EVIDENCE FOR OPEN-SYSTEM BEHAVIOR IN IMMISCIBLE Fe–S–O LIQUIDS IN SILICATE MAGMAS: IMPLICATIONS FOR CONTRIBUTIONS OF METALS AND SULFUR TO ORE-FORMING FLUIDS

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ABSTRACT

Magmatic sulfides are generally accepted as forming by segregation of an immiscible sulfide liquid from a host silicate melt. Immiscible sulfides have been observed in many types of igneous rocks; however, some types of plutonic and volcanic rocks lack sulfides. We have examined a suite of samples from Mount Pinatubo (Philippines), Volcán Popocatépetl (Mexico), Satsuma–Iwojima (Japan) and Mount St. Helens, Bingham Canyon, Tintic District, and Clear Lake (U.S.A.). The samples reflect a range of crystallization histories and compositions; they range from rhyolite to basalt to trachyandesite, with $f(O_2)$ at the time of eruption ranging from below the fayalite – magnetite + quartz (FMQ) buffer to well above the nickel – nickel oxide (NNO) buffer. Textural and chemical evidence from our suite of samples indicate that sulfides initially were present, but were modified prior to complete cooling of the parent melt, giving rise to Fe-oxide globules. The globules formed through: (1) segregation of an immiscible Fe–S–O melt, and possibly, further separation of immiscible Fe–S and Fe–O liquids, and (2) undersaturation with respect to sulfide, causing removal of S from the immiscible sulfide melt. Sulfide undersaturation may have been caused by magma degassing (passively or during eruption), or magma mixing. The recognition of modified magmatic sulfides is important because, with extensive degassing, base and precious metals (*e.g.*, Cu, Au) could be stripped from a melt by a S-rich magmatic volatile phase and entrained into a magmatic-hydrothermal fluid, ultimately giving rise to porphyry-type or related mineralization. For a melt containing 0.01 modal % magmatic sulfides, efficient degassing of only 10 km³ of magma could yield enough Cu to form a giant deposit.

Keywords: magmatic sulfides, immiscible Fe–S–O melt, degassing, magma mixing, Pinatubo, Popocatépetl, Mount St. Helens, Bingham, Tintic, Satsuma–Iwojima, Clear Lake, porphyry deposit.

SOMMAIRE

On accepte en général que les sulfures magmatiques se sont formés par ségrégation d'un liquide sulfuré immiscible à partir d'un magma hôte silicaté. La présence de sulfures immiscibles a été signalée dans plusieurs types de roches ignées; toutefois, il faut aussi dire que certains types de roches plutoniques et volcaniques sont dépourvus de sulfures. Nous avons examiné une suite d'échantillons provenant du mont Pinatubo (Philippines), du volcan Popocatépetl (Mexique), Satsuma–Iwojima (Japon), du mont St. Helens et des localités Bingham Canyon, Tintic District, et Clear Lake (Etats-Unis). Les échantillons font preuve d'une variété de modes de cristallisation et de compositions; ils représentent le spectre de composition allant de rhyolite à basalte à trachyandésite, la fugacité d'oxygène $f(O_2)$ lors de l'éruption allant de conditions inférieures au tampon fayalite – magnétite + quartz (FMQ) dans certains cas à des conditions au delà du tampon nickel – oxyde de nickel (NNO). D'après les critères texturaux et géochimiques, les sulfures étaient présents à l'origine dans notre suite d'échantillons, mais ils ont été modifiés avant le refroidissement final du liquide silicaté parental, ce qui est responsable de la formation de globules d'oxyde de fer. Ces globules se sont formés (1) par ségrégation d'un liquide Fe–S–O immiscible, et peut-être, séparation éventuelle en liquides Fe–S et Fe–O immiscibles, ou (2) sous-saturation par rapport au sulfure, ce qui mena à la perte de soufre du liquide immiscible sulfuré. Cette

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sous-saturation pourrait résulter d'un dégazage du magma, soit passif ou bien au cours d'une éruption, ou bien par mélange de magmas. Il est important de reconnaître les sulfures magmatiques ainsi modifiés, parce qu'avec un tel dégazage important, les métaux de base et les métaux précieux, par exemple Cu et Au, auraient pu être éliminés du magma par une phase volatile magmatique riche en soufre, et entraînés dans un fluide magmatique-hydrothermal, pour se manifester ultimement dans une minéralisation associée à un porphyre, par exemple. Dans le cas d'un magma contenant 0.01% de sulfures magmatiques par volume, un dégazage efficace de 10 km^3 de magma seulement pourrait fournir amplement de cuivre pour former un gisement géant.

(Traduit par la Rédaction)

Mots-clés: sulfures magmatiques, liquide Fe–S–O immiscible, dégazage, mélange de magmas, Pinatubo, Popocatépetl, mont St. Helens, Bingham, Tintic, Satsuma–Iwojima, Clear Lake, gisement de type porphyre.

INTRODUCTION

Understanding the behavior of trace metals during high-level emplacement and differentiation of a magma is critical, because the availability of base and precious metals (*e.g.*, Cu, Au) for partitioning into magmatic or hydrothermal fluids and ultimately for deposition as economic bodies depends largely on the compatibility of these elements with respect to fractionating phases. Iron oxides and especially Fe sulfides are important in sequestering trace metals that otherwise might be released, for example, to a porphyry-Cu mineralizing system (*e.g.*, Keith *et al.* 1996). Results of early experiments by Naldrett (1969) and observations by Skinner & Peck (1969) indicate that magmatic sulfides are the product of segregation of an immiscible sulfide liquid from a host silicate melt. Although support for the hypothesis is not universal (*e.g.*, Fleet *et al.* 1977, Stone *et al.* 1989), the importance of immiscibility of sulfide liquids in ultramafic melts in forming Ni–Cu sulfide ores is well known. In addition, immiscible globules of sulfide are common in intrusive and extrusive mafic rocks from a variety of tectonic settings (*e.g.*, Desborough *et al.* 1968, Mathez 1976, MacLean 1977, Groves *et al.* 1986, Naldrett 1992). It is also widely recognized that an Fe-sulfide phase is commonly formed at some stage during evolution of more silicic magmas (*e.g.*, Whitney & Stormer 1983, Whitney 1984, 1988, Candela 1989, Imai 1994).

Although magmatic sulfides have been observed in many types of igneous rocks, some lack sulfides completely (*e.g.*, Stanton 1994). The question arises, are magmatic sulfides absent in a rock because the sulfides *never* were present in the magma, or because they were modified prior to complete cooling and solidification of the parent melt? In this paper, we describe Fe-oxide and associated Fe-sulfide phases in volcanic and plutonic rocks of varying composition from Clear Lake, California, Mount St. Helens, Washington, Volcán Popocatépetl, Mexico, Satsuma–Iwojima, Japan, Bingham and Tintic Districts, Utah, and Mt. Pinatubo, Philippines (Table 1, Appendix 1). We have selected young samples to screen out overprinting effects of alteration and metamorphism; all of our samples except those from Bingham and Tintic districts are younger than 1 Ma, and some

samples were collected from products of eruptions that occurred in the last century. The documented occurrences suggest that sulfide formation may be more prevalent than many recognize; in addition, they show that early-formed sulfide is highly susceptible to subsequent modification (through resorption or degassing) and therefore may not be preserved. We present textural

TABLE 1. SUMMARY OF SAMPLE LOCATIONS AND DESCRIPTIONS

Sample Location	Suite	Phases Present[1]	$f(O_2)$[2]	Temp (°C)[3]	Rock Type
Clear Lake, California, U.S.A.	Ilmenite series	Pl-Opx-Cpx-Ilm-Po-*FOG*	<FMQ?	1050	rhyolite
Mt. St. Helens, Washington, U.S.A.	I-type, moderate oxidation	Pl-Opx-Hbl-Mgt-Ilm-Ap-*FOG*	>NNO	890–930	dacite to basalt
Volcán Popocatépetl, Mexico	I-type, moderate oxidation	Pl-Opx-Cpx-(Hbl)-Ilm-(Mgt)-Po-*FOG*	>NNO	880–920[6]	dacite to andesite
Satsuma-Iwojima Japan	I-type, moderate oxidation	Pl-Opx-Cpx-Mgt-Ilm-Ap-Po-*Iss-FOG*	NNO+1[8]	952	rhyolite to dacite
Bingham District, Utah, U.S.A.	I-type, high oxidation	Hbl-Bt-Pl-Cpx-Ap-Ol-Po-*Iss-FOG*	>NNO+2[4]		trachy-andesite
Mount Pinatubo, Philippines	I-type, high oxidation	Pl-Hbl-Bt-Qtz-Mgt-Ilm-Anh-Ap-Po-*Iss-Bn-FOG*	NNO+3[7]	780 ± 10[7]	dacite
Tintic District, Utah, U.S.A.	I-type, high oxidation	Pl-Cpx-Bt-Opx-Ap-Mgt-Ilm-Po-*Iss-FOG*	>NNO+4[5]	900–920	trachy-andesite

Abbreviations: $f(O_2)$, oxygen fugacity in log units relative to FMQ (fayalite – magnetite – quartz) and NNO (nickel – nickel oxide) buffer curves. Phase symbols: Pl plagioclase, Ol olivine, Cpx clinopyroxene, Opx orthopyroxene, Hbl hornblende, Bt biotite, Mgt magnetite, Ilm ilmenite, Po pyrrhotite, *Iss* intermediate solid-solution, *FOG* Fe-oxide globule, Bn bornite, *FOG* Fe-oxide globule, Qtz quartz, Ap apatite. [1] Phase assemblages indicate strong disequilibrium conditions. [2] Conditions at the time of eruption; unpublished data of JAS, unless otherwise indicated. [3] Estimated temperature of eruption; unpublished data of JAS, unless otherwise indicated. [4] Determined by Tomlinson (1997). [5] Determined by Choon-Sik Kim (1992). [6] Determined by Athanasopoulos (1997), on products of 1996 dome eruption (likely comparable to temperature of eruption of Tutti Frutti and Pink pumice units). [7] Determined by Rutherford & Devine (1996). [8] Genji Saito, pers. commun.

and chemical evidence for the removal of S from magmatic sulfides resulting from magma mixing and incorporation of S into a magmatic volatile phase (MVP). Metals and S in the MVP may be lost through passive degassing or degassing accompanying eruption; resorption of magmatic sulfides could therefore provide a continuing supply of S for degassing in a convecting magma column (Kazahaya *et al.* 1994, Shinohara *et al.* 1995). Alternatively, S released from immiscible Fe–S–O melts may be incorporated into a magmatic-hydrothermal ore-forming fluid (Hedenquist & Lowenstern 1994), potentially giving rise to porphyry-type or related mineralization. We summarize criteria that assist in the recognition of Fe oxides formed by the removal of S.

