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Economic Geology, v. 110, pp. 1111–1123

SULFUR LIBERATION FROM COUNTRY ROCKS AND INCORPORATION IN MAFIC MAGMAS

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Abstract

A key step in the formation of many magmatic Ni-Cu-PGE sulfide deposits is the addition of crustal sulfur to mafic or ultramafic magmas. Sulfur addition has been proposed to take place via two different types of processes: (1) production of sulfurous fluids within the thermal aureole around an intrusion accompanying breakdown of sulfide- or sulfate-bearing minerals during devolatilization, followed by diffusive or advective transport of these fluids into the magma, and (2) by direct melting and assimilation of wall rock and xenoliths. We consider physical and chemical controls on the timescales of these processes and show that wall-rock and xenolith melting is by far the most efficient and quickest process for adding crustal sulfur, with melting processes taking place on a scale of minutes to years. In contrast, liberation of sulfur from a thermal aureole via diffusion is much slower and requires timescales of millions of years—two orders of magnitude longer than the time required for an intrusion to solidify by diffusion. We conclude that sulfur, which may be liberated in thermal aureoles (produced either via devolatilization reactions or dissolution involving hydrothermal fluids) and which must be transported via diffusional processes, has a negligible effect on the formation of magmatic Ni-Cu-PGE deposits.

Introduction

The addition of crustal sulfur to mafic or ultramafic magmas is generally thought to be of prime significance in the formation of sulfide-rich Ni-Cu-PGE deposits (e.g., Lesher and Stone, 1996; Ripley and Li, 2003, 2013; Naldrett, 2009; Keays and Lightfoot, 2010). In particular, sulfur isotope values provide strong evidence for the importance of crustal S in many deposits (e.g., Noril'sk—Gorbachev and Grinenko, 1973; Grinenko, 1985; Ripley et al., 2003, 2010; Duluth Complex—Ripley et al., 2007; Kabanga—Maier et al., 2011; many komatiites—Lesher et al., 2001; Fiorentini et al., 2012). Some deposits show little isotopic evidence for the importance of crustal sulfur in magmatic sulfide ore genesis, and mantle sulfur has been proposed as the sole sulfur source in these deposits (e.g., Nebo-Babel, Seat et al., 2009; see also Ripley and Li, 2013).

A frequently asked question is how sulfur in crustal rocks is incorporated into magmas of mantle origin. It is important when considering this question to summarize the locations in a magma transport, or conduit, system where the liberation of country-rock sulfur may occur. In Figure 1 we illustrate one flow path, keeping in mind that several such paths through the crust may exist, and systems may mix in the shallow crust if conduits merge or coalesce. One very straightforward observation is that magmas may be contaminated from their margins inward by interacting with the country rocks. There are essentially two types of processes that could lead to sulfur release from country rocks and incorporation in magmas: (1) those in thermal aureoles, where mass is transferred from wall rock to magma as a result of thermal decomposition of wall-rock minerals driven by heat diffused outward from the magma; and (2) mass transfer due to physical incorporation, melting, and/or dissolution of xenolithic blocks of country rock incorporated into the magma body. The purpose of this communication is to evaluate the relative rates and importance of these two types of processes. We utilize both chemical and physical principles to argue that physical incorporation of xenoliths and xenomelts is overwhelmingly the fastest and most plausible mechanism.

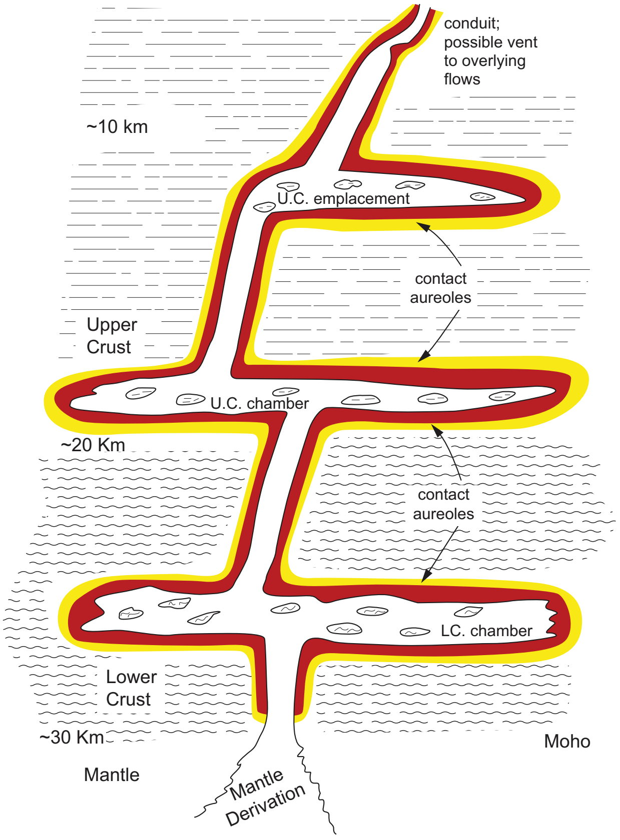

FIG. 1. Schematic illustration of a magma flow path through the crust. The concurrence of several such paths would lead to higher regional country-rock temperatures and a greater mass from which external sulfur could be derived. The red to yellow colors represent contact aureoles and thermal gradients around conduits and chambers.

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Submitted: July 15, 2014
Accepted: October 27, 2014

Principal Minerals That May Supply Sulfur to Mafic Magmas

Sulfur derivation from pyrite

Pyrite is a common accessory mineral in many rock types. Its breakdown to pyrrhotite at high temperatures has led numerous workers to suggest that derivation of sulfur from pyrite is a key process involved in the contamination of mafic magmas by crustal sulfur. Naldrett (1966) first proposed that sulfur in the Alexo deposit was supplied as a result of the thermal breakdown of pyrite to pyrrhotite in a 2- to 3-m-thick zone at the contact between peridotite and volcanic country rocks. Pyrite melts incongruently to pyrrhotite plus liquid at 743°C (e.g., Kullerud and Yoder, 1959; Toulmin and Barton, 1964), but may thermally decompose to pyrrhotite plus vapor at temperatures below the intersection with the sulfur condensation curve (Fig. 2). It has been shown that in many types of atmosphere pyrite completely decomposes to pyrrhotite plus vapor at temperatures well below the melting point (e.g., Lambert et al., 1998; Ripley and Snyder, 2000; Hong and Fegley, 2010).

Ferry (1981), Ripley (1981), Mohr and Newton (1983), and Tracy and Robinson (1988) proposed that reactions in graphitic metasedimentary rocks were important in the production of sulfurous fluid during metamorphism. Ripley (1981) suggested that reactions such as

$$FeS_2 + H_2O + C = FeS + H_2S + CO_2 + CH_4 \qquad (1)$$

occur in sulfidic and carbonaceous metasedimentary rocks. Ohmoto and Kerrick (1977) calculated the composition of fluid produced during the devolatilization of pelitic rocks with f_{S_2} buffered by the coexistence of pyrrhotite plus pyrite. More recently, Tomkins (2010) used the PerpleX (Connolly and Cesare, 1993) and Thermocalc (Holland and Powell, 1998) codes to model metamorphic sulfur liberation. Tomkins (2010) showed that during prograde metamorphism and dehydration of minerals such as chlorite, carbonaceous shales are the most favorable rock type for generating H_2S-rich fluid. The generation of H_2S via reactions between pyrite and H_2O in the low-pressure (<~2 kb) environment begins at temperatures as low as 400°C (e.g., Ripley and Snyder, 2000; Tomkins, 2010). Andrews and Ripley (1989) demonstrated that the conversion of pyrite to pyrrhotite outside of the contact aureole of the Duluth Complex (Fig. 3) occurred prior to major dehydration and graphitization. Andrews and Ripley (1989) suggested that H_2 or CH_4 generated during kerogen maturation may have driven the reaction of pyrite to pyrrhotite (e.g., $FeS_2 + H_2 = FeS + H_2S$) at temperatures less than 400°C.

