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Crystallization of magmatic sulfides: An empirical model and application to Sudbury ores

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Abstract

I present an empirical parameterization of low-pressure melting relations of monosulfide solid solution in the system Ni–Cu–Fe–S–O and use it to argue that sulfide ores at Sudbury are almost exclusively cumulate in origin. In the model the solid is considered to be composed of four components NiS, CuS, FeS and ·S, where ·S represents substitution of a vacancy for a cation. The liquid solution is considered to be a mixture of cations Ni, Fe, and Cu and anions S and O. The exchange of metals and sulfur between solid and melt is treated as a series of reactions of the form $M_l + S_l = MS_s$, where subscripts l and s denote liquid and solid, respectively, allowing the definition of an exchange coefficient $K_D = X_s^{MS}/(X_l^M \times X_l^S)$ where X denotes mole fraction. I have fitted equations of the form $\log K_D = a/T + bX_l S + c$ to the existing database for coexisting sulfide liquid–monosulfide solid solution for each of the liquid components Ni, Cu, and S. The fitted K_D expressions have been implemented in a Matlab program to estimate the compositions of coexisting solid and liquid sulfide phases in the system Ni–Cu–Fe–S–O, using the liquidus temperature approximation of Fleet and Pan (1994), and using a crude approximation to the liquidus surface of magnetite. Ni is found to be incompatible with mss over most of the range of conditions of crystallization of natural sulfide magmas, becoming compatible only at the lowest temperatures and highest Ni and Cu contents attained. Comparison with compositions of sulfide ores from Sudbury demonstrates that many ore compositions are distributed along mixing lines between primary mss and intermediate solid solution (iss) or between high pentlandite (heazlewoodite solid solution; hzss) and iss. The mss–iss trend can be modeled as a mixing line between mss and residual sulfide liquid or between mss and iss cumulates. In the former case, the Ni-rich composition of the mss must reflect continuous equilibration of solids and liquids during cooling to low temperatures close to the sulfide solidus. In the latter case, a significant mass of highly Ni- and Cu-enriched residual sulfide liquid must be interpreted to have left the mss–iss cumulates behind during a late-stage migration process at temperatures well below the solidus temperature of the enclosing silicate rocks. Subsequent crystallization of hzss–iss cumulates from Ni- and Cu-rich residual sulfide liquids produced the second trend between the compositions of pentlandite and chalcopyrite. The balance of evidence favors the hypothesis that most sulfide ores represent cumulate mixtures of iss and mss or of iss and hzss rather than residual Cu-rich sulfide liquids.

1. INTRODUCTION

Phase equilibria between melts and solids in the system Ni–Cu–Fe–S–O are of fundamental importance in controlling a variety of geochemical processes including the fractionation of platinum-group elements (PGE) during mantle melting (e.g., Lorand and Conquere, 1983; Bockrath et al., 2004; Mungall et al., 2006) and the genesis and evolution of magmatic sulfide ore deposits (e.g., Li and Naldrett, 1994; Barnes and Maier, 1999; Mungall et al., 2005). It is commonly observed that large deposits of magmatic sulfides like those at Sudbury and Noril'sk show strong compositional zoning. The most popular interpretation holds that sulfide rock composed of pyrrhotite (po) and pentlandite (pn) containing several wt% Ni and <3 wt% Cu represents a primary magmatic cumulate of

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monosulfide solid solution (mss) whereas sulfide rocks composed of pyrrhotite, pentlandite and chalcopyrite (cp), typically containing <3 wt% Ni but as much as 35 wt% Cu represent fractionated sulfide liquids residual to the removal of the mss cumulates. Veins of sulfide composed primarily of pentlandite, chalcopyrite and cubanite (cb) have been proposed to represent the solid equivalents of extremely fractionated sulfide melts (e.g., Naldrett et al., 1999). Magnetite is generally present in these assemblages as well.

A full understanding of the relevant phase equilibria must derive from a thermodynamic model based upon experimental measurements. Although extensive early experimental work in binary and ternary subsystems of the Ni–Cu–Fe–S–O system established the basic topology of most of the important phase boundaries (Craig and Kullerud, 1969, and references therein; Naldrett, 1969), the complexity of the five-component system complicates simple graphical approaches to understanding the phase equilibria, and recent attention has been focussed on the measurement of coexisting phase compositions in quenching experiments (Fleet et al., 1993; Fleet and Pan, 1994; Ballhaus et al., 2001; Li et al., 1996; Ebel and Naldrett, 1996, 1997; Mungall et al., 2005; Kosyakov and Sinyakova, 2005). Several other studies have been conducted in various systems including some of the components Ni, Cu, Fe, S and O in addition to other major element components, especially the PGE (Fleet and Stone, 1991; Barnes et al., 2001; Sinyakova et al., 1996; Sugaki and Kitakaze, 1998; Makovicky, 2002; Peregoedova and Ohnenstetter, 2002). Attempts to apply thermodynamic solution models have been limited to superliquidus conditions in the system Fe–S–O (Kress, 1997). Although empirical parameterizations of some of the published data set have been published (Fleet and Pan, 1994; Li and Naldrett, 1994; Ballhaus et al., 2001) none of these has addressed the sum of currently available information. Furthermore, available parameterizations are difficult to apply to any conditions outside the range of the experimental data used to calibrate them. Ballhaus et al. (2001) performed their modeling using Nernst partition coefficients (i.e., weight fraction of the element in mss divided by its weight fraction in sulfide liquid) instead of exchange coefficients, an approach that neglects the non-Henrian behaviour of Ni, Cu and Fe, all of which are major elements in sulfide magmas. The parameterization of Fleet and Pan (1994) was based upon least squares fitting of arbitarily defined polynomial expressions to the data without thermodynamic foundations, making them numerically unstable outside their range of calibration.

In this contribution I present some simple thermodynamic expressions to describe the partitioning of metals and sulfur between sulfide melt and monosulfide solid solution, which I then use as the basis of a fairly robust empirical parameterization that I have implemented in a Matlab program to calculate compositions of coexisting liquid and solid sulfides. The model is used to demonstrate that few, if any, of the Cu-rich sulfide rocks found at major sulfide ore deposits like those of the Sudbury igneous complex can represent quenched fractionated sulfide liquids as is commonly proposed.

2. PARAMETERIZATION

2.1. Components of solid and liquid sulfide solutions

Whether they form during partial melting of the mantle or in the crust, natural sulfide magmas typically coexist with silicate melts at temperatures ranging from 850 to 1600 °C and at oxygen fugacities near to that at which the buffering assemblage fayalite, magnetite and quartz exists (i.e., FMQ; e.g., Mavrogenes and O'Neill, 1999). Under these conditions, a sulfide liquid has a cation to anion ratio close to unity (Naldrett, 1969). Depending on oxygen fugacity (fO_2) and sulfur fugacity (fS_2), the liquidus phase might be alloy (reduced), wüstite, magnetite (oxidized) or monosulfide solid solution (mss; high fO_2 and fS_2). Most natural magmas are sufficiently oxidized that only one or both of magnetite and mss will form. Since magnetite in sulfide magmas is generally essentially pure Fe_3O_4, I assume henceforth that it has this simple stoichiometry and will concern myself only with the composition of mss and sulfide liquid.

