The Canadian Mineralogist
Vol. 41, pp. 207-220 (2003)

EXPERIMENTAL EVIDENCE FOR THE CHALCOPHILE BEHAVIOR OF THE HALOGENS

JAMES E. MUNGALL[§] AND JAMES M. BRENAN[§]

Department of Geology, University of Toronto, 22 Russell Street, Toronto, Ontario M5S 3B1, Canada

ABSTRACT

We have investigated the partitioning of F, Cl, Br, and I between coexisting silicate and sulfide liquids at 0.9 to 1.8 GPa pressure and temperatures between 1150° and 1450°C, and the partitioning of Cl between Cu- and Ni-rich sulfide liquid and monosulfide solid-solution (mss) at atmospheric pressure and temperatures of 1000° and 1100°C. We have calculated Nernst partition coefficients, expressed as wt.% halogen in sulfide divided by wt.% halogen in silicate. F remains undetectable in quenched sulfide liquid under all conditions investigated. There is no discernable change in $D_{\mathrm{Cl}}^{\mathrm{sul/sil}}$, $D_{\mathrm{Br}}^{\mathrm{sul/sil}}$ and $D_{\mathrm{I}}^{\mathrm{sul/sil}}$ with temperature. Values of $D_{\mathrm{Cl}}^{\mathrm{sul/sil}}$, $D_{\mathrm{Br}}^{\mathrm{sul/sil}}$ and $D_{\mathrm{I}}^{\mathrm{sul/sil}}$ are scattered around means of 0.038, 0.026, and 0.15, respectively. The increase of pressure from 0.9 GPa to 1.8 GPa causes increases in each of $D_{\mathrm{Cl}}^{\mathrm{sul/sil}}$, $D_{\mathrm{Br}}^{\mathrm{sul/sil}}$ and $D_{\mathrm{I}}^{\mathrm{sul/sil}}$ by about a factor of 2. Chlorine is moderately incompatible with mss; $D_{\mathrm{Cl}}^{\mathrm{mss/liq}}$ varies from 0.09 at 1000°C to 0.19 at 1100°C, indicating that crystallization of mss from sulfide liquid will lead to progressive enrichment of Cl in the residual melt. The melting point of mss in the system Fe–Cu–Ni–S is lowered by the presence of Cl. Our results indicate that the common association of halide minerals with massive sulfide ores, including the deliquescent phase lawrencite, is fully consistent with a purely magmatic origin for the ores. The halogens can be dissolved in sulfide melts, and expelled during final crystallization of the sulfide liquids to form halide minerals within the massive sulfide bodies, or hypersaline fluids when mixed with aqueous fluids in the country rocks. A hallmark of the orthomagmatic fluid derived from a sulfide magma will be extremely high values of Cl/F and Cl/Br due to the preference of Cl for sulfide relative to these other halogens. Recognition of hypersaline fluids with anomalously high Cl/Br might serve as a powerful prospecting tool in the search for Cu- and PGE-rich fractionated sulfide bodies.

Keywords: halogen, solubility, sulfide liquid, silicate liquid, monosulfide solid-solution, partition coefficient.

SOMMAIRE

Nous avons étudié la répartition de F, Cl, Br, et I entre liquides silicaté et sulfuré coexistants à une pression allant de 0.9 à 1.8 GPa et à une température entre 1150° et 1450°C, et la répartition du Cl entre liquide sulfuré riche en Cu et en Ni d'une part, et solution solide monosulfurée (mss) à pression atmosphérique et une température de 1000° et 1100°C. Nous avons calculé les coefficients de partage de Nernst, exprimés en termes de la proportion pondérale d'halogène dans le sulfure divisé par la proportion dans le silicate. Nous n'avons pas détecté de fluor dans le liquide sulfuré, quelles que soient les conditions expérimentales. Il n'y a pas de changement discernable dans les coefficients $D_{\mathrm{Cl}}^{\mathrm{sul/sil}}$, $D_{\mathrm{Br}}^{\mathrm{sul/sil}}$ et $D_{\mathrm{I}}^{\mathrm{sul/sil}}$ avec la température. Les valeurs de $D_{\mathrm{Cl}}^{\mathrm{sul/sil}}$, $D_{\mathrm{Br}}^{\mathrm{sul/sil}}$ et $D_{\mathrm{I}}^{\mathrm{sul/sil}}$ sont dispersées de part et d'autre de 0.038, 0.026, et 0.15, respectivement. Une augmentation de la pression de 0.9 à 1.8 GPa mène à une augmentation des coefficients $D_{\mathrm{Cl}}^{\mathrm{sul/sil}}$, $D_{\mathrm{Br}}^{\mathrm{sul/sil}}$ et $D_{\mathrm{I}}^{\mathrm{sul/sil}}$ selon un facteur de 2, environ. Le chlor est modérément incompatible avec la phase mss; $D_{\mathrm{Cl}}^{\mathrm{mss/liq}}$ varie de 0.09 à 1000°C à 0.19 à 1100°C, indication que la cristallisation de cette phase solide à partir d'un liquide sulfuré entrainera un enrichissement progressif du Cl dans le liquide résiduel. Le point de fusion de mss dans le système Fe–Cu–Ni–S est abaissé par la présence du Cl. Nos résultats montrent que l'association commune des halogénures dans les minerais de sulfures massifs, y inclus la lawrencite, minéral déliquescent, concorde parfaitement avec l'hypothèse d'une origine purement magmatique du minerai. Les halogènes pourraient bien avoir été dissous dans le liquide sulfuré, pour ensuite être rejeté pendant sa cristallisation finale, pour former des halogénures comme minéraux accessoires dans les amas de sulfures massifs, ou bien des fluides hypersalins qui pourront se mélanger avec les fluides aqueux dans les roches encaissantes. Comme signe révélateur d'une phase fluide orthomagmatique dérivée d'un magma sulfuré, on s'attend à voir des valeurs extrêmement élevées des rapports Cl/F et Cl/Br, traduisant l'affinité préférentielle du Cl pour les sulfures en comparaison des autres halogènes. Des signes de la présence d'une telle phase fluide hypersaline ayant un rapport Cl/Br anormalement élevé pourrait fournir un outil précieux dans la prospection pour les amas sulfurés enrichis par fractionnement en Cu et en éléments du groupe du platine.

(Traduit par la Rédaction)

Mots-clés: halogène, solubilité, liquide sulfuré, liquide silicaté, solution solide monosulfurée, coefficient de partage.

[§] *E-mail addresses*: mungall@geology.utoronto.ca, brenan@geology.utoronto.ca

INTRODUCTION

Unusual abundances of halogen-rich minerals are found in close spatial association with base-metal and precious-metal sulfide mineralization cogenetic with igneous rocks in several localities worldwide. A contentious issue regarding such ore deposits concerns the role of deuteric or later hydrothermal processes in concentrating or remobilizing ore metals after termination of magmatic processes. Anomalous abundances of halogens or ratios among halogens have been used by a number of investigators as evidence for the participation of saline hydrothermal fluids in the mineralizing process (*e.g.*, Jago *et al.* 1994, Willmore *et al.* 2000, Hanley 2002). In this article, we briefly review some evidence concerning the nature and mineralogy of halogen-enriched sulfides from several localities and present new experimental results indicating that sulfide melts are capable of dissolving and transporting significant concentrations of halogens in the absence of an aqueous fluid. The results show that observed enrichments in halogens in some mineralized environments are consistent with ore deposition by purely magmatic processes.

REVIEW OF NATURAL OCCURRENCES

Occurrences of halogen-rich minerals have been reported from several major sulfide deposits worldwide. Common ore-associated halogen-bearing phases in which Cl is an essential constituent are halite (NaCl), lawrencite [Fe,Ni)Cl_2], and ferropyrosmalite [$(Fe,Mn)_8Si_6O_{15}(OH,Cl)_{10}$]. Inclusions consisting of nearly 100% halite with subsidiary amounts of water have been interpreted as halide melt inclusions (Ballhaus & Stumpfl 1986). These phases have been described from the Merensky Reef of the Archean Bushveld Complex, South Africa (Ballhaus & Stumpfl 1986), the Copper Zone of the Fraser mine (formerly known as the Strathcona Deep Copper Zone; Springer 1989, Li *et al.* 1992), the adjoining McCreedy East deposit (Jago *et al.* 1994), and the Victor Deep deposit (Jago *et al.* 1994) in the Sudbury Igneous Complex (SIC) of Ontario, Canada, and the Oktyabr'sky mine in the Noril'sk district of Russia (Karpenkov *et al.* 1981, Saini-Eidukat *et al.* 1998). Additional phases reported from magmatic sulfides in minor occurrences as well as in the Oktyabr'sky mine include djerfisherite [$K_6(Cu,Fe,Ni)_{25}S_{26}Cl$] and its potassium – thallium – lead sulfide analogs (Barkov *et al.* 1997, Korobeinikov *et al.* 1998). The Broken Hill massive sulfide deposit has recently been proposed to have undergone partial melting during high-grade metamorphism despite its origin as a hydrothermal deposit (Frost *et al.* 2002), to produce localized concentrations of low-melting-point chalcophile elements such as Ag. The same group of deposits is host to unusual occurrences of silver and copper halide minerals marshite (CuI), miersite [(Ag,Cu)I], iodargyrite (AgI), bromian chlorargyrite [(Br,Cl)Cl], bromargyrite (AgBr) and iodian bromian chlorargyrite [Ag(I,Br)] (Millstead & Creagh 2000). The silver halide phases may thus once have been in equilibrium with a sulfide melt rich in halogens.

