



Modeling the interplay of fO_2 and fS_2 along the FeS-silicate melt equilibrium

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ABSTRACT

In this paper we will discuss a simplified thermodynamic description for the saturation of FeS, either liquid or solid, in magmatic melts. The Conjugated-Toop-Samis-Flood-Grjothheim model [Moretti R. and Ottonello G., 2005. Solubility and speciation of sulfur in silicate melts, the Conjugated-Toop-Samis-Flood-Grjothheim (CTSFG) model. *Geochimica et Cosmochimica Acta*, 69, 801–823] has furnished the theoretical reference frame, since it already accounts for the solubility of gaseous sulfur and the speciation and oxidation state of sulfur in silicate melts. We provide a new model to predict the saturation of magmatic silicate melts with an FeS phase that is internally consistent with these previous parameterizations. The derived model provides an effective sulfogobarometer, which is superior with respect to previous models. For magmas rising from depth to surface, our appraisal of molar volumes of sulfur-bearing species in silicate melts allows us to model oxidation–reduction processes at different pressures, and sulfur concentrations for saturation with either liquid or solid phases. In this respect, the nature of the oxygen fugacity buffer is critical. On the basis of model results on some typical compositions of volcanological interest, the sulfur contents at sulfide saturation (SCSS) have been calculated and the results duplicate the experimental observations that the SCSS is positively correlated with pressure for water-saturated acidic melts and negatively correlated with pressure for water-poor basaltic melts. This new model provides fO_2 – fS_2 pairs of FeS saturation of natural silicate melts. In cases where the redox constraint is lacking, the model can be used to investigate whether the dissolved sulfur content approaches SCSS or not, and if so, to estimate at which fO_2 value the silicate melt is saturated with a sulfide phase.

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1. Introduction

The geochemical literature has shown that understanding sulfur is without a doubt real challenge in advancing our knowledge of magmatic environments. Sulfur is an important element to understand how gas separation takes place from magmas and to define the physico-chemical conditions of the chemically subtle interface between the magmatic and the hydrothermal domains. This narrow transition zone plays a primary role in volcanic processes, as well as in ore deposit geochemistry related to magmatism (Li and Ripley, 2005; Gorbachev, 2006).

Because of its multiple valence states and its high reactivity, sulfur has the extraordinary capability to partition in significant amounts into stable phases that characterize the local chemical environments in which sulfur species equilibrate. Moreover, in all of these environments, sulfur forms nearly pure stable condensed phases that represent the most important indicators of the sulfur capacity of a system. Therefore, these stable phases, such as FeS-dominated liquids and crystalline

monosulfide solid solutions (MSS), including pyrrhotite (Po), buffer or moderate the system and yield valuable insights into the sulfur fugacity of the system, its acid-base characteristics and its redox features, so far modeled only for two-phase melt + gas systems (Moretti and Papale, 2004; Burgisser and Scaillet, 2007). In the case of magmatic systems, we know that multiple reactions involve sulfur as i) dissolved in melts, essentially as SO_4^{2-} and S^{2-} anionic species (e.g., Fincham and Richardson, 1954), ii) condensed in monosulfide solid solutions (e.g. Vaughan and Craig, 1978) or sulfates (Carroll and Rutherford, 1985), iii) condensed in immiscible sulfide liquids, occurring as globules in rocks (Mathez, 1976; Czamanske and Moore, 1977), and iv) volatile components in the gas phase, mainly SO_2 and H_2S (Giggenbach, 1996).

The recent calibration of the Conjugated-Toop-Samis-Flood-Grjothheim model for sulfur solubility and speciation in silicate melts (Moretti and Ottonello, 2005) is the basis for the creation of an internally consistent model of FeS precipitation. This is a major step on the long path toward a full modeling of sulfur release in magmatic-volcanic systems.

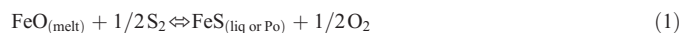
2. Model description

The existing data on sulfide saturation have been used to investigate the P – T – X – fO_2 – fS_2 space described by the Conjugated-Toop-

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Samis–Flood–Grjotheim model (hereafter CTSFG, Moretti and Ottonello, 2005) for dissolution of gaseous sulfur in silicate melts.