There is no significant amount of oxygen in mss, and the amount of oxygen in magnetite is fixed by stoichiometry. There are few data available in the literature describing the compositions of sulfide liquids containing O, and for lack of information with which to constrain more complex models, I assume ideal mixing of O and S on the anion sublattice of the sulfide melt, and therefore assume that the behaviour of the other elements in the melt will not depend on the concentration of oxygen. For modeling purposes, the amount of O in this combined component can be tracked separately (assuming that O does not enter mss) and used to establish a saturation surface for magnetite if a liquid line of descent is to be calculated for the system.

Monosulfide solid solution usually has an excess of sulfur relative to its metal content (e.g., Toulmin and Barton, 1964), requiring the consideration of four components to fully describe its composition in the system Ni–Cu–Fe–S–(O); NiS_s, CuS_s, FeS_s, and a component I will call $^{\cdot}S_s$ (throughout this article the subscripts l and s denote liquid and solid, respectively). The $^{\cdot}S_s$ component comprises sulfur combined with a vacancy substitution for the cation. Recalculation of a mss composition, given in wt%, to these new components requires calculation of mole fractions of Ni, Cu, Fe and S, followed by normalization to 0.5 S to arrive at a nominal monosulfide composition containing 50% S and 50% [cations + vacancies]. The normalization lowers the nominal molar proportion of each of the other components Ni, Cu and Fe; the difference between the sum of these normalized components and 0.5 is the molar proportion of the vacancy. Mole fractions of the new components are thus simply defined:

$$X_s^{S} = X_s^{Cu} + X_s^{Ni} + X_s^{Fe} + X_s^{\cdot} = 0.5 \quad (1)$$

$$X_s^{CuS} + X_s^{NiS} + X_s^{\cdot S} + X_s^{FeS} = 1 \quad (2)$$

$$C_s^{S} = \frac{1}{1 + X_s^{CuS} + X_s^{NiS} + X_s^{FeS}} = \frac{1}{2 - X_s^{\cdot S}} \quad (3)$$

$$C_s^{Cu} = \frac{X_s^{Cu}}{X_s^S + X_s^{Cu} + X_s^{Ni} + X_s^{Fe}} = \frac{X_s^{CuS}}{1 + X_s^{CuS} + X_s^{NiS} + X_s^{FeS}} \quad (4)$$

$$C_s^{Ni} = \frac{X_s^{Ni}}{X_s^S + X_s^{Cu} + X_s^{Ni} + X_s^{Fe}} = \frac{X_s^{NiS}}{1 + X_s^{CuS} + X_s^{NiS} + X_s^{FeS}} \quad (5)$$

$$X_s^{\cdot} = X_s^S - (X_s^{Cu} + X_s^{Ni} + X_s^{Fe}) = 0.5 - (X_s^{Cu} + X_s^{Ni} + X_s^{Fe}) \quad (6)$$

where X_s^S is the mole fraction and C_s^S is the weight fraction of the superscripted component in the subscripted phase.

X_s^{CuS} = mole fraction of the CuS component in mss :

$$X_s^{CuS} = \frac{X_s^{Cu}}{X_s^{Cu} + X_s^{Ni} + X_s^{Fe} + X_s^{\cdot}} = \frac{X_s^{Cu}}{X_s^S} = 2X_s^{Cu} \quad (7)$$

X_s^{NiS} = mole fraction of the NiS component in mss, similarly :

$$X_s^{NiS} = \frac{X_s^{Ni}}{X_s^S} = 2X_s^{Ni} \quad (8)$$

X_s^{FeS} = mole fraction of the FeS component in mss, similarly :

$$X_s^{FeS} = \frac{X_s^{Fe}}{X_s^S} = 2X_s^{Fe} \quad (9)$$

$X_s^{\cdot S}$ = mole fraction of the ·S component in mss,

$$X_s^{\cdot S} = \frac{X_s^{\cdot}}{X_s^S} = \frac{X_s^S - (X_s^{Cu} + X_s^{Ni} + X_s^{Fe})}{X_s^S} = 1 - 2(X_s^{Cu} + X_s^{Ni} + X_s^{Fe}) \quad (10)$$

The process of interest here is the exchange of matter between the sulfide melt and mss. If heterogeneous reactions are written, such as

$$Cu_l + S_l = CuS_s \qquad K^{Cu} \quad (11)$$

then the equilibrium constant depends on the activities of the components of both phases as follows:

$$K^{Cu} = \frac{a_s^{CuS}}{a_l^{Cu} \cdot a_l^S} \quad (12)$$

Assuming that activity coefficients are constants over moderate ranges in composition, I combine them with K^{Cu} to write an exchange coefficient defined in terms of measureable mole fractions of the components

$$K_D^{Cu} = \frac{X_s^{CuS}}{X_l^{Cu} X_l^S} = \frac{2X_s^{Cu}}{X_l^{Cu} X_l^S} \quad (13)$$

and similarly I write for Ni;

$$Ni_l^{+2} + S_l^{-2} = NiS_s \qquad K^{Ni} \quad (14)$$

$$K^{Ni} = \frac{a_s^{NiS}}{a_l^{Ni^{+2}} \cdot a_l^{S^{-2}}} \quad (15)$$

$$K_D^{Ni} = \frac{X_s^{NiS}}{X_l^{Ni} X_l^S} = \frac{2X_s^{Ni}}{X_l^{Ni} X_l^S} \quad (16)$$

and for S;

$$S_l = {}^{\cdot}S_s \qquad K^S \quad (17)$$

$$K_D^S = \frac{X_s^{\cdot S}}{X_l^S} = \frac{1 - (X_s^{CuS} + X_s^{NiS} + X_s^{FeS})}{X_l^S} = \frac{1 - 2(X_s^{Cu} + X_s^{Ni} + X_s^{Fe})}{X_l^S}. \quad (18)$$

If all K_Ds could be described empirically as a function of only X_l^S at a given T, then $X_s^{\cdot S}$ could be given as a function of X_l^S, but the dependence on the relative proportions of the other components cannot be escaped. So the mass balance using F and the molar concentrations C_s^S, X_l^S cannot be calculated, i.e.,

$$FC_s^S + (1 - F)X_l^S = C_o^S \quad (19)$$

is unknown.