Ore deposition in the footwall of the SIC and in the Merensky Reef has been attributed by various authors either to purely magmatic processes (*e.g.*, Li *et al.* 1992, Jago *et al.* 1994, Campbell *et al.* 1983), purely hydrothermal processes (*e.g.*, Farrow & Watkinson 1992, Boudreau *et al.* 1986, Boudreau & McCallum 1992), or to some combination of the two (e.g., Ballhaus & Stumpfl 1986, Farrow & Watkinson 1997, Marshall *et al.* 1999). Evidence cited in support of magmatic deposition of ore generally consisted of 1) the absence of major alteration-induced signatures like those observed in ore-depositing systems universally acknowledged to be hydrothermal in nature (*e.g.*, volcanogenic massive sulfide and porphyry deposits), and 2) the success of geochemical models using well-characterized magmatic processes to account for the range of mineral and rock compositions observed.

Evidence cited in support of the presence of aqueous fluids, and their inferred role in metal transport, has been largely based upon the presence of abundant halogens in the silicate phases and fluid inclusions associated with mineralization. Furthermore, retrograde alteration of anhydrous mineral assemblages to lower temperature hydrous assemblages has been attributed to aqueous fluids. High proportions of Cl to F in hydrous phases have been used to infer the involvement of aqueous fluids in ore deposition (Boudreau & Kruger 1990, Willmore *et al.* 2000). There are two key assumptions behind this inference: first, that only silicate melt and aqueous fluids are capable of transporting halogens, and second, that hydrous minerals crystallize with a low Cl/F where in equilibrium with silicate melt, and with a high Cl/F where precipitated from aqueous fluids. If these two assumptions are correct, then any mineralization associated with chloride minerals or hydrous phases exhibiting high Cl/F must have been affected by or deposited by an aqueous fluid.

On the other hand, if another mobile phase characterized by high Cl/F exists in magmatic systems, then each occurrence of chloride-rich sulfides will need to be assessed individually to determine if there are other lines of evidence to support aqueous deposition. Apart from silicate melt and aqueous fluid, the third fluid phase that commonly exists in magmatic ore-forming environments is an Fe–S–O melt containing Cu and Ni as major constituents and trace amounts of the platinum-group elements (PGE).

Fuge & Johnson (1984) have persuasively argued that I is a moderately chalcophile element, based upon comparison of coexisting sulfide and silicate minerals from a wide variety of environments. It might also be argued that the common occurrence of lawrencite as an accessory phase in globules of Fe–Ni alloy (Taylor *et al.* 1974) in lunar basalts and iron–nickel meteorites (e.g., Mason 1963) constitutes evidence that Cl is siderophile and hence also likely to be chalcophile. The similar occurrence of lawrencite in terrestrial magmatic sulfides also suggests that sulfide melt can contain dissolved Cl.

Taken as a whole, the previous observations indicate that magmatic sulfide (*sensu lato*) mineralization is commonly associated with halogen-bearing phases, perhaps indicating that the sulfide magmas themselves contained the halogens. Since the behavior of halogens in sulfide liquids was hitherto unknown, here we experimentally explore the solubility of halogens in sulfide melts coexisting with either silicate melt or monosulfide solid-solution (mss).

Experimental Approach

Partitioning between sulfide and silicate

We have conducted a series of experiments intended to explore the behavior of the halogens F, Cl, Br and I in magmatic systems containing silicate and sulfide melt, or sulfide melt and mss. Experiments designed to explore the partition of halogens between silicate and sulfide melts were done in a conventional piston–cylinder press at high pressure, whereas melting experiments on sulfides were done in evacuated silica tubes at one bar external pressure. All experiments were conducted in the High Pressure or Hydrothermal Labs at the University of Toronto.

Starting materials for the equilibration of sulfide and silicate melts were prepared from reagent-grade chemicals and from a natural sample of quartz diorite from the Copper Cliff Offset dike, Sudbury, Ontario (CC06; Table 1). The quartz diorite was ignited overnight at 1000°C to dehydrate alteration minerals, then fused at 1400°C overnight to produce a homogeneous dark brown glass. Chips of this glass were weighed and ground with $CaCl_2$ powder in an agate mortar and pestle, and the resulting powder was remelted overnight under air at 1400°C in an attempt to synthesize a glass containing 0.2% Cl. Evaporative loss of Cl to the furnace atmosphere led to the formation of a glass (CC06Cl) containing strong Cl concentration gradients from 0 at the air/melt interface to 0.4% in the middle, making its bulk Cl content impossible to quantify. Since our intention was to measure relative Cl contents of coexisting phases, we elected to use this glass despite its uncertain Cl content. The first experiment contained only powdered CC06Cl and sulfide, but in subsequent experiments, this glass was mixed with combinations of halide salts, and with sulfide, to produce sulfide-saturated silicate melts containing various amounts of the halogens.

TABLE 1. COMPOSITION OF QUARTZ DIORITE CC06

SiO_2 wt.%	55.6	MnO	0.17	P_2O_5	0.18
TiO_2	1.03	MgO	4.78	LOI	0.66
Al_2O_3	15.1	CaO	7.22		
FeO	5.88	Na_2O	2.82		
Fe_2O_3	4.40	K_2O	1.62	Total	98.8

Major elements determined by X-ray fluorescence on fused bead at McGill University Geochemical Laboratories.

Sulfide melt was prepared by mixing powdered elemental Fe, Ni and S (weight proportions $Fe_{65}Ni_5S_{30}$), loading the mixture into an evacuated silica tube, and fusing the mixture at 1200°C for one hour before quenching in water. The resulting quenched sulfide was ground in an agate mortar and pestle and mixed with powdered glass in the proportion $glass_{90}sulfide_{10}$. The sulfide composition chosen is relatively S-poor compared with natural sulfide liquids (*e.g.*, Naldrett 1969), to ensure that sulfide liquid would remain superheated (*i.e.*, mss crystallization would not commence) over the entire range of temperatures investigated in the partition experiments. We suspect that the effect of S content in sulfide melt on halogen partitioning will be subsidiary to the first-order difference in solution behavior of halogens between sulfide liquid and silicate melt.

Reagent-grade chemicals (99.9995% S pieces from Johnson Matthey, 99.998% Fe powder from Alfa Aesar, 99.999% Ni from Aldrich, 98% anhydrous $FeCl_2$ from Anachemia, >97% NaF from British Drug House, and reagent grade NaBr and KI supplied by Fisher) were used to make starting mixtures to be added to the fused quartz diorite. Because the composition of the glass already includes a wide range of trace and minor elements, we did not consider it necessary to use ultrahigh-purity reagents for the halogen components of the experimental mixtures, which are in any case present at low concentrations.

Run conditions for the sulfide/silicate melt partitioning experiments in the piston–cylinder apparatus are summarized in Table 2. All experiments were run using solid NaCl as the pressure medium surrounding a pyrex sleeve. Heat was applied by passing current through a cylindrical graphite resistance furnace that surrounded an assembly made of crushable MgO. Capsules were made of graphite with lids sealed in place by the application of pressure at the beginning of each run. All experiments were maintained within 200 bars of 0.9 GPa throughout their duration using the hot-piston-in technique and pumping periodically to compensate for stress relaxation of the pressure medium. A 10% pressure correction was applied to compensate for frictional loss along the sample–vessel interface. Temperature was maintained to within 1°C of the setpoint using a programmable controller. Temperature was monitored and controlled using a single W5%Re–W26%Re thermocouple, which also served as input to the controller. No correction for the pressure effect on output emf was applied. Experiments were heated to run conditions at a rate of 50°C per minute, and were quenched to below

500°C within 10 seconds by shutting off power to the graphite furnace.

