Oxygen solubility and speciation in sulphide-rich mattes

Raúl O.C. Fonseca^{a,b,*}, Ian H. Campbell^b, Hugh St.C. O'Neill^b, John D. Fitzgerald^b

^a *Steinmann Institut für Geologie, Mineralogie und Paläontologie, Rheinische Friedrich-Wilhelms Universität Bonn, Germany*

^b *Research School of Earth Sciences, Australian National University, Canberra ACT, Australia*

Received 10 October 2007; accepted in revised form 17 March 2008; available online 1 April 2008

Abstract

Sulphide-rich liquids are common in magmatic environments forming over a wide range of temperature, pressure, fO_2 and fS_2 . They are economically important because they sequester valuable metals such as Cu, Ni, Au and Pt from silicate melts. The presence of accessory amounts of primary oxides associated with sulphide mineralisations is often ignored or unexplained. Experimental work has shown that large amounts of oxygen can dissolve into mattes at fO_2 typical of terrestrial environments. At the quartz–fayalite–magnetite fO_2 buffer, the molar fraction of O in the matte exceeds that of S, placing the composition of the matte to the magnetite side of the mss (monosulphide solid solution)–magnetite join in the Fe–S–O system. However, sulphides crystallise before magnetite in most sulphide mineralisations and are much more abundant. Moreover, the speciation of O in a matte is not well known. Here we report the results of an experimental study of the solubility of O in mattes as a function of fS_2 , fO_2 , temperature, and composition. We confirm previous observations that Ni and Cu have a negative effect on the solubility of O in mattes. We show evidence for the existence of FeSO as a structural constituent of mattes in the Fe–S–O system. We present a simple parameterisation of the amount of O dissolved in mattes under relevant geological conditions, and use this parameterisation to discuss mechanisms for the crystallisation of primary spinels associated with sulphides in the Kambalda massive sulphide deposit (Western Australia) and the Sudbury Igneous Complex (Ontario, Canada).

© 2008 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Sulphide liquids, or mattes, occur in many magmatic settings, from Cu–Ni massive sulphide deposits associated with ultramafic flows, to PGE-rich deposits such as the Bushveld complex (South Africa) and Sudbury (Ontario, Canada). Early experimental work by Naldrett (1969), and empirical observations, showed that magmatic sulphides are the product of the segregation of an immiscible sulphide-rich matte from a host silicate melt. The mattes sequester chalcophile metals from their parental silicate melt, which may lead to the formation of important ore deposits such as the Pt-rich Merensky Reef (e.g. Campbell et al., 1983). An immiscible FeS-rich matte can contain

appreciable amounts of O; for example, at the oxygen fugacity of the quartz–fayalite–magnetite (QFM) buffer, often thought to be typical of terrestrial crustal conditions, the matte contains a higher molar proportion of O than S (Nagamori and Kameda, 1965; Naldrett, 1969; Doyle and Naldrett, 1987; Kress, 1997; Nagamori and Yazawa, 2001; further affirmation of this perhaps surprising fact will also be presented in this study).

Furthermore, experimental data predict that at QFM, because the composition of a matte falls on the O-rich side of the magnetite–mss (monosulphide solid solution) cotectic in the Fe–S–O system (Fig. 1), the first phase to crystallise should be magnetite followed by mss, yet in natural assemblages the opposite appears to be true (Doyle and Naldrett, 1987). Two possible explanations have been proposed to explain this. Firstly, estimates of the fO_2 of natural magmas are known to vary from as low as QFM–3 to as high as QFM+3 (e.g. Christie et al., 1986; Ballhaus, 1993). Monosulphide solid solution should crystallise first in magmas that formed at fO_2 lower than QFM, implying that the oxi-

* Corresponding author. Present address: Steinmann Institut für Geologie, Mineralogie und Paläontologie, Rheinische Friedrich-Wilhelms Universität Bonn, Germany. Fax: +49 (0)228 732763.

E-mail address: raul.fonseca@uni-bonn.de (R.O.C. Fonseca).

Fig. 1. Enlargement of the Fe–S–O liquidus diagram, detailing the mss–magnetite and the mss–wüstite cotectics. Modified from Naldrett (1969) and Mungall et al. (2005).

dation state of ore-forming magmas might simply be lower than QFM. Secondly, Celmer (1988) and Yoshiki-Gravelsins and Toguri (1993) have noted that at a given fO_2 the oxygen content of a sulphide-rich matte depends on its Fe/(Ni + Cu) ratio, with O being more soluble in Fe-rich compositions than in Fe-poor compositions. The presence of Cu and Ni in the matte may therefore lower its O content so that its bulk composition is closer to the mss field than is the case for Fe–S–O mattes *sensu strictum* (Naldrett, 1989).

The speciation of oxygen in mattes is not known. Most authors suggest that the composition of a matte is controlled by the following reaction:

with FeO as the principal O species in the matte, and O/(O + S) in the matte varying as a function of the fO_2/fS_2 ratio (e.g. Shima and Naldrett, 1975). However, magnetite (Fe_3O_4), not wüstite ($Fe_{1-x}O$) is the common iron oxide associated with magmatic sulphides (Naldrett, 1969). Kress (2000) proposed a thermodynamic model based on six matte components, S, Fe, FeO, $FeO_{1.5}$, FeS and FeOS. The ternary stoichiometry FeSO has never been recognised in either experimental work or in natural assemblages; however, it was postulated by Kress (2000) as a possible species in sulphide-rich matte since its presence provided the best fit to his associated solution model for available experimental data (Nagamori et al., 1970; Kress, 1997).

Here we report experiments in which the solubility of O in mattes was investigated as a function of fO_2/fS_2 , composition and temperature. We show novel evidence that FeSO is more than a convenient thermodynamic component, as described by Kress (2000), but an actual structural species in mattes in the system Fe–S–O. We quantify the influence of Ni and Cu on the O abundances of mattes through a simple, easy-to-use parameterisation of available data. We show that Ni, and in a lesser extent Cu, have a negative effect on O solubility in a sulphide-rich matte, consistent with previous studies (Celmer, 1988; Yoshiki-Gravelsins and Toguri, 1993; Kress, 2007; Mungall, 2007).

2. EXPERIMENTAL METHODS

The experimental set-up used was the same for all experiments. Each experimental charge consisted of ~1 g of troi-

lite (Fe/S atomic = 1) powder of 99.99% purity placed inside an open capsule, 1 cm in diameter and 2 cm in height, made from pure SiO_2 glass. The crucibles were suspended in a vertical muffle tube furnace equipped for gas mixing, in which both fO_2 and fS_2 were controlled independently using CO_2 –CO– SO_2 gas mixtures. The gas flows were measured using Tylan F2800 mass flow controllers. Two controllers were available for each gas, with ranges between 10 and 200 SCCM (standard cubic centimetres per minute) for CO and CO_2 and 10–100 SCCM for SO_2 . The fO_2 and fS_2 for each run were calculated using the thermodynamic data for gas species in the NIST-JANAF tables (Chase, 1998) according to O'Neill and Mavrogenes (2002). The gas flows used for our experimental runs can be found as an Electronic Annex EA1 to this manuscript. The temperature was held constant to $\pm 5^\circ$ for the duration of each run using a central Pt–Rh thermocouple external to the muffle tube. The achievement of equilibrium was subsequently checked by analysing sulphides run for different times, which showed that at least 24 h are needed for the matte to equilibrate with the gas mixture in the furnace. Experimental charges were left in the furnace for 96 h, at 1200 °C, 72 h, at 1300 °C, and 24 h, at 1400 °C, to ensure equilibrium between the gas mixture and the matte. At the end of each run the charges were quenched by dropping them into a beaker of cold water. The experimental products were then recovered, mounted in epoxy resin and polished for analysis.

3. ANALYTICAL METHODS

3.1. Major elements: wavelength dispersive spectroscopy (WDS)

Both sulphide and alloy phases were analysed using the CAMECA SX100 Electron Microprobe (EMP), in wavelength dispersive mode (WDS), at 15 kV acceleration voltage and 20 nA beam current. Given the heterogeneity at the μm scale of the experimental run products in this study, sulphides were analysed for Fe, S, Ni, Cr, Cu and Si (to track crucible contamination) in area scans in $300 \mu m \times 300 \mu m$ grids with a $10 \mu m$ beam. Standard calibrations were carried out using pure troilite for Fe and S, NiS for Ni, chalcopyrite for Cu, Cr–metal for Cr, and SiO_2 for Si.