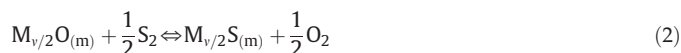
Our approach is not based on the minimization of the Gibbs free energy, because we cannot accurately construct the free energy surface for the system silicate melt+sulfide (melt or solid)+gas. We couple mass balances and equilibrium constants. CTSFG was used to generate $a_{\text{FeO}_{\text{melt}}}$ and $a_{\text{FeS}_{\text{melt}}}$ values from chemical equilibria that were assessed over about 1500 data from the literature about the iron redox state and sulfur solubility (Ottonello et al., 2001; Moretti and Ottonello, 2005). The following equilibrium reaction will be the main objective of our investigation into the coexistence of iron-bearing silicate melts and sulfide, either liquid or solid



We first introduce the main concepts behind the adopted model for sulfur solubility and describe how this takes into account volume properties that allow it to be extended to $P > 1$ bar. We then discuss how sulfide saturation can be effectively modeled to provide a sulfogebrometer that predicts the conditions of sulfide saturation with respect to either a crystalline or immiscible sulfide liquid phase.

2.1. Sulfur dissolving as sulfide in melts: extension to $P > 1$ bar

Sulfur solubility in melts (Moretti and Ottonello, 2003, 2005) is approached by generalizing Eq. (1) into a weighted linear combination of contribution from each metal oxide–metal sulfide pair:



where ν is the charge on cation M and the subscripts m and g refer to melt and gas phase, respectively.

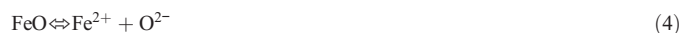
The (1 bar, T of interest) equilibrium constant holds:

$$K_{\text{O-S,M}} = \frac{f_{\text{M}_{\nu/2}\text{S}}}{f_{\text{M}_{\nu/2}\text{O}}} \left(\frac{f_{\text{O}_2}}{f_{\text{S}_2}} \right)^{1/2} = \exp(A'_{\text{O-S,M}} + B'_{\text{O-S,M}}/T) \quad (3)$$

In Eq. (3), the B' term (enthalpic contribution) is based upon metal oxide–metal sulfide exchanges independently evaluated from thermodynamic compilations in the pure liquid phase. The A' term embodies a solvation entropy directly calibrated on an extended database for sulfide capacity, $C_{\text{S}^{2-}} = S_{(\text{wt.}\%)}\left(\frac{f_{\text{O}_2}}{f_{\text{S}_2}}\right)^{1/2}$, (e.g. Fincham and Richardson, 1954), and represents the energy of transfer from the standard state of the pure component in the pure liquid phase to that of the pure component dissolved in the silicate melt phase. This conversion recalls the solvation of ions and ionic complexes in aqueous solutions and is accounted for by means of the Flood and Grjotheim thermochemical cycle (see Moretti and Ottonello, 2005 for more details).

Equilibrium constant 3 is based on activities defined through a Toop–Samis based polymeric treatment (Ottonello et al., 2001, Ottonello and Moretti, 2004, Moretti, 2005) in which Si^{4+} , Al^{3+} , Fe^{3+} and P^{5+} are networks former that build up the polymeric skeleton of the silicate melt, whereas other cations are network modifiers (Ottonello et al., 2001; Moretti, 2005). Water is treated as an amphoteric oxide, dissociating in H^+ and OH^- (Moretti, 2005; Moretti and Ottonello, 2005); sulfide (S^{2-}) and sulfate (SO_4^{2-}) are free anionic species.

In silicate melts the acid–base behavior is well described by the Lux–Flood formalism, such that oxide components are involved into acid–base exchanges of the type $\text{Base} \rightleftharpoons \text{Acid} + \text{O}^{2-}$. Therefore, the following basic dissociation relates $a_{\text{FeO}_{\text{melt}}}$ to its ionic dissociation products:



The equilibrium constant (1 bar, T of interest standard state) of reaction (4), K_4 , was already computed by Ottonello et al. (2001),

whereas the $1/RT \int \Delta V_4 dP$ term needed to shift K_4 to the standard state of P and T of interest was given following Moretti (2005). By considering the molar volume and thermal expansivity of FeO from Lange and Carmichael (1987; see also Table 1) and the volumes of one mole of Fe^{2+} (ionic radius=0.78; Shannon, 1976) and one mole of O^{2-} (ionic radius=1.40; Shannon, 1976), we get the following expression for FeO activities at the standard state of P and T of interest:

$$a_{\text{FeO}_{\text{melt}}} = \frac{[\text{Fe}^{2+}][\text{O}^{2-}]}{K_4^{P,T}} = \frac{(\text{Fe}^{2+})/\sum \text{cations}(\text{O}^{2-})/\sum \text{anions}}{\exp\left(1.1529 - 1622.4/T - \frac{5.53 + 2.92 \cdot 10^{-3}(T-1673)}{RT}\right)} \quad (5)$$