Partitioning between mss and sulfide melt

Starting materials for the experiments were mixtures of metal + sulfur reagents listed above and 99.999% Cu (supplied by Alfa Aesar), which were weighed, then added directly to close-ended fused silica tubes (5 mm O.D. × 3 mm I.D.). Approximately 0.4 wt.% Cl was added as $FeCl_2$ salt to three experiments, whereas the other two were run under the same conditions without any Cl present. Samples were then evacuated and sealed with a welding torch. Experiments involved suspending the sample in the predetermined hotspot of a vertical tube furnace at an initial temperature of 1200°C (~80°C above the liquidus) for one hour, then cooling at 2°C/minute to the final run temperature, and holding for 26 to 40 hours. Experiments were terminated by plunging the sample into an ice–water mixture. Temperature was monitored with a Pt–Pt10%Rh thermocouple located adjacent to the sample in the furnace. Temperature control was achieved using the same controller system employed for the piston–cylinder experiments.

In the sulfide melting experiments, we required the presence of coexisting mss and sulfide melt, thus mandating the choice of a composition richer in S. We chose to use the composition B11–2 (close to $Fe_{54}Cu_5Ni_5S_{36}$; wt.%), whose phase equilibria were previously investigated by Li *et al.* (1996), to facilitate comparison of our results with those of other investigators.

Run products were mounted in epoxy, sectioned with a diamond saw, and polished with carbide grit and diamond paste. Some samples were polished using oil-based media to prevent dissolution of halide phases during preparation; no difference was observed between these samples and others prepared using water-based media.

TABLE 2. SUMMARY OF SULFIDE/SILICATE PARTITION COEFFICIENTS AND RUN CONDITIONS

Run	P GPa	T °C	t hrs	D_F	D_{Cl}	1σ	D_{Br}	1σ	D_I	1σ	Σhalogens
CC06Cl1	0.9	1350	19		0.11	0.03					0.36
CC06Cl2	0.9	1350	24		0.11	0.01					1.00
CC06Cl3	0.9	1350	15	<0.019	0.030	0.005	0.027	0.013	0.169	0.076	4.12
CC06Cl6	0.9	1250	24	<0.021	0.049	0.015	0.022	0.015	0.053	0.037	3.64
CC06Cl7	0.9	1150	22	<0.019	0.030		0.028		0.220		3.65
CC06Cl8	0.9	1450	24	<0.019	0.037	0.018	0.033	0.020	0.159	0.132	4.46
CC06Cl9	0.9	1350	4	<0.019	0.069	0.015	0.065	0.014	0.303	0.103	4.42
CC06Cl10	1.8	1350	18	<0.020	0.062	0.010	0.074	0.023	0.384	0.087	4.63
CC06Cl11	0.9	1350	1	<0.019	0.055	0.014	0.059	0.025	0.301	0.098	4.23
CC06Cl16	0.9	1150	48	n.d.	0.031	0.012	0.023	0.011	0.240	0.090	3.57
CC06Cl17	0.9	1150	24	n.d.	0.028	0.014	0.011	0.007	0.108	0.105	3.66

Analytical methods are described in the text. F was consistently below detection limits in all sulfides analyzed. Reported values of D_F are maximum values based on the detection limit for F in sulfide (0.02%) divided by the concentration of F in the glass. Total halogens refers to the net weight-fraction of halogens measured in the silicate glass portion of each run product.

Analytical methods

Sectioned and polished products were examined and phases identified by optical microscopy and scanning electron microscope (SEM) with an auxiliary energy-dispersion X-ray spectrometer. Individual phases were analyzed quantitatively using a Cameca SX–50 electron microprobe with three wavelength-dispersion X-ray spectrometers. As a standard for halogens and major oxides in silicate glasses, we used a synthetic glass prepared by mixing 1.77, 1.71, 1.99, and 1.74 weight % each of F, Cl, Br and I, respectively, with powdered CC06 glass and homogenizing the mixture overnight at 1400°C in a sealed Pt capsule 5 mm in diameter in the piston–cylinder apparatus. Pentlandite and chalcopyrite were used as standards for Fe, Ni, Cu and S in sulfides from all experiments. The halogen contents of the sulfide phase from the sulfide/silicate partitioning experiments were measured using the same glass standard as was used for the analysis of the glasses. Tugtupite ($NaAlBeSi_4O_{12}Cl$) was used as a chlorine standard for the analysis of sulfides in the mss/sulfide partitioning experiments. An attempt to synthesize a halogenated sulfide standard was unsuccessful because it was not possible to quench the halogen-rich sulfide melt to a homogeneous solid. Halogen contents of the sulfide phases were therefore measured using the same glass standard as was used for the analysis of glasses. There may be some systematic bias in the data resulting from uncompensated matrix-effects owing to the difference in X-ray absorption by sulfide and silicate matrices. This bias is unlikely to be more than a few percent relative, however, and is compensated for in part by the advantages accruing from the use of a single standard for both sets of analyses. Although the composition of the halogen standard is only known by gravimetry (composition "as weighed in"), the resulting uncertainty does not affect our results because we are primarily concerned with relative abundances of halogens in coexisting phases; errors in absolute amounts will not affect the partition coefficients extracted from our data.

We acquired wavelength-dispersion scans of the regions of the *K*α X-ray emission peaks for each of the halogens in the quenched sulfide phase in one of our sulfide/silicate partitioning experiments (Fig. 1) to check for possible interferences and to confirm that the desired emission lines were truly present. Whereas these portions of the X-ray spectrum are flat or monotonic in slope in the pentlandite standard (not shown), the profiles shown (from experiment CC06Cl3) show unequivocally that recognizable peaks exist exactly at the nominal wavelengths of each of Cl, Br and I. No sign of a peak could be discerned for F, indicating either that it is absent from the sulfide, or that low-energy F*K*α X-rays were too severely attenuated by the sulfide to be detected.

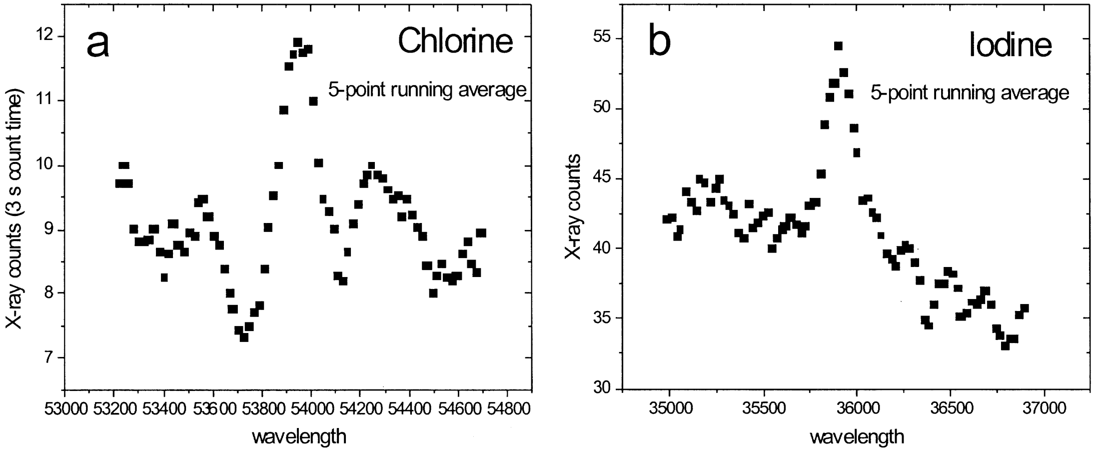

FIG. 1. Wavelength scans of the vicinity of the halogen Kα peaks in a quenched sulfide melt containing about 600 ppm Cl and 1500 ppm I. a: Cl peak; b: I peak. Units are equal to sinθ × 10^5; wavelength is equal to 8.75 Å × sinθ. Backgrounds were measured at +500 and -600 units displacement from the peak position.

Analyses were conducted with an accelerating voltage of 20 kV, beam current of 20 or 30 nA and a slightly defocused beam ~20 μm in diameter. Halogen peaks were counted for 60 to 90 seconds, and backgrounds were collected on both sides of the peaks.

RESULTS

Partitioning between sulfide and silicate melts

The product of a typical experiment at high pressure is shown in Figure 2, a back-scattered electron image. The graphite capsule appears dark owing to its low average atomic number, whereas the silicate glass appears as a dark grey field scattered with bright spots that represent quenched droplets of immiscible sulfide liquid. The detailed view shows that the sulfide liquid quenched to a uniform phase dotted with volumetrically minor brighter specks rich in Ni, which may be crystals of Ni–Fe alloy (*cf.* Karup-Møller & Mackovicky 1998). In some experiments, the sulfide quenched uniformly without apparent phase-separation; the example shown is the most inhomogeneous sample observed.