3.2. Analysing oxygen

Despite being the most abundant element in the Earth, O has been one of the most difficult elements for geochemists and material scientists to analyse accurately, but modern electron microprobe instrumentation makes the precise analysis of O possible. Several previous studies have used the EMP to measure O in sulphides (e.g. Kress, 1997; Gaetani and Grove, 1999; Brenan and Caciagli, 2000; Larocque et al., 2000; Nagamori and Yazawa, 2001; Rose and Brenan, 2001; Andrews and Brenan, 2002; Brenan and Rose, 2002; Mungall et al., 2005; Kress, 2007), however, the lack of suitable standards for O in sulphides is an issue (McGuire et al., 1992),

and the accuracy of many measurements is also hard to evaluate because detailed information on O calibrations and the method used to measure background in sulphides are not given.

In this study, calibrations for O were initially performed using the CAMECA SX100 EMP with the synthetic monolayer crystals PC0 ($2d = 45 \text{ \AA}$) and PC2 ($2d = 100 \text{ \AA}$). Peak and background positions, as well as background geometry, were found to vary from standard to standard, and between standards and the unknown (Fig. 2). The variations in the O $K\alpha$ peak position have been described previously by Liang (1991), who showed that the O $K\alpha$ peak undergoes a significant shift ($0.024\text{--}0.043 \text{ \AA}$) for different O standards, using a W–Si multilayer pseudocrystal ($2d = 59.8 \text{ \AA}$). Liang (1991) observed that “in the direct determination of oxygen, a peak count reduction could occur as a result of this peak shift effect if unsuitable oxygen standards are used”. In this study, early attempts at analysis of nominally O-free samples, using O calibrations done on different standards, yielded either negative concentrations or “phantom” amounts of O in the sulphide, confirming the point made by Liang (1991). Moreover, analysis of O with a PC2 crystal has the additional complication of several interferences associated with high-order Fe L lines, which makes analysis

in Fe sulphides particularly difficult. An additional problem of using WDS for O analysis is that both the minimum beam width (above $1 \mu\text{m}$) and associated interaction volumes (over $5 \mu\text{m}$) are too large for analysis of some of the oxygen-bearing quench phases. Calibrations for O were conducted on rutile (TiO_2), chromite and quartz using the PC0 monolayer pseudocrystal. Because of the peak shift effect, and the fact that the background in the low energy part of the WDS spectrum is curved, calibrations were conducted in peak area mode rather than by the usual peak and background measurements. Given the heterogeneity at the μm scale characteristic of the samples in this study, analysis was initially conducted using an unfocused beam of $10 \mu\text{m}$ width. However, this approach failed to produce reliable results, with the oxygen count rate changing by over a factor of two over a period of hours, probably due to carbon build-up on the surface of the samples. An alternate approach was therefore used in which the sample stage was moved in a boustrophedonic pattern over a distance of $\pm 20 \mu\text{m}$ from the central position, while the beam was kept focused with a constant width of $1 \mu\text{m}$; this method was implemented using a stage-control program *WANDER* written by Ashley Norris. Beam conditions were set at 15 kV acceleration voltage and 20 nA beam current. Counting times for O peaks was set at 180 s and O detection limits were $\pm 0.1 \text{ wt\%}$.

Oxygen was also analysed using a JEOL 6400 scanning electron microscope, in EDS mode. The disadvantages of analysis by EDS are: (i) low peak resolution, (ii) possible peak overlaps, and (iii) lower detection limits when compared to WDS quantitative analysis in peak area mode. The advantages of EDS analyses is that it provides rapid analysis of very small domains in samples, due to its smaller beam width (as low as $0.01 \mu\text{m}$), and smaller interaction volume. Beam conditions were set at 15 kV acceleration voltage and 1 nA beam current. Standard calibrations for O were carried out using albite. Only data that yielded totals between 98.5 and 101.5 wt% were used. About 5% of analysis were rejected on this basis, and the poor results are attributed to bad polishing of the sample or surface charging effects. Standard calibrations were performed immediately prior to the sample analysis. In addition, freshly polished oxygen-free troilite standards were analysed to measure “blank” oxygen levels. It was found that these nominally oxygen-free standards returned oxygen concentrations of $0.81 \pm 0.09 \text{ wt\%}$, due to errors in assigning the baseline under the oxygen $K\alpha$ peak in Fe-rich samples resulting from the close proximity of the Fe $L\alpha$ lines. This value was therefore subtracted from all nominal values of O concentrations. X-ray maps confirmed the presence of oxygen at low concentrations along the grain boundaries of sulphides, even in samples run at the lowest $f\text{O}_2$ (Fig. 3). Image analysis of the X-ray maps, using the ImageJ software, was performed independently of the EDS analysis and showed good agreement with the quantitative analysis. A comparison between data obtained from WDS with background corrected EDS data for the same samples showed good agreement with an $R^2 = 0.97$ (Fig. 4).

Fig. 2. Examples of variations in the peak (a) and background (b) positions of O for different standards and our unknowns given by WDS scans of the O $K\alpha$ X-ray peak using the PC0 and the PC2 pseudocrystal, respectively.

Fig. 3. X-ray maps for O and S for samples with different oxygen concentrations. It was found that even at very low oxygen values, oxygen was present in interstitial grain boundaries, where S was depleted. Discrete O-rich phase featured in the bottom of the 22 wt% O X-ray map, is the crucible material and was not taken into account in the average O content of that particular run.

3.3. X-ray diffraction (XRD) and transmission electron microscope (TEM)

3.3.1. XRD—X-ray diffraction

Nominally metal-free samples of sulphide were ground in acetone, and the resulting powder was mounted for powder X-ray diffraction (XRD). XRD diffraction patterns were determined using a Siemens D-5005 diffractometer (scintillation counter and Co $K\alpha$ radiation). Sample mixtures were sedimented onto a “zero background” quartz plate that was rotated while intensity data were collected from 10° to 90° 2θ in 0.01° increments taking 9 s per step.

Rietveld refinement was carried out using the program DBWS-9807 (Young et al., 1995). R_{Bragg} values were ~ 3 for mss and ~ 2 for wüstite (Fe_{1-x}O).

3.3.2. TEM—transmission electron microscopy

Samples were prepared by crushing in acetone, drying and transferring onto a TEM copper specimen grid precoated for lattice fringe resolution work with a perforated carbon thin film. TEM imaging, diffraction and analysis was carried out at 300 kV using a Phillips CM300T with a LaB6 filament, and a Gatan 794 multi-scan CCD camera. The chemical composition of powdered samples was qualitatively checked

Fig. 4. Comparison of O concentrations in matte obtained in WDS and EDS modes.

using an X-ray energy dispersive spectrometer (XEDS), fitted with an EDAX super-ultra-thin-window Si(Li) X-ray detector.

4. RESULTS

Experimental conditions and compositions are listed in Table 1. Fig. 5 is a plot of O concentrations in the matte as a function of $f\text{O}_2$, which increase with increasing $f\text{O}_2$ to a maximum of ~ 7 wt% (~ 18 at % O) for run FeOS2 at a $\log f\text{S}_2 = -3.0$ and $\log f\text{O}_2 = -10.3$. At higher $f\text{O}_2$ the matte reacts extensively with the “quartz” crucible leading to the formation of a mixture of silicate glass, magnetite and sulphide droplets in the quench (runs FeOS1 and FeOS11). Because the experimental charges in runs FeOS1 and FeOS11 reacted extensively with the silica crucible, we have not used these data. Temperature does not have a significant effect on the solubility of O in matte over the range of temperatures studied (1200–1400 °C).

Fig. 6 are plots of the concentration of O in the matte as a function of $f\text{S}_2$. The O content in the matte is shown to be inversely correlated with $f\text{S}_2$ for all temperatures. The data for 1250 °C of Kress (1997) has higher O concentrations in the matte when compared to our data for 1200 °C, because these runs were carried out at a higher $f\text{O}_2$ ($\log f\text{O}_2 \sim -8.5$ for 1250 °C). Fig. 7 is a plot of excess anions, O^{2-} and S^{2-} , over Fe in the matte as a function of $\text{O}/(\text{O} + \text{S})$, which is proportional to $f\text{O}_2$. Assuming that both O and S are in their 2- state, a positive $(\text{O} + \text{S})\text{-Fe}$ reflects the presence of Fe^{3+} in the matte, whereas a negative $(\text{O} + \text{S})\text{-Fe}$ reflects the presence of Fe^0 in the matte. The Fe^{3+} content of the matte increases with increasing $\text{O}/(\text{O} + \text{S})$ at all temperatures, in agreement with the data in Kress (1997). Negative $(\text{O} + \text{S})\text{-Fe}$, indicating Fe^0 in the matte, occurs at $\text{O}/(\text{O} + \text{S}) < 0.1$, which is supported by the presence of rare Fe nuggets in the quench at lower $f\text{O}_2$ (e.g. run FeOS13).