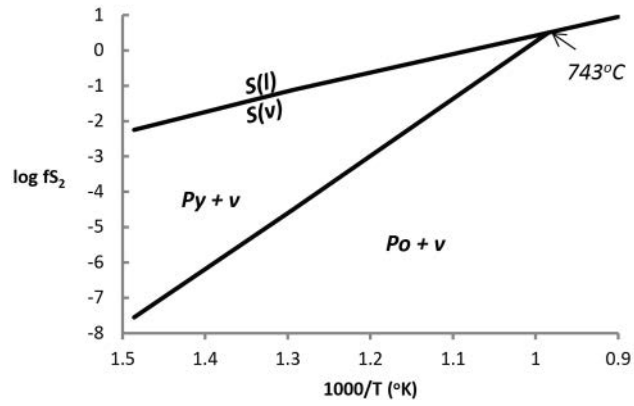

FIG. 2. Log f_{S_2} versus temperature diagram showing the thermal breakdown of pyrite at 743°C. Data from Toulmin and Barton (1964).

Sulfur derivation from pyrrhotite

In pyrrhotite-bearing rocks, the liberation of sulfur is a more difficult process than that described above for pyrite-bearing rocks. At low pressure, the maximum melting point of pyrrhotite is ~1,190°C (e.g., Kullerud and Yoder, 1959). The addition of water may lower this value (e.g., Konnikov, 1997), but melting of pyrrhotite requires temperatures in excess of 1,000°C; these are values that are unlikely to be reached within contact aureoles but may be attained within xenoliths contained in high-MgO magmas (see below). Andrews and Ripley (1989) showed that the mole fraction of H_2S in a metamorphic fluid decreases sharply in the field of pyrrhotite stability relative to that in the pyrite field. Of potentially more significance than thermal degradation alone for pyrrhotite in contact aureoles is the possibility of sulfur liberation via dissolution. The solubility of pyrrhotite is a function of variables such as T, pH, f_{O_2}, and fluid salinity. Crerar and Barnes (1976) and Crerar at al. (1978) showed that $FeCl^+$ is an important species in the dissolution of pyrrhotite. Reactions such as

$$FeS + 2H^+ + Cl^- = FeCl^+ + H_2S \qquad (2)$$

may control the production of H_2S in hydrothermal fluids that are present in the contact aureoles of mafic intrusions (Fig. 4), particularly in rocks where pyrrhotite is the primary sulfide mineral or where pyrite was consumed by prior reactions.

Sulfur derivation from evaporites

The derivation of sulfur from country-rock evaporite minerals has been proposed as a significant process for ore formation in the Noril'sk region (e.g., Gorbachev and Grinenko, 1973; Naldrett and Lightfoot, 1999; Arndt et al., 2003; Li et al., 2009a). Evaporite minerals occur in many sedimentary sequences and the potential for interaction with mantle-derived magmas is high. Two criticisms which are often directed toward an interpretation for ore genesis that involves sulfur derivation from evaporites are that (1) the temperatures of melting of evaporites are high (e.g., anhydrite ~1,450°C, van der Sluis, 2010) and (2) oxidized sulfur that might be derived from evaporites must be reduced to sulfide and reductants such as Fe^{2+} in mafic magmas are limited. Recent experiments by van der Sluis (2010) in the anhydrite-dolomite system indicate that, at high pressures (10 kb), melting of anhydrite occurred at ~1,000°C. Such temperatures indicate that direct melting of evaporite minerals may be viable for sulfur liberation as a result of xenolith assimilation, but certainly is an unlikely process for the production of sulfur in contact aureoles. Direct incorporation of xenoliths is physically far more plausible, as discussed further below.

Two other processes appear to be far more likely in the liberation of sulfur from evaporites. The first, much like the case for pyrrhotite, is dissolution, as discussed below in the context of the incorporation of xenoliths in magmas. Newton and Manning (2005) have shown that the solubility of anhydrite increases markedly with NaCl activity at temperatures between 600° and 800°C. Saline solutions in the vicinity of

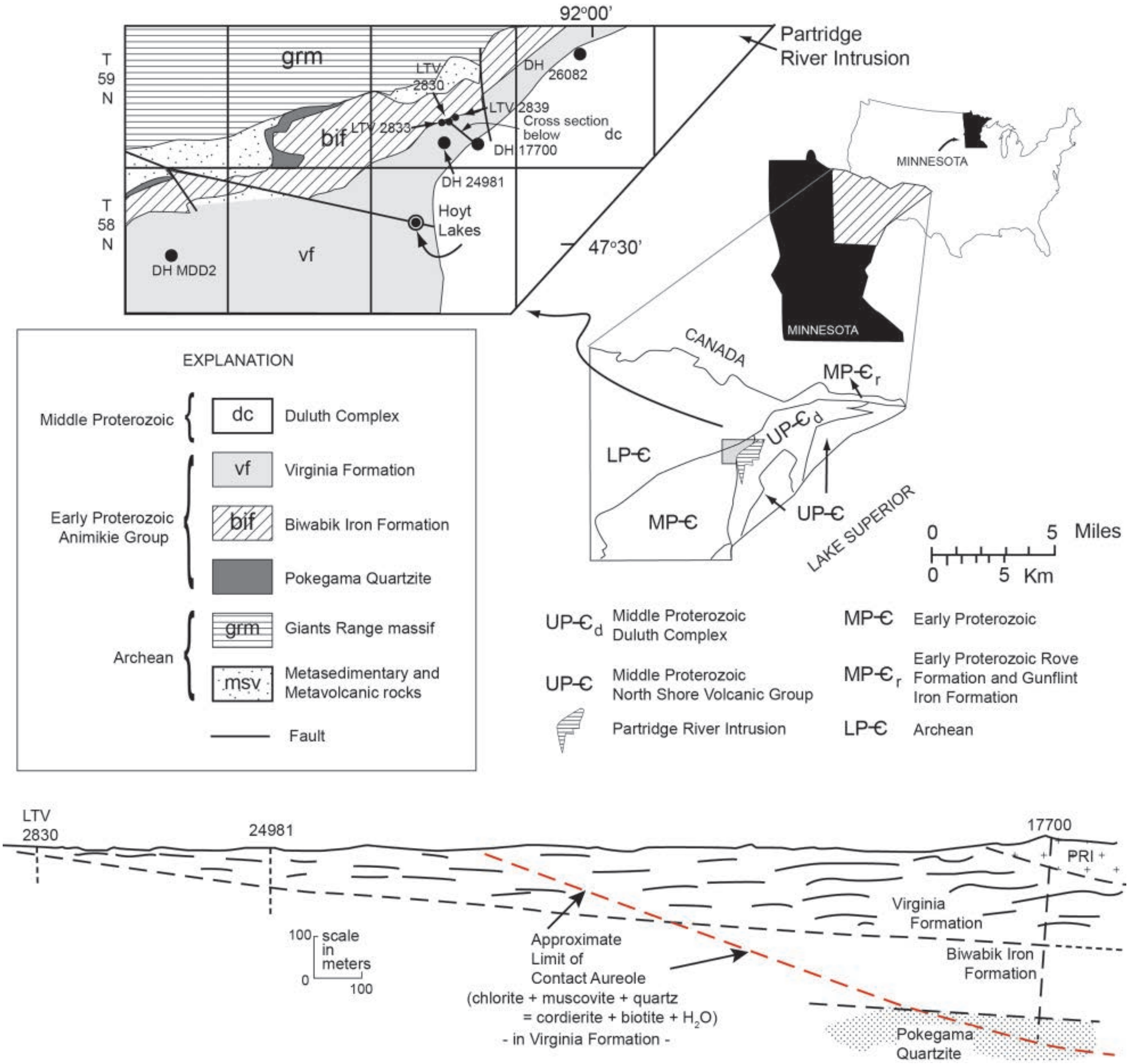

FIG. 3. Geologic map and cross section showing the contact aureole around the Partridge River Intrusion of the Duluth Complex. The approximate limit of the aureole is defined by the dehydration of the chlorite-muscovite assemblage. It is important to note that coarser-grained sulfides in core 24981 are still pyrite, but finer-grained sulfide is pyrrhotite. The conversion of pyrite to pyrrhotite begins before both graphitization of kerogen and dehydration of chlorite + muscovite.