The ideal approach to an empirical parameterization would be to relate K_D to the fO_2 and fS_2 at which each experiment was conducted, permitting the establishment of a true thermodynamic solution model for both solid and liquid phases. Unfortunately, few experiments have been conducted at known fO_2 or fS_2, and the only parameters that present themselves as major controls on K_D are the temperature T and the mole fraction of sulfur in either the sulfide melt or the mss (c.f. Barnes and Maier, 1999). Since the aim of this study is to predict the compositions of solids that would precipitate from a sulfide liquid, and since sulfide phases other than mss are likely to be stable at the lowest temperatures and most metal-rich compositions in a a given system, I have chosen to consider the composition of the solids as being dependent on the liquid composition, rather than letting the liquid composition depend on the solid as was done by Barnes and Maier (1999).

If all relevant K_Ds are known, it is trivial to calculate the instantaneous solid in equilibrium with a known liquid composition at the liquidus temperature, since all K_Ds depend on X_l^S, which is known, and X_s^{FeS} can be calculated by difference. However, given only the bulk composition and a mass fraction F of mss, neither the liquid composition nor the liquidus temperature are known. There is, however, a closure condition on the composition of the liquid and solid phases;

$$X_s^{CuS} + X_s^{NiS} + X_s^{\cdot S} + X_s^{FeS} = 1 \quad (20)$$

$$X_l^{Cu} + X_l^{Ni} + X_l^{Fe} + X_l^S + X_l^O = 1 \quad (21)$$

and conservation of mass between liquid and solid phases:

$$\frac{F}{1 + X_s^{CuS} + X_s^{NiS} + X_S^{FeS}} + (1 - F)X_l^S = X_o^S \quad (22)$$

$$\frac{FX_s^{CuS}}{1 + X_s^{CuS} + X_s^{NiS} + X_s^{FeS}} + (1 - F)X_l^{Cu} = X_o^{Cu} \quad (23)$$

$$\frac{FX_s^{NiS}}{1 + X_s^{CuS} + X_s^{NiS} + X_s^{FeS}} + (1 - F)X_l^{Ni} = X_o^{Ni} \quad (24)$$

Given four unknown compositional parameters in each phase, an unknown liquidus temperature T_{liq}, and a stated mass fraction F of mss in the bulk system, there are nine

unknowns but only eight equations. To solve this system one more equation is required, giving the liquidus temperature as a function of melt composition.

2.2. Calibration of the model

Fleet and Pan (1994) have presented a parameterization of the liquidus temperature of sulfide melt as a function of melt composition. Their model is a polynomial fitted by least squares methods to their own extensive data set; it works nearly as well on the entire published database (Fig. 1). Although there are some published experiments for which the calculated temperature differs from the measured temperature by as much as 50 °C, the empirical fits for K_D (below) do not show very strong dependences on temperature so the resulting errors in K_D will not be very severe.

I have taken all the available data for the compositions of coexisting sulfide melt and mss at known temperatures and used them to establish empirical parameterizations of the equations above. The database excludes any experiments in which other elements such as the PGE were present as major components, because it is unclear how such compositions should be projected from these more complex systems into the nominally four-component system considered here. Simply recalculating compositions to 100% after subtraction of the additional metals would grossly overestimate the amount of S in the remaining components. Assuming that all of the PGE form monosulfide species in both melt and mss and recasting compositions solely in terms of the base metal sulfides would artificially increase the mole fractions of the base metals and therefore interfere with the determination of K_Ds, especially when the PGE in question are either highly compatible or highly incompatible, since the apparent relative change in concentration of the base metals in one phase would be much greater than in the other.

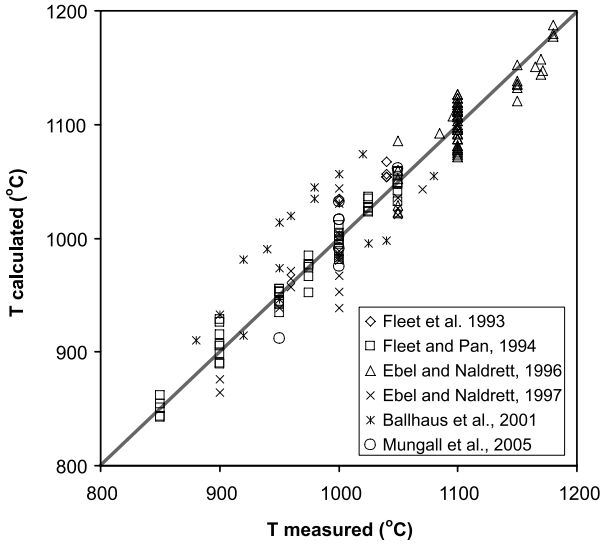

Fig. 1. Comparison of temperatures of equilibration of mss and sulfide liquid as measured and predicted using the model of Fleet and Pan (1994).

I expect the equilibrium constant K for each exchange reaction to depend on temperature according to the following relation:

$$\Delta_R G^o = -RT\ln K = \Delta_R H^o - T\Delta_R S^o, \tag{25}$$

where $\Delta_R G^o$ is the standard state free energy of reaction and R is the ideal gas constant. From Eq. (25) can it can be seen that

$$\ln K = \frac{-\Delta_R H^o}{RT} + \frac{\Delta_R S^o}{R} \tag{26}$$

Calorimetric data are not available for either the solid or the liquid phase, so I am forced to rely upon the common simplifying assumption that the change in heat capacity $\Delta_R C_p$ for the exchange reactions (11), (14), and (17) is zero in each case (i.e., $\Delta_R H$ and $\Delta_R S$ are both constant with respect to T; see for example Anderson, 2005, p. 252) allowing me to combine $\Delta_R G$ and R into fit parameters a, b and c, allowing for a dependance of $\Delta_R G$ on melt composition and temperature as follows:

$$\log K_D^{Cu} = \frac{a^{Cu}}{T} + b^{Cu}X_l^{S^*} + c^{Cu} = \log\frac{X_s^{CuS}}{X_l^{Cu}X_l^{S^*}} = \log X_s^{CuS} - \log X_l^{Cu} - \log X_l^{S^*} \tag{27}$$

$$\log K_D^{Ni} = \frac{a^{Ni}}{T} + b^{Ni}X_l^{S^*} + c^{Ni} = \log\frac{X_s^{NiS}}{X_l^{Ni}X_l^{S^*}} \log X_s^{NiS} - \log X_l^{Ni} - \log X_l^{S^*} \tag{28}$$

$$\log K_D^{S} = \frac{a^{S}}{T} + b^{S}X_l^{S^*} + c^{S} = \log\frac{X_s^{S}}{X_l^{S^*}} = \log X_s^{S} - \log X_l^{S^*} \tag{29}$$

Because the reliability of the data used in this fitting process is difficult to assess quantitatively, and because there are very few data at some temperatures, I did not see any particular benefit to a least squares estimate of goodness of fit, electing instead to fit the curves subjectively in an iterative process. There is no more rigorous way to estimate goodness of fit because the quality of data from each study will be different, and the number of data points from each study is not necessarily in proportion to their aggregate value. The fit parameters a, b and c for each component are listed in Table 1; some comparisons of the fits to the experimental data are presented in Figs. 2 and 3. The assumption of constant $\Delta_R H$ and $\Delta_R S$ is justified by the close approach of the data to a linear dependence on reciprocal temperature,