Parentheses symbolize concentrations. Ion activities, denoted by square brackets, are computed in the Temkin (1945) model by normalizing ion concentrations over the sub-lattice, or matrix, of interest, either cationic or anionic. These are given by summations over cations and anions in Eq. (5) (Ottonello et al., 2001; Moretti, 2005).

The oxide–sulfide equilibrium constant (3) in multicomponent melts may be readily generalized in terms of the Flood–Grjotheim thermochemical cycle (Moretti and Ottonello, 2003, 2005 and references therein):

$$\ln K_{\text{O-S}} = N'_{\text{A}} \ln K_{\text{O-S,A}} + N'_{\text{B}} \ln K_{\text{O-S,B}} + \dots + N'_{\text{M}+1} \ln K_{\text{O-S,M}} + \dots \quad (6)$$

where $K_{\text{O-S,i}}$ terms identify the equilibrium constant of the exchange reaction involving O_2 , S_2 , a metal oxide MO, and its corresponding sulfide, MS, and where N' are the “electrically equivalent fractions” (Flood and Grjotheim, 1952), i.e.:

$$N'_{\text{M}+1} = \frac{v_{\text{M}}^+ n_{\text{M}}}{v_{\text{A}}^+ n_{\text{A}} + v_{\text{B}}^+ n_{\text{B}} + \dots + v_{\text{M}}^+ n_{\text{M}} + \dots} \quad (7)$$

where v_{A}^+ , v_{B}^+ , v_{M}^+ are the charges associated with the cations of interest ($\text{A}^{\nu_{\text{A}}+}$, $\text{B}^{\nu_{\text{B}}+}$, $\text{M}^{\nu_{\text{M}}+}$ etc...). Each $K_{\text{O-S}}$ term enters the linear

Table 1

Partial molar volumes, expansivity and compressibility terms of silicate melt oxide components

Comp.	$\bar{V}_{i,1673\text{K}}$ (cm^3/mol)	a (1 bar) ($10^{-3} \text{ cm}^3/\text{mol K}$)	b (1673 K) ($10^{-4} \text{ cm}^3/\text{mol bar}$)	Source
SiO ₂	26.90±0.06	0.00±0.5	-1.89	(1)
	26.9	0.1 (§)	-1.89	(2)
TiO ₂	23.16±0.26	7.24±0.5	-2.31±0.1	(1)
	23.16	7.24	-2.31	(2)
P ₂ O ₅	82.16	2.62 (§)	-8.93	(2)
Al ₂ O ₃	37.11±0.18	2.62±0.2	-2.26±0.1	(1)
	37.11	2.62	-2.26	(2)
Fe ₂ O ₃	42.13±0.28	9.09±3.5	-2.53±0.1	(1)
	42.13	9.09	-2.53	(2)
Cr ₂ O ₃	36.36	8.22	-1.96	(2)
FeO	13.65±0.15	2.92±1.6	-0.45	(1)
	13.65	2.92	-0.45	(2)
MnO	11.62	2.73	-0.37	(2)
MgO	11.45±0.13	2.62±0.6	0.27±0.1	(1)
	11.45	2.62	-0.4	(2)
CaO	16.57±0.09	2.92±0.6	0.34±0.1	(1)
	16.57	2.92	-1.34	(2)
Na ₂ O	28.78±0.10	7.41±0.6	-2.40±0.1	(1)
	28.78	7.41	-2.4	(2)
K ₂ O	45.84±0.17	11.91±0.9	-6.75±0.1	(1)
	45.84	11.91	-6.75	(2)
Li ₂ O	16.85±0.15	5.25±0.8	-1.02±0.1	(1)
SO ₃	57.71	12.88	-7.39	(2)
H ₂ O	16.44	3.23	-1.79	(2)

(1) Lange and Carmichael (1987) and Lange (1994); (2) value adopted in this study.

(§) a for P₂O₅ was set to be consistent with Al₂O₃.

a for SiO₂ set to 0.1, well within the analytical error of Lange (1994) and Lange and Carmichael (1987).

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