mafic magmas and evaporates could become sulfate rich. Within xenoliths, it would be possible for both melting and dissolution to be important processes involved in the assimilation of sulfate by mafic magmas. The second process involves reactions between anhydrite and siliceous fluids to produce wollastonite, which is commonly observed in contact aureoles in the Noril'sk region (e.g., Duzhikov et al., 1992). Reactions producing wollastonite include

$$CaSO_4 + SiO_2 + H_2O = CaSiO_3 + H_2S + 2O_2 \quad (3)$$

or, in more reduced conditions where hydrogen may be produced via kerogen maturation,

$$CaSO_4 + SiO_2 + 4H_2 = CaSiO_3 + H_2S + 3H_2O. \quad (4)$$

Reduced sulfur (H_2S) may have been generated in contact aureoles of intrusions in the Noril'sk area, as well as within xenoliths, via such reactions. Arndt et al. (2005), Jugo and Lesher (2005), and Thakurta et al. (2008) have shown that organic carbon in sedimentary rocks or graphite in magmas may serve as reductants in the conversion of sulfate to sulfide. In the absence of such reductants, Li et al. (2009a) showed that with FeO as a sulfate reductant, f_{O_2} conditions of a magma could increase from QFM-2 to QFM+1.5. Li et al. (2009b) confirmed that interstitial anhydrite is present within at least some picritic intrusions of the Noril'sk area. Ripley et al. (2010) showed that interstitial anhydrite was characterized by $\delta^{34}S$ values in excess of 18‰ and that sulfate must have been derived from evaporate minerals in country rocks that have similar $\delta^{34}S$ values.

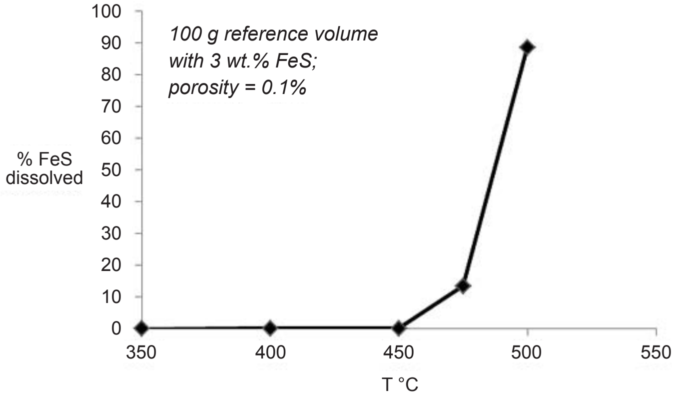

FIG. 4. Percentage of dissolution of pyrrhotite in a 100-g reference volume containing 3 wt % pyrrhotite, following the reaction $FeS + 2Cl^- + 2H^+ = FeCl_2 + H_2S$ (Crerar et al., 1978). Porosity was set at 0.1%, molality of Cl^- at 1, and H_2S at 0.1 initially, increasing to $\sim10^3$ as the reaction progressed. High-temperature equilibrium constants were extrapolated from the 200° to 350°C data of Crerar et al. (1978). Even considering the uncertainties of the calculation, it is clear that pyrrhotite may release considerable quantities of sulfur via reaction with a saline solution at high temperatures.

We return to specific examples of potential S-generating processes in thermal aureoles below, after consideration of mass balance and timescale factors.

Potential Sulfur Supply from Country Rocks

The above examples illustrate that sulfur in contact aureoles or within xenoliths may be assimilated into the intrusion by a number of mechanisms. Of ultimate concern in models for the generation of magmatic Ni-Cu-PGE deposits is the fate of sulfur species produced within country rocks. Can the proposed processes drive incorporation of sulfur into magmas in large enough proportions to account for the mass of sulfur found in the ore deposits? We consider four examples: Partridge River, Eagle, Norilsk-Talnakh, and Voisey's. Ripley and Li (2013) have documented the mass of magma needed to produce these deposits if the sulfur was mantle derived and shown that external sources of sulfur are required, especially in smaller magmatic bodies.

In all contact aureole environments, the biggest problem for local derivation of sulfur is one of mass balance: the amount of sulfur in the mineralized zones is often far larger than the amount of sulfide which could be liberated in the contact aureole. As a specific example, we consider the Virginia Formation-Partridge River Intrusion contact zone (Fig. 3), where the sulfidic Virginia Formation has been postulated to have supplied sulfur for mineralization in the basal portion of the intrusion. The amount of sulfur available in the country rocks of the Virginia Formation is highly variable. To produce a volume of one million m^3 of sulfide-mineralized igneous rocks with 3% disseminated sulfide requires approximately 5×10^7 kg of sulfur. Stable isotope data (e.g., Ripley et al., 2007) indicate that a minimum of 50% of the sulfur was of external crustal origin. To produce enough sulfur, we therefore require a 300-m-thick thermal aureole containing about 0.6 wt % sulfur as pyrite, assuming all of the pyrite is broken down into pyrrhotite and the liberated sulfur somehow transported into the magma.

Some horizons in the Virginia Formation contain bands of sulfide, giving bulk rock sulfur contents of 10% or more. However, most of the Virginia Formation contains far less S, typically less than 0.6 wt %. In areas where sulfide was abundant, the derivation of sulfur by the thermal breakdown of pyrite in the contact aureole would certainly have been feasible; for most portions of the stratigraphy where the concentration of sulfur was lower, in situ processes of sulfur liberation and transport in sufficient quantities to account for the necessary external sulfide in ore zones would have been less certain. A similar conclusion applies to deposits in the Noril'sk area, where the contact aureoles contain many sulfur-poor rock types (Turovtsev, 2002) in addition to those that are sulfur bearing. If evaporates, shales, or coals with $\delta^{34}S$ values near 20‰ are taken as likely contaminants, then a minimum of 50% of the sulfur in the deposits with $\delta^{34}S$ values near 10‰ must be of external origin.

Massive sulfide deposits within near-vertical dike-like bodies, such as the Eagle deposit in Michigan (Fig. 5), present additional problems with respect to sulfur addition linked to sulfur liberation in immediate country rocks. The massive sulfide occurrence at Eagle represents a sulfur accumulation that far exceeds that which could have been derived from contact rocks adjacent to the dike. In the case of Eagle, contact metamorphic effects (cordierite, andalusite, and biotite formation after chlorite and muscovite) in the carbonaceous and sulfidic rocks of the Proterozoic Michigamme Formation are detectable for no more than 20 m from the contact with igneous rocks that extend laterally in sill-like fashion from the conduit and less than 5 m from the contact in the vertical portion of the conduit. The ~5-million-tonne massive sulfide body indicates that external sulfur must have been derived distally from the present location level. Whether sulfide liquid accumulations in vertical conduits moved up the conduit or drained downward remains unsettled; a discussion of that issue is beyond the scope of this paper. However, it is clear from mass balance considerations at Eagle that the orebody does not represent a contact-style deposit where sulfur was derived from within a contact aureole.

We suggest that a similar conclusion applies to the ~30-million-tonne Ovoid massive sulfide deposit at Voisey's Bay (e.g., Lightfoot et al., 2012). The Ovoid occurs in a thickened portion of a dike that appears to link larger underlying and overlying chambers, both of which contain disseminated sulfide mineralization. Country rocks of the Voisey's Bay deposit are granulite facies gneisses (e.g., Li and Naldrett, 2000; Ryan, 2000) and, although contact metamorphic effects are clearly discernible, establishing the geometry of the contact aureoles is difficult (Lee, 1987; Mariga et al., 2006). The Proterozoic Tasuiyak Gneiss locally contains graphitic and pyrrhotite-bearing layers, and has been proposed as a major source of externally derived sulfur for the deposits at Voisey's Bay (Ripley et al., 2003; Hiebert et al., 2013). However, the immediate contact rocks to the Ovoid are relatively low sulfur enderbitic orthogneisses that could not have supplied significant quantities of sulfur to the massive sulfide system (Ripley et al., 1999).