Figs. 8 and 9 are plots of the mole fraction of Fe, S and O as a function of $f\text{O}_2$ and $f\text{S}_2$, respectively, for the temperatures of 1200 °C, 1250 °C (Kress, 1997) and 1300 °C. As found in previous work (e.g. Kress, 1997, and references therein), Fe content of the matte is independent of temperature, $f\text{O}_2$ and $f\text{S}_2$ over the range of experimental conditions studied (Figs. 8 and 9). On the other hand, O substitutes for S in the matte at increasing $f\text{O}_2$ and decreasing $f\text{S}_2$, as shown by their negative correlation in Figs. 8 and 9.

Run FeOSCr1 was saturated with Cr metal and run at 1200 °C and at a $\log f\text{O}_2 = -10.5$ ($\sim \text{QFM}-2$). The aim of run FeOSCr1 was to measure the solubility of Cr in the matte and in the quenched phases. Subhedral to euhedral chromite crystals formed (Fig. 10), indicating that they crystallised before quenching took place. The mss did not contain detectable Cr, whereas the FeSO phase had ~ 0.3 wt% Cr. FeO was not analysed for its Cr content because it is only detectable at the TEM scale ($\sim 0.5 \mu\text{m}$). This result suggests that in Cr-undersaturated natural mattes, most, if not all of the Cr would be concentrated with the FeSO species, albeit in small amounts.

4.1. Identification of stoichiometric FeSO in the matte

The results presented here are similar to those of Kress (1997) who used a rapid quench device to provide a relatively homogeneous sample after quenching, with the absence of quench crystals at the micron scale, which clearly facilitates subsequent bulk analysis, but at the expense of being able to easily identify the quench products. Here, electron backscatter images of relatively O-rich samples (Fig. 11A) show the presence of two phases, mss grains devoid of O content, and an O-rich phase in interstitial spaces (Fig. 11B). X-ray mapping of O and S in run FeOS2 (Fig. 3) shows that O is concentrated in the interstitial spaces between sulphide grains while S is concentrated in O poor areas. Numerous electron microprobe analyses of the O-rich phase (approximately 5 per run) in Fig. 11B showed that it consistently had the stoichiometry of $\text{Fe}_{0.99}\text{S}_{1.00}\text{O}_{1.01}$. X-ray diffraction of one of the more O-rich runs (run FeOS2) identified only three crystalline phases; mss, wüstite and cristobalite (recrystallised fragments of the wall of the crucible), which raised the possibility that the interstitial O-rich phase is a quenched glass with FeSO stoichiometry. TEM analysis of run FeOS2 (Fig. 12) confirmed the presence of a glass (Fig. 12C) with a FeSO stoichiometric composition, suggesting that FeSO existed in the matte as constituent species, which then quenched to a glass, coating grains of mss. It may be possible that glassy inclusions might exist in the mss grains. However, these inclusions were not identified in BSE images.

4.2. Activity of FeO in the Fe–S–O system

Shima and Naldrett (1975) used the a_{Fe} in binary Fe–S liquids at 1200 °C (Nagamori and Kameda, 1965), and 1120 °C and 1400 °C (Bog and Rosenqvist, 1958), to calculate a_{FeO} from Darken and Gurry’s (1946) data for the standard free energy for the reaction:

Table 1
Experimental conditions and major element concentrations

Runs	Experimental conditions				Composition of the matte					
	T (°C)	$-\log/f\text{O}_2$	$-\log/f\text{S}_2$	Fe	S	O (EDS)	O (WDS)	Si	Cr, Cu, Ni ^b	Total
FeOS1	1200	9.0	3.05	52.8 ± 0.5	6.1 ± 1.1	29.8 ± 0.8	N/A	11.1 ± 0.6	bdl	99.8
FeOS2	1200	10.3	2.94	64.8 ± 0.2	27.4 ± 0.2	6.91 ± 0.5	N/A	bdl	bdl	99.1
FeOS3	1200	10.9	2.94	64.1 ± 0.2	33.0 ± 0.4	3.46 ± 0.4	N/A	bdl	bdl	100.5
FeOS4	1200	11.8	2.24	64.0 ± 0.1	32.6 ± 0.4	2.1 ± 0.1	N/A	bdl	bdl	98.7
FeOS5	1200	12.9	2.94	64.6 ± 0.2	34.2 ± 0.2	0.3 ± 0.1	0.6 ± 0.2	bdl	bdl	99.1
FeOS6	1200	12.8	2.94	66.1 ± 0.4	33.6 ± 0.1	0.4 ± 0.1	0.7 ± 0.4	bdl	bdl	100.1
FeOS7	1200	13.1	3.96	66.0 ± 0.9	32.5 ± 0.1	0.9 ± 0.1	1.2 ± 0.4	bdl	bdl	98.9
FeOS8	1200	13.1	4.96	66.07 ± 1.5	33.2 ± 0.6	1.5 ± 0.3	1.2 ± 0.4	bdl	bdl	100.8
FeOS9	1400	10.2	3.48	65.2 ± 0.3	33.0 ± 0.6	1.4 ± 0.5	N/A	bdl	bdl	99.6
FeOS11	1200	12.6	1.66	63.3 ± 0.1	36.3 ± 0.2	1.0 ± 0.1	1.1 ± 0.1	bdl	bdl	99.6
FeOS12	1300	9.6	2.94	58.7 ± 0.4	12.4 ± 0.8	21.9 ± 0.3	N/A	6.1 ± 0.4	bdl	99.1
FeOS12 ^a	1300	9.6	2.94	62.4 ± 3.6	30.7 ± 0.8	5.8 ± 0.7	N/A	bdl	bdl	98.9
FeOS13	1300	13.7	3.05	64.5 ± 0.1	34.7 ± 0.2	0.5 ± 0.1	0.7 ± 0.2	bdl	bdl	99.2
FeOS14	1300	10.2	2.83	65.2 ± 0.4	30.5 ± 0.5	3.7 ± 0.2	4.5 ± 0.3	bdl	bdl	98.8
FeOS15	1300	12	3.05	64.5 ± 0.2	31.4 ± 0.3	2.8 ± 0.2	3.3 ± 0.4	bdl	bdl	98.7
FeOS16	1300	12.7	2.88	64.5 ± 0.2	33.9 ± 0.3	0.9 ± 0.1	0.5 ± 0.03	bdl	bdl	99.3
FeOS17	1300	11.4	2.84	65.2 ± 0.3	33.1 ± 0.3	1.5 ± 0.1	N/A	bdl	bdl	99.8
FeOS18	1300	11.2	2.10	64.2 ± 0.2	34.4 ± 0.1	0.8 ± 0.1	N/A	bdl	bdl	99.4
FeOS19	1300	11.4	3.64	66.2 ± 0.8	31.6 ± 1.2	2.0 ± 0.5	N/A	bdl	bdl	99.8
FeOS20	1300	11.3	1.61	63.8 ± 0.1	35.9 ± 0.1	bdl	N/A	bdl	bdl	99.7
FeOS21	1300	11.3	4.43	67.6 ± 0.5	27.2 ± 0.2	4.4 ± 0.7	4.1 ± 0.04	bdl	bdl	99.2
FeOS22	1300	11.2	3.15	64.7 ± 0.3	32.4 ± 0.2	2.1 ± 0.5	1.8 ± 0.1	bdl	bdl	99.2
FeOS23	1300	11.4	2.48	64.0 ± 0.2	34.6 ± 0.1	1.3 ± 0.1	1.7 ± 0.1	bdl	bdl	98.6
FeOS24	1300	11.3	1.81	63.6 ± 0.1	35.4 ± 0.1	1.1 ± 0.1	1.1 ± 0.2	bdl	bdl	99.0
FeOS25	1350	10.2	1.59	63.7 ± 0.1	35.6 ± 0.1	bdl	0.3 ± 0.1	bdl	bdl	99.3
FeOS26	1200	12.6	3.88	66.7 ± 0.2	30.1 ± 0.2	2.9 ± 0.2	N/A	bdl	bdl	99.7
FeOS27	1400	10.2	1.58	63.0 ± 0.1	35.1 ± 0.2	0.8 ± 0.1	N/A	bdl	bdl	98.9
FeOS28	1200	11.8	1.30	62.3 ± 1.2	38.0 ± 0.9	0.3 ± 0.1	0.4 ± 0.1	bdl	bdl	100.7
FeOS29	1200	10.0	2.94	65.2 ± 0.3	28.0 ± 0.8	7.9 ± 0.9	7.6 ± 1.3	bdl	bdl	100.7
FeOS30	1200	11.9	2.24	63.2 ± 0.6	36.2 ± 0.4	0.7 ± 0.2	0.5 ± 0.1	bdl	bdl	99.8
FeOSCr1	1200	10.5	2.94	62.5 ± 0.1	28.2 ± 0.3	7.7 ± 0.2	7.0 ± 0.3	0.5 ± 0.02	0.14 ± 0.02	99.0
FeOSCu1	1200	10.5	2.94	54.0 ± 0.6	28.3 ± 0.3	6.9 ± 0.1	N/A	0.2 ± 0.01	9.9 ± 0.8	99.3
FeOSCu2	1200	10.5	2.94	57.3 ± 0.3	27.5 ± 0.4	7.3 ± 0.2	N/A	0.3 ± 0.01	6.2 ± 0.2	98.6
FeOSCu3	1200	10.5	2.94	60.1 ± 0.1	27.5 ± 0.4	7.6 ± 0.2	N/A	0.4 ± 0.02	4.3 ± 0.1	99.9
FeOSNi1	1200	10.5	2.94	54.2 ± 0.3	30.5 ± 0.4	4.8 ± 0.1	N/A	0.1 ± 0.02	9.3 ± 0.2	98.9
FeOSNi2	1200	10.5	2.94	57.5 ± 0.3	29.4 ± 0.4	5.9 ± 0.3	N/A	0.2 ± 0.02	5.6 ± 0.3	98.6
FeOSNi3	1200	10.5	2.94	60.5 ± 0.2	28.0 ± 0.3	7.1 ± 0.2	N/A	0.3 ± 0.01	2.8 ± 0.1	98.7

