

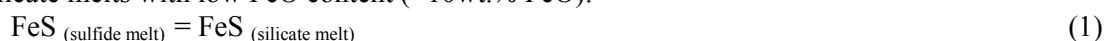
**Physical and chemical factors controlling sulfide-silicate liquation in unhydrous mafic systems  
(from result of computational modeling)**

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Over the last 20 years at least ten models of the sulfide solubility in synthetic and natural silicate melts have been proposed. We chose the reaction of the equilibrium between a silicate melt and immiscible sulfide phase by Poulson and Ohmoto [Poulson and Ohmoto, 1990], which they suggested for silicate melts with low FeO content (<10wt.% FeO):



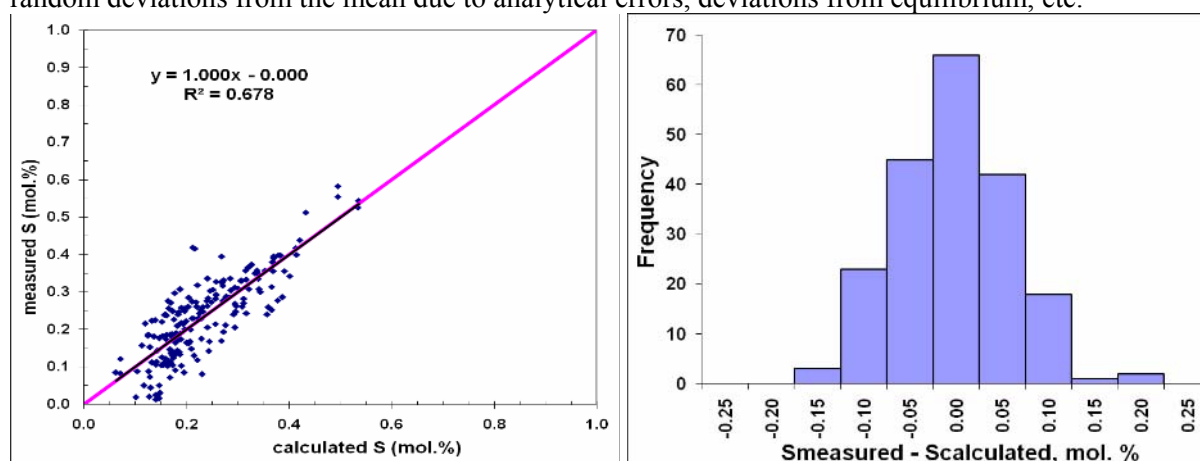
Reaction 1 suggests the relationship:

$$\ln X_S = -(A + \beta P)/T - B - D \lg fO_2 - \sum E_i X_i \tag{2}$$

where the  $X_S$  is the sulfur concentration at sulfide saturation (SCSS) in silicate melt. This reaction and a corresponding equation of the SCSS well reproduce the experimental data. The coefficients in the equation (2) were found by multiple linear regression of experimental data using the option "solver" in MS Excel. The coefficients of the equation are given in Table 1.

A	$\beta$	B	DfO <sub>2</sub>	Si	Ti	Al	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ca	Na	K
0	40.33	-181.94	0.08	190.30	182.34	185.47	212.47	185.77	190.13	190.11	189.07	219.89

The results of the analysis of experimental data using the equation (2) are shown in the graph and the histogram (Fig. 1). The differences between the experimental and calculating values of the SCSS are followed a normal distribution. The histogram clearly demonstrates this distribution. Consequently, the differences between the experimental and calculated values can be considered as random deviations from the mean due to analytical errors, deviations from equilibrium, etc.