Table 1
Fit parameters for exchange coefficients $\log K_D = a/T + bX_l^S + c$ (T in Kelvin)

Element	a	b	c
Ni	4500	4.2	−5.1
Cu	−600	2.5	−0.85
S	3500	12	−9.5

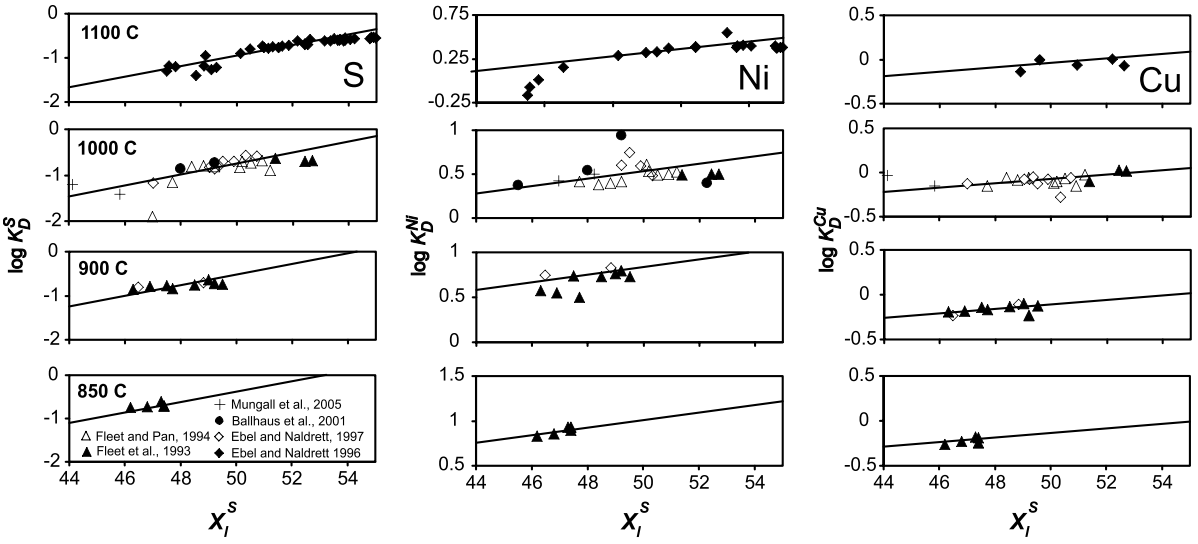

Fig. 2. Experimentally measured values of K_D for S, Ni and Cu at four temperatures. The solid black lines show the curves calculated using the fit parameters in Table 1. Symbols are explained in the bottom left panel.

and although a full solution model for both phases would evidently be preferable the present appproach gives some assurance of a robust empirical fit to the data.

3. APPLICATION

3.1. Computer program Sulfide.m

I have written a short Matlab routine called Sulfide.m (available as electronic annex EA-1) to implement the expressions above with the liquidus temperature model of Fleet and Pan (1994) in order to estimate the temperature and compositions of coexisting mss and sulfide liquid at equilibrium given a bulk composition and a mass fraction of solid. The routine works by making a first guess at the liquid composition and using this to find the liquidus temperature and then the composition of the mss that would result. The bulk composition of the model system is then calculated from the mass fraction of mss as given and the compositions of the phases as calculated. This model bulk composition will differ from the given bulk composition. The sign and magnitude of the difference between given and calculated mole proportions of each component are used to adjust the proposed liquid composition, and the calculation is repeated until the calculated bulk composition converges with the given bulk composition. The program is fairly robust until temperatures below about 850 °C are attained, perhaps because the liquidus temperature calibration of Fleet and Pan was restricted to temperatures between 850 and 1100 °C, and also because the liquid would probably be metastable with respect to iss (Fleet and Pan, 1994), heazlewoodite solid solution (hzss; Sugaki and Kitakaze, 1998; Kosyakov and Sinyakova, 2005) or some other phase at temperatures not far below this limit. Use of the program at temperatures outside the range of temperatures between 850 and 1100 °C should be avoided.

The program Sulfide.m also incorporates parameterizations for the Nernst partition coefficients for trace platinum-group elements and Au between mss and sulfide liquid that were presented by Mungall (2005). These parameterizations are given below; note that they do not include the effects of temperature, due to the paucity of experimental data and the apparent absence of any discernable temperature dependance:

$$\log(D_{Au}) = 0.22X_l^S - 2.2505 \quad (30)$$

$$\log(D_{Ir}) = 0.38X_l^S + 0.5434 \quad (31)$$

$$\log(D_{Ru}) = -5.79X_l^S + 3.6848 \quad (32)$$

$$\log(D_{Rh}) = 1.08X_l^S - 0.0383 \quad (33)$$

$$\log(D_{Pt}) = 10.59X_l^S - 6.222 \quad (34)$$

$$\log(D_{Pd}) = 5.69X_l^S - 3.679 \quad (35)$$

The choice of a saturation surface for magnetite is problematic and can only be approximated crudely. Fig. 4 illustrates the dependence of the O content of magnetite-saturated sulfide melts (Naldrett, 1969; Kaiser and Elliot, 1986; Mungall et al., 2005) on the weight ratio Fe/(Fe + Cu + Ni). The experiments of Naldrett (1969) constitute the Ni- and Cu-free endmember and are fully consistent with the data of Kaiser and Elliot (1986) for magnetite-saturated Cu–Fe–S–O liquids. Cu evidently suppresses the solubility of O in multicomponent sulfide melts. The O contents of Ni- and Cu-rich sulfide melts at the FMQ oxygen buffer but not physically in contact with magnetite (Mungall et al., 2005) fall far below the curve for reasons that are unclear. One possibility is that the melts lost O during quench of the experiments, leading to erroneously low measured O contents. This is unlikely in view of the fact that Ni- and Cu-free sulfide melts that formed in contact with wüstite within the solid oxygen buffer assemblage in two similar experiments retained far higher O contents than their Ni- and Cu-rich counterparts during exactly the same quenching process within the same silica tubes. The results

