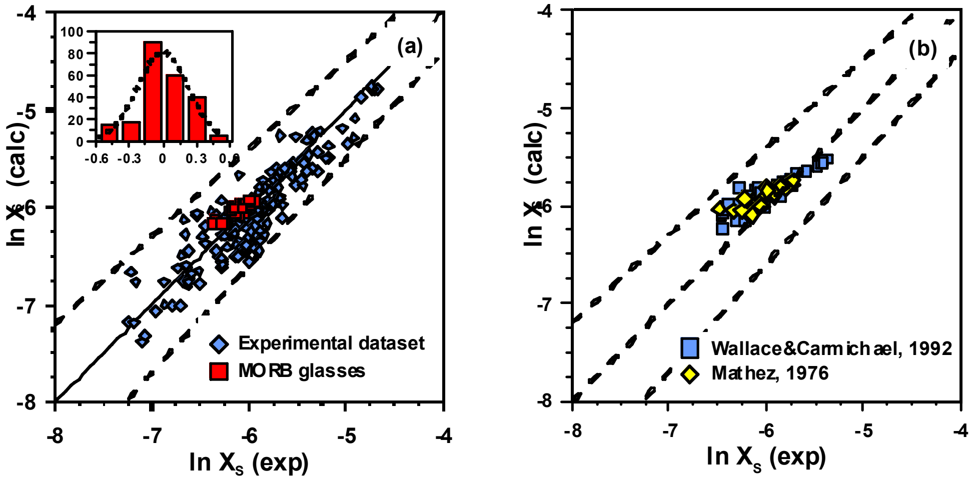

Figure 1. Testing the accuracy of the proposed SCSS model: (a) on the calibration dataset including experimental and sulphide-saturated MORB glasses from the Siqeuros FZ (Danyushevsky, unpublished); (b) on independent dataset of sulphide-saturated MORBs.

Twenty experiments on Fe-Ni sulphides (with less 5 wt% of Cu) coexisting with silicate melts at low to moderate pressures (Gaetani and Grove 1997; Holzheid and Grove 2002; Sattari et al. 2002) have been used for the calibration. Strongly non-ideal FeS-NiS solution was described by a regular solution model of component activities (Hsieh and Chang 1987). Calibrating the effect of NiO on sulphide solubility, we assumed the same mechanism of S dissolution in silicate melts as it has been proposed for the Fe-bearing systems (see above). Thus, the Fe-Ni sulphide precipitation from a S-saturated silicate liquid was described as a combined reaction of the decomposition of these complexes, with Fe/Ni ratio in the silicate melt being the same as in the “average” complex that breaks down. Finally, we were able to calibrate an integral sulphide solubility model that describes Fe-Ni sulphide composition as a function of temperature, fO_2, and bulk magma composition, including FeO, NiO, and S contents in the melt. The new Fe-Ni sulphide model has been incorporated into the COMAGMAT program, which can be used now for calculations of SCSS in Ni-bearing mafic magmas and their derivatives (Ariskin et al. 2010).

2 QUANTIFYING THE EFFECT OF NiO IN NATURAL SYSTEMS

We applied the updated COMAGMAT-5.2 to two compositions representing a komatiite-like (Barnes 2007) and tholeiitic “Talnakh magma parent” (Ariskin and Barmina 2004). Modelling of equilibrium crystallization was carried out at 1 atm pressure and variable NiO contents in the initial melts, ranging from 10 to 1000 ppm. This allowed us to assess differences in SCSS and sulphide compositions that exist between Ni-free and Ni-bearing systems. A marked effect of Ni on the sulphide solubility in the komatiite magma was observed, resulting in a 25% decrease in SCSS for the highest temperature Ni-enriched compositions. However, the modelled SCSS trajectories were found to be closer as temperature decreases, with the effect of the initial Ni content becoming negligible. This is caused by Ni partition into olivine during crystallisation. Similar modelling for the proposed Talnakh magma resulted in a more pronounced effect of NiO. Near its liquidus at 1200ºC, an almost two-fold decrease in SCSS is observed as the NiO content in the melt is increased from 10 to 1000 ppm. Also, a 3-fold increase in the Ni content in the modelled sulphide is observed as the NiO in the melt increases from 100 to 1000 ppm. As an independent test of these calculations, we applied the proposed Ni-SCSS model to a highly Mg- and Ni-enriched sulphide-saturated glass from the the southern Mid-Atlantic Ridge near the Bouvet Triple Junction (Kamenetsky et al. 2001). Its SCSS was calculated to be 0.053 wt%, similar to 0.04 wt% of S observed in the glass.