Sulfur isotope data (e.g., Ripley and Li, 2003) provide strong evidence for the importance of crustally derived sulfur in the formation of many magmatic sulfide deposits. In the example of mineralization in the Partridge River Intrusion referred to above, $\delta^{34}S$ values range from 0% to 10% (Ripley et al., 2007) and vary in concert with the distribution of interstitial sulfide minerals. The correlation between variable $\delta^{34}S$ values and variable sulfide distribution is evidence for the emplacement

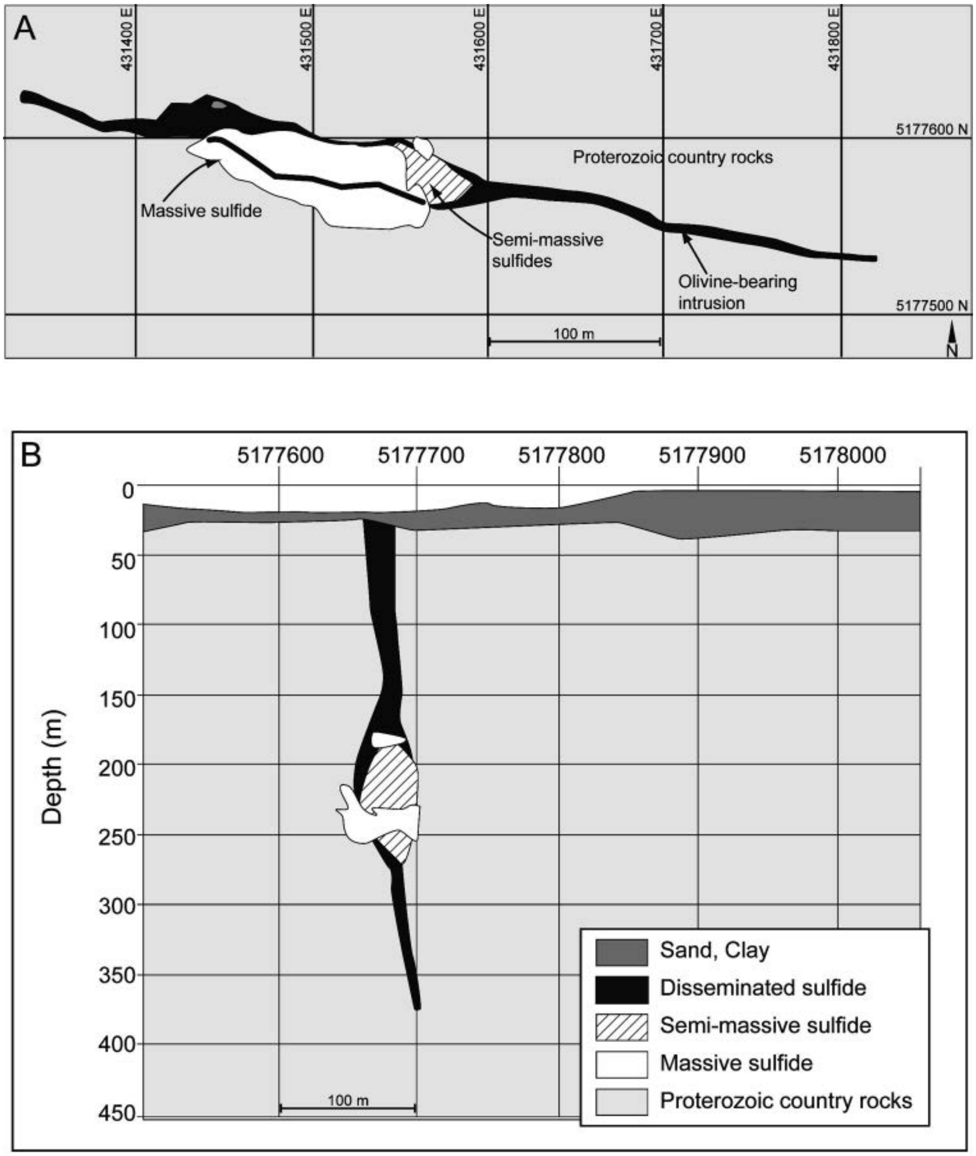

FIG. 5. A. Geologic map of the Eagle Intrusion and associated sulfide occurrences, ~250-m level. B. Cross section of the intrusion showing mineralization types. The deposit is clearly within a dike-like body with a very restricted contact aureole.

of distinct, sulfide-saturated magma pulses, each characterized by distinct δ^{34}S values (Ripley et al., 2007). Another line of evidence for the involvement of distinct magma pulses focuses on copper grades of the mineralization, which vary from ~0.2 to >1.00 wt %. Many of the isotopically distinct mineralized layers contain in excess of 50% chalcopyrite/cubanite in the sulfide assemblage. Such elevated Cu contents could not be produced by in situ addition of sulfur to mantle-derived mafic magmas with Cu contents less than 200 ppm. The geochemical data provide additional evidence against an in situ process for the genesis of sulfide mineralization in the sheet-style intrusions of the Duluth Complex. Geochemical data do not necessarily rule out the derivation of sulfur from a contact aureole, but, taken together with physical constraints, the conclusion for mineralization in the Partridge River Intrusion is that crustal sulfur was derived distally relative to the final magma emplacement site, and via processes distinct from diffusive transport in a local contact aureole.

Although evaluations of the potential for in situ production of sulfur in quantities sufficient for ore formation must proceed on a case by case basis, we suggest that in many intrusions the potential for significant local derivation of sulfide is severely limited by mass balance constraints. This implies that sulfide must be transported through the intrusive system and trapped by some other physical process, and therefore that the sulfide is transported into the magma before the magma viscosity increases dramatically as it cools.

Rates of Thermal and Chemical Processes in Contact Aureoles

The rate of transfer of sulfur from country rocks from thermal aureoles to magma margins is a function of several variables, including the rate of heat transfer into the country rock, the rate of magma crystallization, the nature of reactions that may occur in the country rocks, and the rate and direction of mass transfer of S-bearing fluids. Heat and mass transfer from a magma body into country rocks can be driven by conduction through solid rocks, convection of liquid phases through fracture or pore networks, or by melting and dissolving the country rock itself.

How do we determine which, if any, of these processes are relevant to the formation of magmatic sulfide deposits? In the following sections we outline the fundamental physical timescales for each process and compare these to the timescales for magmatic cooling and solidification. We assume that, to be important in magmatic deposit formation, a candidate process must transport sulfide into the magma before the magma (1) solidifies enough to prevent further addition of sulfur or (2) becomes viscous enough to prevent mixing, transport, and accumulation of sulfide melts.

The next sections discuss processes which are of importance for the transport of sulfur from contact aureoles and then the potential importance of xenoliths. We back up the assumptions used to obtain these timescales with examples of these processes from the field.

Timescales for purely diffusive processes

The mass balance arguments given above show that a thermal aureole must have a thickness on the order of the intrusion thickness in order to generate enough sulfide from the country rock via the decomposition processes discussed in the first section. Given an intrusion of thickness h, we can ask how long it will take to generate such an aureole. If heat transfer is purely by diffusive heat transfer through solid rock, then the timescale t for the growth of an aureole is given by

$$t \sim \frac{h^2}{\kappa},$$

where ~ means "of the same order of magnitude," and κ is the thermal diffusivity of the solid rock (Table 1). Typical measured values for the thermal diffusivity of rock are $\kappa \sim 10^{-6}$ m^2 s^{-1} (Robertson, 1988), so a thermal aureole a hundred meters across ($h \sim 10^2$ m) requires several hundreds of years to develop ($t \sim 10^{10}$ s).

