Sulfide Saturation in Mafic Magmas: Is External Sulfur Required for Magmatic Ni-Cu-(PGE) Ore Genesis?

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Abstract

The importance of externally derived sulfur in the genesis of sulfide-rich, magmatic Ni-Cu-(platinum group element [PGE]) deposits remains a key, yet unresolved, issue. Calculations utilizing a variety of mafic magma types indicate that, in general, sulfide saturation by fractional crystallization occurs after Ni has been depleted due to olivine crystallization. Cu- and PGE-rich layers may form during relatively later stages of closed-system crystallization, but unless the collection of the cotectic proportion of immiscible sulfide is extremely efficient, the mass of sulfide is too small to produce an economic deposit. We show that there are numerous processes that may lead to early sulfide saturation in mafic/ultramafic magmas. Contamination of mantle-derived magmas by silicic rock country rocks or their partial melts will lower the sulfur content needed to induce sulfide liquid saturation, typically by amounts ranging from 200 to 700 ppm. The mixing of magmas, particularly if the result is to lower the liquidus temperature of the mixed magmas, may also lower the sulfur content needed to attain sulfide saturation by similar amounts. An increase in magma fO2 related to the addition of volatiles such as H2O and CO2 is less effective in decreasing the sulfur concentration needed to achieve sulfide liquid saturation. Contamination processes that lead to an increase in the activity of SiO2 in the melt, and hence may promote orthopyroxene rather than olivine crystallization, aid in generating relative Ni enrichment in remaining liquid as a result of the lower DNi (mineral – melt) value of orthopyroxene relative to olivine. Although contamination and magma mixing may produce early sulfide saturation without the addition of externally derived sulfur, Ni-rich sulfide deposits can form in such cases only from large-volume, open systems, where the efficiency of sulfide collection is high. No matter what the liquidus minerals may be, without the addition of country rock-derived sulfur, the mass of sulfide necessary to generate economic Ni-Cu-(PGE) concentrations requires efficient sulfide collection from large, but not necessarily unrealistic, volumes of magma. Small deposits (4–30 Mt of sulfide) may form from the collection of cotectic proportions of sulfide from less than 50 km³ of magma. Larger deposits such as those at Noril’sk could involve more than 200 km³ of magma; this volume of magma is not unreasonable, particularly in rift/plume-related settings. Despite such possibilities, sulfur isotope data clearly indicate that externally derived sulfur has been involved in the formation of many large deposits, and that collection of mantle-derived sulfide in sufficient quantities to produce orebodies is a rare process. We propose that magmatic Ni-Cu-(PGE) sulfide ore formation normally requires significant sulfide supersaturation, and that the addition of sulfur derived from xenoliths is the most viable mechanism for producing sulfide well above the cotectic proportion in mafic/ultramafic magmas.

Introduction

The attainment of sulfide saturation of a magma and the separation of immiscible sulfide liquid, together with the presence of an appropriate physical environment for the collection and concentration of the metal-rich sulfide liquid, are key ingredients for the formation of mafic Ni-Cu-(platinum group element [PGE]) deposits. Experimental studies of the solubility of sulfur in mafic magmas (e.g., Haughton et al., 1974; Shima and Naldrett, 1975; Buchanan and Nolan, 1979; Danckworth et al., 1979; Wendlandt, 1982; Mavrogenes and O’Neill, 1999; Holzheid and Grove, 2002; O’Neill and Mavrogenes, 2002; Clemente et al., 2004; Jugo et al., 2005; Scaillet and Macdonald, 2006; Liu et al., 2007; Moune et al., 2009) have shown that several processes can lead to the attainment of sulfide saturation in a mafic magma. Mavrogenes and O’Neill (1999) showed that the solubility of sulfide in a mafic magma increases with decreasing pressure, and therefore concluded that mafic magmas that are emplaced at relatively shallow depths are unlikely to be sulfide saturated. They noted that, in order for sulfide saturation to be achieved in the low-pressure environment, either extensive fractional crystallization or the introduction of external sulfur must occur. The experimental data on sulfide and sulfate solubility in mafic magmas that are now available can be used to illustrate that several processes of contamination of mafic magma, or mixing of magma types, can lead to the saturation of a mafic magma with sulfide or sulfate liquid. However, one of the major questions still posed with respect to magmatic Ni-Cu-(PGE) ore deposition is if externally derived sulfur is an essential ingredient in the process. Recent articles illustrate the strongly contrasting points of view. For example, Keays and Lightfoot (2010) state that crustal sulfur must be added to mantle-derived magmas to promote ore genesis, whereas Seat et al. (2009) provide evidence from the Nebo-Babel deposit that mantle S can be sufficient to promote ore formation.

The only process for the attainment of sulfide saturation in a mafic magma that does not require some type of interaction with country rocks, or mixing of magmas, is fractional crystallization. The increase in S concentration of a melt as a result of crystallization of olivine, pyroxene, feldspar, etc., may lead to the separation of what is known as “cotectic” proportions of sulfide liquid. Sulfide-poor but PGE-enriched layers such as that found in the Sonju Lake intrusion (e.g., Miller, 1999; Park et al., 2004) are thought to result from fractional crystallization...
of a tholeitic melt. Tao et al. (2007) proposed that sulfide saturation was achieved due to olivine and chromite crystallization in magma that gave rise to PGE-enriched disseminated sulfide zones in the Jinhuaoshan intrusion in China.