No crystals were observed in the silicate portion of any experiments except those at 1150°C, where a small number of blades of orthopyroxene formed at the base of the capsule. Silicate melt quenched to an optically homogeneous brown glass free of vesicles. We varied temperature and halogen content to test their effect on the partitioning of the halogens; in one experiment, we also investigated the effects of increased pressure from 0.9 GPa to 1.8 GPa.

The compositions of coexisting silicate glass and quenched sulfide liquid from one typical experiment are shown in Table 3. A full suite of analytical results is available from the authors or from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada. Compositions of glass and sulfide were measured in closely spaced pairs. The ratio of halogen content in sulfide over silicate was calculated directly for each pair to determine the partition coefficient (*D*). The *D* values for each halogen in each experiment were estimated by taking the average and standard deviation of the individual determinations of *D* for each pair measured in that run product. The resulting *D* values and their standard deviations are presented in Table 2.

The first-order result of this study is that Cl, Br and I dissolve in sulfide melt at concentrations on the order of one tenth those in the coexisting silicate melt, under all conditions investigated. On the other hand, the concentration of F in the sulfide is below detection limits in all experiments, and may be very low in the sulfides.

It is possible that the distribution of the halogens did not have sufficient time to equilibrate between silicate and sulfide melts. Sulfide droplets in our run products are spaced up to 0.01 cm apart, and the slowest-diffusing species in the quartz diorite melt at 1150°C should have had a diffusivity of approximately 3.5 × 10^{-9} cm^2s^{-1} (estimated using the Eyring equation; Mungall 2002), allowing us to estimate that the timescale of equilibration was at least 8 hours. The approach to equilibrium was investigated through a series of experiments at 1350°C with durations of 1, 4, 15 and 24 hours. The results are shown in Figure 3 as D_{Cl} *versus* time. At 1150°C, our experiments lasted 22, 24 hours and 48 hours. Only one sulfide droplet was preserved during preparation of the product of the 22 hour run. Sulfide/

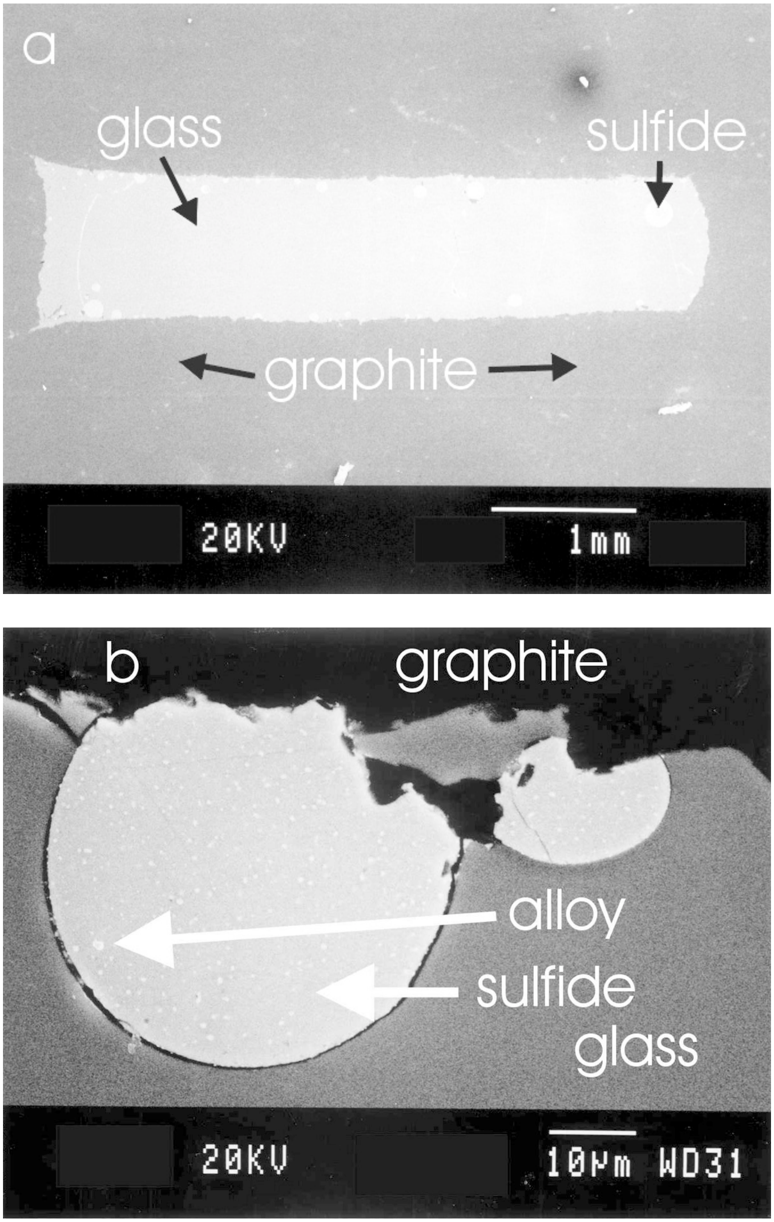

FIG. 2. Back-scattered electron images of the product of a sulfide/silicate partitioning run. a. View of the entire run-product, showing glass and sulfide blebs contained within graphite. b. Detail of a pair of sulfide blebs, showing quench growth of alloy.

silicate melt pairs measured in the 24-hour experiment had a standard deviation almost as large as the average partition-coefficient, whereas the variability of *D* between individual sulfide droplets after 48 hours was about one tenth of the average. In light of the evident variability of *D* at short times, we elected to consider data only from runs with durations greater or equal to 24 hours at T above 1200°C, and greater or equal to 48 hours at T less than 1200°C.

The variations of D_{Cl}, D_{Br} and D_I with temperature and pressure are shown in Figure 4. No increase is evident in D_{Cl}, D_{Br} or D_I with increasing temperature. Values of D_{Cl}, D_{Br} and D_I are scattered around means of 0.038, 0.026, and 0.15, respectively. The increase of pressure from 0.9 to 1.8 GPa caused increases in each of D_{Cl}, D_{Br} and D_I by about a factor of 2; this result has not been confirmed by further experiments, and the inferred positive dependence of D on pressure should be regarded as tentative.

Figure 5 shows values of D_{Cl} measured in experiments containing different amounts of Cl. D_{Cl} is increased by approximately a factor of three as bulk Cl concentration decreases from about 1% to the range close to natural abundances below 4000 ppm. We have not attempted similar measurements for the other halo-

TABLE 3. ANALYTICAL RESULTS FOR EXPERIMENT CC06Cl16

Element concentration in glass* (wt.%)

	Na	Mg	Al	Si	Mn	Ti	K	Ca	O	Fe	S	F	Br	Cl	I	total
Pair 1	3.60	2.71	7.03	24.69	0.06	0.40	1.80	3.94	42.68	10.78	0.11	1.18	0.48	0.85	1.11	101.40
Pair 2	3.50	2.67	6.91	24.48	0.11	0.47	1.76	4.00	42.39	10.71	0.12	1.07	0.50	0.88	1.11	100.67
Pair 3	3.65	2.59	6.99	24.40	0.00	0.43	1.79	3.96	42.26	10.78	0.10	1.12	0.47	0.85	1.06	100.46
Pair 4	3.54	2.66	6.88	24.54	0.04	0.45	1.77	4.01	42.30	10.58	0.08	1.06	0.50	0.88	1.03	100.32
Pair 5	3.59	2.58	6.94	24.31	0.00	0.52	1.78	4.10	42.09	10.57	0.07	1.19	0.50	0.87	1.14	100.27
Pair 6	3.52	2.62	7.03	24.35	0.11	0.45	1.82	4.03	42.26	10.63	0.09	1.07	0.49	0.88	1.12	100.47
Pair 7	3.46	2.65	6.98	24.18	0.05	0.51	1.76	4.17	42.09	10.73	0.09	1.15	0.48	0.90	1.13	100.34
Pair 8	3.58	2.68	6.95	24.56	0.12	0.33	1.77	4.04	42.39	10.60	0.10	1.13	0.48	0.88	1.08	100.68
Pair 9	3.68	2.58	6.95	24.79	0.05	0.31	1.84	3.90	42.54	10.66	0.08	1.14	0.49	0.84	1.12	100.95
Pair 10	3.61	2.50	6.86	24.65	0.00	0.39	1.82	3.94	42.23	10.45	0.08	1.05	0.52	0.88	1.00	99.97
Pair 11	3.42	2.70	6.96	24.51	0.00	0.40	1.80	4.05	42.41	10.94	0.10	1.17	0.48	0.87	1.18	100.97
Pair 12	3.61	2.69	6.92	24.27	0.13	0.42	1.74	4.07	42.25	10.76	0.15	1.10	0.47	0.86	1.16	100.59
Pair 13	3.45	2.66	6.98	24.71	0.08	0.33	1.75	3.93	42.59	10.69	0.10	0.98	0.49	0.86	1.20	100.79