The time taken for the intrusion to cool can be estimated using a similar scaling argument. If we assume that the magma and country rock have similar specific heats, then for the magma to cool, the heat has to be spread out over a similar mass of country rock as the original magma. If the intrusion is several hundred meters across, we have to diffuse this heat out into the country rock over several hundred meters to a kilometer as well ($h \sim 10^3$ m), giving timescales on the order of 30 ka ($t \sim 10^{12}$ s).

Diffusive mass transfer is much slower than diffusive heat transfer. Chemical diffusion obeys the same length-time scaling given above. However, since the chemical diffusivity of rock ($\kappa_c \sim 10^{-10}$ m^{2}s^{-1}, e.g., Cussler, 1997) is four orders of magnitude lower than the thermal diffusivity, the time taken to diffuse sulfur out of a thermal aureole a hundred meters across is on the order of several million years ($t \sim 10^{14}$ s). As this timescale is two orders of magnitude larger than the time taken for the intrusion to cool by diffusion into the country rock, models which require chemical diffusion of sulfide out of the thermal aureole rock are physically implausible.

The effect of advection and diffusion in fluid fractures and grain-boundary networks

Diffusive heat and mass transfer through the country rock can potentially be accelerated by thermally and compositionally driven convection of fluids through country-rock fractures or pores. However, in general, the presence of a hot thermal aureole should tend to drive the warmer fluid away from the intrusion rather than toward it. Hence, a fluid-driven mass flux of sulfur into magmas from roof rocks appears intrinsically implausible. Fluxes driven by the buoyant rise of fluids produced in the floor rocks are conceivable. However, since the magma is cooling as the aureole develops, the boundary of the sill itself can provide an impermeable barrier. Below,

TABLE 1. Explanation of Symbols Used in This Manuscript and Typical Values of Coefficients, Boundary Conditions, and Physical Parameters

		Typical values			
Symbol	Property	Komatiite magma	Basalt magma	Dacitic wall rock	Units
c	Specific heat	730	730	730	J kg^{-1} °C^{-1}
δ	Boundary layer thickness	10^{-4}	10^{-3}	-	M
h	Length scale		Intrusion thickness: 10^2 Xenolith size: 10^{-2}–1		M
J	Convection coefficient	1.8×10^{-5}	5×10^{-6}	-	m s^{-1} °C$^{-1/3}$
κ	Chemical or thermal diffusivity		Thermal: 10^{-6} Chemical: 10^{-10} (via rock), 10^{-7}–10^{-9} (via fluid)		m^2 s^{-1}
L	Latent heat of melting	-	-	5×10^5	J kg^{-1}
m	Melt rate	-	-	-	m s^{-1}
ρ	Density	2,800	2,600	2,100	kg m^{-3}
t	Timescale	-	-	-	S
T_i	Magma temperature	1,400	1,200	-	°C
T_0	Initial country-rock temperature	-	-	500	°C
T_m	Wall-rock melting temperature	-	-	1,000	°C

we add field evidence for the horizontal flow of fluids in the aureole beneath the Partridge River Intrusion of the Duluth Complex. In any case, the development of hydrothermal convection cells occurs on the same timescales as the diffusional growth of the thermal aureole around the magma (since the heat to drive the hydrothermal circulation has to first diffuse through the country rock, e.g., Iyer et al., 2013).

We also consider the transport of H_2O and H_2S into magmas from country rocks via diffusional transport within grain boundary fluids and through fluid fractures and pore spaces. On the scale of an intrusion the process of convection through the country rock is governed by an effective diffusion law, where the effective diffusivity is related to the permeability and porosity of the rock, and the diffusivity of the chemical species in water (Epstein, 1989). Boving and Grathwohl (2001) determined effective diffusivities for limestones and sandstones using iodide tracer experiments. Their values are reported in terms of the ratio of the effective diffusivity to the diffusivity in water, κ/κ_{H_2O}, with values ranging from 10^{-1} to 10^{-3} m^2 s^{-1} over four orders of magnitude of hydraulic conductivity (see their fig. 5). The diffusivity of H_2S in H_2O may be as high as 10^{-6} cm^2/s (Cussler, 1997), giving effective diffusivities on the order of $\kappa \sim 10^{-7}$ to 10^{-9} m^2 s^{-1}. This decreases the time required to diffuse sulfur out of the aureole considered above to several hundreds of thousands of years ($t \sim 10^{11}$ to 10^{13} s); however, this timescale is still an order of magnitude larger than that required for diffusional cooling of the intrusion (see Fig. 6).

The effect of melting on thermal aureole development

Although we consider melting in more detail below, it is important to note that if the heat transfer is high enough to melt the country rock, then, typically, this melting will proceed much faster than heat transfer via diffusion. Not all magmas will melt their hosting rocks, as melting requires (1) an intrusion temperature significantly greater than the melting temperature of the country rock, and (2) magma viscosities sufficiently low for convection to efficiently transport heat from the center of the intrusion toward the walls and roof of the intrusion, or (3) magma flow rates sufficiently high for cooled magma to be swept away from the walls of the intrusion and replaced with fresh hot magma.

If, however, the country rock starts melting, then the latent heat of fusion associated with the melting acts as a significant energy sink. This generates an energy balance where the crystallizing magma releases latent heat and the melting country rock absorbs it (Huppert and Sparks, 1988; Leitch, 2004; Gole et al., 2013). This energy balance implies there will be no significant thermal boundary layer around the intrusion until a large portion of the intrusion has crystallized.

Since the country rock melting also acts as a massive heat sink for an intrusion, this timescale is also the relevant timescale for magma solidification when melting occurs. This is also the relevant timescale for solidification in the case of extrusive komatiite lava flows, as in this case the ambient fluid (air or water) acts as the large heat sink (Turner et al., 1986). We therefore expect that intrusions with significant wall-rock melting will be effectively quarantined from external sulfur within an aureole, except for the sulfur which is entrained from the country-rock melt.

Examples of key processes in intrusion aureoles

Studies of the contact metamorphism of the pelitic Virginia Formation, related to emplacement of the Partridge River Intrusion of the Duluth Complex (Fig. 3), have shown that partial melting and loss of a granitic liquid from the pelitic rocks were restricted to less than 8 m from the contact (Andrews and Ripley, 1989). Temperature of the partial melting and production of cordierite-orthopyroxene hornfels was near 700°C and insufficient for the melting of pyrrhotite. Evidence for transport of the silica-rich partial melt into magma is the presence of a thin horizon of norite rather than troctolite (e.g., Queffurus and Barnes, 2014). However, the presence of a norite layer is a local phenomenon and, in most