Most, but perhaps not all, of the world’s large Cu-Ni-(PGE) deposits exhibit evidence for mixing processes in their evolution, either involving a compositionally distinct mantle-derived magma or a crustal contaminant. Chemical mixing of magmas has been proposed as an integral process in the formation of high-grade PGE deposits, such as those of the Mercenys Reef in the Bushveld Complex and the JM Reef in the Stillwater Complex (e.g., Campbell et al., 1983; Naldrett and von Gruenewaldt, 1989), and has recently been proposed by Godel et al. (2011) as a key process in the generation of the Nebo-Babel deposits. Li and Ripley (2009) showed that mixing of two magmas could lead to the attainment of sulfide saturation in the mixed magma. However, the degree of sulfide saturation is critically dependent on the sulfur contents of the end-member magmas, and the amount of sulfide liquid that may form will typically be small. Sulfide-poor but PGE-rich deposits could result, but it is not clear whether sulfide-rich, large tonnage Cu-Ni-(PGE) deposits could be produced. Another type of mixing involves mafic magmas and partial melt derived from assimilated, siliceous wall rocks. Irvine (1975) deduced that the addition of SiO₂ to a mafic magma could decrease sulfide solubility and promote the formation of an immiscible sulfide liquid. Magma silicification or felsification has been proposed as a mechanism to induce sulfide cation has been proposed as a mechanism to induce sulfide saturation in magmas related to the Ni-Cu-rich ores of the Jinchuan deposit and the PGE-rich occurrences in the Platreef of the Bushveld Complex, respectively. Changes in magma fO₂ are related to changes in key compositional values such as the FeO/Fe₂O₃ ratio. Experimental results suggest that at relatively low fO₂ conditions, where sulfur is the predominant sulfur species, small increases in fO₂ of a magma coupled with decreased amounts of FeO will decrease the S concentration needed to attain sulfide saturation. However, whether this process can account for the large amounts of sulfide in systems such as Jinchuan remains unclear. Perhaps the most obvious contaminant to induce sulfide saturation in magmas is S itself. This was pointed out by Mavrogenes and O’Neill (1999) as a result of their experimental work on the effect of pressure on sulfide solubility, and has been proposed by many researchers based on physical parameters such as the spatial proximity of S-rich country rocks or S isotope results. Sulfur isotope results have provided strong evidence for the introduction of S in komatiite-related deposits (e.g., Naldrett, 1966; Lesher and Groves, 1986; Bekker et al., 2009), the deposits at Noril’sk (Grinenko, 1985; Gorbachev and Grinenko, 1973; Li et al., 2003b), sulfide deposits in the Duluth Complex (e.g., Ripley, 1981; Ripley and Al-Jassar, 1987; Lee and Ripley, 1995; Arcuri et al., 1998; Ripley et al., 2007), Voisey’s Bay (Ripley et al., 1999, 2002), Uitkomst (Li et al., 2002), and the recent discoveries of Kabanga in southern Africa (Maier et al., 2011). In fact, it is often the absence of compelling S isotope evidence that has led researchers to seek alternatives to external S addition to promote sulfide saturation in mafic magmas (e.g., Seat et al., 2009). There are at least two reasons why δ³⁴S values of sulfide ores that fall in the range generally considered to be normal for S in the upper mantle (−0 to 2‰, Ripley, 1999, and references therein) should not necessarily be taken as an indicator that S contamination has not occurred. One is the situation discussed by Ripley et al. (2002) for the Voisey’s Bay deposit. At Voisey’s Bay, only the ores in the Reid Brook zone show δ³⁴S values that are different from those of mantle S. However, when examined in detail, it is clear that the Proterozoic Tasiyuk Gneiss, a locally sulfidic/graphitic pelite that is a likely source of externally derived S, is characterized by a wide range of δ³⁴S values (−17 to +18‰; Ripley et al., 2002). These values are not unusual for sulfide found in sedimentary rocks, and of particular significance is the fact that the weighted average δ³⁴S of the Tasiyuk Gneiss is −1.4‰. Clearly, if homogenization occurred in the magma, anomalous δ³⁴S values should not be expected. This example holds for any situation where the δ³⁴S value of country-rock S is near 0‰. A second possibility is that if sulfides accumulated in a chamber where additional uncontaminated magma passed, isotopic exchange reactions (Ripley and Li, 2003) could result in δ³⁴S values that approach those of mantle values. This process would be expected in conduit systems where magma passage may have led to increases in the tenor of accumulated sulfide. In Archean systems, where sedimentary sulfides may be characterized by δ³⁴S values that depart only slightly from those of mantle values, the use of multiple S isotopes (e.g., δ³⁴S as well as δ³⁴S) has proven valuable in the determination of externally derived S from Archean rocks. Archean sedimentary sulfides often record anomalous Δ³⁴S values (deviation from the terrestrial fractionation line), thought to be linked to low oxygen values in the Archean atmosphere (e.g., Farquhar and Wing, 2003). Anomalous Δ³⁴S values have been utilized by Bekker et al. (2009) to confirm the importance of crustal S in komatiite-related deposits. For magmatic deposits where Archean rocks are unlikely to have supplied S to the magma, Δ³⁴S will be of little value as an indicator of external S addition where δ³⁴S values are near 0‰. There can be little argument that crustal S has played a significant role in ore genesis in those deposits where S isotope values are strongly anomalous. In their recent paper, Keays and Lightfoot (2010) used chalcophile element geochemistry of basaltic rocks at Noril’sk compared to those of the Deccan to arrive at their conclusion that crustal S is essential for the genesis of magmatic Ni-Cu deposits. Others (e.g., Lehmann et al., 2007; Seat et al., 2009) refute such a claim, and the question remains if other mechanisms which can promote sulfide saturation in a magma can lead to the generation of magmatic Ni-Cu sulfide orebodies. In this paper we review many of the processes that can lead to the attainment of sulfide saturation in a mafic magma and attempt to constrain some key parameters that are of importance in situations where the addition of externally derived S to a magma is not indicated, and hence may not be of significance.
for Ni-Cu-(PGE) ore formation. We utilize the equation of Li and Ripley (2009) to estimate the concentration of sulfur at sulfide saturation (SCSS) in a mafic magma; the equation is based on experimental results from a variety of sulfide-saturated and compositionally variable systems (see above) and gives results that are similar to the equation of Liu et al. (2007). We use the equation in conjunction with the MELTS routine of Ghiroso and Sack (1995) to evaluate how processes such as fractional crystallization, compositional variations related to contamination, and changes in intensive parameters such as $f_O^2$ affect the attainment of sulfide saturation in magmas. We also evaluate the importance of the mass of magma involved in potential ore-forming systems where the introduction of externally derived S may not have occurred.