Element concentration in sulfide (wt.%)

	Fe	S	Ni	total	F	Br	Cl	I
Pair 1	63.24	31.88	5.21	100.70	0.000	0.017	0.030	0.319
Pair 2	63.56	32.16	5.29	101.34	0.000	0.017	0.033	0.282
Pair 3	62.90	31.60	6.16	101.07	0.000	0.014	0.034	0.362
Pair 4	63.41	31.85	5.62	101.21	0.000	0.016	0.024	0.284
Pair 5	63.52	31.73	5.55	101.06	0.000	0.005	0.009	0.246
Pair 6	63.10	32.20	4.64	100.22	0.000	0.014	0.029	0.244
Pair 7	63.16	34.77	3.66	101.62	0.000	0.001	0.030	0.000
Pair 8	64.14	31.59	5.14	101.14	0.000	0.010	0.016	0.240
Pair 9	63.45	31.87	5.04	100.67	0.000	0.003	0.019	0.297
Pair 10	62.95	31.28	5.32	99.95	0.000	0.012	0.026	0.358
Pair 11	63.86	31.26	5.75	101.18	0.000	0.012	0.050	0.250
sulfide rim 11	64.66	32.03	4.59	101.43	0.000	0.001	0.022	0.129
Pair 12	64.11	32.31	4.61	101.32	0.000	0.011	0.027	0.261
sulfide rim 12	64.72	32.32	4.47	101.94	0.000	0.010	0.060	0.368
Pair 13	63.76	31.27	5.15	100.33	0.000	0.000	0.044	0.106
sulfide rim 13	63.41	30.32	6.15	100.09	0.000	0.023	0.038	0.153

* O concentration by stoichiometry.

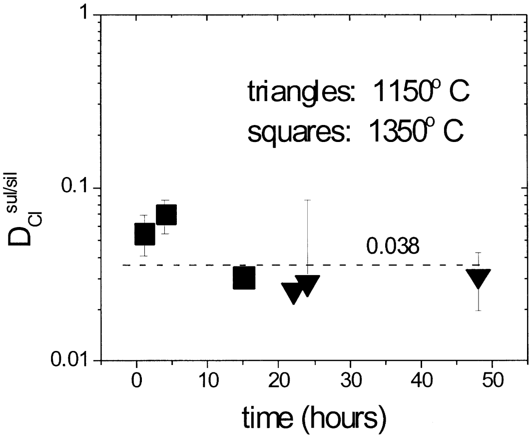

FIG. 3. Variation of sulfide/silicate D_{Cl} with time. The dashed line indicates the average value for the temperature range from 1050% to 1450°C.

gens. Clearly, Henry's law is not obeyed by Cl, so that the *D* values reported here are not constant Nernst partition coefficients. We suspect that at bulk Cl concentrations at or below 4000 ppm, the *D* values may be constant as Cl becomes a true trace element, but have not been able to confirm this owing to analytical constraints at these low concentrations.

Partitioning between mss and sulfide melt

The product of a typical sulfide melting experiment is shown in Figure 6. Equant grains of homogeneous mss are surrounded by quenched sulfide melt consisting of submillimetric trellis-textured intergrowths of mss, intermediate solid-solution (iss), and a series of minor phases that are concentrated along grain boundaries between earlier-formed phases. These minor phases could not be identified positively, but energy-dispersion X-ray analysis shows them to be dominated

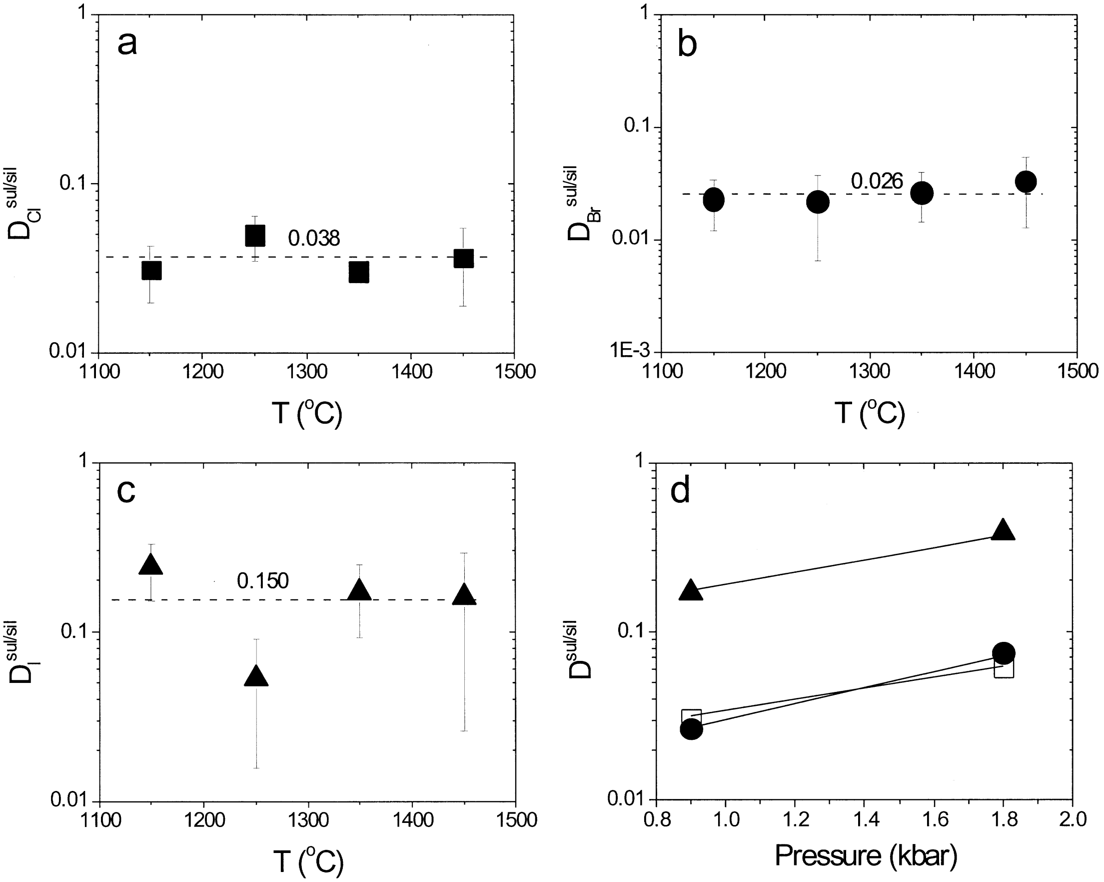

FIG. 4. Sulfide/silicate partition coefficients for Cl, Br and I as functions of temperature (a, b, c) and pressure (d). The anomalously low value for $D_I^{sul/sil}$ at 1250°C may be a consequence of too short a duration. There appears to be a significant increase in *D* for all halogens over the pressure range from 0.9 to 1.8 GPa.

by Cu and Fe halide salts and minor silica. Phase proportions of mss and quenched sulfide melt were established by measuring the major-element compositions of mss and quenched melt and using mass balance based upon the concentration of Fe in both phases. Owing to the extreme inhomogeneity in the distribution of chlorine in the quenched sulfide melt, the amount of chlorine in this phase was calculated from mass-balance considerations, using the initial (weighed) Cl content of the experiment, the measured Cl abundance in mss, and phase proportions.

The run conditions and results of melting experiments done in evacuated silica tubes are shown in Tables 4 and 5. Two important observations can be made from these results. The first is that Cl is moderately incompatible with mss. $D_{Cl}^{mss/liq}$ varies from 0.09 at 1000°C to 0.19 at 1100°C, indicating that crystallization of mss from sulfide liquid will lead to progressive enrichment of Cl in the residual melt. The second is that the melting point of mss in the system Fe–Cu–S is substantially lowered by the presence of Cl. Whereas the Cl-free experiment at 1100°C contained 66% mss and only 34% melt, the same mixture of Fe,Cu and S contained only 18–23% mss and 77–82% melt with ~0.5% Cl added to the system. A smaller but still significant increase in melt fraction, from 23 to 28%, was observed when ~0.5% Cl was added to the same composition at 1000°C.