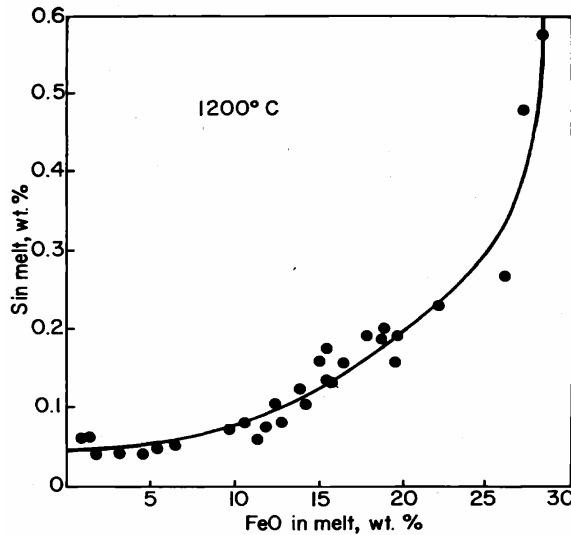


**Fig.1.** The graph of calculated and measured SCSS and the histogram of differences between measured and calculated SCSS, (200 experiments).

The average value of differences very close to zero, and is -0.00008wt. %, confidence interval at 95% significance level is  $\pm 0.0086$  wt. %. Thus, the coefficients of equation (2), found by multiple linear regression, accurately reproduce the experimental data.

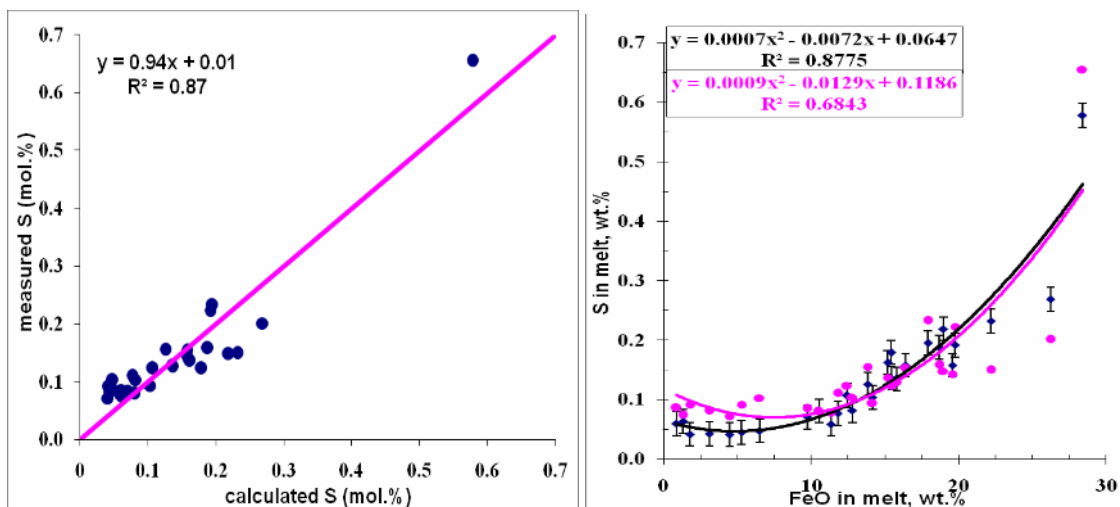
**Influence of melt composition on the SCSS.**

Many researchers stressed the observation that sulfur solubility is closely related to the FeO concentration in the melt. The sulfur content increases with the basicity of the melt, and in similar melts - especially with the increasing concentration of FeO in it. Researchers refer to the paper of Haughton [Haughton et al., 1974], in which the authors increased the concentration of FeO, adding iron to the charge, without changing the ratio of other ingredients. As a result, Houghton received a parabolic dependence of sulfur concentration on the content of FeO. (Fig. 2)



**Fig.2.** Effect of melt composition (here-FeO) on the concentration of sulfur. [Haughton et al., 1974]

Our equation reproduces Haughton's data, as well as the dependence of sulfur concentration on the content of FeO (Fig. 3, 4). Figure 3 shows that the equation (2) reproduces the experimental data by Haughton well. Fig. 4 shows the calculated and experimental dependence of sulfur content on the FeO content in silicate melts for the Haughton's experiments. Especially convincing is close coincidence of parabolic trends. Blue symbols are the experimental data, and purple symbols represent values calculated using the equation (2).