It should be noted that the equation for SCSS by Li and Ripley (2009) does not take into account chalcophile elements such as Ni and Cu. Ariskin et al. (2010) and Evans et al. (2008) have shown that chalcophile elements, in addition to Fe, may exert a significant control on the solubility of S in mafic to ultramafic magmas. The potential influence of Ni and Cu on sulfur solubility is particularly important when assessing the role of mantle-derived S in ore genesis. As S is held primarily within Ni, Cu, and Fe sulfide minerals in the mantle,complexing with these metals is to be expected. This will be true for high-degree or second-stage mantle melts, where immiscible sulfide liquid may ultimately dissolve in silicate liquids. There is no reason for the breaking of S-Cu or S-Ni bonds in favor of S-Fe, and both Ni and Cu must exert a control on the capacity of a mafic magma to dissolve sulfide. If S is introduced into a mafic/ultramafic melt, the mass action effect will strongly favor the formation of Fe-S complexes. O’Neill and Mavrogenes (2002) have stated that the sulfide capacity of a melt with ~10% FeO is controlled mostly by the Fe content. Until additional experimental data that treat the effects of chalcophile element concentration on sulfide solubility over a broad range of compositions are available, we are unable to update our regression equation.

### Fractional Crystallization and Sulfide Saturation

In Figure 1 we illustrate the sulfide saturation curves for a high-Al olivine tholeiite (HAOT—Table 1) liquid thought to be a reasonable parental magma for troctolite rocks (e.g., Duluth Complex and, potentially, Voisey’s Bay; Ripley et al., 2007; Scoates and Mitchell, 2000), a high-FeO picritic liquid thought to be a potential parental magma for rocks that host the Eagle deposit (Ding et al., 2010), and a high-FeO, siliceous high-MgO basalt liquid similar to the B1 magma type proposed by Barnes et al. (2010) as a potential parental magma for rocks in lower and lower Critical zones of the Bushveld Complex. In this discussion the magmas are assumed to be anhydrous; the effect of H$_2$O on the sulfide saturation curve is discussed below. For the high-Al olivine tholeiite (Fig. 1a) the sulfide saturation value rises slightly from that of the 1-kb liquidus due largely to iron enrichment in the liquid related to crystallization of plagioclase and olivine in a ratio of 3:1 (Table 2). It is not until later in the sequence, and particularly when spinel becomes a liquidus mineral, that the sulfide saturation value begins to decrease. In the case of a picritic parental magma, the S content required for saturation at the liquidus is considerably higher than that required to saturate the HAOT liquid, but the saturation value decreases as olivine initially crystallizes, followed by olivine plus clinopyroxene (Fig. 1b; Table 2). Where clinopyroxene and plagioclase begin to crystallize, the FeO content of the residual magma rises, and the S content required for sulfide liquid saturation increases as well. In the case of the FeO-rich, siliceous high-MgO basalt, the SCSS progressively declines, as initial olivine crystallization is quickly followed by orthopyroxene (~3.5% crystallization), and then clinopyroxene and plagioclase. These three examples illustrate the types of variations in the SCSS trajectories that may characterize mafic magmas.

Treating S as a perfectly incompatible element during silicate crystallization, we indicate when fractional crystallization should induce sulfide saturation in the HAOT and picritic magmas. A value of 1,000 ppm S is representative of a melt

### Table 1. Composition of Magmas Used to Assess SCSS (values in wt %)

<table>
<thead>
<tr>
<th>Column</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>47.77</td>
<td>46.56</td>
<td>48.95</td>
<td>52.30</td>
<td>55.37</td>
<td>48.00</td>
<td>47.26</td>
<td>71.42</td>
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<td>TiO$_2$</td>
<td>1.20</td>
<td>1.25</td>
<td>2.84</td>
<td>1.17</td>
<td>0.38</td>
<td>1.81</td>
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<td>Al$_2$O$_3$</td>
<td>19.90</td>
<td>19.40</td>
<td>12.82</td>
<td>12.70</td>
<td>11.53</td>
<td>11.69</td>
<td>6.55</td>
<td>13.70</td>
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<td>FeO$_3$</td>
<td>0.71</td>
<td>1.62</td>
<td>2.05</td>
<td>1.17</td>
<td>1.32</td>
<td>1.54</td>
<td>0.28</td>
<td>0.28</td>
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<tr>
<td>FeO</td>
<td>10.37</td>
<td>10.74</td>
<td>10.06</td>
<td>5.57</td>
<td>8.16</td>
<td>10.91</td>
<td>8.53</td>
<td>1.20</td>
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<tr>
<td>MgO</td>
<td>7.10</td>
<td>6.92</td>
<td>7.73</td>
<td>13.08</td>
<td>13.79</td>
<td>13.67</td>
<td>30.23</td>
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<td>CaO</td>
<td>0.60</td>
<td>9.44</td>
<td>12.52</td>
<td>9.56</td>
<td>6.58</td>
<td>9.53</td>
<td>5.04</td>
<td>5.04</td>
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<tr>
<td>Na$_2$O</td>
<td>2.67</td>
<td>2.60</td>
<td>2.51</td>
<td>3.73</td>
<td>1.85</td>
<td>1.75</td>
<td>0.45</td>
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<td>K$_2$O</td>
<td>0.50</td>
<td>0.49</td>
<td>0.51</td>
<td>0.43</td>
<td>1.02</td>
<td>0.48</td>
<td>0.10</td>
<td>4.03</td>
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<td>H$_2$O</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Columns: 1) High-Al olivine tholeiite; Ripley et al., 2007; liquidus T = 1,229°C
2) High-Al olivine tholeiite, 1 wt % H$_2$O; Ripley et al., 2007; liquidus T = 1,169°C
3) Ocean island tholeiite; Kent et al., 1999; liquidus T = 1,205°C
4) Siliceous high-MgO basalt; e.g., Barnes, 1989; liquidus T = 1,347°C
5) High-FeO, siliceous high-MgO basalt; e.g., Barnes et al., 2010; liquidus T = 1,382°C
6) High-FeO picrite; Ding et al., 2009; liquidus T = 1,337°C
7) Komatiite; Barnes, 2007; liquidus T = 1,617°C
8) Partial melt from pelite; Hoffer and Grant, 1980
FIG. 1. Sulfur content at sulfide liquid saturation versus wt % of magma crystallization. The sulfur axis refers either to the sulfur content at sulfide liquid saturation or, in the case of fractional crystallization, to the sulfur content of the remaining liquid. Fractionating assemblages are given in Table 2. All calculations were done using a pressure of 1 kbar. Note the relatively small differences between the HAOT at QFM and QFM-2 (a), and a similar relationship for the high-FeO picrite (b). Trends for the contaminated magmas, and the hydrous HAOT, are similar, with much lower SCSS values than their anhydrous and uncontaminated counterparts. Sulfur enrichment due to fractional crystallization is illustrated for initial concentrations of 800, 1,000, and 1,500 ppm. Sulfide saturation is attained at less than ~20% crystallization in contaminated magmas with 1,000 ppm S. Of particular note is the fact that orthopyroxene is the fractionating phase rather than olivine and plagioclase in the HAOT magma contaminated with 15% SiO₂ (Table 2). Although the S content of the magma contaminated with SiO₂ only would drop to 850 ppm, saturation would still be attained at ~10% crystallization. Orthopyroxene is the fractionating phase at ~3.5% crystallization for the high-FeO, siliceous high-MgO basalt (c). Because D^Ni(mineral-melt) values are lower for orthopyroxene relative to olivine, the crystallization of orthopyroxene may be relevant for the formation of Ni-rich sulfide orebodies where sulfide saturation was attained after significant magma crystallization.
SULFIDE SATURATION IN MAFIC MAGMAS: IS EXTERNAL SULFUR REQUIRED FOR MAGMATIC Ni-Cu-(PGE) ORE GENESIS?

