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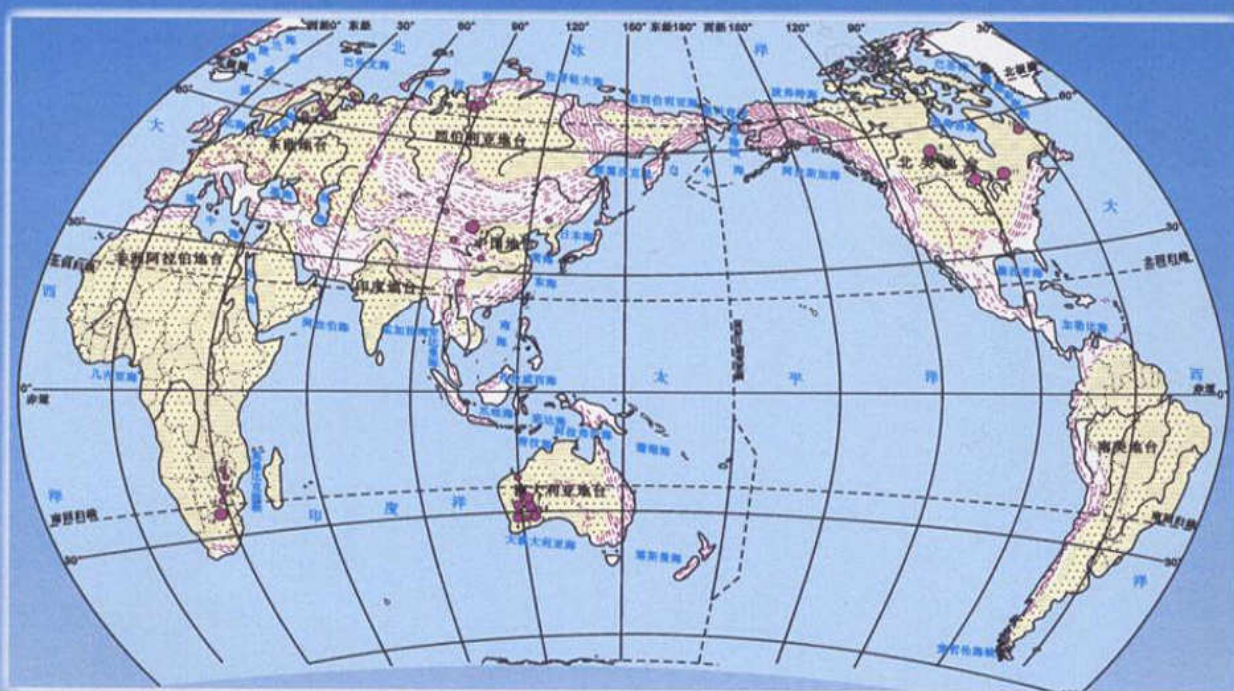
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硫化物溶解度模型的检验与镁铁质母岩浆形成层状 侵入体过程中硫饱和度的计算

Testing of sulfide solubility models and calculations of SCSS during crystallization of mafic magmas parental to layered intrusions