**Fig. 3.** Agreement between calculated and experimental data. [Haughton et al., 1974].

**Fig. 4.** A plot of sulfur content on the content of FeO in wt.%

But it does not mean that only the content of FeO effects on the concentration of sulfur in the melts. Experiments with high and low FeO contents are well reproduced, and even overlapped on the plot (Fig. 5).

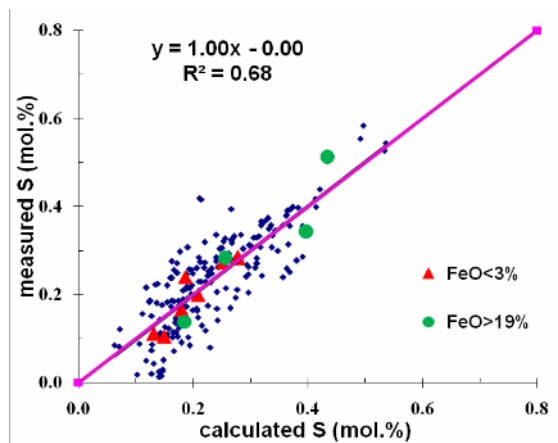


Fig.5. The data of experiments with high and low FeO contents.

If we increase only the concentration of one of the oxides, without changing the proportions of the other components, we obtain a significant positive dependence of sulfur concentration on  $TiO_2$ ,  $Al_2O_3$  and FeO, and the negative dependence on  $SiO_2$ , MgO, CaO. Changing the concentrations of  $Na_2O$  in the melt effects slightly (Fig. 6, 7).

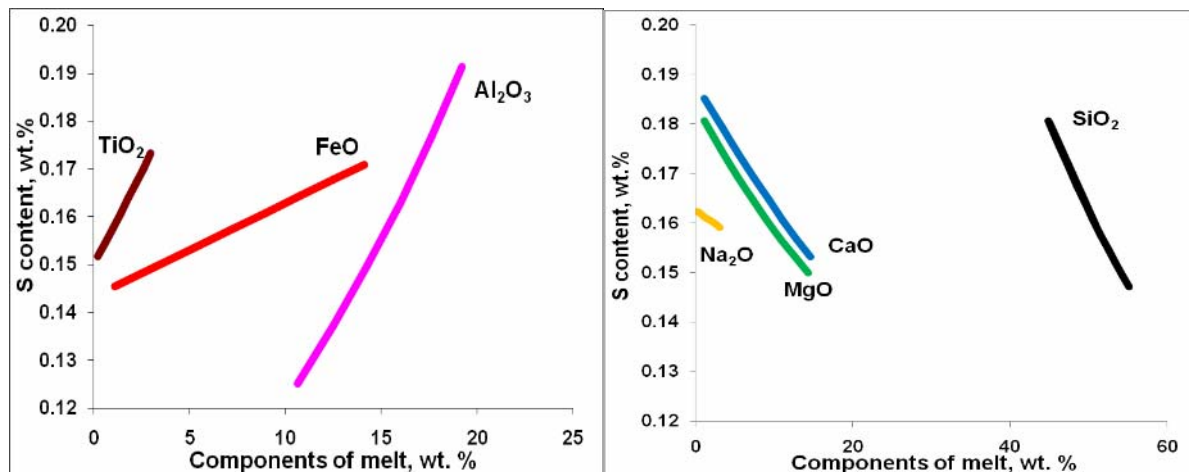


Fig.6, 7. S solubility in melt as a function of melt coposition, at constant temperature ( $T = 1400^\circ C$ ) and pressure ( $P = 10kbar$ ).

For this analysis, we chose a typical basaltic composition from the work [Liu et al., 2007]. Thus, we can refute the view that the sulfur content in the melt is controlled only by the concentration of FeO. Concentrations of all cations in the melt influence on sulfur solubility.