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REVIEW OF RELEVANT LITERATURE
ON IMMISCIBLE Fe–S–O MELTS

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Nickel–copper sulfide deposits hosted by ultramafic and mafic rocks are widely accepted as resulting from segregation of an immiscible sulfide liquid (*e.g.*, Naldrett 1989, Lesher 1989). This hypothesis is not universally accepted, and there is evidence that sulfidation of host rocks during late-magmatic processes may be important (*e.g.*, Fleet *et al.* 1977, Stone *et al.* 1989, Stone & Fleet 1991). However, the importance of immiscibility in the formation of orthomagmatic sulfide deposits is widely recognized (*e.g.*, Naldrett 1981, Frost & Groves 1989). An immiscible Fe–S liquid can contain appreciable amounts of O, and in fact may contain a higher *molar* proportion of O than S at the fayalite – magnetite + quartz (FMQ) buffer (Naldrett 1969, Doyle & Naldrett 1987). Thus, the original immiscible melt may be designated Fe–S–O or Fe–O–S, depending on the relative proportions of O and S. To simplify the discussion of these compositionally variable liquids, we propose the term *immiscible Fe(–S–O) melt* or *IFM*.

Following segregation, and depending on the bulk composition, pyrrhotite and magnetite will crystallize from IFM. The modal proportions of these minerals observed in natural sulfide ores is problematic, because the $f(O_2)$ of most mafic magmas is near, and above, the FMQ buffer (Sato & Wright 1965, Fudali 1965, Mathez 1984); an immiscible liquid in equilibrium with such a melt will fall into the stability field of magnetite (Naldrett 1969), and magnetite will crystallize first. However, solidification products of some IFM seem to contain only pyrrhotite; Naldrett (1989) proposed that the presence of Cu and Ni in the sulfide melts lowers their O contents, so that their bulk compositions fall closer to the pyrrhotite than to the magnetite field.

In the formation of Fe-oxide globules, the initial stage involves segregation of IFM from a silicate liquid. The final product(s) of solidification will depend on the initial proportions of S and O. IFM with a very high S:(S+O) ratio (approaching 1) would form monosulfide solid-solution (*Mss*), and later, with fractionation, intermediate solid-solution (*Iss*) if Cu is present; these would ultimately crystallize as pyrrhotite and chalcopyrite. IFM with an intermediate molar S:(S+O) ratio (>0.5) would crystallize *Mss* first, then magnetite. IFM with a low S:(S+O) ratio (<0.5) would crystallize magnetite first, then *Mss*. In melts with higher $f(O_2)$ [*i.e.*, very low S:(S+O) ratio], sulfate becomes dominant, and anhydrite is the stable S-bearing species. The magnetite that crystallizes from IFM is distinct from titaniferous magnetite phenocrysts formed by normal fractional crystallization directly from a melt. Andersen *et al.* (1998) observed that magnetite associated with sulfides in the Skaergard intrusion is Ti-poor, unlike cumulus magnetite.

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METHODOLOGY

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The rocks in our suite of samples cover a range of compositions and crystallization histories (see Table 1 and Appendix 1); most are andesitic to rhyolitic calc-alkaline rocks. Host-rock types include rhyolite, dacite, andesite, basalt, and trachyandesite of calc-alkaline affinities. The phases listed in Table 1 do not represent equilibrium assemblages; in all suites except that from Mount St. Helens, mineral assemblages and textures indicate that mixing between silicic and mafic magmas occurred (Stimac 1991, Hattori 1993, Athanasopoulos *et al.* 1996, Kress 1997, Keith *et al.* 1997).

At the University of Manitoba, analyses were carried out using a Cambridge Instruments Stereoscan 120 scanning electron microscope (SEM) equipped with a KEVEX 7000 energy-dispersion X-ray spectrometer (EDS). Back-scattered-electron (BSE) images were processed and stored using a Kontron IBAS image-analysis system. Energy-dispersion X-ray spectra were acquired with long count-times (up to 300 seconds) to identify minor elements for the selection of appropriate standards and design of programs for electron-microprobe (EMP) analyses.

Electron-microprobe analyses were done using a Cameca SX–50 electron microprobe (also at the University of Manitoba) equipped with three wavelength-dispersion X-ray spectrometers (WDS) and one EDS spectrometer. Beam diameter was 1 μm, current was 20 nA, and accelerating voltage was 15 eV. On the basis of peaks present in the EDS spectra, EMP analyses were acquired using three programs. Program 1 for sulfides determined the following elements (standards in parentheses): Fe (pyrite), Cu (chalcopyrite), Ni (pentlandite), Co (cobaltite), and S (pyrite); results are summarized in Table 2. Program 2 for spinels determined SiO_2 (diopside), TiO_2 (ilmenite), Al_2O_3 (spinel), Cr_2O_3 (chromite), FeO (magnetite), MnO (spessartine), MgO (spinel), ZnO (gahnite), and V_2O_3 (vanadium metal); results are summarized in Table 3. Program 3 for Fe-oxide globules determined FeO (magnetite), TiO_2 (ilmenite), Al_2O_3 (spinel), SiO_2 (diopside), Cr_2O_3 (chromite), CuO (chalcopyrite), NiO (pentlandite), CoO (cobaltite), and SO_3 (pyrite); results are summarized in Table 4. Mag-

netite standards were analyzed using both the spinel program (Table 3) and IFM program (Table 4).

The concentrations of invisible Au in sulfide and Fe-oxide globules were determined using a Cameca ims-4f ion microprobe in the Materials Technology Laboratory at the Canada Centre for Mineral and Energy Technology (CANMET) in Ottawa, Ontario. The primary beam consisted of positive Cs ions; negative secondary ions were counted. A mass interference with $^{133}Cs^{32}S_2$ was reduced by operating in high-mass-resolution mode. Minimum detection-limits of 10 ppb were obtained. External standards implanted with ^{197}Au were used to quantify the results. Larocque & Cabri (1998) provided details of data reduction.