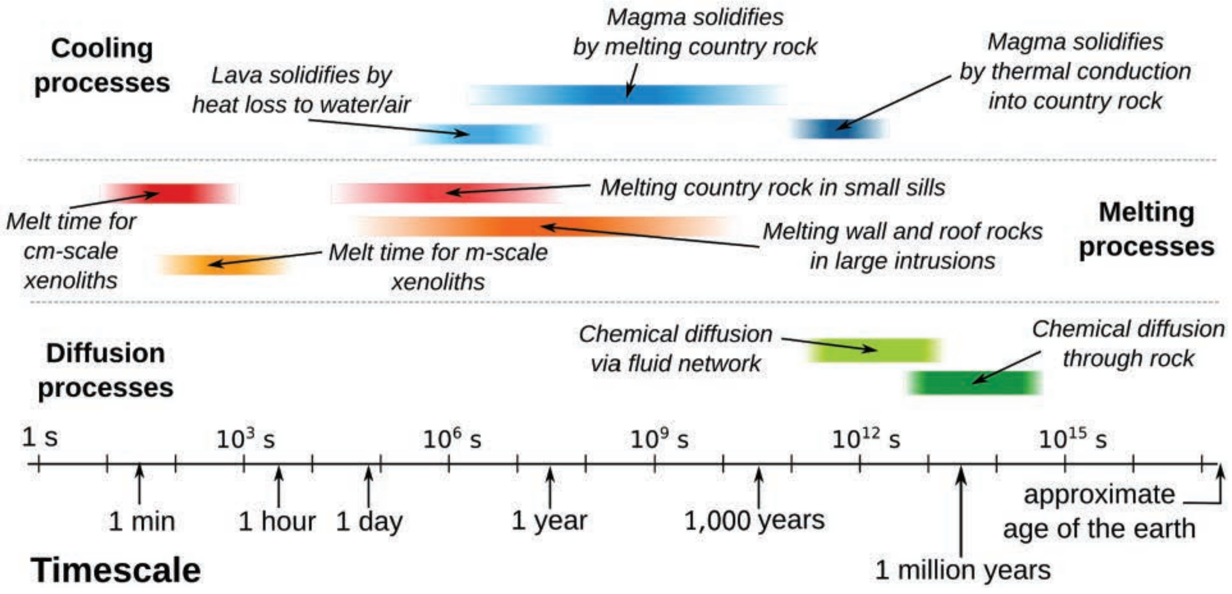

FIG. 6. Relative timescales of diffusion in contact aureoles, melting of wall rocks and xenoliths, and cooling of magmas.

localities, evidence for the transport path of the siliceous partial melt is absent (Ripley and Alawi, 1988). The presence of pyrite in core 24981 (Fig. 3) indicates that the breakdown of pyrite to pyrrhotite may have released sulfur over a ~300- to 400-m thickness below the contact with the Partridge River Intrusion. The presence of chlorite and muscovite in core 24981, with no evidence of H_2O loss, constrains dehydration fronts to have moved outward. Andrews (1987) used a 1-D heat conduction model with a magma temperature of 1,200°C to track temperature variations and fluid production in the aureole. He concluded that the aureole formed within 66,000 years, and that fluid was channeled through fractures in the country rock or horizontally along bedding planes, in part due to compaction. The presence of layer-parallel quartz-carbonate-sulfide veins in the Virginia Formation (Williams et al., 2010) attests to the flow of hot fluids along bedding planes. No evidence exists for the presence of near-vertical fractures in the contact aureole that may have supplied fluids from dehydration reactions. It would be expected that, because of pressure differences between magma and country rocks, any such fractures would have been forcibly filled with magma.

In the case of the Virginia Formation, it is therefore conceivable that diffusive transport of sulfur from a 300- to 400-m-wide zone of dehydration could have occurred within the time predicted by Andrews (1987) for the production of the zone of dehydration. However, there are at least three arguments against such a model for sulfur transport. Firstly, not all the sulfur which had been liberated from the aureole reached the magma, as field relations suggest that sulfur-bearing fluid was advected away from the intrusion along bedding planes. Secondly, magmas that gave rise to the mineralized zones in the Duluth Complex are thought to have been emplaced as relatively thin sheets, much less than 100 m in thickness (see evidence detailed above). As thermal diffusivity is considerably larger than H_2S diffusivity, calculations suggest that a magma would have solidified well before diffusive transport of sulfur could have been effective. For example, Petford and Gallagher (2001) calculated crystallization times of less than 4,000 years for a mafic sill of 1 km in thickness emplaced into the lower crust. This is a much shorter timescale than the millions of years required for chemical diffusion across several hundred meters of thermal aureole. Thirdly, reactions between silicate and oxide minerals and H_2S may have limited the amount of sulfur available for transport into the magma. Andrews and Ripley (1989) noted that in the contact aureole pyrrhotite formed at the expense of biotite and ilmenite. Fe/Mg ratios of ferromagnesian minerals in the aureole are strongly related to sulfur abundance. Using bulk rock analyses, they concluded that sulfur had been conserved in the contact aureole as a result of sulfidation reactions involving Fe-bearing silicates and oxides.

Contact aureoles developed around sills in the Noril'sk area appear to be the best example where evaporitic sulfur may have contributed to magmatic sulfide ore genesis (e.g., Gorbachev and Grinenko, 1973; Grinenko, 1985; Arndt et al., 2003; Li et al., 2003, 2009b). Aureoles may be thick when compared to the thickness of sills (200–300-m-thick aureoles to a comparable thickness of sill; Likachev, 1994; Pang et al., 2012), which attests to continual heat introduction as magma flowed through the conduit system. Sulfur generation from the evaporitic strata has been linked largely to dissolution and transport via Cl-rich hydrothermal fluids (e.g., Ripley et al., 2003; Li et al., 2009b; Pang et al., 2012). Sulfur may also have been generated via wollastonite-forming reactions, but the apparent localized nature of wollastonite (Pang et al., 2012) occurrences suggests that this method could not have been of major significance. It should be noted that the country rocks at Noril'sk also contain pyrite-bearing shales and coals (Grinenko, 1985; Pang et al., 2012). Although it is clear that sulfur (oxidized from evaporites and reduced from pyrite-bearing shales and coals) could have been generated in the contact aureoles of intrusions in the Noril'sk region, the physical method via which large masses of sulfur produced in an aureole may have been introduced into a reasonably rapidly crystallizing magma meets the same limitations as those discussed above.

Sulfur Derivation from Xenomelts

The presence of country-rock xenoliths in intrusive sequences that host sulfide mineralization suggests that much of the external sulfur that was important in ore formation was derived from the xenoliths. Digesting xenoliths in the melt directly also ensures that sulfur transfer will not be impeded by solubility limits in the magma.

The rate of magma interaction with xenoliths is a first-order control in evaluating the effectiveness of sulfur removal from the fragments. Xenolith digestion can proceed via a number of chemical and physical mechanisms, including melting, chemical dissolution, and xenolith disaggregation (Sparks and Huppert, 1984; Woods, 1992). These mechanisms proceed at different rates, and the process which is dominant will depend on the local magma flow conditions, the relative physical and chemical properties of the xenoliths, host magma, and any xenolithic melt that is produced, and the style of convection and mixing in the host magma (Fig. 7).

The physics of wall-rock and xenolith digestion in a quiescent magma is an example of a Stefan problem, a type of free boundary problem that has a rich history (Stefan, 1891). In these problems, there is a substance undergoing a phase change (e.g., melting from solid to liquid) at a phase interface. The rate at which the phase boundary moves is determined by the thermodynamic disequilibrium at the boundary interface, and may be driven by thermal or chemical gradients. For example, in the case of a single component substance undergoing a phase change from solid to liquid, it is the difference in heat flux at the phase interface which determines the melting rate. In this simple case, the problem can be solved directly (see the examples in Carslaw and Jaeger, 1959, p. 282–296). Once compositional variations are introduced, the conditions determining the motion of the phase interface become more complex, as both dissolution and melting are possible. Melting occurs when the rate of heat supplied to a solid interface exceeds the rate at which this heat can be conducted into the solid, such that the temperature of the solid is raised above its solidus. Dissolution occurs when the solid and melt have different compositions and the solubility limit governing the concentration of the solid in the melt has not been exceeded. Heat transfer to the solid from the liquid is not essential in this case. A useful example from Woods (1992) considers salt and water: not only can cold ice cubes melt in warm fresh water, but (relatively) warm ice can dissolve in colder, salty