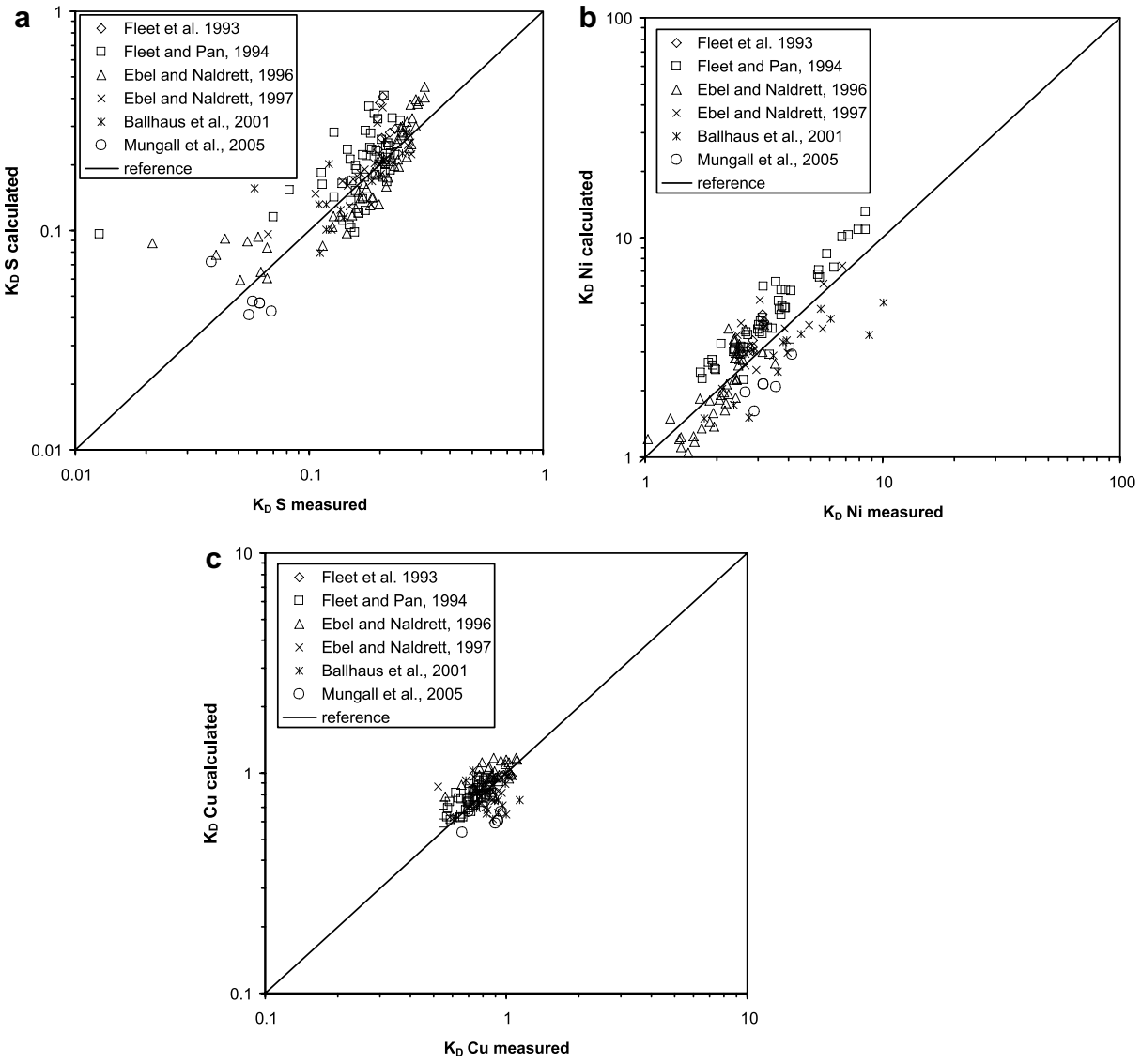

Fig. 3. (a) Comparison of all measured and predicted values of exchange coefficients K_D^S. (b) Comparison of all measured and predicted values of exchange coefficients K_D^{Ni}. (c) Comparison of all measured and predicted values of exchange coefficients K_D^{Cu}.

appear to indicate that Ni decreases the capacity of a sulfide melt to dissolve O at a given oxygen fugacity much more effectively than does Cu. In the model used here, I have chosen an arbitrary limit of 4 mole % (i.e., about 1.5 wt% O) for the solubility of O in sulfide melt containing Ni concentrations typical of magmatic sulfides because it is hard to justify any more detailed treatment of the problem. Since the program works by specifying F initially, and since O is quantitatively excluded from mss, it is straightforward to determine the amount of O in excess of magnetite solubility at a given F, remove a sufficient amount of magnetite to return O concentration to 4 mole %, and to remove the corresponding amount of Fe required to form the magnetite before beginning the rest of the calculation.

The melt composition and temperature at which iss will begin to crystallize is constrained by so few experimental data points that it cannot be predicted in arbitrarily defined melt compositions with any confidence. Other workers (e.g., Ballhaus et al., 2001) have proposed that iss might become a liquidus phase when the liquid composition had itself reached a composition near to the iss composition, as demonstrated by Fleet and Pan (1994) who were able to equilibrate mss, iss, and sulfide melt at a temperature of 850 °C (compositions shown in Fig. 5). Kosyakov and Sinyakova (2005) described the compositions of heazlewoodite solid solution (hzss) formed at equilibrium with mss from sulfide melt containing 30–40 mole % Ni at temperatures below the mss–hzss pseudoperitectic at 865 °C (Sugaki and Kitakaze, 1998), but again the data are too sparse to permit an empirical parameterization.

3.2. Model results

In Fig. 5 I show the results of several runs of the program Sulfide.m, each starting from a different initial

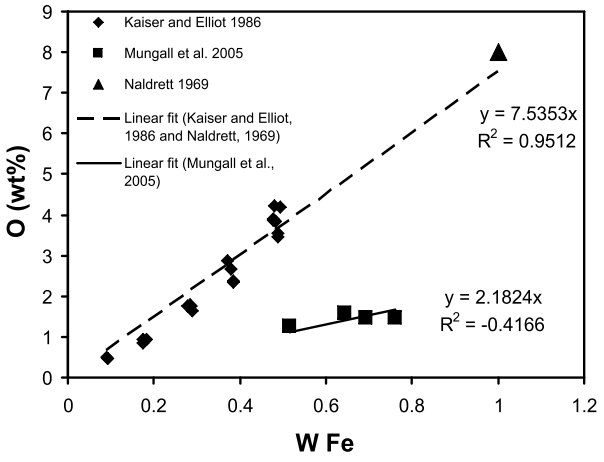

Fig. 4. Oxygen content of magnetite-saturated sulfide melts. W Fe is defined by Kaiser and Elliot (1986) as Fe/(Fe + Cu) in wt%.