^a Sulphide droplets.

^b This column represents Cr content in run FeOSCr1, Cu content in runs FeOS Cu1–3 and Ni content in runs FeOSNi1–3.

Following Shima and Naldrett (1975), –log/*f*O₂ and –log/*f*S₂ have been contoured for a part of the Fe–S–O ternary phase diagram using the matte compositions determined in this study for *f*O₂ and *f*S₂ at temperatures of 1200 °C and 1300 °C (Fig. 13A and B). Superimposed on Fig. 13A and B, are the *a*_{FeO} curves calculated for 1200 °C by Shima and Naldrett (1975).

Naldrett (1969) pointed out that by controlling *f*O₂ and *f*S₂ for a liquid in the Fe–S–O system at any given temperature and pressure, one also controls the composition, and from reaction 2, the *a*_{FeO} of the matte. When a matte segregates from a given silicate melt, the condition of thermodynamic equilibrium requires the *a*_{FeO} in both the matte and silicate melt to be the same. As in Shima and Naldrett (1975), the *a*_{FeO} will decrease with increasing *f*S₂, so that

the lower the *a*_{FeO} of the silicate melt, the higher the *f*S₂ needs to be for the segregation of a Fe–S–O matte to occur. For example, if a silicate melt at 1200 °C and with a log/*f*O₂ of –10 has an *a*_{FeO} of 0.1, the minimum log/*f*S₂ necessary to trigger segregation of a Fe–S–O matte, is ~–2.2, which is in close agreement to the determined value of –2.6 determined by Shima and Naldrett (1975) under the same conditions. Despite the similarity between this study and Shima and Naldrett (1975), the *f*S₂ contours are slightly different in both studies. The most likely explanation is that different methods were used to analyse O: EMP in this study versus O calculated by difference in Shima and Naldrett (1975).

The above discussion assumes that Fe is the only cation to enter the sulphide-rich matte. The presence of Ni and Cu triggers matte segregation at a different *f*S₂ than in the pure Fe–S–O system, since these elements are likely to influence the *a*_{FeO} of the system.

Fig. 5. O concentrations in matte as a function of oxygen fugacity at 1200 °C, 1250 °C (Kress, 1997), 1300 °C and 1350 °C (Gaetani and Grove, 1999). Datasets for different temperatures show good agreement between them, indicating that temperature has a negligible effect to the solubility of O in the matte.

4.3. The solubility of O in a S-rich Fe–S–O matte as a function of fS_2 , fO_2 and T

Kress (2000) developed an algorithm based on an associated solution model for sulphide liquids in the system Fe–S–O. The model is quite computationally complex and difficult to implement. Here we present a simple parameterisation of the experimental results that allows the solubility of O in sulphide-rich mattes to be calculated as a function of fO_2 , fS_2 and temperature. The parameterisation was obtained by least-squares fitting to a number of datasets from the literature, as listed in Table 2. Several criteria were used to decide which data were reliable. Firstly, only data that was obtained through experimental studies carried out at 1 atm in furnaces equipped for accurate simultaneous control of fO_2 and fS_2 by gas mixing were considered. Secondly, data from studies where no analytical methods for analysis of O are described were rejected. Thirdly, any obvious outliers from groups of data were also excluded. The rationale for the exclusion of obvious outliers, hinges on the fact that small disruptions in the SO_2 , CO and CO_2 gas flows, can change the stoichiometry of sulphides considerably resulting in obvious outliers in a composition versus fO_2 or fS_2 plot. Therefore, by default, outliers that represent more than two standard deviations from the mean are rejected. Finally, data that displayed an obvious analytical bias, i.e. H extraction versus EMP, were also excluded. An example of analytical bias is shown by the O solubility data in mattes, from Nagamori and Kameda (1965), which systematically displays higher concentrations of O for the same fO_2/fS_2 when compared to other data obtained by EMP (Fig. 14). A summary of the data sources, the range of conditions investigated, the analytical method used and the number of data rejected for each study are given in Table 2.

Fig. 15 shows the range of compositions (a) and conditions (b) covered by each of the studies considered. The range of fS_2 , fO_2 and T covered by each one of the stud-

Fig. 6. Solubility of O in matte as a function of fS_2 at (a) 1200, (b) 1250 (Kress, 1997) and (c) 1300 °C. O solubility in the matte decreases with increasing fS_2 for all temperatures and values of fO_2 .

ies described in Table 2 is limited but by combining all of the studies a large range of conditions is obtained, which is pertinent to the crust and the upper mantle (Fig. 15A). In terms of the composition of the matte, all of the studies, regardless of temperature have a Fe/(S + O) molar ratio very close to one (Fig. 15B), characteristic of sulphide-rich mattes of the upper mantle. Studies of S-containing liquid metals with $Fe/(S + O) \gg 1$ (e.g. Jana and Walker, 1997; Fleet et al., 1999; Lazar et al., 2004) were not considered.

The filtered data were fit to the following equation:

$$\ln[O]_{\text{matte}} = A + \frac{B}{T(K)} + C \ln fO_2 - D \ln fS_2 \quad (3)$$

where A , B , C and D are empirical fitting constants. The result of this fit is:

Fig. 7. Excess anions over Fe ((O + S)–Fe) as a function of O/(O + S). Assuming that S and O have valences of 2–, excess of anions over Fe reflects the presence of ferric iron in the matte with increasing O/(O + S), whereas at low O/(O + S) negative (O + S)–Fe reflect the presence of Fe⁰.

$$\ln[\text{O}]_{\text{matte}} = -2.99 + \frac{17550}{T(\text{K})} + 0.334 \ln f\text{O}_2 - 0.149 \ln f\text{S}_2 \quad (4)$$

with $\chi^2_v = 2.55$.

Some of the studies quoted in Table 2 did not quote uncertainties, in which case we assumed $\sigma \log_{10} f\text{O}_2$ and $\sigma \log_{10} f\text{S}_2 = 0.1$; $\sigma[\text{O}]_{\text{matte}} = 0.1 + 0.1[\text{O}]_{\text{matte}}$; if $[\text{O}]_{\text{matte}}$ was reported as zero we assumed it to be 0.1 ± 0.1 . Note that our empirical parameterisation returns coefficients *C* and *D* that are different from the values expected thermodynamically from the stoichiometry of reaction 1, namely +0.5 and –0.5, respectively. This discrepancy with thermodynamic behaviour has been found previously (e.g. Nagamori and Kameda, 1965; Blatov et al., 1997; Kress, 1997; Nagamori and Yazawa, 2001).

Fig. 16, is a plot of the O concentrations measured in the matte against the O concentrations in the matte as calculated through Eq. (4). The agreement between measured and calculated O contents of the matte is excellent, except at lower concentrations of O where calculated concentrations tend to be slightly higher than the measured ones. This is plausibly the result of poor data quality at very low O concentrations due to difficulties in measuring O at very low concentrations by EMP. Fig. 17 is a plot of the difference between measured and calculated O concentrations in the matte as a function of $f\text{O}_2$, here shown as relative to QFM, and for different intervals of $f\text{S}_2$. The aim of this diagram was to test whether there was any prevalence of outliers for a given range of conditions. Outliers do not show any preference to particular intervals of $f\text{O}_2$ and $f\text{S}_2$, and display a random distribution.