3 CALCULATIONS FOR OL-RICH CUMULATE PILES AND GABBRONORITIC MELTS

Using the Fe-Ni sulphide version of COMAGMAT, we have carried out a set of calculations simulating crystallization of Ol-rich cumulate piles assumed to be a precursor of Pl-lherzolites and dunites from the Dovyren intrusion (Northern Baikal area, Russia). The pluton is a lens-shaped body (~26×3 km) of late Proterozoic age which is sub-conformable with its host rocks. The complex is well exposed due to post-intrusive folding. The modal layering of the intrusion includes a bottom unit of plagioclase lherzolites (100-150 m) followed by a succession of cumulates including: sulphide bearing dunites (Ol+Chr, 800-900 m) → troctolite (Ol+Pl+Chr, ~700 m) → Ol gabbro (Pl+Ol+Cpx) → gabbronorites (Pl+Ol+Cpx±Opx±Pig). The most primitive rocks of this intrusion have been found in a roughly 5 m thick chilled zone composed of picro-dolerites which are replaced upward by Ol-rich peridotites (Ariskin et al. 2009). The FeO-MgO trend displayed by the lowermost Pl-lherzolites suggests that they originally contained olivine ~Fo_{88} at ~1300ºC. We applied the COMAGMAT-5.2 model to six Ni-rich chilled rocks in an attempt to simulate changes of their equilibrium melting-crystallization relationships with decreasing temperature. These calculations were carried out at 1 atm pressure under QFM conditions, with crystal increment of 0.5%. Assuming the NiO and S contents of the chilled rocks to correspond to their original values, all of the calculated crystallization trajectories suggest sulphide-undersaturated conditions of the proposed parental magma at temperatures > 1250ºC. This is considered as evidence for a later appearance of sulphides in more crystallized olivine cumulus at lower temperatures.

Another important observation is the effect of bulk cumulate composition on SCSS in the residual melts. Two calculations have been performed. The first involved modelling of post-cumulus equilibrium crystallization of the inter-cumulus melt for a high-magnesia picro-dolerite in the temperature range from 1320ºC (11 wt% MgO in the melt, equilibrium with Fo_{88}) to ~1100ºC. The second involved the same initial melt but assumed to be free of Ol crystals. The principal difference between these two calculations is the onset of sulphide saturation. In the case of "Ol cumulus pile", the first sulphide appears at 1209ºC, slightly earlier than plagioclase and pyroxenes appeared on the liquidus (Table 1). In the case of "Ol-free magma", the first sulphide appears at a much lower temperature (≤1173ºC) in the stability field of Ol-Pl-Opx-Cpx assemblage. These differences in the evolution of the same primitive melt are explained by the effect of different bulk NiO contents in the modelled systems. The proposed parental melt contained only 500 ppm NiO as compared to 2300 ppm NiO in the cumulus picrodolerite (Table 1). This implies that the presence of a large amount of Ni-enriched Ol crystals should be considered as a "Ni-buffer" which does not allow for NiO content in the melt to decrease significantly during crystallization and solidification of cumulus piles. Such a buffering is considered to decrease SCSS in the residual trapped liquid, as follows from the pronounced effect of Ni on sulphide solubility (see above).

Table 1. Modelled differences in onset of sulphide saturation in partly crystallized Ol cumulus and crystallizing independently high-Mg melt.

Initial Ol-cumulus (1320ºC): 2315 ppm NiO, 0.030 wt% S	Initial melt (1320ºC): 517 ppm NiO, 0.067 wt% S
Before onset of *Opx*	After onset of *Opx*
T = 1209ºC	*T* = 1173ºC
Fo in *Ol* = 86.3	*Fo* in *Ol* = 80.1
NiO in melt = 254 ppm	NiO in melt = 150 ppm
SCSS = 0.078 wt%	SCSS = 0.099 wt%
Ni in sulphide = 17.7 wt%	Ni in sulphide = 12.2 wt%

4 CONCLUSIONS

A new version of the COMAGMAT program has been developed to predict sulphide solubility in mafic magmas more accurately as compared to previous models which were calibrated for "FeS liquid" - silicate melt equilibrium and did not consider the effect of NiO on the sulphide composition and SCSS. Results of application of the new model to Ol cumulates from the Dovyren intrusion in Russia have demonstrated that because of the effect of NiO on SCSS and due to the enrichment in NiO, olivine cumulates possess a greater potential for early precipitation and separation of Ni-rich sulphides in the inter-cumulus liquid compared to genetically related gabbronoritic melts, which may be separated from the original cumulus piles to crystallize independently. We believe that this effect may play an important role in the formation of Ni-rich sulphide komatiite-related deposits.

5 ACKNOWLEDGEMENTS

This research is supported by AngloAmerican, BHP Billiton and Votorantim Metais through AMIRA project P962, by the Australian Research Council funding to the Centre of Excellence in Ore Deposits, University of Tasmania, and the Russian Foundation for Basic Research (project 08-05-00194).

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