TEXTURAL AND CHEMICAL CHARACTERISTICS OF FE-OXIDE GLOBULES

Fe-oxide globules (Figs. 1, 2) occur in igneous rocks from diverse locations and of diverse compositions and cooling histories (Table 1); however, their documentation has been rare (Keith *et al.* 1991, 1997, 1998, Cannan 1993, Hook 1995, Stimac & Hickmott 1996, Larocque *et al.* 1998). The lack of recognition of Fe-oxide globules as something genetically distinct from either magmatic Fe-oxide phenocrysts or primary magnetite that has crystallized from IFM is attributable in part to the variability in associated minerals such as sulfides (causing them to be dismissed as products of
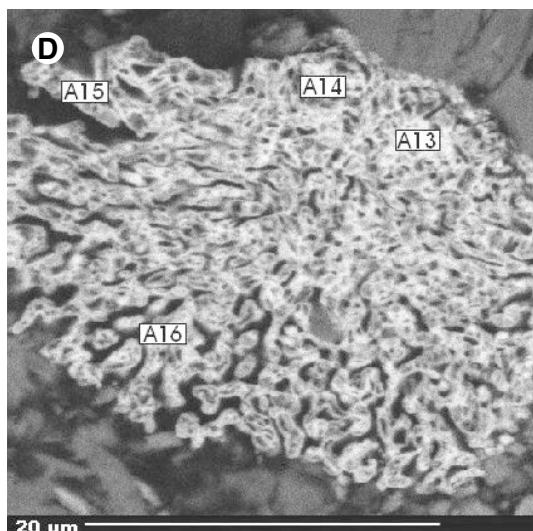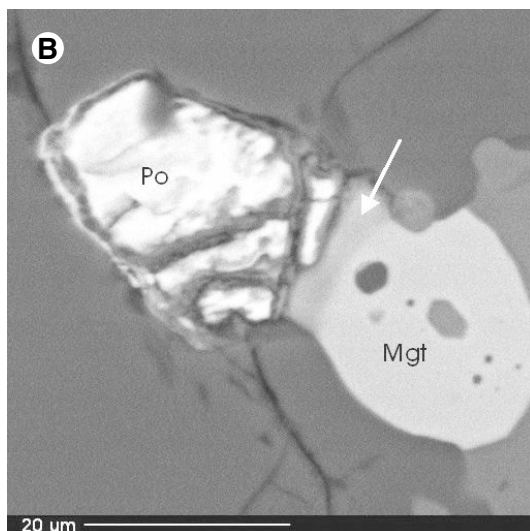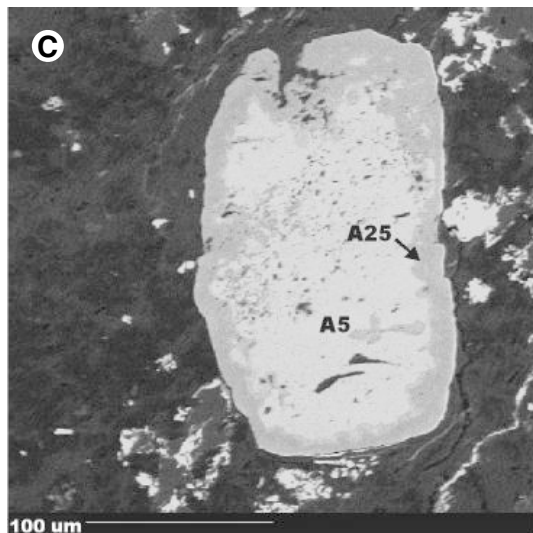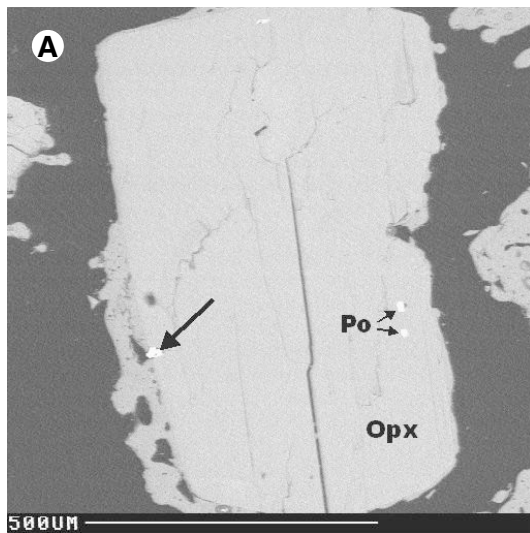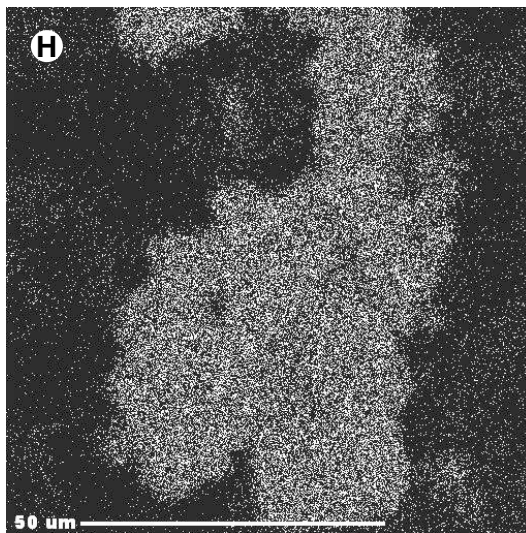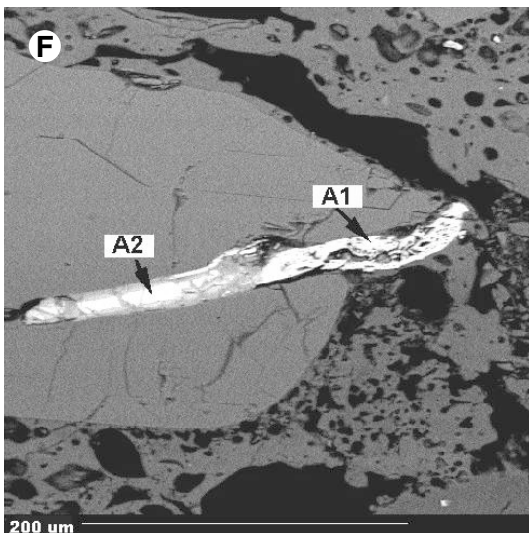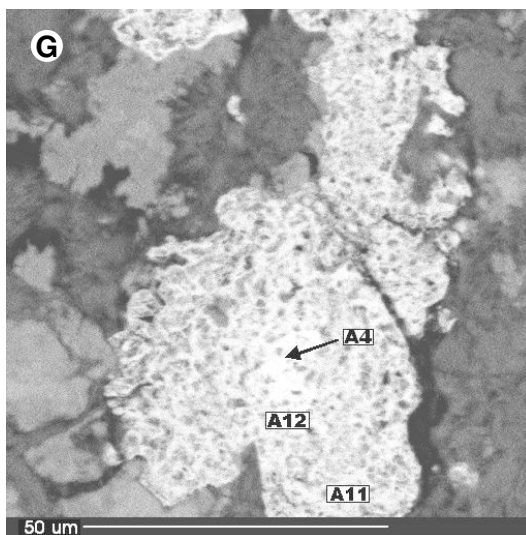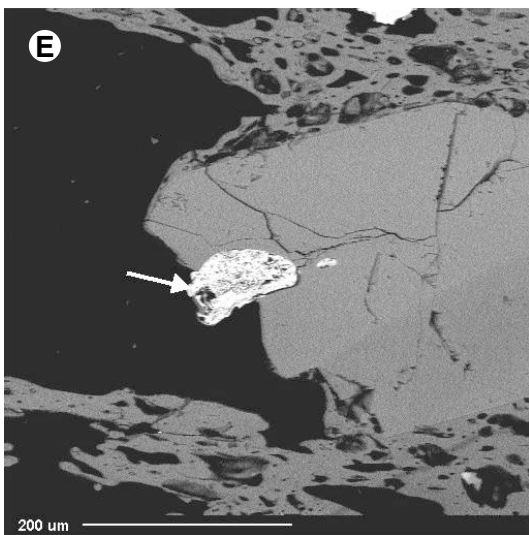
postmagmatic oxidation of sulfides), as well as the wide variety of textures exhibited by the globules. The wide range in compositions of Fe–Ti oxide phenocrysts in igneous rocks (Frost & Lindsley 1991) also complicates the situation.

Figures 1 and 2 show SEM images and photomicrographs, respectively, of globules consisting of Fe oxide and Fe sulfide. In our suite of samples, Fe oxides occur in isolation as well as intergrown with magmatic sulfides. The oxides are generally globular in shape; however, they range from spherical to irregular globules. There is a continuum in texture and composition between the globules and magmatic sulfides coexisting in the same polished section. Simple Fe-sulfide globules

typically consisting of pyrrhotite are included within mafic phenocrysts (Fig. 1A; see also Larocque *et al.* 1998, Fig. 3A). Minor chalcopyrite, bornite, or Cu-rich zones occur as a rim on pyrrhotite in some globules (Fig. 2A). In many samples, sulfides are intergrown with magnetite (Figs. 1B, 2B). The intergrowths may consist of distinct, coarse grains (Fig. 2B) or a fine-grained mixture of sulfide and oxide (Fig. 2C).

In addition to simple examples, many globules in our samples are texturally and compositionally variable. Some globules have a massive core of sulfide rimmed by Fe oxide (Fig. 1C). The boundary between the sulfide core and oxide rim is less distinct than those observed in sulfides that have undergone obvious post-emplace-

ment oxidation along cleavage planes or fractures, caused by interaction with meteoric fluids (see Larocque *et al.* 1998, Fig. 3C). Other globules are composed entirely of Fe oxide with a frothy texture, much like vesicular glass (Fig. 1D). These globules occur surrounded by volcanic glass, or on the margins of mafic phenocrysts, especially broken or resorbed ones (Figs. 1A, E). The globules generally yield a poor polish, which also may have played a role in the rarity of their documentation. Some of the frothy globules are composed of