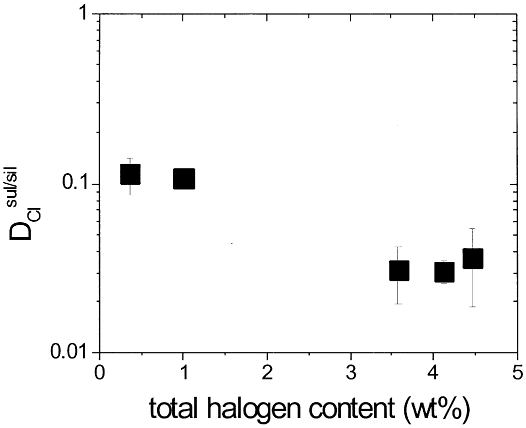

FIG. 5. Variation of D_{Cl} with total halogen content of silicate melt. Values at the lowest abundances of halogen are significantly higher than at greater abundances, and are probably representative of partitioning behavior in nature.

TABLE 4. SUMMARY OF mss/MELT PARTITIONING: EXPERIMENTAL CONDITIONS AND RESULTS

Run	T °C	t hrs	D_{Cl}	D_{Cu}	D_{Ni}
MSSCl1	1100	40	0.16	0.44	0.83
MSSCl2a	1100	26	0.19	0.29	0.76
MSSCl2b	1100	26	----	0.19	0.65
MSSCl3a	1000	26	0.09	0.22	1.18
MSSCl3b	1000	26	----	0.21	0.89

Experiments MSSCl2b and MSSCl3b were run without Cl. Partition coefficients were calculated by measuring the composition of mss and using Fe mass balance with the known initial compositions of the charges to estimate composition of the sulfide liquid.

DISCUSSION

Halogens in massive sulfide ores

This work constitutes a reconnaissance study to evaluate the extent to which the halogens exhibit chalcophile behavior. It would be premature to attempt detailed modeling of the fractionation of halogens in sulfide-bearing systems based upon the present data, but several important qualitative points can be made.

The partitioning of Cl between sulfide and silicate melt is clearly affected by the amount of Cl present in the bulk system, such that $D_{Cl}^{sul/sil}$ reaches a maximum near 0.1 at the trace concentrations anticipated in natural magmas. The partition coefficients of Br and I are likely to show the same behavior, so that the reported values of $D_{Br}^{sul/sil} = 0.02$ and $D_{I}^{sul/sil} = 0.2$ measured in systems containing about 1 wt.% of each halogen should both be considered to be minimum values for natural systems.

TABLE 5. SUMMARY OF COMPOSITIONS OF Mss AND QUENCHED SULFIDE LIQUID (MELT) IN SULFIDE MELTING EXPERIMENTS

Experiment	phase	Fe	Cu	Ni	S	Cl	total	% Mss	% Melt
MSSCl1	Mss	55.46	2.79	4.04	37.78	0.17	100.24	23	77
	1σ	*0.20*	*0.16*	*0.10*	*0.18*	*0.01*			
	Melt	51.60	6.34	4.84	36.33	0.53	99.63		
	1σ	*0.54*	*0.76*	*0.20*	*0.46*	*0.19*			
MSSCl2a	Mss	57.12	1.42	3.78	37.79	0.29	100.40	18	82
	1σ	*0.19*	*0.10*	*0.13*	*0.20*	*0.01*			
	Melt	53.22	4.75	4.97	36.23	0.40	99.58		
	1σ	*0.33*	*0.40*	*0.14*	*0.50*	*0.06*			
MSSCl2b	Mss	57.04	2.13	3.70	37.60	0.00	100.48	66	34
	1σ	*0.41*	*0.19*	*0.22*	*0.23*	*0.00*			
	Melt	48.09	11.31	5.73	34.29	0.00	99.42		
	1σ	*0.86*	*1.32*	*0.36*	*0.40*	*0.00*			
MSSCl3a	Mss	56.21	2.70	3.89	37.50	0.33	100.63	72	28
	1σ	*0.19*	*0.12*	*0.03*	*0.21*	*0.01*			
	Melt	48.60	12.26	3.28	33.00	0.70	97.84		
	1σ	*0.37*	*0.60*	*0.11*	*0.26*	*0.11*			
MSSCl3b	Mss	56.17	2.89	4.18	37.17	0.00	100.41	77	23
	1σ	*0.22*	*0.03*	*0.03*	*0.13*	*0.00*			
	Melt	47.56	13.79	4.68	32.89	0.01	98.92		
	1σ	*1.32*	*1.85*	*0.32*	*0.46*	*0.01*			

Halogen contents of sulfide liquids were calculated by mass balance based on the measured Fe contents of both mss and quenched liquid. 1σ refers to the standard deviation of data measured with the electron microprobe.

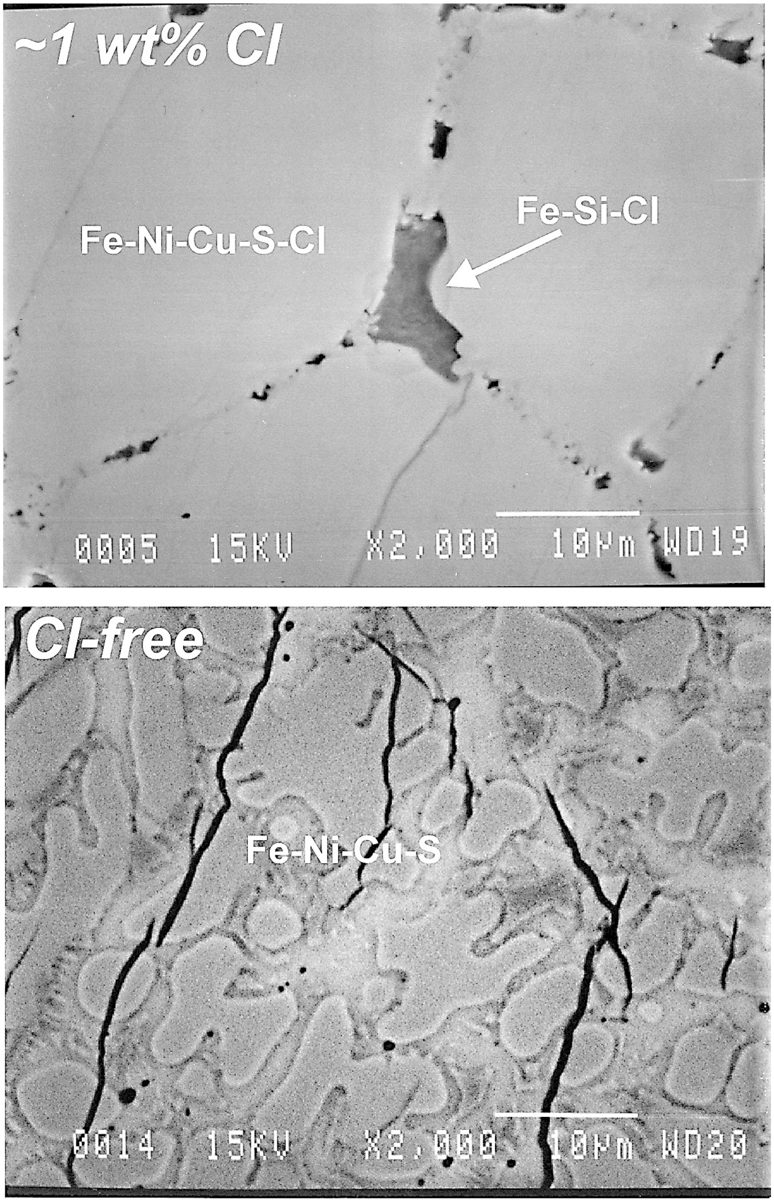

FIG. 6. Back-scattered electron images of quenched sulfide liquid. Textures in the lower figure are typical of quenched volatile-free sulfide liquids. In the Cl-rich experiment shown above, the trellis-texture is absent owing to exceptionally rapid crystal-growth, presumably due to reduced viscosity of the melt. Phases between ~100 μm homogeneous patches include an Fe–Si–Cl phase like ferropyrosmalite, and open cavities representing escaped Cl-rich vapor exsolved during the quench.

These partition coefficients, coupled with the observation that Cl is incompatible in mss during sulfide fractionation, allow an explanation for the common observation of halogen-rich minerals in magmatic sulfide ores. If a sulfide melt has equilibrated with a silicate melt containing 1,000 ppm Cl, we should expect it to contain about 100 ppm Cl. If the sulfide melt is segregated from the parent silicate melt to form a separate sulfide magma, then the onset of fractional crystallization will lead to enrichment of Cl in the residual melt. A classic magmatic interpretation of the petrogenesis of a fractionated sulfide magma has been proposed for the vein stockworks of the Fraser Copper Zone, at Sudbury. These veins are extremely rich in Pt, Pd, Au and Cu, apparently as a result of a protracted process of fractional crystallization of mss from a sulfide melt that was originally equilibrated with the Main Mass magma of the SIC (Li *et al.* 1992). The veins are also characterized by the ubiquitous presence of halogen-rich minerals as inclusions within the sulfide minerals of the veins. Some of the halide minerals, notably lawrencite, $FeCl_2$, are deliquescent and would seem to be unlikely ever to have coexisted with an aqueous fluid. The country rock surrounding the veins is substantially enriched in Cl over similar rocks at a distance from the veins, and is moreover characterized by an elevated ratio of Cl/Br, which has been impossible to explain by appealing to normal processes of halogen fractionation in aqueous solutions (Hanley 2002).