Fig. 18 is a comparison between the mole fractions of S in the matte as a function of $f\text{S}_2$ (a), and of O in the matte as a function of $f\text{O}_2$ (b), with the predicted mole fractions for both O and S based on a thermodynamic model of the system Fe–S–O by Kress (2000), and the empirical fit by Eq. (4). The agreement between the Kress model and our empirical fit is striking with regard to O concentrations

Fig. 8. Mole fraction of O, S and Fe as a function of $f\text{O}_2$ at constant $f\text{S}_2$ (10^{-3} bar) for the temperatures of (a) 1200, (b) 1250 (Kress, 1997) and (c) 1300 °C.

in the matte as a function of $f\text{O}_2$. However, the Kress model and the empirical fit do not agree with regard to how the molar fraction of S changes with $f\text{S}_2$, especially at $\log f\text{S}_2$ higher than –1.5 and lower than –4.5. This discrepancy may be explained by the fact that our empirical fit is constrained by a larger dataset ($n \sim 300$) than that used by Kress (2000).

4.4. The effect of Cu and Ni on the solubility of O in matte

As discussed previously the relevance of the Fe–S–O system to natural systems hinges on our knowledge of the effects of other cations, such as Cu and Ni. Several experiments were carried out to investigate the effect of composition on the solubility of oxygen in matte. Temperature

Fig. 9. Mole fraction of O, S and Fe as a function of fS_2 at constant fO_2 ($\sim 10^{-11.3}$ bar) for the temperatures of (a) 1200, (b) 1250 (Kress, 1997) and (c) 1300 °C.

and $\log fO_2$ were kept at a constant 1200 °C and -10.5 (QFM-2), respectively, with varying amounts of Cu and Ni added to the starting composition (0–10 wt%). Fig. 19 is a plot of O solubility in matte as a function of Ni/Fe and Cu/Fe. It is evident that Ni/Fe has the largest effect on the solubility of O in the matte, which decreases by almost ~50% at a Ni/Fe of 0.17. The Cu content of the matte has a more subtle effect, with the O content decreasing by less than 10% at a Cu/Fe of 0.16.

Previous studies (Kaiser and Elliott, 1986; Celmer, 1988; Yoshiki-Gravelsins and Toguri, 1993; Brenan and Caciagli, 2000; Rose and Brenan, 2001; Brenan and Rose, 2002; Mungall et al., 2005; Kress, 2007), have shown that increasing the molar fractions of Ni and Cu in the matte led to a decrease of the molar fraction of O in the matte.

Fig. 10. Subhedral to euhedral chromite crystals that have crystallised directly from the sulphide-rich matte in run FeOSCr1. Dark grey crystals are chromite and light grey matrix are mss + FeSO.

Fig. 11. (A) Backscatter electron image of run FeOS2. Round light coloured grains are mss, whereas the dark phase in the interstitial spaces consists of stoichiometric FeSO. White crystals are PtFe quench nuggets. (B) Textural relationship between FeS and FeSO interstitial phase in run FeOSCr1. It is clear that the FeSO phase (marked by white arrows) is in the interstitial spaces between grains of FeS.

The relationship between O solubility in Fe–S–O mattes and its Cu content, determined in this study is different to that of Ni, a conclusion that disagrees with the work

Fig. 12. Selected area diffraction pattern (SADP) of phases found in the sulphide-rich quenched samples. Numbers depicted in (A) and (B) are lattice parameters.

of Yoshiki-Gravelsins and Toguri (1993). However, Yoshiki-Gravelsins and Toguri (1993) compared their experimental results for Ni–Fe–S–O mattes with previous studies (Kaiser and Elliott, 1986) where the experiments were conducted at different T , fO_2 and fS_2 , making it impossible to compare the effect of Cu and Ni on the solubility of O in mattes with confidence. Kaiser and Elliott (1986) and Somsiri and Gaskell (1995) studied the solubility of O in Cu–Fe–S mattes as a function of fS_2 , fO_2 and melt composition. They fitted their experimental results to the following equation:

$$[O]_{\text{matte}} = a \times fO_2^b \times fS_2^c \times (1 + 9 \times W_{\text{Fe}})^d \quad (5)$$

where $[O]_{\text{matte}}$ is the O content of the matte in wt%; a , b , c and d are empirical fitting constants; and W_{Fe} is the Fe/(Cu + Fe) weight ratio of the matte. At 1200 °C, Kaiser and Elliott (1986) obtained:

$$[O]_{\text{matte}} = 2.5 \times fO_2^{0.200} \times fS_2^{-0.142} \times (1 + 9 \times W_{\text{Fe}})^{2.19}. \quad (6)$$

Eq. (6), although useful for Cu-rich compositions cannot be applied to situations where Ni is also present. Moreover, neither Kaiser and Elliott (1986) or Somsiri and Gaskell (1995) included the effect of T on their fits. What is needed is a parameterisation that allows the calculation of O solubility in the matte as a function of Ni and Cu contents of the matte as well as T , fO_2 and fS_2 . By expanding the data fit for the Fe–S–O system described by Eq. (4) to accommo-

date for the effects of Cu and Ni to the solubility of O the following fit is produced:

$$\begin{aligned} \ln[O]_{\text{matte}} = & -2.99 + \frac{17550}{T(K)} + 0.334 \ln fO_2 - 0.149 \ln fS_2 \\ & - 0.425[Ni]_{\text{matte}} - 0.337[Cu]_{\text{matte}} \\ & + 1.99 \times 10^{-4}[Ni]_{\text{matte}}^2 - 2.83 \times 10^{-4}[Cu]_{\text{matte}}^2 \\ & - 0.0064[Ni]_{\text{matte}} \times [Cu]_{\text{matte}} \end{aligned} \quad (7)$$

where $[Ni]_{\text{matte}}$ and $[Cu]_{\text{matte}}$ are the concentrations of Ni and Cu in the matte in weight percent, and $\chi_v^2 = 3.28$.

Fig. 20 is a comparison between measured and calculated O contents in Cu–Ni–Fe–S–O mattes. As with the Fe–S–O system, the fit between the calculated and measured O is excellent as shown by the reasonably small value of χ_v^2 displayed by the fit.

The implication for natural systems is that the presence of Ni, and to a lesser extent Cu, in a matte will decrease its molar proportion of O relative to S. As a result, the composition of a matte in the Fe–Cu–Ni–O–S system may not fall on the O-rich side of the magnetite–mss cotectic at an fO_2 defined by the QFM buffer depending on the Ni and Cu contents of the matte. Ni and Cu-rich mattes are likely to crystallise mss first rather than magnetite, in agreement with empirical observations (e.g. Doyle and Naldrett, 1987).

Fig. 13. Empirical contours of $-\log f_{S_2}$ and $-\log f_{O_2}$, and calculated contours of the a_{FeO} (Shima and Naldrett, 1975) in a portion of the ternary phase diagram for the system Fe-S-O at 1200 °C and 1300 °C following Shima and Naldrett (1975) but contoured in the light of the data presented in this study.

5. DISCUSSION

5.1. Implications of oxygen solubility in mattes

Most natural occurrences of magnetite associated with magmatic sulphides are the result of desulphurisation, either by high-grade metamorphic fluids (e.g. Curaçá Valley, Brazil; Maier and Barnes, 1996), and late-magmatic hydrothermal fluids (JM reef, Stillwater, USA; Li and Ripley, 2006), or in most cases, the result of direct precipitation from a silicate melt. In addition to the aforementioned modes of magnetite formation, there are cases where magnetite is associated with sulphide and appears to have crystallised directly from an immiscible sulphide-rich matte.

Our results indicate that a natural sulphide-rich matte should increase its O abundance as mss crystallises. What happens to the dissolved oxygen is not very well known. Naldrett (1969) suggested that sulphide-rich mattes are closed systems with respect to their O content. Indeed, massive sulphides, such as the Ovoid body in the Voisey's Bay Ni-Cu-Co deposit, display abundant disseminated magnetite, which is uniformly distributed within the ore (Naldrett et al., 2000) and not concentrated in the matte/silicate-melt boundaries, like in deposits such as Kambalda (Western Australia—Frost and Groves, 1989) or Sudbury (Ontario, Canada—Magyarosi et al., 2002). The Ovoid body in Voisey's Bay, may then be considered a closed system with regards to its O content. Other ore deposits, do not display such a clear picture with regards to the fate of the matte's O abundances. For example, the Kambalda massive Ni-sulphide deposit features, in addition to rare disseminated magnetite (Heath et al., 2001), has Cr-rich magnetite within the massive sulphide ore, in close proximity to komatiitic melt inclusions (Frost and Groves, 1989). Moreover, in some sections of the Sudbury igneous complex (e.g. Copper Cliff South Mine) up to 5 wt% primary magnetite associated with the massive sulphide ore are present (e.g. Magyarosi et al., 2002). Moreover, (Magyarosi et al., 2002) describes that magnetite is more common along the disseminated/massive ore interface and not uniformly disseminated in the massive ore like in the Voisey's Bay massive sulphide. The distribution of magnetite in the massive sulphides in both Kambalda and Sudbury seems to be in contrast with that observed in the Voisey's Bay massive sulphide. Further understanding on how the magnetites and Cr-rich spinels formed in Sudbury and Kambalda respectively is then necessary to understand the fate of oxygen dissolved in sulphide-rich mattes.