submicrometric intergrowths of Fe oxides (Fig. 2D), likely magnetite and hematite (on the basis of reflectance and bulk composition). Between these two end-members are globules showing internal gradations between Fe sulfide and Fe oxide. Where in contact with groundmass glass along the margins of resorbed phenocrysts, Fe sulfide in the interior of the phenocryst grades out into porous Fe oxide at the grain margin (Fig. 1F). Where surrounded by groundmass glass, frothy globules consisting of Fe oxide grade into a core
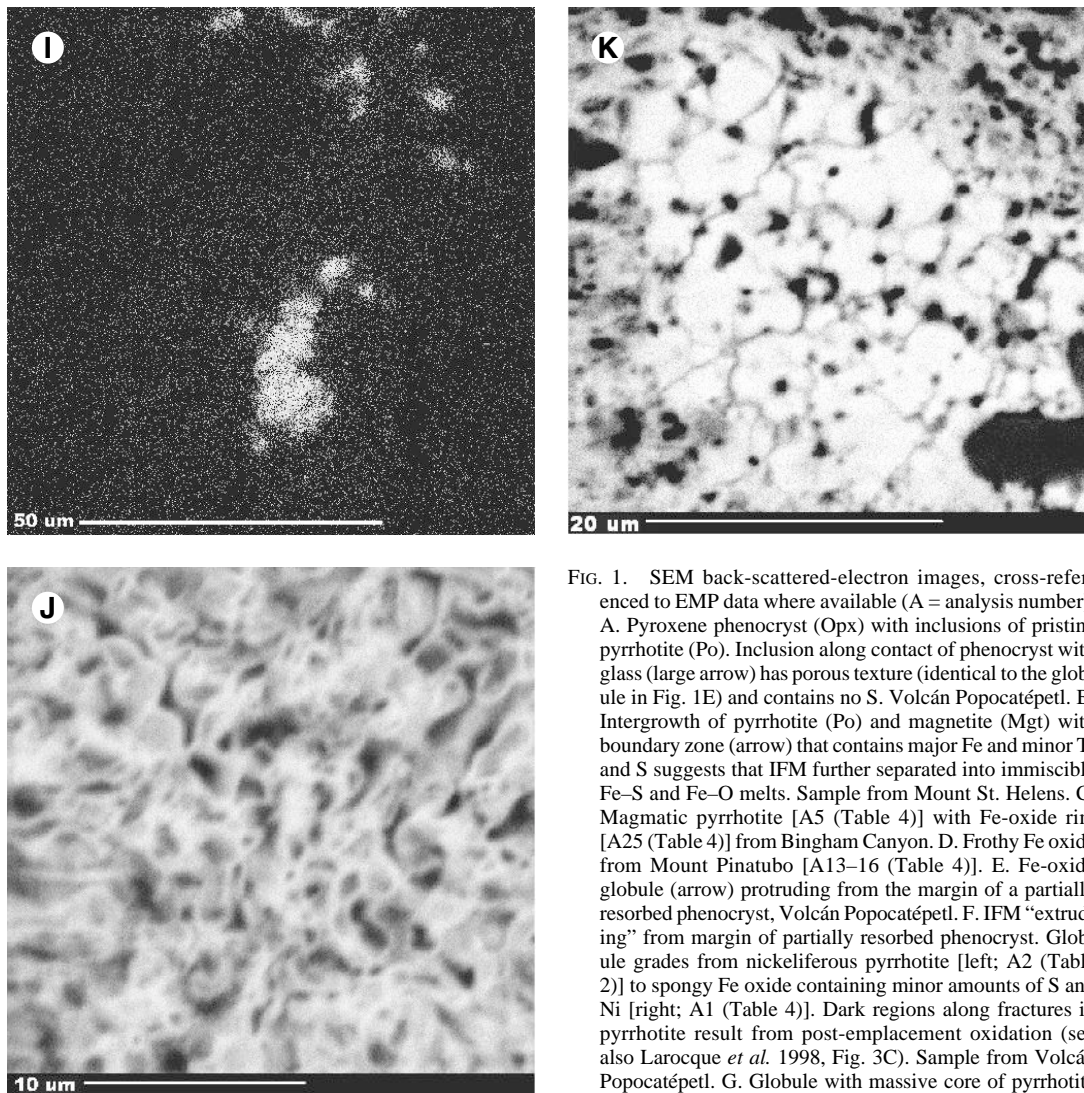

FIG. 1. SEM back-scattered-electron images, cross-referenced to EMP data where available (A = analysis number). A. Pyroxene phenocryst (Opx) with inclusions of pristine pyrrhotite (Po). Inclusion along contact of phenocryst with glass (large arrow) has porous texture (identical to the globule in Fig. 1E) and contains no S. Volcán Popocatépetl. B. Intergrowth of pyrrhotite (Po) and magnetite (Mgt) with boundary zone (arrow) that contains major Fe and minor Ti and S suggests that IFM further separated into immiscible Fe–S and Fe–O melts. Sample from Mount St. Helens. C. Magmatic pyrrhotite [A5 (Table 4)] with Fe-oxide rim [A25 (Table 4)] from Bingham Canyon. D. Frothy Fe oxide from Mount Pinatubo [A13–16 (Table 4)]. E. Fe-oxide globule (arrow) protruding from the margin of a partially resorbed phenocryst, Volcán Popocatépetl. F. IFM "extruding" from margin of partially resorbed phenocryst. Globule grades from nickeliferous pyrrhotite [left; A2 (Table 2)] to spongy Fe oxide containing minor amounts of S and Ni [right; A1 (Table 4)]. Dark regions along fractures in pyrrhotite result from post-emplacement oxidation (see also Larocque *et al.* 1998, Fig. 3C). Sample from Volcán Popocatépetl. G. Globule with massive core of pyrrhotite [A4 (Table 2)] grading out into frothy Fe oxide, from Mount Pinatubo [A11–12 (Table 4)]. H. SEM X-ray map showing distribution of Fe in (G). I. SEM X-ray map showing distribution of S in (G). J. Close-up of frothy Fe oxide in (G). K. Close-up of sulfide core in (G).

of Fe sulfide (Figs. 1G–K). Figure 1A shows a pyroxene phenocryst with inclusions of magmatic pyrrhotite in the interior of the grain, and a spongy Fe-oxide globule along its contact with the groundmass. In our suite of samples, most sections that contain Fe-oxide globules surrounded by glass also have mafic phenocrysts containing globular inclusions of pyrrhotite. Typically, the Fe-oxide globules have a similar modal abundance to, but are larger in diameter than, sulfides or oxides present in the same sample (Fig. 2E).

Tables 2, 3, and 4 summarize EMP data for Fe sulfides, Fe–Ti oxide phenocrysts, and Fe-oxide globules, respectively. The analytical total for some pyrrhotite samples (*e.g.*, those from Bingham and Tintic) is low, whereas in others it is more typical (Table 2). Concentrations of Ni in pyrrhotite range from below detection to 4.6 wt.%. Concentrations of Cu in pyrrhotite also range from below detection to 4.6 wt.% (Table 2). Typical compositions of titaniferous magnetite phenocrysts (Table 3) from the sample suite are included to highlight their differences from Fe-oxide globules (Table 4). Magnetite standards were analyzed using the EMP programs for both spinels and Fe-oxide globules.

Analytical totals for EMP analyses of Fe-oxide globules as well as S-rich cores in the globules are low, with most ranging from 72 to 91 wt.% (Table 4; see also Stimac & Hickmott 1996). The low totals are due, in part, to the porous nature of the globules, and difficulty in obtaining a good polish on the surface. Because of the frothy texture of the Fe oxide, the original void space is now partially filled by glass. To compensate for the fine intergrowth between Fe oxide and glass, we included SiO_2 and Al_2O_3 in the EMP program for Fe-oxide globules. The SiO_2 contents in the globules are

significant, ranging up to 8.1 wt.%; however, they are not sufficiently high to explain the low totals, even though not all glass-derived elements were included in the EMP program. One obvious problem, likely due to the difficulty in polishing the samples, is the high Al_2O_3 content (higher than SiO_2) in samples from Mount St. Helens; we attribute this to the presence of polishing compound (alumina).

Whereas the factors described above may have played a role, the main reason for low EMP totals for Fe-oxide globules relates to assumptions about valence

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES
OF MAGNETITE[1]

Anal. #	Location	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	Fe$_2$O$_3$	MnO	MgO	ZnO	V$_2$O$_5$	Total
1	Pinatubo	0.8	1.0	0.2	28.3	66.2	1.2	0.4	0.1	0.3	98.5
2	Pinatubo	3.6	2.0	0.1	25.0	64.4	1.1	1.6	0.3	0.0	98.1
3	Popocatépetl*	10.9	1.3	0.4	38.5	44.3	0.6	2.4	0.1	0.9	99.4
4	Popocatépetl*	10.5	1.3	0.4	38.2	46.2	0.5	2.5	0.1	0.9	100.5
5	Popocatépetl*	10.3	1.3	0.4	37.9	46.4	0.5	2.5	0.2	1.0	100.5
6	Popocatépetl*	12.7	1.5	0.2	40.4	41.1	0.5	2.0	0.1	0.7	99.2
.	Standard	0.0	0.1	0.3	29.9	68.1	0.1	0.0	0.1	0.5	99.1
	Standard	0.0	0.1	0.2	30.1	68.1	0.2	0.0	0.1	0.5	99.3

[1] all data in weight per cent. * Data from Athanasopoulos (1997).

TABLE 4. RESULTS OF ELECTRON-MICROPROBE ANALYSES
OF Fe-OXIDE GLOBULES*

Anal. #	Location	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO	SO$_3$	CoO	NiO	CuO	Total
1	Popocatépetl	5.8	0.0	0.0	0.0	62.0	4.9	0.0	4.5	0.0	71.4
2	Popocatépetl	1.2	0.0	0.5	0.0	85.7	0.1	0.2	0.4	0.0	86.8
3	Popocatépetl	4.5	0.2	2.8	0.0	75.9	0.1	0.1	0.3	0.1	79.2
4	Popocatépetl	0.4	0.0	0.2	0.0	81.7	0.2	0.2	2.5	0.2	84.9
5	Popocatépetl	1.0	0.2	0.5	0.0	86.1	0.1	0.2	0.6	0.0	87.5
6	Popocatépetl	0.6	0.0	0.3	0.0	87.1	0.0	0.0	0.2	0.1	87.8
7	Popocatépetl	0.3	0.0	0.1	0.0	89.9	0.0	0.1	0.4	0.0	90.4
8	Popocatépetl	1.1	0.0	0.3	0.0	79.9	0.0	0.3	2.3	0.2	83.1
9	Popocatépetl	0.5	0.0	0.2	0.0	84.7	0.1	0.4	2.7	0.4	88.4
10	Popocatépetl	0.1	0.0	0.3	0.0	77.0	0.7	0.7	7.6	0.3	86.5
11	Pinatubo	1.1	0.1	0.3	0.0	84.1	0.3	0.2	0.1	0.1	85.1
12	Pinatubo	1.3	0.1	0.4	0.1	83.6	2.1	0.2	0.1	0.0	86.5
13	Pinatubo	0.2	0.0	0.1	0.0	80.9	0.1	0.1	0.1	0.0	81.4
14	Pinatubo	0.2	0.0	0.1	0.0	82.1	0.1	0.1	0.0	0.1	82.6
15	Pinatubo	0.3	0.0	0.1	0.0	76.7	0.1	0.0	0.0	0.0	77.0
16	Pinatubo	0.2	0.0	0.1	0.0	77.1	0.1	0.1	0.1	0.0	77.5
17	Pinatubo	0.2	0.1	0.1	0.0	90.3	0.2	0.1	0.1	0.1	91.0
18	Pinatubo	7.3	0.0	0.2	0.0	64.9	12.7	0.1	0.3	0.3	78.5
19	Pinatubo	0.1	1.9	2.1	0.0	83.8	0.0	0.0	0.0	0.2	86.2
20	Tintic	11.0	0.2	2.7	0.0	74.9	0.1	0.1	0.0	0.5	78.2
21	Tintic	0.1	0.0	0.1	0.0	88.1	0.0	0.1	0.2	0.0	88.5
22	Bingham	2.1	0.0	0.0	0.0	72.2	1.1	0.3	0.4	0.1	74.1
23	Bingham	3.2	0.0	0.7	0.0	67.1	1.1	0.0	0.0	0.2	69.1
24	Bingham	3.7	1.6	0.3	0.0	67.3	0.8	0.1	0.0	0.0	68.5
25	Mt. St. Helens	6.9	0.2	4.1	0.0	58.0	10.1	0.1	0.1	2.3	74.6
26	Mt. St. Helens	0.8	0.1	4.5	0.0	65.0	8.2	0.1	0.0	0.3	78.1
	Mgt Standard	0.0	0.0	0.1	0.3	92.7	0.0	0.0	0.1	0.0	93.3
	Mgt Standard	0.0	0.0	0.1	0.3	93.0	0.0	0.0	0.0	0.0	93.4
	Mgt Standard	0.0	0.0	0.1	0.3	93.7	0.0	0.1	0.0	0.0	94.3