Table 2. Fractionating Minerals from the Magmas Illustrated in Figure 1

<table>
<thead>
<tr>
<th>Magna</th>
<th>fO₂ (first appearance)</th>
<th>Minerals¹</th>
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<tbody>
<tr>
<td>HAOT</td>
<td>QFM-2</td>
<td>pl</td>
</tr>
<tr>
<td></td>
<td>1.233</td>
<td>pl</td>
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<td>1.198</td>
<td>pl,ol</td>
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<td></td>
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<td>pl,ol,sp</td>
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<tr>
<td></td>
<td>1.078</td>
<td>pl,ol,sp</td>
</tr>
<tr>
<td>HAOT, 1% H₂O</td>
<td>QFM</td>
<td>ol</td>
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<tr>
<td></td>
<td>1.169</td>
<td>pl,ol</td>
</tr>
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<td>1.079</td>
<td>pl,ol,sp</td>
</tr>
<tr>
<td></td>
<td>1.069</td>
<td>pl,ol,sp</td>
</tr>
<tr>
<td>HAOT + 10% pelite melt</td>
<td>QFM-2</td>
<td>pl</td>
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<td></td>
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<td>pl,ol</td>
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<td></td>
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<td>HAOT + 30% SiO₂ melt</td>
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<td>1.032</td>
<td>ol,opx,sp</td>
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¹ cpx = clinopyroxene, ol = olivine, opx = orthopyroxene, pl = plagioclase, sp = spinel

derived from 20% melting of a mantle with 200 ppm S (Palme and O’Neill, 2004). Lower degrees of melting may produce melts with higher S concentrations, but, if sulfide saturation is attained, immiscible sulfide may be retained in the mantle (e.g., Keays, 1995; Naldrett, 2011). In the case of a magma such as a HAOT, which may be itself derived from fractional crystallization of a more primitive liquid, the S concentration of the derivative liquid may be more elevated. However, troctolitic rocks from the Duluth Complex that show no evidence for crustal contamination contain from 500 to 600 ppm S and suggest that the parental HAOT contained far less than 1,000 ppm S (Ripley et al., 2007). For comparative purposes, we show S trajectories as a result of fractional crystallization for initial concentrations of 800, 1,000, and 1,500 ppm. In the case of the picritic magma, saturation at 1 kb is reached at ~40% crystallization for a starting magma with 1,000 ppm S. For the HAOT, ~40% crystallization is also required to induce sulfide liquid saturation. Of additional note is that, due to the shallow trend of the SCSS curve where plagioclase and clinopyroxene are liquidus minerals (Table 2), and the positive slope where Fe enrichment accompanies the cessation of olivine crystallization, only small amounts of immiscible sulfide liquid can be generated as a result of fractional crystallization until late stages of the process. In strong contrast, sulfide saturation is attained in the high-FeO, siliceous high-MgO basalt at ~17% fractional crystallization for a magma with an initial S concentration of 1,000 ppm.

Concentrations of platinum group elements and Cu are expected to increase during fractional crystallization due to their high degree of incompatibility. This is not the case for Ni, which is readily accepted into the olivine structure. Distribution coefficients for Ni between olivine and liquid in sulfide-undersaturated conditions are a strong function of MgO contents and range between 4 and 20 at MgO concentrations from 22 to 4 wt % (see summary in Li et al., 2003a). For the picritic parental magma (assuming an initial concentration of Ni = 300 ppm), where the ratio of olivine crystallized to plagioclase plus clinopyroxene at the point of sulfide saturation is ~1.7, the concentration of Ni in the residual liquid drops to 127 ppm using an olivine/liquid D value of 7. The drop in Ni concentration for the HAOT at the 40% crystallized point, where sulfide saturation is predicted, is similar (139 ppm) due in part to an olivine/liquid D value of 15. The drop in Ni concentration is far less extreme for the high-FeO, siliceous high-MgO basalt, where orthopyroxene replaces olivine as a liquidus phase before sulfide saturation is attained. Because the DiNi (orthopyroxene-liquid) value for orthopyroxene (~1–3, Hashizume and Hariya, 1992; Frei et al., 2009) is considerably lower than the DiNi (olivine-liquid) value, higher concentrations of Ni will be available for partitioning into sulfide liquid. Of obvious concern is whether sulfide-saturated magmas where prior crystallization of olivine is indicated and that contain less than 140 ppm Ni can produce Ni sulfide-rich orebodies. We will return to this point below, but end the current discussion with an example where fractional crystallization appears to have played a strong role in the distribution of S and metals in an intrusion.