5.1.1. Sudbury (Ontario, Canada)

The Sudbury Igneous Complex (SIC) is thought to have formed through a meteoritic impact (e.g. Grieve, 1994), which led to the formation of a silicate melt that was well above its liquidus temperature (1700 °C according to Keays and Lightfoot, 2004). The initial high temperature of the SIC melt made it able to dissolve as much as 5000 ppm S (Keays and Lightfoot, 2004). As it cooled down to its liquidus temperature (ca. 1180 °C), the silicate melt became sulphide saturated, producing the mass sulphide ores present today (Keays and Lightfoot, 2004). Keays and Lightfoot (2004) estimated that the f_{O_2} when the silicate melt reached its liquidus temperature was ~QFM-1. They calculated a Ni and Cu tenor of the sulphide liquid in equilibrium with the silicate melt and they obtained 4.2 wt% Ni and 4.5 wt% Cu. At 1180 °C, QFM-1 and an f_{S_2} of 0.12 bars (estimated based on the relationship between a_{FeO} in the silicate melt, f_{O_2} and sulphur content following O'Neill and Mavrogenes, 2002), the calculated solubility of O in a matte under these conditions using Eq. (4), gives a maximum O content of 5.31 wt% (~20 wt% magnetite in the matte). However, the observed magnetite content of the SIC's sulphide is between 2 and 5 wt% of primary magnetite, far below the calculated 20 wt%, which indicates that the matte may have

Table 2

List of sources of data used for the empirical fit described by Eq. (4)

Data source	<i>n</i>	Rejections ^a	Range of $-\log/S_2$	Range of $-\log/O_2$	Range of <i>T</i> (°C)	Analytical method
This study	51	2	1.3–4.96	9.6–15.0	1200–1400	EMP and SEM
Nagamori and Kameda (1965)	59	All ^b	1.05–2.6	9.4–12.0	1300	H extraction
Kaiser and Elliott (1986)	71	None	1.62–2.98	8.33–9.56	1195	H extraction
Somsiri and Gaskell (1995)	36	None	1.6–2.3	8.5–13.72	1300	IR analysers
Blatov et al. (1997)	25	All ^c	1.06–2.26	7.53–11.45	1300	Unknown
Kress (1997)	15	2	1.24–3.05	8.5–13.72	1097–1348	EMP
Brenan and Caciagli (2000)	6	3	2.06–4.0	8.1–10.1	1300	EMP
Nagamori and Yazawa (2001)	12	None	2.65–3.48	9.6–12.0	1200	EMP
Rose and Brenan (2001)	29	7	1.6–4	8–11.1	1300	EMP
Andrews and Brenan (2002)	6	None	1.7–3	8.1–8.6	1300–1400	EMP
Brenan and Rose (2002)	11	4	1.6–1.9	8.1–9.5	1300	EMP
Mungall et al. (2005)	4	None	1.25–2.2	11.2–12.8	950–1050	EMP
Kress (2007)	32	11	1.09–4.02	7.69–13.57	1248–1449	EMP

^a By default, outliers which represent more than two standard deviations from the mean are rejected.^b Data plots slightly higher than the general trend shown by the data. Possible analytical bias.^c Data of poor quality. No analytical methods described in the manuscript.

Fig. 14. O solubility in matte as a function of $\log(fO_2/fS_2)$. Note that despite differences in temperature; overall almost of the datasets represented in the figure agree very well with each other. With the exception of a few outliers (run numbers are identified in the figure, exp52 and exp86 are taken from Nagamori and Yazawa, 2001; Kress, 1997, respectively), only the dataset of Nagamori and Kameda (1965) plots at consistently higher O concentration than other datasets, probably due to an analytical bias.

lost as much as 75% of its O content through diffusion to the overlying SIC melt. The diffusion of O from the massive sulphide into the overlying SIC cumulate pile is consistent with the larger concentration of magnetite in the disseminated ore (Magyarosi et al., 2002), and with the low diffusion rate of O in silicate melts compared with mattes ($\sim 10^{-7}$ cm²/s—Liang et al., 1996—compared to ~ 2 cm²/s in sulphide—Jorgensen and Moyle, 1986), allowing the nucleation of magnetite at the massive ore–disseminated ore interface (Fig. 21A). As the matte cools, mss starts crystallising and the remaining O in the matte increases leading to the crystallisation of sparse magnetite in the massive ore (Fig. 21B). Note that Szentpéteri et al. (2002) also document the presence of Ti-magnetite, in addition to magnetite associated with the Sudbury massive sulphides (Copper Cliff North Area). The Ti-magnetite is likely the result of direct precipitation from the silicate melt, and therefore it cannot have precipitated from the sulphide-rich matte.

5.1.2. Kambalda (Western Australia)

Frost and Groves (1989), in their study of magmatic contacts between immiscible sulphide and komatiite melts in the Kambalda sulphide ores (Western Australia), identified Cr-rich magnetite in close textural association with the Ni-rich sulphide ore. The spinel is localised in the sulphide matrix adjacent to komatiite inclusions in the massive ore and it is concentrated near, but not on, sulphide–komatiite contacts. Subsequent observations by Heath et al. (2001) showed that, in addition to the Cr-rich spinel described by Frost and Groves (1989), primary magnetite is found in the matrix ore (1–9 wt%) and to a lesser extent in the massive ore (less than 1 wt%). Magnetite enrichment is more pronounced along the boundary between massive- and disseminated-ore types (Woolrich et al., 1981; Heath et al., 2001), which is explained by Naldrett (1969) as the result of fO_2 enhancement due to differences in the diffusion coefficients of O in mattes and silicate melt. These observa-

Fig. 15. (a) Oxygen and sulphur fugacity distribution of the different datasets used in this study. (b) $\text{Fe}/(\text{S}+\text{O})$ molar ratio versus temperature. The range of $\text{Fe}/(\text{S}+\text{O})$ molar ratios shown here represents sulphide-rich mattes characteristic to the upper mantle.

tions seem to indicate that a sulphide-rich matte can be considered an open system with regard to its oxygen content, a view which differs from that of [Naldrett \(1969\)](#) who suggested that massive sulphide-rich mattes would form a closed system.

The magnetite present in the ore as well as the Cr-rich spinel, are thought to be primary in origin ([Frost and Groves, 1989](#); [Heath et al., 2001](#)). It is necessary to characterise the mechanisms that allowed the crystallisation of these two different types of primary magnetites in order to understand how O behaves during the fractional crystallisation of sulphide-rich mattes. [Ewers et al. \(1976\)](#) suggested that the presence of Cr-rich spinels in massive sulphide ores, such as Kambalda, crystallised directly from the sulphide-rich matte. However, direct crystallisation of chromite from a matte is inconsistent with the fact that Cr-rich spinels in Kambalda are not found in sulphide ore, which would be the case if they crystallised directly, but they are concentrated near ore–komatiite interfaces. We re-evaluated the interpretation of [Ewers et al. \(1976\)](#) in view of the structural matte constituents that were iden-

Fig. 16. Comparison between measured O in matte and O solubility in the matte calculated through Eq. (4). The results of the fit are excellent as shown by its high χ^2_v value.

Fig. 17. Plot of the difference between measured O and O calculated through Eq. (7), versus f_{O_2} at different intervals of f_{S_2} . The outliers identified this way show no dependence on either f_{O_2} or f_{S_2} .

tified previously and in the light of run FeOSCr1, which was carried out to determine the solubility of Cr in a matte.

Our results, as well as Cr solubility data from sulphides featured in [Brenan and Rose \(2002\)](#), show that in a Cr-saturated matte, chromite will crystallise before mss. However, in Kambalda, the sulphide-associated Cr-rich spinel is found in intergrowths with sulphides, indicating that the Cr-rich spinel crystallised at the same time or shortly after the onset of sulphide crystallisation. Because sulphide crystallised before the Cr-rich spinel, the residual matte will become increasingly rich in the FeSO component and therefore O. The scarcity of any kind of spinel in the crystallised sulphide ([Frost and Groves, 1989](#); [Heath et al., 2001](#)) shows that the matte lost most of its O to the overlying silicate melt. The excess O reacted with the Cr from the

Fig. 18. Comparison between melt composition data as a function of fO_2 (a) and fS_2 (b) and the associated asymmetric regular solution thermochemical formulation for the system Fe–S–O of Kress (2000). The full line represents the expected O and S concentrations of the matte as calculated through Eq. (4).