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1 Introduction

Over the last 20 years, at least ten models for sulfide solubility in silicate melts have been proposed (Ariskin A.A et al., 2008; Boudreau, A.E., and Simon, A., 2007) These models may be divided to three groups: ① those designed for systems open to sulfur fugacity . ② models based on the “sulfur capacity” concept (Fincham C. J. B. and Richardson F. D. , 1954), in which the effect of f_{S_2} is accounted for implicitly, and ③ models describing system closed to sulfur, in which the sulfide saturation surface is considered to be a function of melt composition (including S_2), with temperature, pressure and f_{O_2} being external intensive parameters (Holzheid, A. and Grove, T.L., 2002; Li, C., and Ripley, E.M. ,2005; Liu, Y et al., 2007; Mavrogenes, J. A. and O’Neill, H. St. C. ,1999). Most of the models were constructed to calculate sulfur contents at sulfide saturation (SCSS) for a particular magma composition, or a series of basalts formed due to mafic magma fractionation. Some of these models can be applied to volcanic gaseous systems (Moretti, R. and Ottonello, G. , 2005; Moretti R. and Baker, D.R , 2008; Wallace, P. and Carmichael, I.S.E., 1992), whereas their applicability to magma crystallization processes, especially within closed intrusive chambers (where f_{S_2} is unconstrained) is under question. Same problem exists for the “sulfur capacity models” combining results from iron-free and Fe-containing systems at fixed f_{S_2}/f_{O_2} ratios (O’Neill, H. St. C. and Mavrogenes, J. A., 2002), although such models are still popular in metallurgical studies (Nilsson, R et al., 1994; Nzotta M. M et al. ,1999; Shankar A et al., 2006). In this paper we present results of comparisons of the accuracy of three recent SCSS models , followed by a consideration of the basic principles for the development of a new model, capable of more accurate calculation of sulfide solubility in mafic magmas. Examples of computer modeling of changes in the SCSS during crystallization of parental magmas for several fertile layered intrusions will be given.

2 Testing on experimental compositions

A set of 330 experimental S-saturated silicate melts were used to test the accuracy of selected SCSS models (Fig. 1). Our approach was to test the S-solubility equations both for the calibration array and over the entire experimental database, see Fig. 2. In general, all of the models describe the data which were used for their calibration reasonably well (commonly within <10% error of $\ln(X_S)$), however when the entire database is tested,

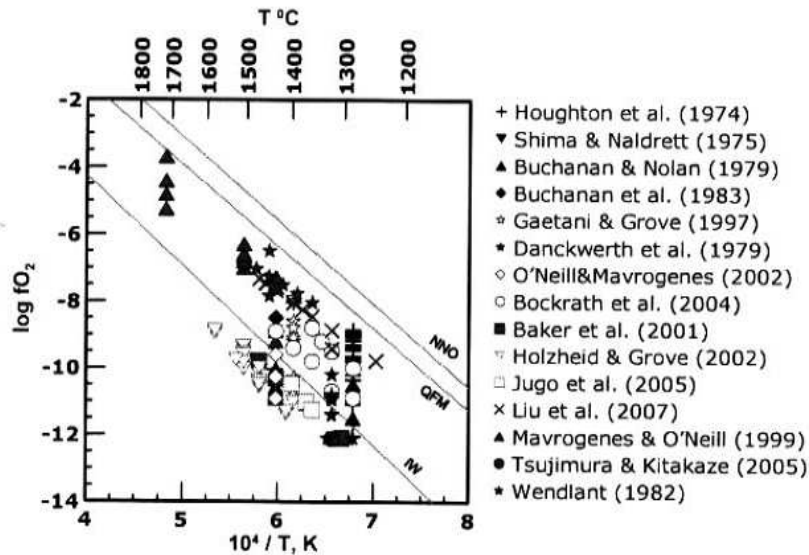


Fig. 1 The range of temperatures and log f_{O_2} for the experimental dataset selected to test the SCSS models at nominally anhydrous conditions