If the Cu–PGE veins resulted from approximately 95% fractional crystallization of sulfide magma originally containing 100 ppm Cl, they would have been emplaced into the vein stockwork carrying about 2,000 ppm Cl. As the results of the quenching of the partitioning experiments show, the halogens are rejected even during the quench by rapidly growing sulfide minerals at relatively low temperatures, so it is likely that they would eventually be expelled from the sulfide magma as a fluid or halide melt during the final stages of solidification.

Orthomagmatic fluids emanating from sulfide magmas

The nature of the expelled fluid is a matter of conjecture, but it is worth digressing here to consider the probable volatile budget of a fractionated sulfide magma. Whereas we have shown that the sulfide melt is likely to contain appreciable concentrations of the halogens, it is unlikely that there will be any significant amount of H_2O present. There have been two experimental studies aimed at establishing the role of H_2O in the the fractionation of sulfide magmas. Naldrett (1969) described the results of attempts to dissolve H_2O in melts in the system Fe–S–O corresponding to natural sulfide magmas. He found that the addition of H_2O to the sulfide system had no measurable effect on the liquidus phase relations, and concluded that the solubility of H_2O in the sulfide melt is insignificant. This finding is in sharp contrast to our observation of substantial freezing point depression in the system Fe–Cu–S upon the dissolution of Cl in the melt.

The other study of the effect of H_2O on sulfide melting relations was done by Konnikov (1997), who added H_2O to compositions along the Fe–S join. Konnikov observed a freezing point depression of about 100°C, which he attributed to the dissolution of 10 wt.% H_2O in the FeS melt. His results are in complete disagreement with those of Naldrett (1969), and demand an explanation. The simplest way to account for the discrepancy is to note that at the initial conditions of Konnikov's experiments, the intrinsic $f(O_2)$ within his Pt capsules was several log units below that of his buffering assemblage (NNO) in his pressure vessel. This disequilibrium would have required a diffusive flux of H_2 out of the capsule until such time as the $f(O_2)$ within the capsule was at NNO. The net result must have been an addition to the sulfide melt, not of H_2O, but of O alone, moving the melt composition from the composition of pyrrhotite toward the O apex. The liquidus temperature where this line intersects the mss–magnetite cotectic is close to 1050°C (Naldrett 1969), very close to the liquidus temperature observed by Konnikov (1997) and inferred by him to result from dissolution of H_2O. Konnikov observed abundant magnetite in the quench phases in his run products. If the H_2O added by Konnikov to his experiments had persisted as H_2O, without diffusive loss of H_2, then there should not have been any magnetite in his experimental products. It therefore appears unlikely that Konnikov was actually observing the dissolution of H_2O, but rather that he had oxidized his system to the magnetite–mss cotectic.

We conclude that the solubility of H_2O in sulfide melt is probably negligible, whereas that of Cl might be expected to near the wt.% level in a fractionated sulfide magma. The result of final cooling and crystallization of a sulfide magma is therefore likely to be the emission of a fluid nearly devoid of H_2O but very rich in halogens. Since the solubility of alkali cations in a sulfide melt is very low, the halogens are most likely to react with transition metals and silica to produce the commonly observed array of halogen-bearing phases, including lawrencite and ferropyrosmalite, within the cooling body of sulfide. Halides leaving the sulfide magma would immediately encounter aqueous fluids in their surroundings, bringing those fluids to supersaturation in more common halide minerals such as halite, and causing a net enrichment of Cl in the host rocks. Small volumes of aqueous fluid passing through the lawrencite-bearing sulfide rock after its final crystallization would react with some of the unstable iron chloride to produce halite and more common Fe minerals.

The observation that the alteration halo surrounding the sulfide veins at the Fraser Copper Zone is characterized by elevated Cl:Br can be understood by considering the relative partitioning behavior of Cl and Br between sulfide liquid and silicate melt. The measured value of $D_{Cl}^{sul/sil}$ is double that of $D_{Br}^{sul/sil}$, so that the Cl:Br ratio of a sulfide melt should be twice that of a coexisting silicate melt. The observed fractionation of Cl from Br in the alteration halo surrounding the Fraser Copper Zone is entirely consistent with the hypothesis that the sulfide veins are purely magmatic in origin, and that the halogen-enriched alteration-induced halo results from reaction with an orthomagmatic fluid released from a sulfide magma.

The recognition of elevated Cl/Br in an extensive alteration-induced halo surrounding the Fraser Copper Zone has led to the suggestion that this ratio be used as a geochemical indicator of proximity to hidden orebodies (Jago *et al.* 1994, Hanley & Mungall, in press). The results of the present study show that elevated Cl:Br is expected to be a hallmark of magmatic sulfide. In systems where large volumes of sulfide magma have undergone extreme fractional crystallization, such as in the footwall deposits of the Sudbury area, or in the Noril'sk camp in Russia, extensive zones of hydrothermal alteration are expected to have developed in which high total abundance of Cl and high Cl/Br reflect mixing of orthomagmatic sulfide-derived halogen-dominated fluids with local groundwaters in the host rocks.

The proposed action of an orthomagmatic fluid derived from a sulfide magma (this study, Li *et al.* 1992, Jago *et al.* 1994) does not refute the suggestions of investigators who favor a hydrothermal mechanism for the generation of many of the characteristic alteration-induced mineral assemblages at Sudbury and elsewhere. Rather, we are proposing an additional end-member to the several previously recognized fluid end-members in the Sudbury footwall. Observations by Fleet & Wu (1993) of high mobility of the PGE in sulfur- and Cl-rich dry (*i.e.*, H_2O-free) fluids are consistent with our suggestion that the sulfide-derived orthomagmatic fluid was dry, and with the observation that the PGE are preferentially concentrated in Cl-rich mineral assemblages both within and surrounding veins of massive sulfide in the footwall of the SIC (Jago *et al.* 1994).

Halogens in disseminated stratiform sulfide deposits

As was mentioned in the introduction, controversy about the relative importance of magmatic and deuteric processes in the concentration of PGE in stratiform deposits like the Merensky Reef has largely revolved around the evidence for high Cl:F and high bulk Cl concentrations at and below the stratigraphic level of the reef. The high Cl:F ratio we observe in our experimental sulfide melts is sympathetic to the trends observed in natural stratiform PGE deposits, suggesting a possible magmatic influence. However, there is a fundamental difference between the Sudbury footwall ores and the stratiform PGE sulfide deposit of the Merensky Reef that renders the Sudbury footwall model inapplicable to stratiform PGE deposits. The Sudbury footwall ores, once injected into the footwall away from the SIC, evolved in a system entirely free of silicate melt. In contrast, the Merensky reef sulfide was always in contact with an evolving interstitial silicate melt. The partitioning data described here show that the concentrations of halogens in silicate melt greatly exceed their concentrations in coexisting sulfide, so that the halogen content of sulfide melt will not exert any significant influence on the halogen budget of the whole system as long as the sulfide and silicate remain in contact. Consequently, the arguments that have been advanced by Boudreau and co-workers (Boudreau *et al.* 1986, Boudreau & Kruger 1990, Boudreau & McCallum 1992, Willmore *et al.* 2000) regarding the importance of fluid – melt – mineral equilibria in determining the halogen geochemistry of cooling intrusions are completely unaffected by our results. We therefore concur with the suggestion that hydrothermal transport of the halogens and PGE in the partially molten piles of cumulates in large intrusions is likely to be an important control on the final disposition of the PGE.

Halogen partitioning at high pressure

A final point concerns the significantly higher partition coefficients measured in the single experiment conducted at 1.8 GPa. Although it would be rash to place great importance on the observation of a positive dependence of D on pressure, it is intriguing to speculate that the process of core formation in the early Earth and planetesimals might have been accompanied by a significant transfer of halogens from the silicate mantle into the core. Continued increase of halogen partition coefficients as pressure increased into the 10 GPa range might lead to weakly or even strongly compatible behavior for the halogens, with the result that a large part of the halogen budget that is presently missing from the silicate Earth might reside in the core rather than having been lost owing to its volatility. If it could be shown that a significant portion of the iodine originally present in the silicate Earth might have been sequestered in the Earth's core at an early time in Earth history, then currently accepted estimates of the timing of accretion and core formation based on $^{129}I–^{129}Xe$ decay systematics (*e.g.*, Dickin 1995) would require revision. Confirmation of this suggestion must await high-pressure experiments on partitioning.