**Influence of temperature on the SCSS.**

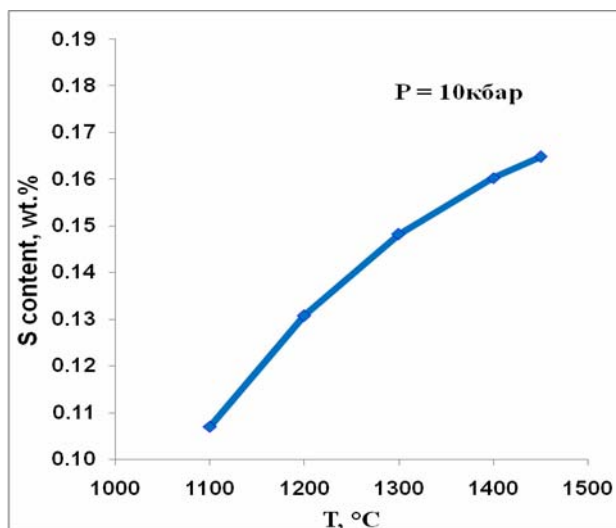
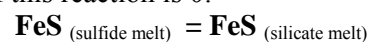


Fig. 8. S solubility in melt as a function of temperature at constant pressure ( $P = 10kbar$ ). (MORB from paper [Liu et al., 2007])

Despite a zero coefficient of the inverse temperature, the temperature dependence exists in terms of non-zero pressure due to the existence of another member of equation (2), which depends on the inverse temperature. This is the second term  $\beta R/T$ . At constant non-zero pressure with increasing temperature, the SCSS increases (Fig. 8).

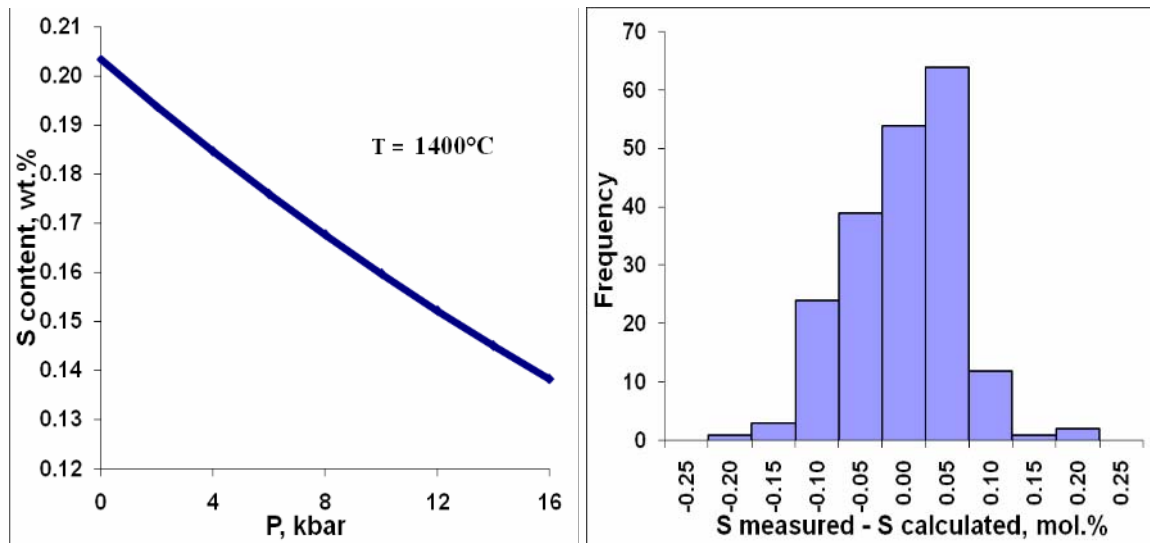
**Influence of pressure on the SCSS.**

Carmichael suggested that the volume effect of this reaction is 0:



In the other words, the pressure should not affect the SCSS. Other investigators consider that it is required experiments in a

large range of pressures, to make the effect obvious. [Wendland, 1982; Mavrogenes and O'Neill, 1999]. In a wide range of pressure effect is obvious (Fig. 9). In addition, the analysis of experimental data, without taking into account the pressure histogram, become asymmetric, i.e. distribution of the difference between the experimental and calculated values cease to be random (Fig. 10).