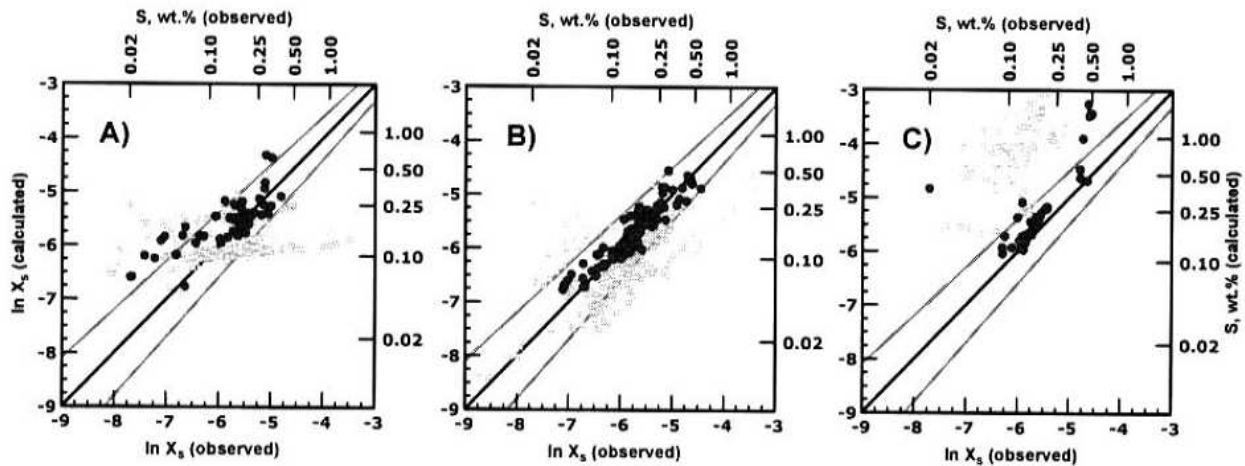


Fig. 2 Results of testing the Holzheid & Grove's (a), O'Neill & Mavrogenes's (b), and Li & Ripley's (c) models on the calibration (red) and whole (grey) experimental dataset

the average error for the calculated sulphur concentration is of 20-30%. This is particularly evident for the the model, which adequately fits their own experiments at 1400°C, however it significantly overestimates S contents in the melt at lower temperatures.

3 Testing on tholeiitic magma compositions

53 MORB sulfide-bearing glasses from the Siqueiros FZ, East Pacific Rise (Danyushevsky, unpublished data) were used to test the SCSS calculations by same models (Bychkov K.A. et al., 2008). These glasses crystallized at temperatures ~1200-1100°C, based on their calculated Ol liquidus temperatures (Ford, C.E et al., 1983). This provides a good test for the application of the models to low-T ferrobasic compositions under reducing and anhydrous conditions. Calculations using the models fitted well the measured sulphur concentration near 1200°C, but failed to reproduce a strong positive correlation between FeO and S contents in the observed MORB glasses. The model reproduced general direction of the natural trend, but significantly overestimated the amount

of S dissolved in the melts (Fig. 3a). Similar problem is evident when the Li&Ripley model is applied to a different set of sulfide-saturated MORB glasses (Mathez, E. A., 1976) (Fig. 3b).