* all data in weight per cent.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES
OF SULFIDES[1]

Anal. #	Location	Mineral	S	Fe	Co	Ni	Cu	Total
1	Popocatépetl	Po	36.8	49.3	0.2	3.9	4.6	94.8
2	Popocatépetl	Po	38.0	53.8	0.1	4.6	0.0	96.5
3	Popocatépetl	Po	38.7	54.4	0.0	4.6	0.0	97.7
4	Pinatubo	Po	33.6	66.7	0.2	0.7	1.0	102.2
5	Bingham	Py	45.3	50.7	0.0	0.1	0.1	96.3
6	Bingham	Py	45.0	51.1	0.1	0.0	0.0	96.3
7	Bingham*	Po	38.9	54.9	0.2	1.6	0.0	95.6
8	Bingham*	Po	39.0	57.2	0.1	0.2	0.0	96.4
9	Bingham*	Po	38.5	55.1	0.1	1.8	0.0	95.6
10	Bingham*	Po	38.6	56.2	0.1	0.6	0.0	95.7
11	Tintic*	Po	37.8	55.7	0.1	0.0	0.0	93.6
12	Tintic*	Po	37.4	57.4	0.3	0.3	0.0	95.4
13	Tintic*	Po	37.4	56.3	0.1	0.2	0.2	94.2
14	Tintic*	Po	37.5	56.0	0.1	0.4	0.2	94.2
15	Mount St. Helens	Po	34.1	67.1	0.2	0.6	0.3	102.2
16	Mount St. Helens	Po	32.0	68.5	0.2	0.7	0.4	101.8
17	Mount St. Helens	Po	33.3	67.3	0.2	0.7	0.3	101.8
	Standard	Py	46.2	53.2	0.0	0.0	0.1	99.6
	Standard	Py	45.9	54.1	0.0	0.0	0.0	100.1

[1] all data in weight per cent. Symbols: Po: pyrrhotite, Py: pyrite.
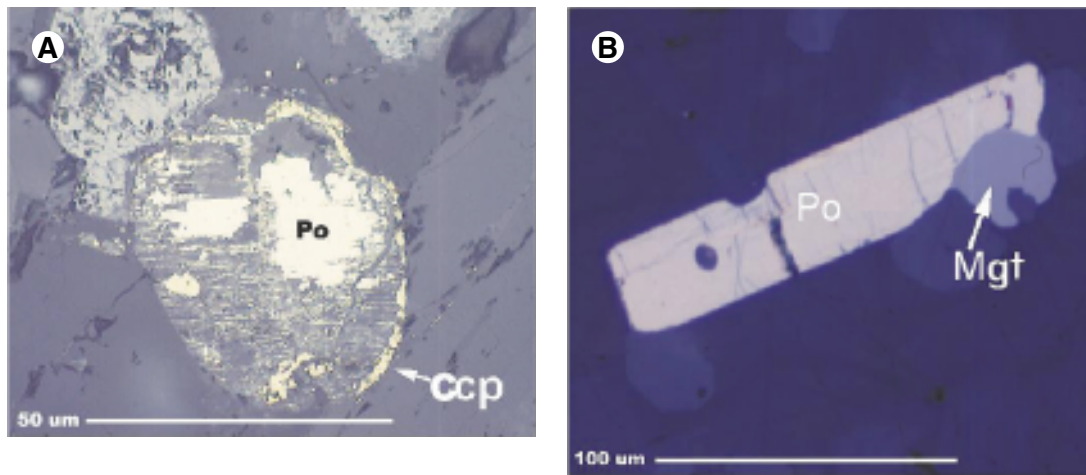* data from Hook (1995, Appendix) and Cannan (1993, Tables 18 and 20).

Fig. 2.   Photomicrographs in reflected light. A. Desulfurized sulfide bleb with core of pyrrhotite (Po) surrounded by Fe oxide and rimmed by chalcopyrite (Ccp). Tintic District, Utah. B. Blade of pyrrhotite (Po) intergrown with magnetite (Mgt). Satsuma–Iwojima. C. Crystallized IFM consisting of complex intergrowth of Fe sulfide and Fe oxide, from Clear Lake. D. Fine-grained intergrowth of Fe oxides (likely hematite and magnetite) with distinct reflectances. E. Spongy Fe-oxide globule (top right) and magnetite phenocrysts (center and left), from Satsuma–Iwojima.

state. Although the globules contain a mixture of Fe^{2+} and Fe^{3+}, all Fe was designated as FeO in the EMP program. Because of the highly variable compositions of the globules, it was not possible to partition Fe between Fe^{2+} and Fe^{3+} with any confidence, as is done for spinels. Some Fe-oxide globules contain appreciable amounts of S (up to 36 wt.% as SO_3); in others, it is below detection. However, S-free globules may be distinguished from coexisting magnetite by their generally lower TiO_2 contents (less than 2 wt.%) and highly variable FeO contents (48 to 86 wt.%). In addition, most globules contain detectable NiO and CuO. Globules in samples from Popocatépetl have NiO contents ranging up to 7.6 wt.%; the highest concentrations exceed those of Ni in some coexisting sulfides. Globules from Mount St. Helens contain up to 2.3 wt.% CuO, whereas coexisting sulfides contain 0.3 to 2.0 wt.% Cu. In contrast, Cu and Ni were not detected in magnetite in any samples by EMP.

Ion-microprobe analysis using external implanted standards requires rastering of the primary beam over an area, and counting of secondary ions from the center of that area (Larocque & Cabri 1998). As a result, ion-microprobe quantification of invisible Au in magmatic sulfides and Fe-oxide globules is difficult; the sulfide domains typically have a small diameter, the Fe oxides can be irregular in shape, and the rastered areas typically measure 50–500 μm on a side. However, we were able to analyze some Fe-oxide globules from Satsuma–Iwojima (Fig. 2E); they contain up to 200 ppb Au; the depth-profiling capability of the ion microprobe clearly indicated that Au is distributed homogeneously through-

out the grains and is not present in metallic Au or sulfide inclusions. Preliminary analyses of magmatic sulfides from Bingham (using a 50-μm raster) indicate that they contain between 50 and 60 ppb Au.

FORMATION OF SPONGY FE OXIDES BY
DEGASSING OF IFM

Keith *et al.* (1991) and Cannan (1993) were the first to describe "spongy" Fe oxides that were interpreted as oxidized sulfide globules in latites from the East Tintic Mountains in Utah. They documented vitrophyres with magmatic sulfides consisting mainly of pyrrhotite and chalcopyrite. Sulfide grains in the groundmass or sulfide inclusions that are not completely isolated within host phenocrysts exhibit textures and compositional changes attributed to degassing and oxidation. The blebs retain the globular shape of the parental sulfide melt, but now consist of remnant pyrrhotite in a residual matrix of Fe oxide and pyrite. Segregations of chalcopyrite typically are preserved in the globules. Cannan (1993) reported low totals (less than 99 wt.%, and usually less than 95 wt.%) for electron-microprobe (EMP) analyses of magmatic sulfides, and explained these as an expression of O.