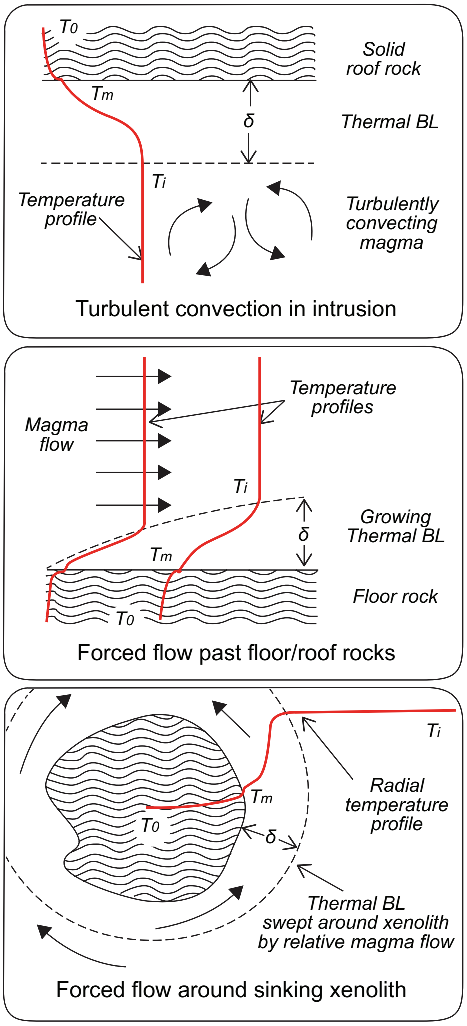

FIG. 7. The geometry of xenolith and wall-rock melting under turbulent, laminar, and buoyant magma flow conditions. Each scenario shows the basic geometry, including temperature profiles and the structure of the thermal boundary layer (BL) around the melting wall rocks or xenoliths.

water. In magmatic systems the chemical diffusivity (of order 10^{-10} m^2 s^{-1}) is several orders of magnitude smaller than the thermal diffusivity (10^{-6} m^2 s^{-1}), so xenolith melting is dominant when the temperature of the host melt is significantly greater than the melting temperature of the xenolith, while dissolution is dominant at (relatively) lower host melt temperatures. Hence, incorporation of anhydrite into mafic magma would necessarily involve dissolution, not melting. We do not consider chemical dissolution further here, except to note that the timescales required for dissolution are typically longer than those for melting in magmatic systems (Kerr, 1994a, b).

Thermal and compositional variations between the xenolithic melt and the host magma will also generate density variations that can drive fluid flow (Turner, 1979; Fig. 7). These convective flows may be thermal, compositional, or double diffusive, and they accelerate the rate of xenolith melting compared to a purely diffusive regime by increasing the heat or solute supply rates at the xenolith or country rock's surface (Huppert and Sparks, 1988). Similarly, turbulent or laminar flow of the host magma relative to the melting rock will also increase the melting rate, whether this is via forced flow of the magma past wall rock (Huppert and Sparks, 1985, 1989; Kerr, 2001) or due to the relative motion of the xenoliths settling through the magma (Kerr, 1994a, b; see Fig. 7).

Disaggregation is driven by selective melting, dissolution, or weakening of xenolithic material, and subsequent mechanical breakup due to the forces exerted by the magma. Since this will depend, in general, on the magnitude of viscous and inertial forces exerted by the magma flow and the intrinsic strength of the country rocks and xenoliths, it is a more difficult process to quantify in a dynamic magma setting. However, given that the country rock still has to partially melt or significantly heat up prior to disaggregation, and this heating process will still be rate-limited by thermal diffusion, we can assume that disaggregation will occur over a timescale similar to the melting processes discussed below.

Rates of xenomelt incorporation from walls and floor near convecting magmas

We first consider melting near a vigorously convecting intrusion of thickness h. The approximate timescale for the onset of significant country rock melting near the intrusion is

$$t \sim \frac{h}{J(T_i - T_m)^{1/3}}$$

(simplified from Huppert and Sparks, 1988, equation 7c), where J is a coefficient encapsulating the effects of magma convection on the heat transfer (a grouping of physical properties, including the thermal diffusivity κ, expansion coefficient α, density ρ, viscosity υ, and gravity g), T_i is the initial magma temperature, and T_m the effective melting temperature of the country rock. Komatiites typically have $J \approx 1.82 \times 10^{-5}$ m s^{-1} °C$^{-1/3}$ and $T_i \approx 1{,}400$°C, while typical values for basalts are $J \approx 5 \times 10^{-6}$ m s^{-1} °C$^{-1/3}$ and $T_i \approx 1{,}200$°C (Table 2; Gole et al., 2013). For an intrusion 100 m thick in dacitic country rock with a melting temperature of 1,037°C, these values give convection melting timescales of 7 days ($t \sim 10^5$ s) for komatiite and 30 days ($t \sim 10^6$ s) for basalt.

The rate at which the wall rock can melt is controlled by the rate at which heat can be delivered from the interior of the magma across a thermal boundary layer at the intrusion contact (and a similar argument holds for chemical dissolution of the contact, with thermal properties replaced by their chemical equivalents). Flow in the magma, which could be due to convection or forced magma flow, will act to keep the thermal boundary layer at some quasi-stable thickness δ. The heat flux due to thermal conduction across this boundary layer to the melting wall rock is then just $\rho c\kappa(T_i - T_m)/\delta$ over every square meter of the intrusion contact, where ρ, c, and κ are the magma density, specific heat, and thermal diffusivity, respectively. The energy required to melt the wall rock is the latent heat of melting L plus the energy required to bring the rock up to its melting temperature, T_m, from some initial temperature, T_0, so that the total energy required to melt the walls is $\rho L + \rho c(T_m - T_0)$ per cubic meter of rock. Balancing the energy flux in with the energy required to melt the rock gives a melting rate estimate of

$$m \sim \left(\frac{c\kappa(T_i - T_m)}{L + c(T_m - T_0)} \right) \frac{1}{\delta}.$$

TABLE 2. Typical Timescales and Rates of Sulfide Addition from Different Physical Processes

Physical process	Timescale for sulfide incorporation	Timescale for intrusion cooling by same process
Diffusion	$t \sim 10^{11}$–10^{14} s (thousands to millions of years)	$t \sim 10^{12}$ s (thousands of years)
Wall/floor melting	$t \sim 10^{5}$–10^{6} s (days)	$t \sim 10^{5}$–10^{7} s (days to months)
Xenolith melting	$t \sim 10^{3}$–10^{4} s (hours to days)	N/A

The stable boundary layer thickness will be different for different flow settings. In the specific case of a turbulently thermally convecting intrusion, the boundary layer thickness is given by

$$\delta = \frac{J(T_i - T_m)^{1/3}}{\kappa}$$

(Turner, 1979). We take some rough values for a dacitic wall rock of $L = 5 \times 10^5$ J kg^{-1}, $\rho = 2600$ kg m^{-3}, and $c = 730$ J kg^{-1} m^{-3}, with a melting temperature of 1,000°C and an initial temperature of 500°C (Gole et al., 2013). With the values of J and T_i for the komatiite magma, we obtain thermal boundary layers of $\delta \sim 10^{-2}$ m, giving melting rates of about 2.3 m per day. For the basaltic magma, we obtain $\delta \sim 10^{-1}$ m with melt rates of about 20 cm per day. As magma near the intrusion boundary cools, the melt rate slows drastically from these values; however, detailed analysis shows that overall melting rates are still on the order of a few meters per year at the roof of a basaltic magma chamber within the continental crust (Huppert and Sparks, 1988).

These values are calculated for turbulently convecting flows, where the turbulence keeps the magma well mixed, keeping hot material close to the country rock (i.e., the boundary layer thickness δ is small). However, melting can also occur for laminar flows—a study by Kerr (2001) determined the thermal boundary layer thickness for forced laminar flows of magma and showed that melting will still take place, albeit with melting velocities on the order of 1 to 10 cm per day, a rate much slower than those given above. These predictions are supported by observations of thermal erosion at rates of centimeters per day in basaltic tholeiitic flows on Hawaii by Kauahikaua et al. (1998).