CONCLUSIONS

The halogens Cl, Br and I can dissolve in sulfide liquids at concentrations as great as 4 wt.% combined. Although these elements are preferentially incorporated in coexisting silicate melt, moderate concentrations are observed in a coexisting immiscible sulfide liquid. Fluorine appears to be entirely lithophile, being dissolved in the sulfide phase at undetectably low concentrations.

During crystallization of mss from a sulfide liquid, the halogens are retained in the residual liquid, so that protracted fractional crystallization of natural magmatic sulfides can be expected to generate Cu-, PGE- and Cl-rich anhydrous residual sulfide melts. Injection of these melts into solid silicate host-rocks containing connate waters should produce a spectrum of halide and halogen-bearing minerals and brines associated with elevated abundances of the PGE and values of the Cl:Br ratio, as is observed in the footwall-hosted Cu–PGE vein stockworks of the Sudbury Igneous Complex.

Recognition of halogen-rich halos with distinctively high Cl/Br should provide exploration geologists with a useful and inexpensive tool for the detection of hidden orebodies rich in Cu and the PGE at Sudbury and wherever highly fractionated sulfide magmas have existed.

ACKNOWLEDGEMENTS

Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada. The manuscript benefitted greatly from careful and thoughtful reviews by John Mavrogenes, Ania Peregoedova and Robert F. Martin. Special thanks are due to Jacob Hanley and Claudio Cermignani for their contributions to the analytical work.

REFERENCES

BALLHAUS, C.G. & STUMPFL, E.F. (1986): Sulfide and platinum mineralization in the Merensky Reef: evidence from hydrous silicates and fluid inclusions. *Contrib. Mineral. Petrol.* **94**, 193-204.

BARKOV, A.Y., LAAJOKI, K.V.O, GEHOR, S.A., YAKOVLEV, Y.N. & TAIKINA-AHO, O. (1997): Chlorine-poor analogues of djerfisherite–thalfenisite from Noril'sk, Siberia and Salmagorsky, Kola Peninsula, Russia. *Can. Mineral.* **35**, 1421-1430.

BOUDREAU, A.E. & KRUGER, F.J. (1990): Variation in the composition of apatite through the Merensky cyclic unit in the western Bushveld Complex. *Econ. Geol.* **85**, 737-745.

________, MATHEZ, E.A. & MCCALLUM, I.S. (1986): Halogen geochemistry of the Stillwater and Bushveld complexes: evidence for transport of the platinum-group elements by Cl-rich fluids. *J. Petrol.* **27**, 967-986.

________ & MCCALLUM, I.S. (1992): Concentration of platinum-group elements by magmatic fluids in layered intrusions. *Econ. Geol.* **87**, 1830-1848.

CAMPBELL, I.H., NALDRETT, A.J. & BARNES S.J. (1983): A model for the origin of the platinum-rich sulfide horizons in the Bushveld and Stillwater complexes. *J. Petrol.* **24**, 133-165.

DICKIN, AP. (1995): *Radiogenic Isotope Geology*. Cambridge University Press, Cambridge, U.K.

FARROW, C.E.G. & WATKINSON, D.H. (1992): Alteration and the role of fluids in Ni, Cu and platinum-group element deposition, Sudbury Igneous Complex contact area, Onaping–Levack area, Ontario. *Mineral. Petrol.* **46**, 67-83.

________ & ________ (1997): Diversity of precious-metal mineralization in footwall Cu–Ni–PGE deposits, Sudbury, Ontario: implications for hydrothermal models of formation. *Can. Mineral.* **35**, 817-839.

FLEET, M.E. & WU, T.-W. (1993): Volatile transport of platinum-group elements in sulfide–chloride assemblages at 1000°C. *Geochim. Cosmochim. Acta* **57**, 3519-3531.

FROST, B.R., MAVROGENES, J.A. & TOMKINS A.G. (2002): Partial melting of sulfide ore deposits during medium- and high-grade metamorphism. *Can. Mineral.* **40**, 1-18.

FUGE, R. & JOHNSON, C.C. (1984): Evidence for the chalcophile nature of iodine. *Chem. Geol.* **43**, 347-352.

HANLEY, J.J. (2002): *The Distribution of the Halogens in Sudbury Breccia Matrix.* M.Sc. thesis, University of Toronto, Toronto, Ontario.

JAGO, B.C., MORRISON, G.G. & LITTLE, T.L. (1994): Metal zonation patterns and microtextural and micromineralogical evidence for alkali- and halogen-rich fluids in the genesis of the Victor Deep and McCreedy East footwall copper orebodies, Sudbury Igneous Complex. *In* Proceedings of the Sudbury – Noril'sk Symposium (P.C. Lightfoot & A.J. Naldrett, eds.). *Ontario Geol. Surv., Spec. Publ.* **5**, 65-75.

KARPENKOV, A.M., RUDASHEVSKIY, N.S., & SHUMSKAYA, N.I. (1981): A natural chloride of palladium and bismuth – the phase of composition $Pd_4Bi_5Cl_3$. *Int. Geol. Rev.* **24**, 1229-1233.

KARUP-MØLLER, S. & MACKOVICKY, E. (1998): The phase system Fe–Ni–S at 900°C. *Neues Jahr. Mineral., Monatsh.*, **8**, 373-384.

KONNIKOV, E.G. (1997): Experimental studies of the melting processes in a pyrrhotine–water system. *Geol. Ore Deposits* **39**, 474-479.

KOROBEINIKOV, A.N., MITROFANOV, F.P., GEHOR, S., LAAJOKI, K., PAVLOV, V.P. & MAMONTOV, V.P. (1998): Geology and copper sulfide mineralization of the Salmagorskii ring igneous complex, Kola Peninsula, NW Russia. *J. Petrol.* **39**, 2033-2041.

LI, CHUSI, BARNES, S.-J., MAKOVICKY, E., ROSE-HANSEN, J. & MAKOVICKY, M. (1996): Partitioning of nickel, copper, iridium, rhenium, platinum, and palladium between monosulfide solid solution and sulfide liquid: effects of composition and temperature. *Geochim. Cosmochim. Acta* **60**, 1231-1238.

________, NALDRETT, A.J., COATS, C.J.A. & JOHANNESSEN, P. (1992): Platinum, palladium, gold and copper-rich stringers at the Strathcona mine, Sudbury: their enrichment by fractionation of a sulfide liquid. *Econ. Geol.* **87**, 1584-1598.

MARSHALL, D., WATKINSON, D., FARROW, C., MOLNÁR, F. & FOUILLAC, A.-M. (1999): Multiple fluid generations in the Sudbury Igneous Complex: fluid inclusion data, Ar, O, H, Rb and Sr evidence. *Chem. Geol.* **154**, 1-19.

MASON, B. (1963): *The Pallasites*. American Museum of Natural History, New York, N.Y.

MILLSTEAD, P.W. & CREAGH, D.C. (2000): The formation of silver and copper halides at Broken Hill, New South Wales, Australia. *Fourth Int. Conf. Mineralogy and Museums (Melbourne), Program and Abstracts,* 72-73 (abstr.).

MUNGALL, J.E. (2002): Empirical models relating viscosity and tracer diffusion in magmatic silicate melts. *Geochim. Cosmochim. Acta* **66**, 125-143.

NALDRETT, A.J. (1969): A portion of the system Fe–S–O between 900 and 1080°C and its application to sulfide ore magmas. *J. Petrol.* **10**, 171-201.

SAINI-EIDUKAT, B., RUDASHEVSKY, N.S. & POLOZOV, A.G. (1998): Evidence for hibbingite–kempite solid solution. *Mineral. Mag.* **62**, 251-255.

SPRINGER, G. (1989): Chlorine-bearing and other uncommon minerals in the Strathcona Deep Copper Zone, Sudbury district, Ontario. *Can. Mineral.* **27**, 311-313.

TAYLOR, L.A., MAO, H.K. & BELL, P.M. (1974): Identification of the hydrated iron oxide mineral akaganéite in Apollo 16 lunar rocks. *Geology* **2**, 429-432.

WILLMORE, C.C., BOUDREAU, A.E. & KRUGER, F.J. (2000): The halogen geochemistry of the Bushveld Complex, Republic of South Africa: implications for chalcophile element distribution in the lower and critical zones. *J. Petrol.* **41**, 1517-1539.

Received June 22, 2002, revised manuscript accepted January 25, 2003.