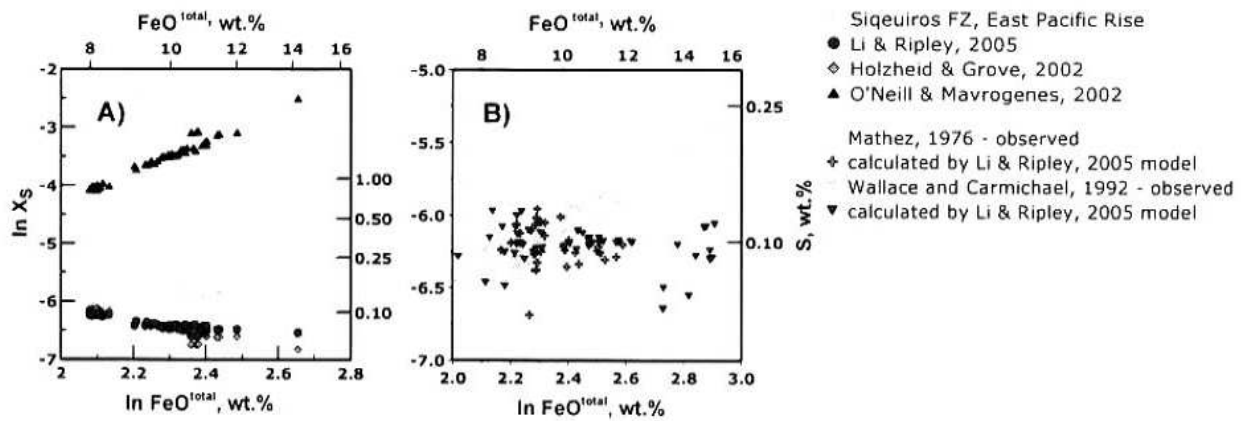


Fig. 3 Results of testing the SCSS models (Holzheid, A. and Grove, T.L.,2002; Li, C., and Ripley, E.M., 2005; O'Neill, H. St. C. and Mavrogenes, J. A., 2002) on sulfide-saturated MORB glasses (A) the Siqueiros FZ (Danyushevsky, unpublished), (B) data from (Wallace, P. and Carmichael, I.S.E., 1992; Mathez, E. A., 1976)

4 Principles for development of a new SCSS-model

The reason for the above discrepancies is likely due to over-estimating the effect of temperature over the effect of melt composition by the first two models, whereas model significantly overestimates the amount of S dissolved in the melt at temperatures < 1400°C. We have proposed a different sulfur solubility mechanism with an appropriate thermodynamic formulation that can reproduce much better both the experimental and natural data on the SCSS at reducing conditions and 1 atm. The technique is based on the assumption for the existence of complex sulfide species in reducing silicate melts, which are similar to cationic iron-sulfur clusters in gas systems (Koszinowski, K. et al., 2002). These clusters are assumed to be formed due to a sequence of reaction, such as:



In this case, sulfide precipitation from iron-bearing melts is described by a combined reaction of decomposition of the iron-sulfur clusters:



where z is a number representing the average weighted size of clusters in the melt. Following eq.2 and mass balance constraints, it can be demonstrated that sulfur content in any sulfide-saturated melt may be approximated by a general equation:

$$\ln X_S = (z-1) \ln X_{\text{FeO}} - z \ln \Sigma \text{cat} - \ln K_{\text{FeS}\downarrow} \quad (3)$$

where X_{FeO} and Σcat are the FeO content and sum of cations in 1 mole in the melt; and $K_{\text{FeS}\downarrow}$ is the equilibrium constant of eq.(2). To calibrate the dependence of z and $K_{\text{FeS}\downarrow}$ on temperature and melt composition, we used a set of 82 anhydrous 1-atm experimental glasses and 53 natural MORB glasses from the Siqueiros FZ (see Fig. 3a). The final equation which can reproduce the calibration database within 10% includes 14 fitted parameters and allows one to realistically predict sulfide saturation in magmas crystallized between 1400-1100°C.

Additional testing on experimental and natural compositions demonstrates that our model can describe both the well-known parabolic dependence of the SCSS on melt FeO at 1200°C (Houghton, D. R. et al., 1974), and increased S-solubility in fractionated MORB glasses as the crystallization temperature is decreased down to 1100°C (Fig. 4).

