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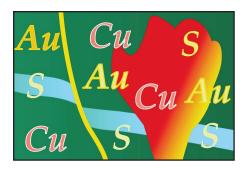## Sulphur Solubility in Felsic Magmas: Implications for Genesis of Intrusion-related Gold Mineralization

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SUMMARY

Sulphur solubility and the state of sulphide/sulphate saturation in felsic magmas play an important role in the formation of intrusion-related gold systems. The solubility of sulphur in felsic magmas is mainly controlled by temperature, pressure, redox condition(s), melt composition, and sulphur diffusion, although the sulphur source is considered an essential factor controlling the ultimate sulphide content in the melt. Decreasing temperature and increasing pressure usually result in a decrease of sulphur solubility if the oxygen fugacity ($f(O_2)$) remains constant. Sulphide is dominant in melts under reduced conditions ($f(O_2)$) near or below the fayalite–magnetite–quartz (FMQ) buffer), whereas sulphate predominates under relatively oxidized conditions ($f(O_2)$) above FMQ+2). Felsic melts with low ferrous-iron (FeO) content have lower sulphur solubility compared to more mafic compositions. Speciation of sulphur in the melt and related degassing behaviour are probably controlled by sulphur diffusivity.

The formation of granitoid intrusion-related gold deposits is largely controlled by whether or not sulphur is saturated in the melt, although gold endowment in the magma is also a factor. For example, sulphide undersaturation in a granitic melt may indicate a greater potential for generating Type-1 intrusion-related gold deposits, in which gold is derived from magmatic fluids directly evolving from granitic magmas. However, if a granitic magma becomes sulphide saturated, the residual melt would be depleted in gold because of immiscible sulphide melt segregation, and thus has a low potential for generating Type-1 gold deposit(s). Late-stage hydrothermal fluids with low pH and a relatively high oxidation state may leach gold that was incorporated into sulphide minerals, during a sulphide saturation event occurring early in the evolution of a granitoid magma. If gold that is liberated via resorption and destruction of early sulphide minerals interacting with hydrothermal fluids is then concentrated in a suitable geological structure, such as shear or fault zones and/or hydrofracture systems, it may form a Type-2 intrusion-related gold deposit. The implications for mineral exploration are that Type-1 gold deposits are likely associated with more evolved granite phases in a composite intrusive suite that is undersaturated in sulphide; these deposits may be hosted by the intrusion or occur within the contact metamorphic aureole. In contrast, Type-2 deposits are most likely related to less evolved granitoids that are saturated in sulphide; they are typically controlled by structures such as shear zones, and may be proximal or distal (beyond the metamorphic aureole). Type-1 deposits likely form at higher temperatures (e.g. proximal skarns) from ore fluids having higher salinities compared to Type-2 deposits. The relative economic importance of Type 1 and Type 2 needs to be evaluated to build specific exploration strategies for these deposits.

SOMMAIRE

La solubilité du soufre et l'état de saturation sulfure/sulfate dans les magmas felsiques jouent un rôle important dans la formation de systèmes aurifères au sein d'intrusifs. La solubilité du soufre dans les magmas felsiques est principalement fonction de la température, la pression, les conditions d'oxydoréduction, la composition du magma, et de la diffusion du soufre, bien que la source de soufre soit un facteur essentiel de la teneur ultime en soufre dans le magma. Une diminution de la température et une augmentation de la pression mènent généralement à une diminution de la solubilité du soufre à fugacité d'oxygène ($f(O_2)$) constante. Les sulfures prédominent dans des magmas de contextes réducteurs ($f(O_2)$), c.-à-d. près ou sous le niveau du tampon fayalite-magnétite-quartz (FMQ), alors que les sulfates prédominent sous contextes relativement oxydants ($f(O_2)$), c.-à-d. au-dessus FMQ+2). Les magmas felsiques à faible teneur ferreuse (FeO) ont une plus basse solubilité en soufre que ceux de compositions plus mafiques. La spéciation du soufre dans le magma

ainsi que son comportement de dégazage sont probablement fonction de la diffusivité du soufre.