Fig. 19. Oxygen concentrations in matte as a function of Cu/Fe and Ni/Fe atomic ratios.

komatiite melt inclusions leading to the crystallisation of spinel near, but not at, the boundaries between komatiite melt inclusions and matte (Fig. 22). The precipitation of Cr-rich spinel is enhanced by the relative low solubility of

Fig. 20. Calculated O contents in the matte versus measured O. The agreement between measured O and calculated O is excellent.

Figure 21 is a schematic diagram illustrating the possible occurrence of spinel associated with magmatic sulphides. The diagram is divided into two main regions: 'Disseminated ore' (top) and 'Massive ore' (bottom). The 'Disseminated ore' region contains 'Silicate melt' and 'Olivine'. The 'Massive ore' region contains 'Matte' and 'Spinel'. Arrows indicate the movement of spinel from the disseminated ore into the massive ore, where it can form bands of cumulate spinel (C) or be disseminated (B).

Fig. 21. Possible occurrence of spinel associated with magmatic sulphides. (A) Spinel at the massive ore–disseminated ore interface. (B) Spinel disseminated through the massive sulphide ore. C bands of cumulate spinel that have settled in the massive sulphide ore.

Cr in sulphide-rich matte as shown in run FeOSCr1 and by Brennan and Rose (2002). This hypothesis is in agreement with the observations of Frost and Groves (1989) who argue that “only limited O will have dissolved in the komatiite melt enclosed in massive sulphides, the excess being concentrated along the sulphide–silicate contacts”. A similar mechanism was proposed by Dowling et al. (2004) (see Fig. 22) to explain the presence of chromites on the komatiite–ore interface of the Silver Swan ore body (Black Swan area, Western Australia). Kambalda’s massive sulphides are Ni-rich, with Ni/Fe ~ 0.30 , and relatively Cu-poor with only ~ 1 wt% Cu (Cowden et al., 1986). Murck and

Fig. 22. (A) Komatiite melt inclusions in sulphide-rich matte with O dissolved. (B) As the matte crystallises mss, the molar fraction of O increases and reacts with the Cr diffusing out of the komatiite melt inclusions, forming spinel near the boundaries between the matte and the inclusions.

Campbell (1986), studied the behaviour of chromium in basic and ultrabasic melts, and showed that the fO_2 of a melt can be estimated from the composition of the coexisting spinel from the following relationship:

$$fO_2 \propto X_{Fe^{3+}} / (X_{Cr^{3+}} + X_{Al^{3+}} + X_{Fe^{3+}}) \quad (8)$$

where X represents the mole fraction of the element in question. Using the compositional data for the spinels associated with Kambalda sulphides of Frost and Groves (1989), $X_{Fe^{3+}} / (X_{Fe^{3+}} + X_{Al^{3+}} + X_{Cr^{3+}}) = 0.14$. The fO_2 value that corresponds to a given ratio depends also on temperature. In Fig. 5 of Murck and Campbell (1986) a $X_{Fe^{3+}} / (X_{Fe^{3+}} + X_{Al^{3+}} + X_{Cr^{3+}})$ of 0.14 corresponds to an fO_2 close to the QFM buffer at 1400 °C. From Eq. (7), a matte with a Ni/Fe of 0.3 (~20 wt% Ni) at QFM, a fS_2 of 0.1 bars and 1400 °C should have 7.3 wt% O in the matte. Under these circumstances, sulphide will crystallise before Cr-rich spinel, since the composition of the matte will fall on the O-poor side of the sulphide–spinel cotectic. However, X_O in the matte will increase until such point where the sulphide/spinel cotectic is reached and co-crystallisation of spinel, chalcopyrite and pentlandite will occur, which is consistent with the textural intergrowths characteristic of the sulphide-associated spinels in the Kambalda ores (Frost and Groves, 1989). Unlike Sudbury, the Kambalda matte lost the bulk of its O content to the overlying silicate melt, which is consistent with the observations of Heath et al. (2001) that the massive ore has negligible amounts of magnetite. The crystallisation of Cr-rich spinel near the ore–komatiite melt interface is taken to be evidence of that O loss.

6. CONCLUDING REMARKS

The solubility of O in sulphide-rich mattes can be quantified and parameterised as a function of fO_2 , fS_2 , temperature and melt composition, by a series of empirical fits to experimental data from this study and the literature. The empirical expressions described here, are of potential use to estimate the initial O content of natural Cu- and Ni-bearing sulphide-rich mattes under supra-liquidus conditions.

We found that in the case of Kambalda and Sudbury, the sulphide-rich matte likely lost much of its dissolved O through diffusion towards the overlying silicate melt. The diffusion of O, out of the sulphide-rich matte and into the silicate melt, may have led to the precipitation of magnetite and/or chromite near or on the boundaries between the matte and the silicate melt. We conclude that most massive sulphide-rich mattes represent open systems in relation to their O content. We have also found evidence for the presence of the FeSO stoichiometry, previously predicted by Kress (2000), as a main O-bearing species and a true structural constituent of a sulphide-rich matte.

ACKNOWLEDGMENTS

We thank Michael Shelley, William Hibberson, David Clark, Dean Scott, for their help throughout the experimental work. Ashley Norris for his assistance while using the CAMECA SX100 electron microprobe; Frank Brink for his help while using the JEOL 6400 SEM. This article benefited greatly from insightful comments and constructive criticism from Guilherme Mallmann, Reid Keays, Stephen J. Barnes, Jim Mungall and Tony Naldrett, and reviews by Edward Ripley, Pedro Jugo, Chusi Li and an anonymous reviewer.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2008.03.009](https://doi.org/10.1016/j.gca.2008.03.009).

REFERENCES

- Andrews D. R. A. and Brenan J. M. (2002) The solubility of ruthenium in sulfide liquid: implications for platinum group mineral stability and sulfide-melt/silicate-melt partitioning. *Chem. Geol.* **192**, 163–181.
- Ballhaus C. (1993) Redox states of lithospheric and asthenospheric upper mantle. *Contrib. Mineral. Petr.* **114**, 331–348.
- Blatov I. A., Burylev B. P., Tsemekhman L. S. H. and Litvinov S. L. (1997) Thermodynamics of the reaction of components of the Fe–S–O system in equilibrium with a CO–CO₂–SO₂ gas phase at 1300 °C. *Russian Metall.: Metally* **6**, 37–40.

