

# THE EFFECT OF NI ON SULPHIDE SOLUBILITY IN MAFIC MAGMAS: 1. CALIBRATION OF A NEW SCSS MODEL AND MODELING SULPHIDE COMPOSITIONS AS A FUNCTION OF NIO IN S-SATURATED MELTS

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Most of existing SCSS models relate variability of sulphide saturation in mafic to ultramafic magmas to the effects of pressure, temperature, and FeO content in the melt (Wallace & Carmichael, 1992; Mavrogenes & O'Neill, 1999; O'Neill & Mavrogenes, 2002; Holzheid & Grove, 2002; Li & Ripley, 2005-2009; Liu, 2007). We present results of development of another SCSS model [1-3] which includes the effect of NiO content as well. Despite relatively low concentration, this element is shown to have an even stronger effect than that of the temperature and pressure (at least at crustal conditions), so that substantial variations in onset of sulphide immiscibility in magmas containing similar amounts of FeO are predicted. Examples of application of the Ni-dependent SCSS model to tholeiitic and komatiite magmas are given below.

To describe SCSS in basaltic melts at low  $fO_2$  earlier we proposed the existence of complex sulphide species  $(Fe_nS)_{2(n-1)+}$  ( $n=2,3,4,\dots$ ), so that precipitation of liquid FeS could be described by a combined reaction of decomposition of the iron-sulfur complexes in the melt [1, 2]. The proposed mechanism of sulphide solubility was used to calibrate a new SCSS equation based on a set of 82 anhydrous 1-atm experimental glasses and 53 natural S-saturated MORBs [3]. As a result, this SCSS model (with 14 fitted parameters) could reproduce the calibration database within 10% at 1100-1400°C. However, this ability to predict sulfur saturation of mafic melts in equilibrium with a stoichiometric FeS is not sufficient to apply the model to natural magmas. Results of thermodynamic modelling sulphides in silicate slags indicate that due to a high non-ideality of the Cu-Ni-Fe sulphide solution (e.g. [4, 5]) even small amounts of Ni and Cu may have strong effect on S capacity of the metallurgical systems.

In attempt to account for the effect of "minor" elements we have updated the proposed SCSS model incorporating NiS as the second principal component of sulphide solution. Twenty experiments on Fe-Ni sulphides (with less 5 wt. % of Cu) coexisting with silicate melts at low to moderate pressures [6-8] were used for the calibration. Strongly non-ideal FeS-NiS solution was described by a regular solution model of component activities [5]. 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 [1]. 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 sulphide liquid being the same as in the 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 [9] which can be used now for calculations of SCSS in Ni-bearing mafic magmas and their derivatives.

We applied the updated COMAGMAT-5.1 to two compositions representing a komatiite-like [10] and tholeiitic parent ("Talnakh magma", after [9]). 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 closing together as the temperature decreases, with the effect of the initial Ni content becoming negligible. This is because of Ni partition into olivine during crystallisation. Similar modelling for the proposed Talnakh magma [9] resulted in more pronounced effect of NiO. Near its liquidus at 1200°C 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. Dependence of Ni contents in sulphides vs Fo content in olivine is considered as a function of NiO content in the initial tholeiitic melt.

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### **Biography**

Kirill Bychkov Graduated from the Moscow State University, Petrology Department in 2005. From 2007 he is enrolled as a PhD student at CODES, University of Tasmania investigating the effects of pressure, temperature and melt composition on the sulphide saturation and developing computer models of silicate-sulphide cocrystallisation