The Sonju Lake intrusion is a relatively small (~1,200 m thick) layered body in the Beaver Bay Complex associated with the ~1.1 Ga Duluth Complex (Miller and Ripley, 1996). Miller (1999) and Park et al. (2004) have described the presence of Cu- and PGE-enriched zones in the layered sequence at the level of Fe oxide-rich gabbro (Fig. 2). Miller (1999) suggested that the “reef” represents the level at which sulfide saturation was achieved in the crystallizing magma. Li and Ripley (2005) confirmed that sulfide saturation should have been achieved at the time that spinel became a liquidus mineral using an equation which is the predecessor to that used.
in this manuscript (Li and Ripley, 2009). What is particularly important is the fact that at the level of the Cu and PGE enrichment, the concentration of Ni has dropped to values of less than 20 ppm. The field and geochemical evidence strongly suggests that Ni was sequestered by olivine prior to the attainment of sulfide saturation in the magma. The Sonju Lake intrusion perhaps represents an end-member case where extensive Ni depletion occurred prior to the arrival of sulfide saturation in the magma by fractional crystallization.

Contamination and Sulfide Saturation

Assimilation of volatiles

The addition of volatile species such as H₂O, CO₂, CH₄, and H₂S to a magma may occur without melting or dissolution of major minerals. We will treat the potential for the addition of volatile S species to a magma below. The role of H₂O in the solubility of S in mafic magmas has received only minor attention (e.g., Liu et al., 2007; Gorbachev and Bezman, 2011; Moune et al., 2009), and further experimental study is required to assess the importance of species such as H₂S and HS⁻ in sulfide dissolution within mafic magmas. The addition of H₂O to a magma is frequently linked to an increase in fO₂ and decrease in FeO content (and hence the capacity of a magma to dissolve sulfide) via a reaction such as the following:

\[ \text{H}_2\text{O} + 2 \text{FeO} = \text{Fe}_2\text{O}_3 + \text{H}_2 \]

However, Carmichael (1991) and Righter et al. (2008) have discussed the uncertainty of H₂O addition to a magma resulting in an increase of magma fO₂. This is particularly true if H₂O dissolution is via molecular H₂O rather than an OH⁻ complex. Even without a substantial change in fO₂, the SCSS of an H₂O-bearing mafic magma may be much lower relative to the anhydrous counterpart. In Figure 1a the SCSS curve for an HAOT with 1 wt % H₂O at QFM is shown to be lower than that of the anhydrous variety by ~280 ppm at liquidus temperatures. Ripley et al. (2007) have shown that a value of 1 wt % H₂O is reasonable for many of the magmas that produced sulfide-bearing intrusions in the Duhuth Complex. A large part of the H₂O may have been derived via assimilation of fluid produced as country rocks were dehydrated. In the case of the high-FeO, siliceous high-MgO basalt, the addition of 1 wt % H₂O lowers the SCSS by ~135 ppm at the liquidus, and by greater values throughout the course of crystallization. The effect is very similar to that produced by the assimilation of a pelite-derived partial melt (see below). Although additional study of the effect of H₂O addition on the solubility of S in mafic-derived partial melt is warranted, it appears that hydrous magmas may attain sulfide liquid saturation much sooner than low-H₂O magmas.

A similar uncertainty in terms of increases of magma fO₂ is associated with assimilation of CO₂. Dissolution mechanisms
of carbonic species in a magma are important in evaluating potential magma \( f_{O_2} \) increases. At relatively high pressure, \( \text{CO}_2 \) dissolves as \( \text{CO}_2^+ \) (e.g., Blank and Brooker, 1994) with relatively little variation in magma \( f_{O_2} \). Stanley et al. (2011) found no correlation between \( \text{CO}_2 \) concentration and the ratio of \( \text{Fe}^{2+} \) to total \( \text{Fe} \) in a basaltic liquid. In contrast, Wenzel et al. (2002) proposed that \( \text{CO}_2 \)-rich fluids released during the decomposition of dolomitic xenoliths in the Ioko-Doyyen intrusion resulted in locally elevated magma \( f_{O_2} \) values. Mollo et al. (2010) suggested the opposite—that carbonate assimilation involving magma-\( \text{H}_2\text{O}-\text{CO}_2 \) interaction may lead to a decrease in magma \( f_{O_2} \) values. Methane may be a component of fluids produced by dehydration of carbonaceous pelites (e.g., Ohmoto and Kerrick, 1977; Andrews and Ripley, 1989). The assimilation of \( \text{CH}_4 \) is expected to reduce the \( f_{O_2} \) of the magma and may be of significance in the reduction of sulfate in magmas with oxidation states that permit sulfate plus sulfide coexistence or the presence of sulfate only (e.g., Jugo et al., 2005; Jugo, 2009). The assimilation of graphite, perhaps accompanied by \( \text{CH}_4 \), by relatively oxidized, sulfate-bearing magmas has also been proposed as an important process for decreasing magma \( f_{O_2} \) and causing the reduction of sulfate in the magma to sulfide (e.g., Nixon, 1998; Jugo and Lesher, 2006; Thakurta et al., 2005a, b). Tomkins et al. (2012) have also suggested the assimilation of graphite-bearing felsic magmas by oxidized arc basalts as a mechanism to promote magma reduction and the formation of immiscible sulfide liquid.

The assessment of sulfur-free volatile assimilation on sulfide solubility in mafic magmas remains difficult because \( f_{O_2} \) changes in natural magmas are often linked with assimilation processes that alter magma compositions other than \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratios. Li and Ripley (2005) showed that \( f_{O_2} / f_{S_2} \) ratios in many of the experiments listed above can be expressed as a function of melt composition. The effect of crystallization at QFM rather than QFM-2 on sulfide saturation in the HAOT and high-\( \text{FeO} \) picritic liquids is shown in Figure 1a and b. Saturation values at QFM are lower than those at QFM-2, as expected, but the effect is small compared to variations in sulfide saturation values related to assimilation of nonvolatile elements (see below). Jugo (2010) also noted that changes in \( f_{O_2} \) below ~QFM resulted in little change in the magma \( \text{Fe}^{2+}/\sum \text{Fe} \) ratio, and hence little change in the SCSS. Increases in the magma \( f_{O_2} \) above QFM result in decreases in the \( \text{Fe}^{2+}/\sum \text{Fe} \) ratio, as well as oxidation of sulfide to sulfate. Due to the increase in \( S \) solubility within oxidized magmas, the concentration of \( S \) needed to obtain sulfide liquid saturation also rises (e.g., Jugo, 2009).