Examples of xenomelt incorporation in komatiite flows

Ni-rich sulfide mineralization associated with komatiites provides an example where the addition of crustal sulfur has been pivotal to the ore-forming process. In many komatiite systems, it has been shown that sulfur was derived from sulfidic country rocks in the immediate substrate of komatiite flow channels, and was deposited as ribbon-shaped accumulations of magmatic sulfide liquid on the floors of these channels (Huppert et al., 1984; Lesher et al., 1984). The key evidence for the physical process was first obtained at Kambalda, where the ore-bearing channels are defined by the distribution of a distinctive sulfidic sediment unit, present at the contact between the basal komatiite flow and the footwall basalt outside the channels, where it is typically 2 to 5 m thick, but characteristically absent within them (Gresham and Loftus-Hills, 1981). Evidence of erosion of footwall rocks at the base of komatiite flows is known from numerous other localities. Houlé et al. (2012) describe an erosional basalt contact in footwall andesites beneath the Alexo deposit. The Perseverance komatiite complex hosts a very large (>50 Mt) basal sulfide deposit occupying a channel at least 50 m deep within footwall dacites (Barnes, 2006). Other examples of country-rock xenoliths and erosional contacts associated with komatiite-hosted ores are found at Hunter Road, Zimbabwe (Prendergast, 2001), and in the Raglan camp in northern Quebec (Lesher, 1999).

A clear example of this process is preserved in the Silver Swan deposit near Kalgoorlie in Western Australia, where partially melted xenoliths of dacite are incorporated into the actual orebody, disaggregating as they ascend buoyantly through the dense sulfide liquid (Dowling et al., 2004). Such observations are relatively rare and are particularly easy to see in this locality owing to the visual contrast between xenoliths and massive sulfides (compared to the normal difficulty of recognizing xenoliths in highly altered komatiite host rocks), but illustrate an important principle that footwall erosion is primarily driven not by melting of the floor in place but by incorporation of footwall xenoliths followed by melting.

Another example of this process is the presence of a distinctive “ocellar xenomelt” lithology at Victor Shoot, Kambalda, reported by Frost and Groves (1989). This unit represents accumulation of completely molten xenoliths of the contact sediment that has melted, disaggregated into a sulfidic and felsic component, then separated—the felsic melt floated to the top of the flow, while the sulfide component became incorporated into the basal orebodies. This observation leads into the next section of this discussion, which deals more generally with the process of xenolith incorporation into magmas.

Rates of xenomelt incorporation from melting xenolithic blocks

Similarly to melting of wall rocks, xenolith melting rates are controlled by the initial temperature of the xenolith and the physical properties of the magma which control the local free or forced flow around the xenolith. The local magma flow is important, as it controls the thickness of the melt layer which forms around the xenolith as it melts—a thick melt layer insulates the xenolith from further melting by the magma, while xenoliths with thin melt layers that are actively stripped away by flow of the host magma melt much more rapidly. To obtain a timescale for melting a xenolith of diameter h, we can follow a line of reasoning similar to that in the wall-rock melting case and balance the flow of heat across a thermal boundary layer of thickness δ with the latent heat required to melt the xenolith, giving the estimate

$$t \sim \frac{h\,L}{\kappa c(T_i - T_m)}\,\delta$$

for the time for the xenolith to melt completely (e.g., McLeod et al., 1996, equation 2).

Here again, the local magma flow determines the thickness δ of the thermal boundary layer. As a simple case, we take a xenolith settling through a static magma under its own buoyancy, for this case

$$\delta = \left(\frac{\upsilon\kappa h}{g'}\right)^{1/4}$$

(McLeod et al., 1996), where υ is the dynamic viscosity of the magma and g' is the reduced gravity due to the density difference between xenolith and magma. For a cm-size dacitic xenolith in a basalt, we obtain $\delta \sim 4 \times 10^{-3}$ m and, in komaiite, $\delta \sim 3 \times 10^{-3}$ m. From these estimates, we obtain melting times of $t \sim 20$ s (in komatiite) and $t \sim 10^2$ s (a few minutes, in basalt) for a centimeter-scale xenolith up to $t \sim 10^3$ s (about an hour, in komatiite) and $t \sim 10^5$ s (several days, in basalt) for a meter-sized xenolith.

This rough estimate assumes homogeneous xenolith melting temperatures. For heterogeneous mixtures of minerals, residual minerals with higher melting temperatures will tend to be dissolved in the magma, a much slower process than melting (Kerr, 1994a). They can also be separated from the melted portion of the xenolith via disaggregation and settling. This separation process is complex and has been considered in detail by McLeod and Sparks (1998). Their theory predicts melt rates on the order of 1 to 10 mm per hour, with complete melting after a few tens of hours (depending on xenolith size), consistent with our rough estimate above. From these timescales, we can assume that the xenoliths will melt rapidly over a few hours once incorporated into the magma and, therefore, the rate-limiting step for incorporating xenolithic sulfur via melting is the melting and erosion of the wall rock.

This is consistent with observations of residual xenoliths in the field. For example, in the Duluth Complex xenoliths of Virginia Formation range in size from a few centimeters in thickness to large (hundreds of meters in length and width), raft-like bodies which are suggestive of delamination of the footwall. Most of the xenoliths show strong evidence of partial melting (e.g., 44–48% SiO_2 compared to 60% or more in equivalent unmetamorphosed pelitic rocks) and are orthopyroxene-bearing hornfels where pyrite has been converted to pyrrhotite. However, in the core of many of the larger xenoliths, the low-grade assemblage of chlorite-muscovite-quartz-plagioclase-pyrite-kerogen still persists. In the Basal Breccia sequence of the Voisey's Bay Intrusion (e.g., Li and Naldrett, 2000; Mariga et al., 2006), small but abundant xenoliths are present with a refractory assemblage of hercynite, magnetite, Ca-rich plagioclase, and corundum. Pelitic and quartzofeldspathic xenoliths underwent extensive partial melting. Pelitic protoliths were locally sulfidic, containing pyrrhotite as well as graphite; however, no sulfide remains in the xenoliths. It is clear that xenoliths in the Partridge River Intrusion have not been as completely digested as those in the Basal Breccia sequence at Voisey's Bay. The most likely reason for this relates to the prolonged interaction with magma pulses in the conduit at Voisey's Bay compared to the less dynamic nature of emplacement of single magma sheets in the Duluth Complex.

Conclusions

Sulfide (primarily pyrite and pyrrhotite) and evaporate minerals in a variety of rock types may release sulfur via processes such as thermal degradation during devolatilization, dissolution (usually involving saline fluids) and, in some cases, direct melting. In many contact aureoles, mass balance considerations clearly show that sulfur in quantities sufficient to explain sulfide-rich mineralization is not available. Where sufficient sulfur could potentially be available, mass transfer may be limited by variables such as transport mechanism (particularly diffusion through a grain boundary fluid) relative to crystallization rate of the magma, and sulfidation reactions involving Fe-bearing silicate and oxide minerals. Timescales for diffusive transfer of sulfur from contact aureoles are at least an order of magnitude less than those of diffusive cooling of magma and severely limit the possibility for sulfur derivation from contact aureoles.

The alternative to the addition of sulfur to a magma via transport through a contact aureole is delivery of sulfur derived from xenoliths. Sulfur may be liberated via devolatilization and fluid production, dissolution, or direct melting in the high-temperature environment. Xenoliths derived from thermomechanical erosion near the base of high-temperature komatiite lavas undergo melting; the process is responsible for the addition of sulfur and ultimate generation of Ni-rich sulfide deposits. Melting rates of xenoliths in mafic magmas are rapid and sulfur liberated from xenoliths is capable of causing sulfide supersaturation in a large volume of surrounding magma. Pyrrhotite derived from xenoliths may melt directly to form sulfide liquid droplets without dissolving into the silicate magma. These processes of xenolith assimilation provide the potential to generate large volumes of immiscible sulfide liquid that could then be collected into suitable traps.

Acknowledgments

We thank a long list of colleagues whose focus is the genesis of Ni-Cu-PGE deposits for their encouragement and suggestion to write this manuscript. This manuscript was greatly improved by careful reviews from Paul Golightly and Peter Lightfoot. Ed Ripley and Chusi Li acknowledge the National Science Foundation for many years of support for the study of magmatic ore deposits and for current grant EAR 1249702. Jess Robertson and Steve Barnes are funded by fellowships from the CSIRO Office of the Chief Executive. This is a contribution from the CSIRO Mineral Resources National Research Flagship.

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