Stimac & Hickmott (1996) described porous, globular Fe-oxides in intermediate-to-silicic volcanic rocks from Satsuma–Iwojima and the Bishop Tuff. The globules typically are included within Fe–Ti oxides, Fe–Cu sulfides, and mafic silicates; however, single globules also were observed in pristine, non-hydrated glass. They reported low totals (between 84 and 88 wt.%, assuming
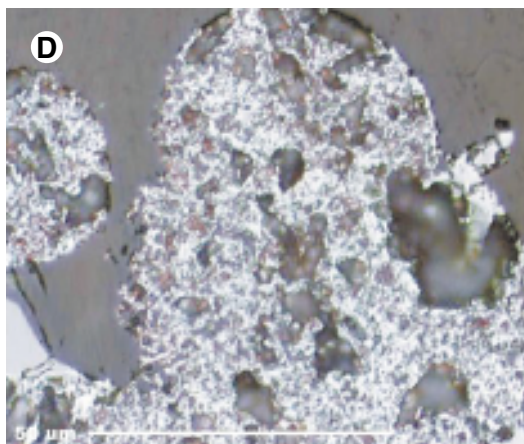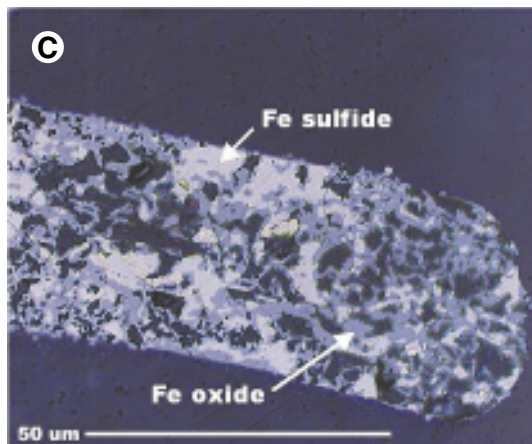
all Fe as FeO) in EMP analysis of globules; Si, Al, Cu, Ni, and S were detected as minor constituents by EMP, and trace abundances of Cu, Zn, Ga, As, Sr, Nb, Mo, and Pb were detected by proton-induced X-ray emission (PIXE) analysis.

Stimac & Hickmott (1996) proposed three possible origins for the formation of Fe–O(–S) globules in volcanic rocks: (1) oxidation of an Fe–S(–O) melt, (2) separation of an Fe-oxide liquid from a silicate melt, and (3) separation of an Fe–O(–S) melt from an existing immiscible Fe–S(–O) melt. In fact, all three of these processes may be involved in producing the variety of textures and compositions observed in Fe-oxide globules. In addition, we propose that destabilization of sulfide and removal of S from IFM can explain the textural and compositional characteristics of Fe-oxide globules in many of our samples.

If globules form exclusively by oxidation of an Fe–S(–O) melt (*e.g.*, Candela 1989), then they should be similar in size, shape, and occurrence to one another, and most abundant in magmas with high $f(O_2)$. However, globules in rocks from Satsuma–Iwojima attain much larger sizes (up to several hundred μm) than coexisting magmatic sulfides (<50 μm) and magnetite phenocrysts (Fig. 2D). Moreover, Fe-oxide globules are present in magmas with $f(O_2)$ ranging from below the FMQ buffer to well above the NNO buffer at the time of eruption (Table 1). Wallace & Carmichael (1994) determined that in lavas with $f(O_2)$ ranging from NNO–1 to NNO+2, the dominant form of dissolved S is S^{2-}. Thus, oxidation of IFM alone is an unlikely mechanism for the formation of Fe-oxide globules in most of our samples, although it may play a role in some of the systems at very high $f(O_2)$.

The immiscibility of Fe–S(–O) liquids in silicate melts is well known (*e.g.*, Naldrett 1981). However, Fe–O liquids also may demonstrate immiscibility with respect to silicate melts (*e.g.*, Gibbon & Tuttle 1967,
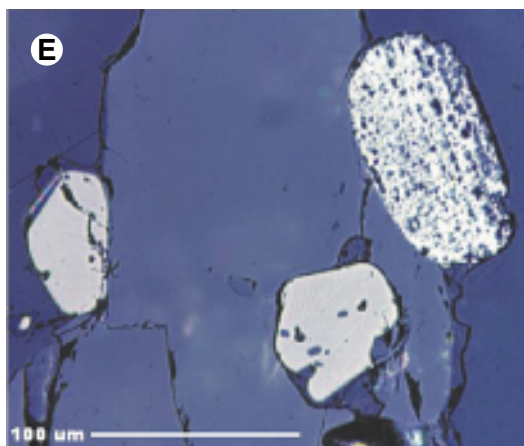
Philpotts 1967), giving rise, for example, to magnetite-rich flows associated with andesite and rhyodacite in Chile (Henriquez & Martin 1978). Separation of an immiscible Fe–O liquid from a silicate melt alone cannot account for the textural characteristics of Fe-oxide globules, and the fact that many contain a core of Fe sulfide. However, we have observed evidence for separation of an immiscible Fe–S–O liquid into immiscible Fe–O(–S) and Fe–S(–O) melts, with pyrrhotite crystallizing from the former and magnetite from the latter. Evidence for this "second segregation" can be seen in Figure 1A, where a diffusional boundary exists between pyrrhotite and magnetite. Similarly, Desborough *et al.* (1968) proposed that *Mss*, a Cu–Fe sulfide similar to cubanite, and Ti-free magnetite unmixed from an immiscible liquid phase in basaltic magma in Hawaii. Ripley *et al.* (1998) documented evidence for immiscibility of sulfide and Fe–Ti–P-rich fluids. However, the separation of an Fe–O(–S) melt from an Fe–S(–O) melt cannot explain all of the textural and chemical characteristics of globules in our suite of samples. In addition to evidence for a "second segregation", there is strong

evidence for the removal of S from IFM; this could only have occurred as a result of undersaturation of sulfide in the parent magma.

Sulfide solubility in silicate melts is a function of temperature, FeO content of the melt, $f(O_2)$, and $f(S_2)$ (*e.g.*, Haughton *et al.* 1974, Wendlandt 1982, Carroll & Rutherford 1985, Wallace & Carmichael 1992). Thus, in a sulfide-saturated melt, sulfide undersaturation can be brought about by the appropriate change in any of these parameters, or a shift in chemical equilibrium such as those brought about by fractional crystallization or magma mixing (*e.g.*, Keith *et al.* 1996, 1997, Stimac & Hickmott 1996). It has been proposed that an immiscible Fe–S–O liquid can behave as an O reservoir that strives to maintain chemical equilibrium with the surrounding silicate melt, and the dissolved-oxygen content of the immiscible liquid changes in response to changing redox ratios in the silicate melt (Carmichael & Ghiorso 1986, 1990). Similarly, IFM may represent a S reservoir that might incorporate or liberate S in response to changing conditions in the system. Stone & Fleet (1991) proposed that sulfide globules that exhibit disequilibrium compositions relative to their host magmas and minerals formed by sulfidation of earlier-formed magmatic sulfides during quenching and cooling of eruption pumice and lava at Kilauea Volcano. Saturation of S resulting from quenching of erupted lava may have caused expulsion of S-rich gas from quenched glass (Moore & Fabbi 1971, Stone *et al.* 1989). If the boundary between silicate melt and sulfide liquid is open to inward diffusion of O and S, and outward diffusion of O, surely it follows that IFM may release S in order to restore equilibrium when the concentration of S in the magma has been lowered. Two obvious mechanisms for a decrease in S content are (1) degassing, either passively or during eruption, and (2) mixing of a S-rich or sulfide-saturated magma with one that is S-poor or sulfide-undersaturated. However, any process that decreases the concentration of dissolved S in a melt could destabilize IFM.

As previously stated, all samples except those from Mount St. Helens show evidence of magma mixing. Injection of mafic melts into felsic magma chambers is strongly suspected to have triggered eruptions at Pinatubo (Hattori 1993, Pallister *et al.* 1996, Kress 1997), Popocatépetl (*e.g.*, Kolisnik 1990, Athanasopoulos *et al.* 1996), Clear Lake (Stimac 1991), and Satsuma–Iwojima (*e.g.*, Saito *et al.* 2000), and also appears to have been important at Bingham at the time of ore formation (Keith *et al.* 1997, Waite *et al.* 1997). The relative proportion of end-member magmas that underwent mixing to produce the hybrid rocks preserved in our suite of samples varies. However, mingling of the appropriate amounts of a mafic, sulfide-saturated magma and a more felsic, sulfide-undersaturated melt could give rise to a hybrid melt in which sulfide would be destabilized. The specific changes in the hybrid melt (relative to the mafic melt) that would bring about sul-

fide undersaturation include: (1) a decrease in the temperature, (2) a possible increase in $f(O_2)$, resulting in oxidation of sulfide to sulfate, (3) a possible decrease in $f(S_2)$. These changes could be counteracted by a decrease in FeO content (resulting from either dilution or oxidation or both), which would tend to promote sulfide saturation. As stated by Haughton *et al.* (1974), "all of the controlling variables change during cooling and crystallization of a magma, and each or all of them may bring a magma to saturation"; they also may all change during magma mixing, and bring a melt to undersaturation. Thus the specific compositions and proportions of the end-member melts will determine the impact on sulfide solubility in the hybrid melt. However, under the right circumstances, magma mixing could cause IFM to be destabilized and S to partition back into the silicate liquid.

In addition to magma mixing, a decrease in pressure accompanying an eruption also would strongly affect sulfide saturation, as S would partition into a magmatic volatile phase (MVP). Even if eruption did not occur, high-level emplacement of a mafic melt likely would result in passive degassing. Volcanic emissions of metals and sulfur through passive degassing are well known (*e.g.*, Hedenquist & Lowenstern 1994), and the $f(S_2)$ of a melt could be lowered significantly through convection in a magmatic conduit (Kazahaya *et al.* 1994, Shinohara *et al.* 1995).