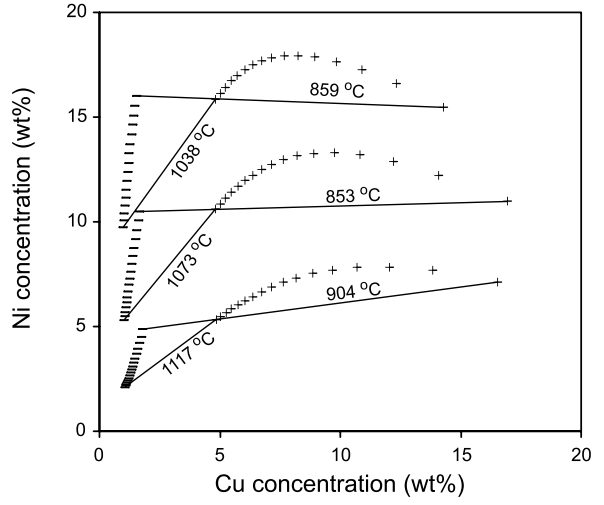

Fig. 5. Compositions of mss and sulfide liquid during equilibrium crystallization of three different starting compositions, calculated using the program Sulfide.m. Liquid and solid compositions are represented by crosses and horizontal lines, respectively. Each symbol represents a 5% increase in the solid fraction F. The final liquid is at $F = 0.75$ (top) and $F = 0.80$ (two lower trends). Tie-lines connect coexisting liquid and mss pairs, and are labeled with the temperature of equilibration.

sulfide melt composition and showing the compositions of coexisting mss and sulfide melt at a succession of temperatures in terms of Ni and Cu concentrations. The temperatures at which selected mss–melt pairs coexist are indicated. The lines with highest concentrations shown indicate the distribution of Ni and Cu between extremely metal-rich liquid and mss, representing a system richer in Ni and Cu than typical primary sulfide magmas. Under these circumstances, Ni shows incompatible behaviour at the onset of mss crystallization and only begins to drop at the lowest temperatures in an equilibrium crystallization scenario as shown. The set of data in the middle show that with initial Ni and Cu concentrations well in excess of 10% and 5%, respectively, Ni remains incompatible with mss throughout the cooling process. The lowest set of data shows the distribution of Cu and Ni expected in a sulfide magma with initial composition similar to typical natural sulfide ores, at about 5% each of Ni and Cu. In this case, Ni initially shows incompatible behaviour, and it does not begin to enter mss in appreciable concentrations until the temperature has dropped below the range over which the model is calibrated; iss or hzss should be expected to appear on the liquidus before significant depletion of Ni could occur in the liquid due to mss fractionation alone.

The model results are in full agreement with published experimental data, in which the partition coefficient for Ni is seen to be >1 in systems rich in Ni and Cu but generally <1 in those systems with Ni and Cu contents similar to natural magmas. Many attempts with the model have shown that it is in fact impossible to propose a starting composition with or without oxygen, at any S content, for which Ni shows compatible behaviour in mss at any temperature above 850 °C unless one begins with an uncommonly Ni- and Cu-rich sulfide melt.

3.3. Comparison to natural sulfide compositions

In Fig. 6 I show the compositions of mineralized samples from several deposits in the McCreedy–Strathcona–Onaping, Lindsley, and Victor Deep-Nickel Rim deposit areas in the Sudbury basin (A.J. Naldrett, personal communication 2000; Naldrett et al., 1999: cf. Ballhaus et al., 2001; Mungall et al., 2005), recalculated to 100% sulfides using a sulfide norm calculation written in Matlab (available as electronic annex 2). The procedure used to recalculate compositions employs S, Cu, and Ni concentrations as follows. The data are recast into moles of each element per 100 grams of sample, and the amounts of S required to balance Cu and Ni in endmember sulfide minerals (millerite NiS, pentlandite $Ni_{4.5}Fe_{4.5}S_8$, bornite Cu_5FeS_4, chalcopyrite $CuFeS_2$) are calculated for each sample. If the amount of S required to form pentlandite and chalcopyrite exceeds the amount of S in the sample, then the amount of S required to form bornite and pentlandite is calculated. If the amount of S that would be required to form bornite and pentlandite exceeds the amount of S present, then all Cu is assumed to be incorporated in bornite, and the Ni is apportioned between millerite and pentlandite so as to consume all the S; otherwise, all Ni is assigned to pentlandite and Cu is apportioned between bornite and chalcopyrite so as to consume all S. If there is S left over after formation of the Ni and Cu minerals, it is used to make pyrrhotite with the composition FeS. Once the number of moles of each mineral have been calculated, their equivalent masses are determined and a sulfide norm is found by summing the masses of the sulfide minerals and normalizing to 100% sulfide. The factor used to normalize each mineral proportion to the 100% sum is then used to multiply each element concentration, including trace elements like the PGE, to the nominal concentrations they would have if the sulfide portion of the rock could be considered

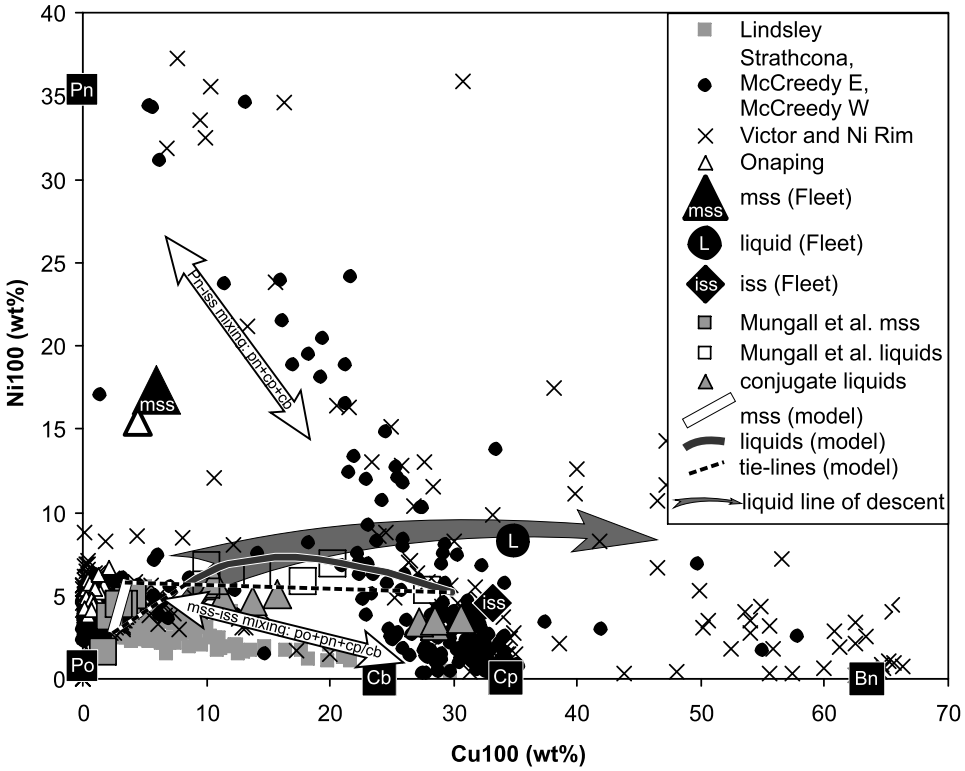

Fig. 6. Ni and Cu contents of model sulfide liquids and mss compared to data from the Sudbury Igneous Complex. Compositions of 100% sulfides were calculated using the Matlab routines described in the text. The compositions of common sulfide minerals pyrrhotite (po), pentlandite (pn), chalcopyrite (cp), cubanite (cb), and bornite (bn) are shown. The compositions of sulfide melt and mss reported by Mungall et al. (2005) are shown; the model results for these phases starting from the same composition are shown for comparison. Conjugate immiscible sulfide melts reported by Ballhaus et al. (2001) are also shown. The two solid curves show the compositions of mss and liquid calculated for a system whose composition matches the experimental liquid with the lowest Cu content shown. The open and solid triangles labeled 'mss' show the model and measured compositions of mss in equilibrium with iss and the experimental liquid 'L' (Fleet and Pan, 1994). White arrows illustrate the ranges of compositions attainable by cumulate mixtures of mss, iss, and pn, with the resulting low-temperature mineral assemblages indicated.