**Assimilation of siliceous country rocks**

We utilize two compositions of contaminants to illustrate the effect of the assimilation of siliceous country rocks on the sulfide saturation state of a mafic magma. One composition is the granitic partial melt produced from a pelite in the experiments of Hoffer and Grant (1980; Table 1). The second is simply addition of \( \text{SiO}_2 \) only, as may result from magma interaction with an \( \text{SiO}_2 \)-rich sedimentary or metamorphic rock, or as may result from disequilibrium and polystage melting of pelitic rocks (e.g., Ripley and Alawi, 1988; Mariga et al., 2006). The Hoffer and Grant (1980) melt contains 4% \( \text{H}_2\text{O} \), so the potential effect of \( \text{H}_2\text{O} \) on sulfide saturation is included in the assessment.

In Figure 3, we have compared the sulfide saturation value at the liquidus temperature (1 kb) for a variety of mafic magmas and the corresponding values at the liquidus for the same magmas after 10% assimilation of the Hoffer and Grant (1980) partial melt. All sulfide saturation values decreased from a high (in terms of differences between contaminated and un-contaminated liquids) of 681 ppm \( S \) in a komatiitic liquid to a low of 246 ppm in a siliceous, high-\( \text{MgO} \) basalt liquid. As expected, the more siliceous the initial magma, the less decrease recorded by the addition of the partial melt. Starting basaltic compositions with 47 to 48 wt% \( \text{SiO}_2 \) showed decreases in sulfide saturation values from 365 to 488 ppm. The computations illustrate the exceptionally strong effect that assimilation may have on komatiitic and picritic magmas, but, in all cases, the assimilation of a granitic contaminant by a mafic magma lowers the SCSS and may lead to early generation of a sulfide liquid.

We utilize the \( \text{SiO}_2 \)-only contaminant with the HAOT to illustrate a potentially important change in the mineralogy of fractionating phases in the contaminated magma (Table 2). With 10% contamination by the Hoffer and Grant (1980) melt, all resultant magma compositions retained olivine as an early crystallizing mineral. With the addition of 15% \( \text{SiO}_2 \) to the HAOT composition, not only is the sulfide saturation value decreased by 569 ppm, but the liquidus phase changes to orthopyroxene. In the case of the high-\( \text{FeO} \), siliceous high-\( \text{MgO} \) basalt, the elevated initial \( \text{SiO}_2 \) concentration drives the early crystallization of orthopyroxene, without assimilation of a siliceous contaminant (although such assimilation may have been responsible for the elevated \( \text{SiO}_2 \) content initially). As noted above, because of the lower \( D^{\text{NiO}} \) (orthopyroxene-liquid) value for orthopyroxene relative to olivine (Hashizume and Hariya, 1992; Frei et al., 2009), increased concentrations of \( \text{Ni} \) will be available to sulfide liquids where similar percentages of orthopyroxene crystallize rather than olivine. We suggest that such a process may be significant for norite-hosted, \( \text{Ni} \)-rich orebodies. In this case, not only does assimilation reduce the capacity of the magma to dissolve sulfide, but \( \text{Ni} \) availability is also enhanced relative to magmas from which olivine is the primary early crystallizing ferro-magnesian mineral. Figure 3 also illustrates that very little, if any, fractional crystallization is required to promote sulfide saturation in contaminated siliceous magma. To summarize, analysis of sulfide solubility systematics of mafic magmas clearly shows that assimilation of siliceous contaminants will cause a significant drop in the \( S \) concentration needed for the attainment of sulfide saturation. In most cases, little, if any, fractional crystallization of the contaminated magma is required to achieve sulfide saturation. Where the \( \text{aSiO}_2 \) is sufficiently elevated, orthopyroxene, rather than olivine, is an early crystallizing mineral and, because of the lower \( D^{\text{NiO}} \) value of orthopyroxene relative to olivine, additional \( \text{Ni} \) is available for incorporation into a sulfide liquid. Fractional crystallization of most low-\( \text{SiO}_2 \) mafic magmas will not promote sulfide saturation until 20 to 40% crystallization. Although PGE and \( \text{Cu} \) contents may continue to rise with crystallization, significant \( \text{Ni} \) will be sequestered in olivine. Assimilation of volatiles such as \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) may or may not result in \( f_{O_2} \) increases of the crystallizing magma,
but, in any case, the drop in the sulfide saturation value caused by \( f_{\text{O}_2} \) increase (up to \(-QFM\)) alone is minor compared to that caused by assimilation of Si-rich contaminants.

**Mixing of magnas**

Li and Ripley (2005) confirmed that mixing of two magnas may induce sulfide saturation of the resultant magma. We will not dwell on this point as the systematics are much the same as contamination involving country rock. We illustrate that the SCSS for a mixture of 70% high-Fe picrite with 30% of HAOT containing 1 wt % \( H_2O \) is lower than that of the uncontaminated picrite by \(-300 \) ppm. This amount is slightly less than that produced by assimilation by the HAOT of 10% of the melt produced by pelite partial melting (Fig. 3), but illustrates that mixing of chemically distinct magnas is a viable mechanism to reduce the sulfur concentration necessary to saturate a resultant magma in sulfide liquid. In the case of the picrite-HAOT mixture, the FeO content of the mixed magma differs only slightly from either of the end-members; the principal control on the lowering of the saturation value is the drop in the liquidus temperature of the mixed magma.