The wide variety of textures and compositions of globules can be explained as a function of the timing of S removal relative to the segregation–crystallization sequence. Magmatic sulfides that yield low totals in EMP analysis may have been quenched before the oxide component could separate (Beatrice Clemente, pers. commun., 1998). If quenching of O within sulfide is possible, then sulfides with oxide rims (Fig. 1C) may represent immiscible melts that were quenched before S could completely diffuse out. It is common for Fe oxides to occur along the contact between sulfides and silicates in igneous rocks (*e.g.*, Ewers & Hudson 1972, Woolrich *et al.* 1981, Groves *et al.* 1986), and this can be interpreted as resulting from chemical exchange between the sulfide and silicate. However, this explanation is unsatisfactory for the occurrence of a Fe-oxide rim on grains of sulfide in our samples for a number of reasons. First, in samples that also contain sulfide blebs included in phenocrysts, oxides have *not* been observed at the contact between sulfide bleb and silicate host in *any* of the samples. Furthermore, the frothy textures observed (*e.g.*, Fig. 1G) do not resemble typical oxide reaction-rims.

Frothy textures and the presence of silicate glass in some Fe-oxide globules suggest that S actually bubbled out of IFM as a vapor rather than being removed through chemical diffusion. Waite *et al.* (1997) documented evidence for S-rich vapor at Bingham; they interpreted Co-rich sulfide occurring along fractures in clinopyroxene and olivine as products of sulfidation of Fe–

Mg silicates by a S-rich vapor, as Co tends to concentrate in a vapor phase relative to a coexisting sulfide liquid (Stone *et al.* 1989). Varying S-contents between different globules and gradations in S-content within individual globules indicate that the process of S removal may be arrested, or may go to completion. Fine intergrowths of magnetite and hematite may have formed by post-crystallization re-equilibration of a metastable quenched Fe-oxide. High-temperature subsolidus processes such as degassing also may be important (*cf.*, Stone *et al.* 1989).

It is possible that mixing of a sulfide-saturated mafic melt with a more oxidized, H_2O-saturated felsic magma would result in oxidation of globular magmatic sulfides (as distinct from simple removal of S from IFM). The difficulty arises in identifying a geologically reasonable reaction for the process. Many investigators discuss oxidation–reduction reactions involving free oxygen (*e.g.*, Sack *et al.* 1980, Candela & Holland 1986); however, the abundance of free O_2 in most magmas is very low. No single, universally applicable, balanced equation for the process can be written, as the amount of O dissolved in an immiscible melt can be highly variable (Naldrett 1969, Doyle & Naldrett 1987), and thus the stoichiometry of the original immiscible melt is not constant.

The high porosity of most globules is consistent with a volume change that may have occurred during oxidation of sulfide or, more likely, because of the presence of a vapor phase. We propose that removal of S from IFM occurs according to the following unbalanced general reaction:

$$Fe–S–O_{(l)} \rightarrow Fe–O_{(l)} + S_{2(g)}\uparrow \qquad (1)$$
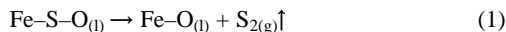
Kress (1997) proposed that mixing of sulfide-saturated basaltic magma with sulfate-saturated dacitic magma results in "purging" of S from the resulting hybrid andesitic magma because of the minimum in S solubility in dacite at the S^{2-}/SO_4^{2-} redox boundary (Carroll & Rutherford 1987, Hattori 1993). The mixing would result in destabilization of both sulfides (in the mafic end-member) and sulfates (in the felsic end-member) and degassing of both H_2S and SO_2. We believe that the presence of H_2O vapor facilitates S loss; upon bubbling out of IFM, S_2 may react with H_2O vapor exsolved from the melt as follows:

$$^3/_2S_{2(g)} + 2H_2O_{(g)} \rightarrow 2H_2S_{(g)} \uparrow + SO_{2(g)}\uparrow \qquad (2).$$
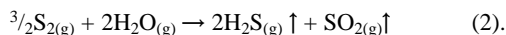
It is possible that, where it is in direct contact with the silicate melt, IFM may react directly with H_2O dissolved in the melt to produce globular Fe-oxide and gaseous H_2S and SO_2; however, it is unlikely that H_2O would diffuse appreciably from the melt into IFM. Thus, it is necessary to invoke removal of S from IFM. Thermodynamic calculations relevant to reaction (2) occurring at 1200°C indicate that for a closed system, the reaction

will not occur spontaneously (Appendix 2). However, under open-system conditions (*i.e.*, removal of H_2S and SO_2 through passive degassing, degassing accompanying eruption, or entrainment into a circulating magmatic-hydrothermal system), the reaction may proceed as written.

The preservation of sulfides in degassing magmatic systems depends on a number of factors. If sulfides become included in silicate or oxide phenocrysts, they will be unaffected by the shift in equilibrium that occurs upon degassing or eruption. Similarly, if the melt is rapidly quenched, as in the case of seafloor basalts, then volatile diffusion will be inhibited. However, if these conditions are not met, S and associated base and precious metals may be removed.

Carroll & Rutherford (1987) proposed that igneous anhydrite is an important source of S that ultimately was incorporated into a vapor phase during eruption of El Chichón volcano, Mexico, in 1982, accounting for the large volume of S-rich gases that were emitted to the atmosphere. Imai *et al.* (1993) stated that the high S content of the magma erupted by Mt. Pinatubo in 1991 was caused by inhibition of sulfide fractionation because of the high $f(O_2)$ of the magma. We propose that the anomalously high volumes of S emitted during some eruptions may be due to resorption of magmatic sulfides or their direct degassing, giving rise to an SO_2-rich vapor phase, as postulated by Wallace & Gerlach (1994). We calculated the amount of S that could be degassed from a magma if all magmatic sulfides were resorbed or directly degassed, and obtained a value of 1.56 Mt of S per km^3 (Appendix 3). This is equal to 3.12 Mt of SO_2 or 1.66 Mt of H_2S per km^3. These values are in line with some estimates of S emissions from historic eruptions. For example, Thordarson *et al.* (1993) used the "petrological method" (a comparison of the concentrations of dissolved S contained in matrix glass to that in melt inclusions) to calculate that the eruption of Laki, Iceland, in 1783–1784 degassed 135 Mt of SO_2 (for the estimated 15 km^3 of magma erupted, this translates into 9 Mt SO_2 per km^3). If immiscible sulfide globules in a hypothetical magma contained 10 wt.% Cu prior to separation of *Mss* and *Iss*, then complete degassing could yield 0.5 Mt Cu per km^3 [note that Hattori (1993) reported 30 wt.% Cu in sulfides from Mt. Pinatubo]. Efficient degassing of only 10 km^3 of magma could therefore yield enough Cu to form a giant deposit (*sensu* Clark 1996).

CRITERIA FOR DISTINGUISHING FE OXIDES OF DIFFERENT ORIGINS

In rocks where Fe-oxide globules are associated with magmatic sulfides, the origin of oxide globules may be easily deduced. However, some rocks preserve no primary sulfides, and it becomes important to develop diagnostic criteria to distinguish degassed magmatic sulfides from Fe-oxide phenocrysts in sulfide-absent rocks. The textures observed in degassed sulfides de-

pend largely on the timing of S removal relative to segregation and crystallization. However, the following textural and chemical characteristics of Fe oxides support a degassing origin for them, especially where more than one characteristic is present.

The following textural criteria are useful: 1) globular form, 2) frothy, porous, or spongy texture, typically yielding a poor polish, 3) gradation from a core with a massive appearance to a rim with a frothy or porous texture, 4) larger diameter than magmatic sulfides or unequivocal Fe–Ti oxide phenocrysts (indicating expansion), 5) similarity in distribution to magmatic sulfides, if present (*e.g.*, on margins of phenocrysts which contain sulfide inclusions), 6) occurrence of pristine sulfides included in phenocrysts, especially where sulfides are absent or modified in the groundmass, and 7) occurrence of sulfidation rims on mafic phenocrysts.

The following are useful chemical criteria: 1) absence or very low concentrations of Ti (because Ti does not partition into IFM), 2) high and variable concentrations of SiO_2 and Al_2O_3 (due to the presence of glass in original void space), 3) highly variable total-Fe contents, 4) presence of S at weight percent concentrations, 5) decrease in S content from core to rim of globule, 6) low analytical totals for EMP data on magmatic sulfides, 7) similar minor- and trace-element composition of co-existing magmatic sulfides (presence of Cu, Ni, Au), and 8) gradation in texture and composition of grains partially included in silicate phenocrysts.

IMPLICATIONS FOR ORE FORMATION AND EXPLORATION

Various investigators have discussed the role of magmatic sulfides in storing and releasing metals to the magmatic component of an ore-forming fluid (Candela 1989, Keith *et al.* 1991, 1996, Waite *et al.* 1997). Recognition of the presence of Fe oxides arising from destabilization of magmatic sulfides is important, because it indicates that many systems that may have been enriched in base and precious metals now show no evidence of those early characteristics. This possibility has critical implications for metal exploration, because some intrusive rocks that have no magmatic sulfides may actually represent source magmas for porphyry-type and related ore deposits. In our suite of samples, the connection between magmatic sulfides and Fe-oxide globules is clear because the host rocks cooled rapidly, preserving remnants of early-formed sulfide. However, because of their slow rate of cooling, some intrusive rocks that are comagmatic with volcanic rocks that do contain magmatic sulfides are themselves devoid of sulfides (Keith *et al.* 1991).