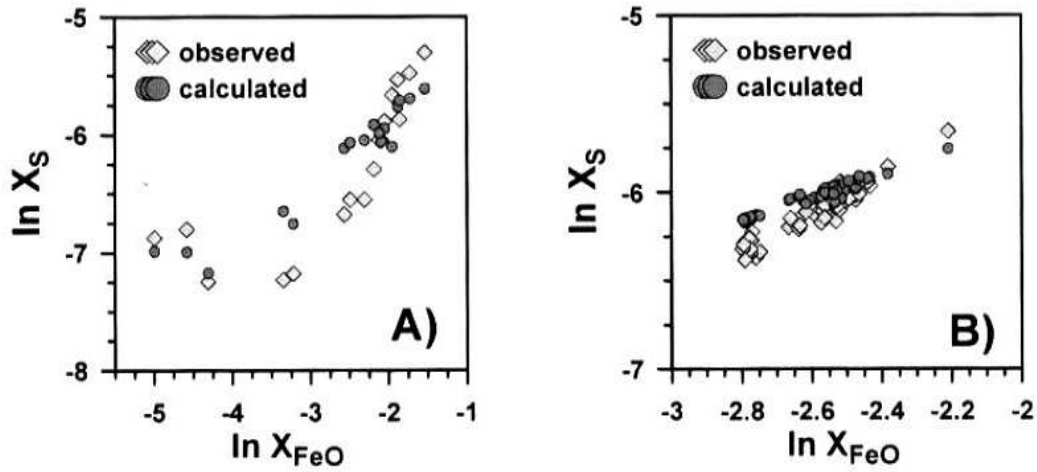


Fig. 4 Comparison of the SCSS vs FeO dependences observed in experiments (Houghton, D. R. et al., 1974) and sulfide-saturated MORBs from the Siqueiros FZ with those calculated by our model

5 Applications to parental magmas of layered intrusions

The proposed SCSS equation has been integrated into a new version of the COMAGMAT model that now permits one to follow changes in the SCSS during crystallization of multiply-saturated basaltic magmas. Fig. 5 displays results of such calculations for five magma compositions assumed to be parental for fertile and barren layered intrusions (Ariskin, A. A. and Barmina, G. S., 2004).

The general effect for all of the proposed parents is to decrease sulphide solubility during crystallization up to an inflection point where PI begins to crystallize. It happens in the temperature range of 1175-1220°C: starting from this point SCSS is to increase (Fig. 5a) due to enrichment of the residual liquids in FeO (Fig. 5b). Genetically important are systematic differences between the assumed parents. It appears that at temperatures ~ 1200°C, both KOM and DOV melts are characterized by the lowest SCSS of 0.14-0.16 wt% as

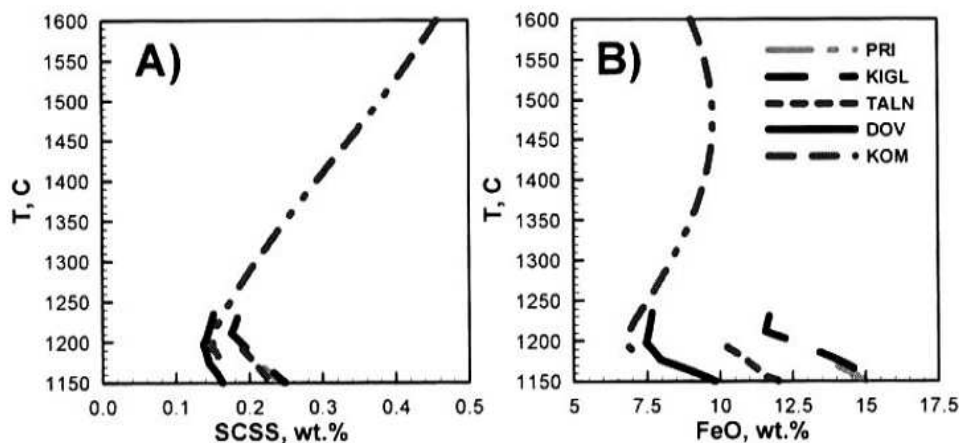


Fig. 5 Modeled changes in SCSS in terms of the temperature (A) and FeO content in the melt (B)

Fertile layered intrusions: PRI, Partridge River Intrusion (Minnesota, USA, h=500 m), TALN, Talnakh (NW Siberian Platform, Russia, h~150 m); DOV, Iloko-Dovyren (Northern Transbaikalia, Russia, h=3.2 km); KOM, assumed parent for komatiite-hosted nickel sulfide deposits. Barren complexes: KIGL, Kiglapait (Labrador, Canada, h=9 km). Data for PRI, TALN, and KIGL are from . Information on the Dovyren parental magma is from Ariskin et al. (2009). The KOM composition is from Barnes, S.J., (2007)

compared to tholeiite-like magma types. Highest sulfide solubility is found in the highly FeO-enriched derivatives of the KIGL and PRI magmas.

Results of modeling of bulk silicate-sulfide ratios (sulfide proportions) for a range of multiply-saturated cotectics crystallizing from same parental magmas are given in (Ariskin et al., 2009).

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