separatedly from the gangue silicates and magnetite. A copy of the Matlab routine SulfideNorm.m used to calculate the sulfide norm is available on the online Supplementary data or from the author. Also shown in Fig. 6 are the compositions of mss that was equilibrated with sulfide melt at geologically reasonable fO_2 and fS_2 (Mungall et al., 2005), iss from a single experiment by Fleet and Pan (1994), and the compositions of chalcopyrite, pentlandite and pyrrhotite from magmatic sulfide ores of the Kelly Lake deposit at Sudbury that have reached chemical equilibrium at temperatures well below magmatic temperatures (Huminicki et al., 2005). The point for cubanite is taken from our recent unpublished data.

The procedure of estimating Cu and Ni contents with a sulfide norm calculation can be criticized for forcing estimated compositions to show a low variance imposed by the normalization calculation itself. Beswick (2002) avoided this problem by plotting compositional data with metal/sulfur ratios. It should therefore be noted that the data displayed here in Figs. 5 and 6 appear essentially identical in plots of Ni/S versus Cu/S, which cannot be affected by assumptions of modal mineralogy. This is because most rock-forming sulfide minerals in magmatic systems are essentially monosulfides of transition metals with similar atomic weights. Any inferences drawn from the present choice of diagram are equally well supported by the ratio plots, but the sulfide norm plots are preferable due to their familiarity.

The compositions of all other sulfide deposits from the Sudbury basin follow the same trends with minor differences, but are not shown because the excessive amount of data obscures the main trends. The recently discovered low-sulfide variant of PGE deposit (e.g., Farrow et al., 2005) are not displayed in this diagram. It is debatable whether all of the disseminated, low-sulfide and extremely PGE-rich samples in this suite are magmatic in origin, despite their obvious association with a primarily magmatic system.

The data shown in Fig. 6 are dominated by a trend from values near to the composition of magmatic mss (intermediate to low-temperature pyrrhotite and pentlandite) to the composition of iss. This is consistent with the observation that such ores are almost invariably composed of chalcopyrite and an assemblage of pyrrhotite and pentlandite; the norms of these samples contain only chalcopyrite, pentlandite and pyrrhotite. Another trend falls along the join

between pentlandite and chalcopyrite. A relatively small subset of the data, which comprises those vein samples found to contain some combination of bornite or millerite with the other sulfide phases, scatters to higher values of Ni above the main mss–iss trend.

The compositions of sulfide melts and mss cumulates as calculated using the program Sulfide.m for a bulk composition initially containing $X_l^S = 0.492$ (i.e, 35.8 wt% S) and no oxygen are shown in Fig. 6, superimposed on the data for natural ores. The composition chosen corresponds to the liquid in experiment MSS8 of Mungall et al. (2005), without oxygen (O has been replaced by an equivalent number of moles of S). Incorporation of moderate O concentrations in the model were not found to affect the results notably in the Ni–Cu diagram, but to avoid criticism of the model relating to the inclusion of O and uncertainty over the magnetite saturation surface I have chosen to focus on modeling of the O-free system. The liquid trend line starts at the composition of the bulk system at $F = 0$, and extends to $F = 0.4$. Tie-lines connect the initial and final liquids to the mss compositions with which they would coexist. The initial liquidus temperature is 1083 °C, and at $F = 0.4$ the temperature is 835 °C.

It should be noted that the liquid trend shown is an equilibrium crystallization trend—the compositions of liquids resulting from fractional crystallization of mss cumulates would trend towards higher Ni concentrations than the model trend, following approximately along the grey arrow in the back ground (labeled in the legend as 'liquid line of descent').

For comparison with the experimental determination of mss composition that coexisted with iss and Cu-rich liquid (Fig. 6; data from Fleet and Pan, 1994), the composition of mss calculated to be in equilibrium with the experimental liquid is shown in Fig. 6 with the small open triangle immediately below the solid triangle labeled 'mss'. The correspondance is quite close (model T was 861 °C as compared with 850 °C in the actual experiment), and confirms that the model can reproduce experimentally observed compatible behaviour for Ni.

The model calculations presented in Figs. 5 and 6 are entirely consistent with the sum of available experimental data for mss–sulfide liquid equilibrium, and demonstrate that the Ni and Cu contents of the Cu-rich and Ni-poor samples at the right hand extreme of the main trend near the cp composition can only be interpreted to represent quenched sulfide liquid compositions if one pushes the model to extremely low temperatures of equilibration below the probable temperature at which iss and pn or hzss begin to crystallize. Although individual deposits show trends from slightly different Ni contents at the low-Cu end, most of them share the tendency to cluster tightly around the mss–iss control line. The more Cu-rich end of the mss–iss trend has commonly been interpreted to represent the compositions of fractionated sulfide liquids (Li and Naldrett, 1994; Naldrett et al., 1999; Ballhaus et al., 2001). In a recent paper (Mungall et al., 2005) we argued that if these compositions do indeed represent liquids, the sum of major and trace element data would require that these liquids remained in equilibrium with the mss cumulates to a very low temperature. The present study can be seen as a test of that hypothesis, and the present conclusion is that the compatible behaviour required for Ni to satisfy these relations cannot be achieved because Ni remains incompatible in mss to low temperatures unless the system contains far more Ni than the Sudbury ores. There are no published experimental mss–melt pairs in which the liquid has such low Ni contents whilst remaining in equilibrium with Ni-rich mss, and the model reflects this. Furthermore, it would seem to be a remarkable coincidence that in no case did the main liquid line of descent deviate from the mixing line between the two common liquidus phases mss and iss, if indeed the Cu-rich compositions along this trend do represent liquids in equilibrium with mss.

An alternate explanation for the existence of the mss–iss trend is that all of the samples along this trend are cumulates, comprising mixtures of igneous mss and iss that were deposited from liquids whose compositions were considerably more Ni-rich. In this interpretation the liquid was efficiently removed from the cumulates late in the evolution of the system, to leave solid mixtures of mss and iss lacking any great amount of trapped liquid. In this case, once cooling was complete, most of the mass of the sulfide magma system would reside in cumulate minerals lying along the mss–iss control line. The residual sulfide liquid may thus be represented by the Ni-rich veins and similar segregations with compositions scattered through the field between pentlandite, bornite, chalcopyrite and mss as observed, especially for samples from the McCreedy, Strathcona, Victor and Ni Rim deposit areas. As shown in Fig. 5, various starting compositions would lead to the formation of fractionated liquids highly enriched in both Ni and Cu over a wide range of possible compositions.