Although a lower SCSS value may result relative to that of fractional crystallization by any of the processes mentioned above, the mixing of mafic magnas alone will be unlikely to produce sulfide saturation unless both end-members are close to their saturation values. This feature has been pointed out by Naldrett (2011) and is illustrated in what is essentially an end-member case for the high-FeO picrite-HAOT mixture shown in Figure 4. The degree of sulfide supersaturation (defined as the difference in the sulfur concentration and that of the SCSS, which is the minimum necessary to promote the formation of sulfide liquid droplets) that may be attained as a result of mixing is a strong function of the shape (concavity) of the SCSS curve. Figure 4a illustrates that the concavity of the high-FeO picrite-HAOT mixture is so slight that only mixtures of magnas very near the end-member saturation values will attain sulfide saturation upon mixing. In contrast, where variations in SCSS values of mixtures are more strongly concave (e.g., Li and Ripley, 2005) or vary as shown in Figure 4b for an ocean island tholeiite-HAOT mixture, mixing of mafic magnas can be a mechanism to produce sulfide supersaturation. Figure 4b illustrates that even in this case the mixing process will be effective only if the end-members are within \(-100 \) ppm of their sulfide saturation values. Tomkins et al. (2012) have shown how the mixing of an S-bearing oxidized arc basalt with a reduced graphite-bearing felsic melt could result in reduction of sulfate and sulfide supersaturation in the mixed magma.

**Addition of externally derived sulfur**

Perhaps the most efficient means of causing prolonged sulfide supersaturation in a mafic magma is through the addition of S derived from country rocks. As outlined above, in many localities the combination of isotopic (e.g., Ripley and Li, 2003) and geochemical (e.g., Keays and Lightfoot, 2010) data strongly points to the involvement of externally derived S in
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Fig. 4. Comparison of SCSS trajectories for mixed magmas: (a) high-FeO picrite and HAOT, and (b) ocean island tholeiite and HAOT. Mixing of mafic magmas is potentially important for the attainment of sulfide supersaturation where end-member S concentrations are close to those required for sulfide saturation and the shape of the SCSS curve for the mixture is strongly concave or has a pronounced inflection.

The Importance of Magma Volume and Chamber Shape

Given that mafic magma may reach sulfide saturation as a result of fractional crystallization, and much sooner via contamination involving a siliceous end-member or by magma mixing, the question remains whether an economic sulfide accumulation may be produced without the addition of external S. In all cases described above, except those of xenolith digestion or thermomechanical erosion, the amount of sulfide liquid produced is that of, or very near, the cotectic proportion (Barnes, 2007; Li and Ripley, 2009). Both Barnes (2007) and Li and Ripley (2009) describe methods to calculate the cotectic proportion of sulfide. The amount of sulfide liquid produced per crystallization increment is small (generally <1.5 wt %), and very efficient collection is required to produce horizons with more than ~2 vol % sulfide. In the case of a magma with a sulfide saturation value that has been decreased due to contamination and mixing, the mass of collectible sulfide is constrained by the initial concentration of sulfide in the system. This is an obvious point, but one of extreme importance when considering ore-forming systems. For example, for the Sonju Lake intrusion the parental magma is estimated to have contained no more than 1,000 ppm S. Miller and Ripley (1996) estimate that the intrusion is considerably larger than its exposed area of 9 km², with a strike length of ~20 km. We estimate a potential volume of ~30 km³ of magma, but of particular significance is the fact that, even with the improbable collection of all available sulfide, only a ~2-m-thick massive sulfide horizon could be produced in the intrusion. As stated above, Ni concentration dropped to extremely low values prior to sulfide saturation. When sulfide saturation was attained in the intrusion as a result of fractional crystallization, the R-factor would have been ~260, assuming sulfide saturation affected all portions of the remaining 60% liquid. A 2-m-thick massive sulfide would grade ~3 wt % Cu (100 ppm Cu in the parent magma) and 1.3 ppm Pt (3.5 ppb Pt in initial liquid). A 2-m-thick massive sulfide would be an unlikely candidate for a Cu ore, but a PGE reef could be produced. In the Sonju Lake intrusion, the zone of PGE and Cu enrichment is dispersed over ~100 m rather than 1 or 2 m, with grades of ~0.06% Cu and 30 ppb Pt, but less than 70 ppm Ni. These are expected values for dispersion of the immiscible liquid with the composition described above.

Without the addition of external S, most magmas that crystallize as closed systems (whether uncontaminated or after contamination involving S-poor country rocks) are unlikely to produce sufficient quantities of sulfide to form economic deposits, unless the volume of magma from which sulfide is derived is large. Barnes (2007) evaluated whether cotectic amounts of sulfide were sufficient to account for the large, disseminated sulfide orebody at Mt. Keith. Large, disseminated sulfide-bearing intrusions are logical candidates where...
crystallization of cotectic proportions of sulfide may have been responsible for ore generation. Barnes (2007) concluded that sulfide in excess of cotectic amounts was required to produce the Mt. Keith orebody and proposed the mechanical deposition of transported sulfide, formed in response to the introduction of sulfur from country rocks.