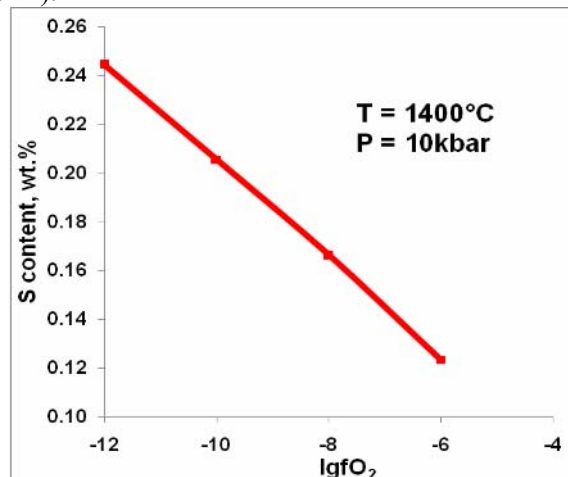
**Fig. 9.** S solubility in melt as a function of pressure at constant temperature ( $T = 1400^{\circ}\text{C}$ ) (MORB from paper [Liu et al., 2007])

**Fig.10.** Histogram of differences between measured and calculated SCSS, without pressure.

Consequently, the pressure significantly affects the sulfide-silicate equilibrium. With the increasing of pressure, the SCSS decreases. Negative correlation of SCSS with pressure explains, why the sulfide mineralization occurs in the middle and upper parts of layered intrusions. As the melt ascends, the SCSS value increases and the melt becomes undersaturated in sulfide; only as it cools and crystallizes does the melt again reach the SCSS.

#### **Influence of oxygen fugacity on the SCSS.**

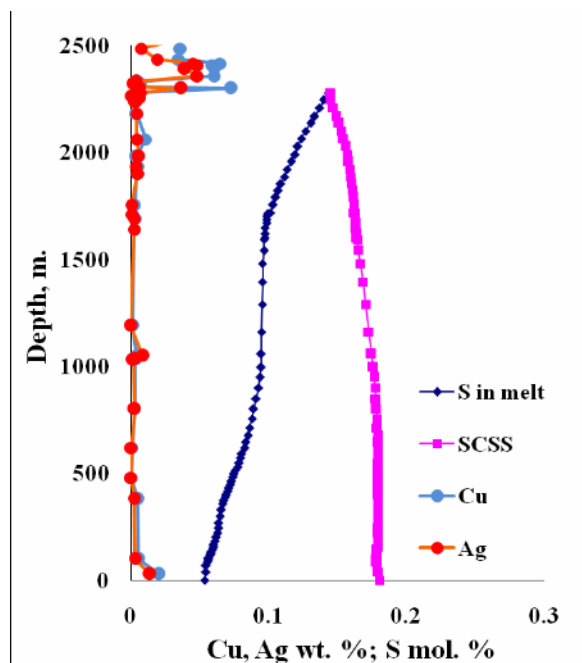
Our findings show that the SCSS decreases strongly with increasing oxygen fugacity without change other parameters (Fig. 11).



**Fig.11.** S solubility in melt as a function of oxygen fugacity at constant temperature ( $T = 1400^{\circ}\text{C}$ ) and pressure ( $P = 10\text{kbar}$ ). (MORB from paper [Liu et al., 2007])

#### **Testing of the SCSS model as an example of the layered intrusion Tsypringa.**

Using the SCSS model we can predict at what stage of formation of the intrusion liquation of sulfide and silicate melts happens, and to determine the level of occurrence of platinum species in the massif. The sharp increase in the content chalcophile elements in rocks at an altitude of about 2300 meters from the base of the intrusion corresponds to the liquation of sulfide melt in the chamber of the intrusion and the formation of sulfide mineralization. (Fig.12)



**Fig. 12.** The distribution of Cu and Ag in the vertical structure of the intrusion Tsipringa according to data of N.F. Pchelintseva [Semenov *et al.*, 1995] and the evolution of sulfur in the melt during the crystallization of primary magma (according to results of computational modeling) and changing the SCSS (calculated by equation (2)).

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