After the appearance of iss on the liquidus of the sulfide magma, the compositional path followed by the residual liquid would move in some direction away from both mss and iss in Fig. 6. It was suggested by Naldrett et al. (1999) that this residual liquid trend might follow the trend of data evident in Fig. 6 extending from iss toward the composition of pentlandite (Pn). I would suggest that, in light of the evidence for a cumulate nature for most of the samples clustered around the mss–iss trend, a similar trend linking iss and pentlandite might also reflect a primary accumulation of these two phases from a liquid whose composition fell far to the right, perhaps falling within the scatter of data from the Ni Rim and Victor deposits with >40% Cu. A high form of pentlandite (heazlewoodite solid solution of Kosyakov and Sinyakova (2005))) has been shown to form in a peritectic reaction from mss and Ni-rich sulfide liquid at 865 °C (Sugaki and Kitakaze, 1998). One might therefore envision a crystallization sequence from early mss to mss + iss and eventually iss + hzss after hzss replaces mss on the liquidus, with successive batches of cumulate sulfides composed of each of these three assemblages. Low-temperature re-equilibration will allow Ni-rich mss to break down to pyrrhotite and pentlandite, whereas Ni-rich iss will break down to cubanite, chalcopyrite and pentlandite, producing the commonly observed final sulfide assemblages po + pn—po + pn + cp—cb + cp + pn (illustrated in Fig. 6 as broad arrows). Magnetite is likely to be a liquidus phase and to

persist during subsolidus recrystallization throughout the evolution of the sulfide ore.

A complete description of the crystallization process once iss or a Ni-rich phase such as hzss or pn reaches the liquidus must await further experimental determinations of the relevant phase equilibria. It suffices to say for now that it is nearly impossible to continue to support the concept that Cu-rich, Ni-poor sulfide compositions clustered near the composition of iss represent liquids residual to the removal of mss from primary sulfide magmas at Sudbury.

The notion that most natural sulfide compositions, including the Cu-rich and Ni-poor examples, are cumulate rather than representing quenched liquids runs counter to common current perception, but upon reflection it should not seem surprising. We do not expect to find liquid compositions preserved in plutonic silicate rocks—no petrologist would be surprised to learn that a silicate rock comprising only two magmatic minerals (e.g., harzburgite) was a cumulate rock whose parent melt had since departed, so why should one feel otherwise about an mss–iss rock? It would be passing strange if magmas belonging to the five-component system Fe–Ni–Cu–S–O, with initial compositions entirely dictated by silicate–sulfide partitioning during liquation from parent silicate melts, were repeatedly found to crystallize entirely within the low-variance three-phase assemblage mss–iss–magnetite. For example, the five-component liquids at equilibrium with mss at fO_2 and fS_2 chosen to represent typical magmatic conditions with fO_2 at FMQ (Mungall et al., 2005) cannot be recast purely in terms of the four minerals chalcopyrite, pentlandite, pyrrhotite and magnetite. In our experiments there was a small but significant excess of metal over sulfur and oxygen. If a natural sulfide ore is thought to have crystallized from a sulfide magma that intially formed at equilibrium with a silicate melt at FMQ, then either excess metal must have departed from the rock which is now composed only of the common minerals chalcopyrite, pyrrhotite, pentlandite and magnetite; or an anion must have been added to the sulfide during cooling to combine with the excess metal—the probable carrier that removed the excess metal was an exceptionally metal-rich sulfide melt with a composition resembling those samples at the extreme right of Fig. 6.

Furthermore, considering the much greater rates of equilibration of sulfide phases compared with silicates (e.g., Kress, 1997), the very low viscosity of sulfide melts, and the ease with which sulfide melt can continue to migrate through a solid matrix of silicate minerals once the silicate melt has crystallized (Mungall, 2002; Mungall and Su, 2005), we should not expect to find many plutonic examples of quenched sulfide liquids. The amount of residual sulfide liquid extracted from the mss–iss cumulates need not be very large. The ubiquitous Cu- and Ni-rich vein systems below the contact type deposits at Sudbury can be interpreted as having crystallized from these fugitive liquids; however even these narrow sharp-walled veins may consist of cumulus iss and a nickel-rich phase (pentlandite or heazlewoodite solid solution). Fugitive components not accomodated in the solid assemblage within these vein systems may in turn have departed into the host rocks to participate in the formation of the low-sulfide PGE deposits (e.g., Farrow et al., 2005) which are spatially associated with magmatic sulfide veins but which themselves were deposited from a phase of questionable identity. In other words, it is likely that none of the compositions plotted in Fig. 6 represents a liquid—all are probably cumulate rocks.

Ballhaus et al. (2001) documented the existence of immiscible pairs of sulfide liquids in some of their experiments, a finding that was used by Beswick (2002) to argue that the principal control on sulfide differentiation at Sudbury was sulfide liquid immisicibility. The compositions of four different conjugate pairs measured by Ballhaus et al. (2001) are shown in Fig. 6. The Cu-rich liquids correspond fairly closely to the composition of the cluster of Cu-rich ores from Sudbury near to the composition of chalcopyrite. The Cu-poor liquids are rather more Cu-rich than the mss-rich material that forms the bulk of the ore samples at Sudbury. It is surprising that other researchers who have done melting experiments on similar compositions have failed to observe stable immiscible sulfide liquids. For example, several of the liquids described by Mungall et al. (2005) have compositions intermediate between the conjugate liquids reported by Ballhaus et al. (2001), and yet in our experiments we did not observe any immiscible phase separation. Pending independent confirmation that stable immiscibility is a real phenomenon in natural sulfide magmas, rather than a metastable quench phenomenon, I will consider only crystallization–differentiation as the dominant control on the evolution of sulfide magmas.

4. CONCLUSIONS

The partition of metals and sulfur between monosulfide solid solution and sulfide melt can be quantified and parameterized in terms of a series of simple exchange reactions. The parameterization is of potential use wherever the compositions of coexisting sulfide melt and mss are of interest in geological processes. A first order result of the application of the model to crystallization of sulfide magmas is the observation that Ni tends to be an incompatible element in all plausible sulfide magma compositions until very low temperatures and high Ni, Cu contents are reached. Comparison of the model to natural sulfide compositions from the Sudbury district shows that the vast majority of ore samples, including those Cu-rich compositions that have previously been considered to represent residual liquids, are probably cumulates dominated by mixtures of magmatic mss and iss. Veins rich in both Ni and Cu are most likely to represent compositions approaching those of the actual sulfide liquids that originally equilibrated with the cumulus phases. Like most plutonic rocks, most natural sulfide ores do not preserve bulk compositions representative of magmatic liquids.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2007.03.026.

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