If degassing were pervasive, base and precious metals (*e.g.*, Cu, Au) could be stripped efficiently from a melt by a S-rich magmatic volatile phase, ultimately giving rise to economic, porphyry-type mineralization (Hedenquist & Lowenstern 1994). In contrast, systems that contain abundant magmatic sulfides may be less desirable targets for exploration because the S and base metals remained trapped in the melt, unavailable for partitioning into an ore-forming hydrothermal system. Borrok *et al.* (1999) speculated that compatible behavior of Cu due to segregation of immiscible sulfide liquid in intrusions in the Wasatch Mountains in Utah accounts for the paucity of porphyry-copper deposits there relative to the nearby Oquirrh Mountains. Of course, it is possible that some igneous rocks containing no magmatic sulfides *never* contained any, or that S and metals removed from immiscible sulfides might be lost to the atmosphere through eruption or passive degassing (creating an impact on climate); we would not expect these rocks to be related to mineralization. Nonetheless, for sulfide-free igneous rocks, the ability to distinguish between Fe oxides formed by normal fractional crystallization from those formed by destabilization of sulfides could potentially aid explorationists in distinguishing between promising and unpromising rock-types. Finally, given the strong evidence for mixing between hotter, mafic melts and cooler, more felsic melts in most of the samples we studied, and its apparent importance in destabilizing IFM, it seems that magma mixing may be an important process in the formation of magmatic-hydrothermal ore deposits.

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APPENDIX 1. SAMPLE LOCATIONS AND DESCRIPTIONS

Mount St. Helens, Washington

Mount St. Helens is a calc-alkaline andesitic to dacitic stratovolcano located in the southern portion of the Cascade volcanic arc and related to subduction of the Juan de Fuca plate beneath North America. Gabbroic xenoliths from the 1980–1983 dacite dome of Mount St. Helens have been described by Heliker (1995). Sample MSH12 is a gabbroic xenolith consisting of plagioclase, clinopyroxene, with accessory Fe–Ti oxides and trace amounts of olivine. Samples were collected by Jim Stimac.

Clear Lake, California

The Clear Lake volcanic suite is a compositionally diverse group of lavas and tuffs erupted from about 2.1 Ma to 0.01 Ma (Stimac 1991). The magmatism in the area is most likely related to northward migration of the Mendocino Triple Junction, and the transition from a subduction to a transform regime. Andesitic to rhyolitic rocks have calc-alkaline affinities, but show chemical, isotopic, and textural evidence for a large metasedimentary crustal component, and are volcanic analogs to ilmenite-series granites (Stimac & Hickmott 1994). The sample we studied is from the rhyolite of Thurston Creek, which contains contains about 1% phenocrysts of plagioclase, orthopyroxene, and ilmenite. Pyrrhotite is present in trace amounts as inclusions in ilmenite and orthopyroxene and as rare single grains in unhydrated glass. Chalcopyrite is present at the margins of some pyrrhotite grains (Stimac & Hickmott 1994). Samples were collected by Jim Stimac.

Bingham mining district, Utah

The Bingham mining district is located in the Oquirrh Mountains in the eastern Great Basin in Utah. Volcanic rocks that flank the eastern margin of the Bingham Canyon porphyry-Cu deposit range in composition from minette lavas to rhyolite domes (*e.g.*, Keith *et al.* 1997). Sample Bing 52 is from a latite dike, and contains phenocrysts of plagioclase, amphibole, biotite, and Fe–Ti oxides with accessory apatite, quartz, and zircon. Sulfide blebs occur in association with mafic phenocrysts as well as in the groundmass. Samples were collected by Jeff Keith.

Tintic mining district, Utah

The East Tintic volcanic field in central Utah consists of intermediate-to-silicic volcanic and shallow intrusive rocks formed by composite volcanoes and small calderas (*e.g.*, Keith *et al.* 1991, Moore 1993). Compositions range from shoshonite to trachyte, although latite

is the dominant rock-type. Sample TJ55 contains phenocrysts of plagioclase, hornblende, biotite, with lesser olivine, clinopyroxene, and Fe–Ti oxides, and minor apatite and zircon. Magmatic sulfides occur in association with mafic phenocrysts. Samples were collected by Jeff Keith.

Volcán Popocatépetl, Mexico

Volcán Popocatépetl (Popo) is located within the Trans-Mexican volcanic belt, a zone of Late Tertiary and Quaternary volcanism related to oblique subduction of the Cocos Plate beneath North America (Nixon 1982). The modern stratocone of Popo consists of numerous interlayered lava and pyroclastic deposits of andesitic to dacitic composition (Robin 1984, Kolisnik 1990). During the past 20,000 years, activity has been characterized by large Plinian eruptions that produced pumice-fall and ash-flow deposits (Macías *et al.* 1995). Samples were collected from the Tutti Frutti and Pink pumice units by Jim Stimac and Claus Siebe. The Tutti Frutti contains poorly vesiculated, moderately dense fragments of andesite pumice with phenocrysts of hornblende, pyroxene, and Fe–Ti oxides. Plagioclase rarely is present and probably is xenocrystic. Abundant sulfide inclusions are present in both mafic phenocrysts and glass, and commonly are associated with spongy Fe-oxide. The Pink pumice contains phenocrysts of plagioclase, pyroxene, and Fe–Ti oxides. It is slightly less dense than the Tutti Frutti pumice, and slightly more silicic in composition. It also contains minor olivine and Fe–Cu sulfides. The olivine phenocrysts exhibit a reaction rim consisting of pyroxene and vermicular magnetite, resulting from destabilization of olivine (see also Larocque *et al.* 1998).

Mount Pinatubo, Philippines

Mount Pinatubo is a calc-alkaline basaltic to dacitic center located in the frontal Bataan arc of the Philippines. Samples consist of highly porphyritic white pumice from the June 15–16, 1991 eruptions. The glassy dacitic pumice has phenocrysts of plagioclase, pyroxene, biotite, quartz, magnetite, and ilmenite, as well as rare olivine reacted to orthopyroxene or amphibole (Imai *et al.* 1993, Pallister *et al.* 1996). Samples were collected by Wendel Duffield and provided by Grant Heiken.

Satsuma–Iwojima, Japan

Satsuma–Iwojima, located at the southern tip of Kyushu, Japan, is a volcanic island forming part of the largely submerged Kikai caldera complex. The age of eruption and formation of the Kikai caldera is approxi-

mately 6300 years. The most abundant rock-types are rhyolitic to dacitic tuffs and lava flows, but basaltic to andesitic rocks also are present (Ono *et al.* 1982, Saito *et al.* 2000). Satsuma–Iwojima is calc-alkaline, with some rocks transitional to the tholeiitic suite. Sample F93–26 is a vitric, welded rhyolitic ash-flow tuff of the Koabi unit, with phenocrysts of plagioclase, orthopyroxene, clinopyroxene, magnetite, and ilmenite. Trace phases include apatite and pyrrhotite, and globular Fe oxides. The sample was collected by Fraser Goff.

APPENDIX 2. THERMODYNAMIC CALCULATIONS

Data for the following calculations were taken from Faure (1998, Appendix B).

Constants: $R = 1.987$ cal • deg^{-1} • mol^{-1}

For the reaction:

$$^{3}/_{2} S_{2(g)} + 2 H_2O_{(g)} \rightarrow 2 H_2S_{(g)} \uparrow + SO_{2(g)} \uparrow \quad (2)$$
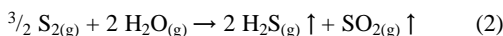
$\Delta H_R° = \Sigma n_i H°_{fi}$ (products) $- \Sigma n_i H°_{fi}$
(reactants) $\quad (3)$
$= [2 (-4.93) + (-70.94)] - [3/2 (+30.68)$
$+ 2 (-57.79)]$
$= -11.24$ kcal/mol or -47.03 kj/mol

Thus, the reaction is exothermic. The change in the Gibbs free energy in the standard state is given by:

$\Delta G_R° = \Sigma n_i G°_{fi}$ (products) $- \Sigma n_i G°_{fi}$
(reactants) $\quad (4)$
$= [2 (-8.02) + (-71.66)] - [3/2 (+18.96)$
$+ 2 (-54.636)]$
$= -6.868$ kcal/mol or -28.74 kj/mol

Also, $\Sigma G_R° = -RT\ln K \quad (5)$

Rearranging equation (5):

$$K_{To} = 10^{-(-6.868/1.364)} = 10^{5.04} \quad (6)$$

Thus, the reaction will proceed as written at STP. However, to evaluate the reaction under magmatic conditions requires solving the van't Hoff equation [equation (7)]; we assume that enthalpy of reaction does not vary with temperature between 25° and 1200°C. At 1200°C:

$\log K_T = \log K_{To} - (\Delta H_R° / 2.3025R)$
$(^{1}/_T - ^{1}/_{298.15}) \quad (7)$
$= 2.03 - (-11.24 \times 10^3 / 4.575)$
$(^{1}/_{1473.15} - ^{1}/_{298.15}) = 4.54$
$K_T = 10^{-4.54}$

Thus, at 1200°C, the reverse reaction is strongly favored.

APPENDIX 3. CALCULATION OF AMOUNT OF S DEGASSED

We used an average modal abundance for magmatic sulfides of 0.01%; however, note that sulfides range up to 0.1% in modal abundance in sample suites from Utah (Cannan 1993, Hook 1995). Assuming that the modal proportion of sulfide is equal to the volume proportion:

1 km^3 = 10^{15} cm^3
0.0001×10^{15} cm^3 = 10^{12} cm^3 sulfide/km^3 of magma

Average density of pyrrhotite = 4.6 g/cm^3, so 1 km^3 contains 10^{12} cm^3 sulfide $\times$ 4.6 g/cm^3 = 4.6×10^{12} g pyrrhotite

Using an average S content of pyrrhotite of 34 wt.%:

4.6×10^{12} g $\times$ 0.34 = 1.56×10^{12} g S/km^3 = 1.56 Mt S/km^3, or 3.12 Mt SO$_2$/km^3, or 1.66 Mt H$_2$S/km^3.