In a very large volume system such as the impact melt sheet at Sudbury, concentrations of 600 to 1,000 ppm S (as estimated by Keays and Lightfoot, 1999; Lightfoot et al., 2001) are consistent with the estimated mass of sulfide in the Sudbury ores (Lesher and Thurston, 2002; Keays and Lightfoot, 2004; Fig. 5). For a system such as Noril’sk (sulfide content between 275 and 750 Mt; Lightfoot and Hawkesworth, 1997; Naldrett, 2011), the amount of sulfide present far exceeds that which could be collected from closed-system crystallization of magma that produced tabular, ~1,000-m-thick (or less) sills. If contamination not involving S addition is a key process for the attainment of saturation, then open-system processes are likely to have been operative to result in the concentration of sufficient quantities of sulfide. The mass and grade of sulfide at Noril’sk have been the focus of many studies, virtually all of which focus on sulfide collection from passing magmas in a conduit system, followed by some type of metal upgrading (e.g., Brügmann et al., 1993; Naldrett and Lightfoot, 1999; Arndt et al., 2003; Kerr and Leitch, 2005; Lightfoot and Keays, 2005; Li et al., 2009). Figure 5 illustrates that for the Noril’sk ores, the estimated sulfide mass, if collected from magma with ~1,000 ppm S available as immiscible sulfide, would require between ~34 and 100 km³ of magma. For comparison, the 30-Mt Ovoid orebody at Voisey’s Bay (Lightfoot et al., 2012) would have required sulfide collection from ~3.7 km³ of magma. For both of these systems the required amounts of magma may not be unreasonable; the involvement of 100 km³ in an ore-forming system represents only a small fraction of that which generated the Siberian Traps (e.g., Reichow et al., 2009). For the small but high-grade (~3.5% Ni) Eagle deposit, the 4-Mt sulfide orebody could have been generated from as little as 0.5 km³ of magma containing 1,000 ppm S. A more realistic estimate for the Eagle deposit also serves to illustrate that Ni contents in parental magmas of ~150 ppm may give rise to sulfide assemblages with tenors similar to those found in many deposits. Figure 1b shows that sulfide saturation of a picritic magma contaminated with a partial melt from a pelite may occur at ~15% crystallization. The Ni content of the liquid at this time would be ~155 ppm. Crystallization of an additional 10% involves clinopyroxene and results in the Ni content of the liquid falling to no less than 140 ppm. The computed mass of immiscible sulfide available for collection from the residual liquid over this interval is ~0.3 wt %, resulting in an R-factor of ~335. With Ni contents in the residual liquid of 140 to 150 ppm, R-factors of 200 to 350 will produce Ni tenors in the sulfide liquid of 2 to 3 wt %. Hence, collection of this sulfide could generate an orebody similar in grade to many of the world’s large deposits. For the small, 4-Mt orebody at Eagle, the amount of silicate magma needed based on the above calculation is ~2 km³. These values would appear to be very reasonable quantities of magma to be delivered in a developing rift system. The example from the Sonju Lake intrusion also serves to emphasize that if the amount of mantle-derived sulfide present in a moderate-sized, sheet-type intrusion were to have been collected in a restricted magmatic conduit, an

**Fig. 5.** Plot of tonnes of sulfide in ore versus S concentration in a source magma. Cubic kilometers of magma are shown assuming that all the sulfur in magma is collected to generate the ore. For example, if only 200 ppm S is available as immiscible sulfide during magma crystallization, deposits similar in size to those at Noril’sk (between 275 and 750 Mt) can be generated from between 200 and 300 km³ of magma. Small orebodies such as Eagle can be formed by collection of immiscible sulfide from less than 10 km³ of magma.
economic ore accumulation could have resulted. The conduit environment provides a physical setting where small amounts of sulfide from large volumes of magma may collect; in addition, subsequent upgrading may occur as sulfide-undersaturated magmas utilize the conduit and partially dissolve the accumulated sulfide (e.g., Kerr and Leitch, 2005; Li et al., 2009). Ni enrichment of a low-Ni sulfide that initially formed from a system where Ni was sequestered by olivine could also occur. Maier et al. (2001) pointed out the importance of conduits in the formation of magmatic Ni-Cu-PGE sulfide deposits, as well as the lack of such deposits in large layered intrusions. The point here is that geochemical data are consistent with the mineralization that is found in intrusions such as Sonju Lake being related to processes that did not involve the introduction of external S (or even significant contamination of any type). Had this sulfide been able to accumulate in a conduit setting, there appears to be little reason to suspect that an orebody could not have resulted. Barnes et al. (2011) have recently described an Ni-rich disseminated sulfide orebody that occurs as a stratiform layer in the Fazenda Mirabela intrusion of Brazil. The authors note that this is a very unusual occurrence produced as a result of mixing of two compositionally distinct magmas, one of which contained suspended sulfide droplets. Additional research of this type is vital to enhance our understanding of all processes that may lead to the formation of magmatic Ni-Cu-(PGE) deposits.

Conclusions

An assessment of mechanisms that can promote sulfide saturation in mafic magmas indicates that externally derived S may not be required for Ni-Cu-(PGE) ore formation in open systems where the volume of magma involved is large and an efficient process of sulfide collection is operative. Conduits provide a physical environment where sulfide collection and upgrading may occur, related in part to the passage of multiple pulses of magma. The fact that many large Ni-Cu-(PGE) sulfide deposits show strong evidence for the incorporation of crustally derived S suggests that efficient collection of mantle-derived sulfide is a rare process, and that sulfide supersaturation is often required. Sulfide supersaturation in magmas is accomplished via the liberation of sulfur from xenoliths in intrusions or by similar transport due to thermomechanical erosion near the base of komatiite lava flows.

Closed-system fractional crystallization of mantle-derived magmas will be unlikely to produce sulfide accumulations of sufficient size for economic exploitation. Sulfide saturation in most uncontaminated mantle-derived magmas will not occur via fractional crystallization until ~20 to 40% crystallization. Sulfide accumulations that may form will be Ni poor because of sequestration of Ni by early crystallizing olivine. Systems with sufficient volume have the potential to generate Cu-rich PGE reefs. The contamination of mafic magmas by siliceous country rocks, or mixing of magma types, will cause a reduction in the S concentration necessary for the attainment of early sulfide saturation of between ~200 and 700 ppm. This facilitates sulfide saturation but does not necessarily trigger it. Where the aSiO2 is sufficiently elevated to cause orthopyroxene rather than olivine crystallization, more Ni is available for incorporation into sulfide. Ni sulfide-rich ores could form preferentially in orthopyroxene-bearing rocks, but only from large-volume systems.

Addition of volatiles such as H2O and CO2 to mafic magmas is frequently linked to an increase in magma fO2 and a lowering of the SCSS. Assimilation of oxygen-bearing volatiles does not necessarily result in an increase of magma fO2; in addition, at QFM and below an increase in fO2 results in only small changes in the SCSS of the magma. Assimilation of siliceous, and potentially hydrous, partial melts derived from country rocks and mixing of chemically distinct magmas are more viable processes for decreasing the SCSS of a mafic magma, relative to increased fO2 alone. Methane, as well as graphite, may serve as a reductant in high fO2 magmas where sulfate is predominant and the solubility of S is considerably higher than in reduced magmas.

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