- Bog S. and Rosenqvist T. (1958) Thermodynamics of metal sulfides. *Nor Tek-Naturvitensk* **12**, 1–20.
- Brenan J. and Rose L. A. (2002) Experimental constraints on the wetting of chromite by sulfide liquid. *Can. Mineral.* **40**, 1113–1126.
- Brenan J. M. and Caciagli N. C. (2000) Fe–Ni exchange between olivine and sulphide liquid: implications for oxygen barometry in sulphide-saturated magmas-contrasting compositions and phase relations in eruption pumice and Kilauea Iki lava lake. *Geochim. Cosmochim. Acta* **64**(2), 307–320.
- Campbell I. H., Naldrett A. J. and Barnes S. J. (1983) A model for the origin of the platinum rich sulfide horizons in the Bushveld and Stillwater complexes. *J. Petrol.* **24**(2), 133–165.
- Celmer R. (1988) *The Distribution of Minor Elements in Nickel Matte Smelting*. National Library of Canada.
- Chase M. W. (1998) *NIST-JANAF Thermodynamic Tables*. National Institute of Standards and Technology, Washington, DC, USA.
- Christie D. M., Carmichael I. S. E. and Langmuir C. H. (1986) Oxidation states of mid-ocean ridge basalt glasses. *Earth Planet. Sci. Lett.* **79**, 379–411.
- Cowden A., Donaldson M. J., Naldrett A. J. and Campbell I. H. (1986) Platinum-group elements and gold in the komatiite-hosted Fe–Ni–Cu sulfide deposits at Kambalda, Western Australia. *Econ. Geol.* **81**, 1226–1235.
- Darken L. S. and Gurry R. W. (1946) The system iron–oxygen. I: The wüstite field and related equilibria. *J. Am. Chem. Soc.* **67**, 1398–1412.
- Dowling S. E., Barnes S. J., Hill R. E. T. and Hicks J. D. (2004) Komatiites and nickel sulfide ores of the Black Swan area, Yilgarn Craton, Western Australia. 2: Geology and genesis of the orebodies. *Miner. Deposita* **39**(7), 707–728.
- Doyle C. D. and Naldrett A. J. (1987) Oxygen content of “sulfide” magma and its effect on the partitioning of nickel between coexisting olivine and molten ores. *Econ. Geol.* **82**, 208–211.
- Ewers W. E., Graham J., Hudson D. R. and Rolls J. M. (1976) Crystallization of chromite from nickel–iron sulphide melts. *Contrib. Mineral. Petr.* **54**(1), 61–64.
- Fleet M. E., Liu M. and Crockett J. H. (1999) Partitioning of trace amounts of highly siderophile elements in the Fe–Ni–S. *Geochim. Cosmochim. Acta* **63**(17), 2611–2622.
- Frost K. M. and Groves D. I. (1989) Magmatic contacts between immiscible sulfide and komatiite melts: implications for the genesis of Kambalda sulfide ores. *Econ. Geol.* **84**, 1697–1704.
- Gaetani G. A. and Grove T. L. (1999) Wetting of mantle olivine by sulfide melt: implications for Re/Os ratios in mantle peridotite and late-stage core formation. *Earth Planet. Sci. Lett.* **169**, 147–163.
- Grieve R. A. F. (1994) An impact model of the Sudbury structure. In *Proceedings of the Sudbury-Noril'sk Symposium*, pp. 119–132. Ontario Geological Survey Special 5, Ottawa.
- Heath C., Lahaye Y., Stone W. and Lambert D. (2001) Origin of variations in nickel tenor along the strike of the Edwards Lode nickel sulfide orebody, Kambalda, Western Australia. *Can. Mineral.* **39**, 655–671.
- Jana D. and Walker D. (1997) The influence of sulfur on partitioning of siderophile elements. *Geochim. Cosmochim. Acta* **61**(24), 5255–5277.
- Jorgensen F. R. A. and Moyle F. J. (1986) Gas diffusion during the thermal analysis of pyrite. *J. Therm. Anal. Calorim.* **31**(1), 145–156.
- Kaiser D. L. and Elliott J. F. (1986) Solubility of oxygen and sulfur in copper–iron mattes. *Metall. Trans. B* **17B**, 147–157.
- Keays R. R. and Lightfoot P. C. (2004) Formation of Ni–Cu–platinum group element sulfide mineralization in the Sudbury impact melt sheet. *Mineral. Petr.* **82**(3), 217–258.
- Kress V. (1997) Thermochemistry of sulfide liquids. I: The system O–S–Fe at 1 bar. *Contrib. Mineral. Petr.* **127**, 176–186.
- Kress V. (2000) Thermochemistry of sulfide liquids. II: Associated solution model for sulfide liquids in the system O–S–Fe. *Contrib. Mineral. Petr.* **139**, 316–325.
- Kress V. (2007) Thermochemistry of sulfide liquids. III: Ni-bearing liquids at 1 bar. *Contrib. Mineral. Petr.* **154**, 191–204.
- Larocque A. C. L., Stimac J. A., Keith J. D. and Humnicki M. A. E. (2000) Evidence for open-system behavior in immiscible Fe–S–O liquids in silicate magmas: implications for contributions of metals and sulfur to ore-forming fluids. *Can. Mineral.* **38**, 1233–1249.
- Lazar C., Walker D. and Walker R. J. (2004) Experimental partitioning of Tc, Mo, Ru, and Re between solid and liquid during crystallization in Fe–Ni–S. *Geochim. Cosmochim. Acta* **68**(3), 643–651.
- Li C. and Ripley E. M. (2006) Formation of Pt–Fe alloy by desulfurization of Pt–Pd sulfide in the J–M reef of the Stillwater complex, Montana. *Can. Mineral.* **44**, 895–903.
- Liang L. C. (1991) Study of oxygen peak shifts among some minerals using a tungsten–silicon multilayer pseudo-crystal. *X-Ray Spectrom.* **20**, 89–90.
- Liang Y., Richter F. M., Davis A. M. and Watson E. B. (1996) Diffusion in silicate melts. I: Self diffusion in CaO–Al₂O₃–SiO₂ at 1500 °C and 1 GPa. *Geochim. Cosmochim. Acta* **60**(22), 4353–4367.
- Magyarosi Z., Watkinson D. H. and Jones P. C. (2002) Mineralogy of Ni–Cu–platinum-group element sulfide ore in the 800 and 810 orebodies, Copper Cliff South Mine, and P–T–X conditions during the formation of platinum-group minerals. *Econ. Geol.* **97**, 1471–1486.
- Maier W. D. and Barnes S. J. (1996) Unusually high concentrations of magnetite at Caraíba and other Cu–sulfide deposits in the Curaçá valley, Bahia, Brazil. *Can. Mineral.* **34**, 717–731.
- McGuire A. V., Francis C. A. and Dyar M. D. (1992) Mineral standards for electron microprobe analysis of oxygen. *Am. Mineral.* **77**, 1087–1091.
- Mungall J. E. (2007) Crystallization of magmatic sulfides: an empirical model and application to Sudbury ores. *Geochim. Cosmochim. Acta* **71**(11), 2809–2819.
- Mungall J. E., Andrews D. R. A., Cabri L. J., Sylvester P. J. and Ubrett M. (2005) Partitioning of Cu, Ni, Au and platinum-group elements between monosulfide solid solution and sulfide melt under controlled oxygen and sulfur fugacities. *Geochim. Cosmochim. Acta* **69**(17), 4349–4360.
- Murck B. W. and Campbell I. H. (1986) The effects of temperature, oxygen fugacity and melt composition on the behavior of chromium in basic and ultrabasic melts. *Geochim. Cosmochim. Acta* **50**, 1871–1887.
- Nagamori M., Hatakeyama T. and Kameda M. (1970) Thermodynamics of Fe–S melts between 1100 and 1300 °C. *Trans. Jpn. Inst. Met.* **11**, 190–194.
- Nagamori M. and Kameda M. (1965) Equilibria between Fe–S–O system melts and CO–CO₂–SO₂ gas mixtures at 1200 °C. *Trans. Jpn. Inst. Met.* **6**, 21–30.
- Nagamori M. and Yazawa A. (2001) Thermodynamic observations of the molten FeS–FeO system and its vicinity at 1473 K. *Metal. Mater. Trans.* **32B**(5), 831–837.
- Naldrett A. J. (1969) A portion of the system Fe–S–O between 900 and 1080 °C. *J. Petrol.* **10**, 171–201.
- Naldrett A. J. (1989) Sulfide melts-crystallization temperatures, solubilities in silicate melts and Fe, Ni, and Cu partitioning between basaltic magmas and olivine, In *Ore deposition associated with magmas*, (eds. J.A. Whitney and A.J. Naldrett). Rev. Econ. Geol., New Mexico Bureau of Mines & Mineral Resources 4 (Chapter 2), pp. 5–21.

- Naldrett A. J., Singh J., Krstic S. and Li C. (2000) The mineralogy of the Voiseys Bay Ni–Cu–Co deposit, northern Labrador. *Econ. Geol.* **95**, 889–900.
- O'Neill H. S. C. and Mavrogenes J. A. (2002) The sulfide capacity and the sulfur content at sulfide saturation of silicate melts at 1400 °C and 1 bar. *J. Petrol.* **43**(6), 1049–1087.
- Rose L. and Brenan J. (2001) Wetting properties of Fe–Ni–Co–Cu–O–S melts against olivine: implications for sulfide melt mobility. *Econ. Geol.* **96**(1), 145–157.
- Shima H. and Naldrett A. J. (1975) Solubility of sulfur in an ultramafic melt and the relevance of the system Fe–S–O. *Econ. Geol.* **70**, 960–967.
- Somsiri C. and Gaskell D. R. (1995) The activities of sulfide and oxide components and the solubility of oxygen in copper–iron–sulfur–oxygen mattes at 1300 °C. *Metal. Mater. Trans. B* **26**(6), 1157–1164.
- Szentpéteri K., Watkinson D. H., Molnár F. and Jones P. C. (2002) Platinum-group elements–Co–Ni–Fe sulfarsenides and mineral paragenesis in Cu–Ni–platinum-group element deposits, Copper Cliff North Area, Sudbury, Canada. *Econ. Geol.* **97**, 1459–1470.
- Woolrich P., Cowden A. and Giorgetta N. E. (1981) The chemical and mineralogical variations in the nickel mineralization associated with the Kambalda dome. *Econ. Geol.* **76**, 1629–1644.
- Yoshiki-Gravelsins K. S. and Toguri J. M. (1993) Oxygen and sulfur solubilities in Ni–Fe–S–O melts. *Metal. Mater. Trans. B* **24B**, 847–853.
- Young R. A., Sakthivel A., Moss T. S. and Paiva-Santos C. O. (1995) DBWS-9411 an upgrade of the DBWS*.* programs for Rietveld refinement with PC and mainframe computers. *J. Appl. Cryst.* **28**, 366–367.

Associate editor: Edward M. Ripley