La formation de gisements d'or associés à des intrusions granitoïdes est principalement fonction de la saturation en soufre du magma, bien que la dotation en or du magma soit aussi un facteur. Par exemple, la sous-saturation en sulfure dans un magma granitique peut indiquer un plus grand potentiel de génération de gisements d'or de type-1 associés à des intrusions, dans lesquels l'or provient de fluides magmatiques issus directement des magmas granitiques. Toutefois, si un magma granitique devient saturé en sulfures, le magma résiduel serait appauvri en or en raison de la ségrégation des sulfures immiscibles du magma, et aura donc un faible potentiel de génération de gisements d'or de type-1. Les fluides hydrothermaux tardifs avec un faible pH et un état d'oxydation relativement élevé peuvent exsuder de l'or incorporé aux minéraux sulfurés dans un événement de saturation de sulfure précédant de l'évolution d'un magma granitoïde. Si l'or qui est libéré via la résorption et la désagrégation des minéraux sulfurés existants par réaction avec des fluides hydrothermaux est alors concentré dans une structure géologique propice, comme des zones de cisaillement ou de faille, et/ou des systèmes de fracturation hydraulique, il peut former un gisement d'or de type-2 à caractère intrusif. Dans une perspective d'exploration, on doit retenir que les gisements d'or de type-1 sont plus susceptibles d'être associées avec des phases plus évoluées de granites dans une suite intrusive composite qui est sous-saturée en sulfure; ces gisements peuvent exister au sein de l'intrusion ou dans l'auréole du métamorphisme de contact. Contrairement, les gisements de type 2 sont plus probablement liés à granitoïdes moins évolués qui sont saturés qui sont saturés en sulfure; ils sont généralement dépendants de structures telles que des zones de cisaillement, et peuvent se trouvés plus loin du magma (au-delà de l'auréole métamorphique). Les gisements de type-1 sont susceptibles de se former à des températures élevées (dans des skarns proximaux) à partir de fluides minéralisés ayant des salinités plus élevées que celle des gisements de type-2. La relative importance économique des gisements de type 1 et de type 2 doit être évaluée pour établir des stratégies d'exploration correspondantes.

INTRODUCTION

Understanding the behaviour of sulphur in felsic magmas and their derivative hydrothermal systems is increasingly important in the study of gold mineralization, particularly for recently recognized intrusion-related gold systems, in which gold is commonly associated with other ore-forming sulphide and oxide minerals (Newberry and McCoy 1995; McCoy et al. 1997; Thompson et al. 1999; Poulsen et al. 2000; Rowins 2000; Thompson and Newberry 2000; Lang and Baker 2001; Fan et al. 2003; Groves et al. 2003; Baker et al. 2005; Simon et al. 2007; Frank et al. 2011). Sulphur solubility and saturation in granitoid (*sensu lato*) magmas (here the concept of granitoid rocks with felsic compositions used in Pearce et al. (1984), i.e. intrusive rocks containing over 5% modal quartz is adopted) are among the most important factors controlling the formation of intrusion-related gold deposits because of the close relationship between gold and sulphur in these systems. Intrusion-related gold deposits are characterized by:

i) formation within a continent well inboard of inferred or recognized convergent plate boundaries;

ii) a spatial and temporal association with dominantly metaluminous, subalkalic granitoid intrusions of felsic to intermediate composition that span the boundary between ilmenite and magnetite series, or reduced I-type granites;

iii) a metal assemblage that includes Bi, As, and Te, and lesser amounts of W, Mo, Sn, Pb, and Sb;

iv) a reduced sulphide mineral assemblage commonly including pyrrhotite, pyrite, arsenopyrite, and loellingite;

v) a low sulphide mineral content, typically less than 5% (by volume) of veins;

vi) restricted zones of fracture-controlled hydrothermal alteration; and

vii) CO_2-rich hydrothermal fluids (Newberry and McCoy 1995; McCoy et al. 1997; Thompson et al. 1999; Thompson and Newberry 2000; Lang and Baker 2001; Chi 2002; Ishihara and Murakami 2004; Yang and Lentz 2005a, b; Yang et al. 2004, 2006, 2008; Hart 2007; Chi et al. 2008; Thorne et al. 2002, 2008; Bineli Betsi and Lentz 2011; Kontak and Kyser 2011; McFarlane et al. 2011).

Notwithstanding ii) above, it is noted that gold mineralization is also associated with some alkaline intrusions, and giant alkaline intrusion-related gold deposits have been reported (e.g. Müller and Groves 1993; Sillitoe 2002). The characteristics listed here are well established in Alaska (USA) and Yukon and New Brunswick (Canada), and suggest that gold and associated mineralizing elements are mainly derived from the intrusions (Newberry and McCoy 1995; McCoy et al. 1997; Thompson et al. 1999; Thompson and Newberry 2000; Lang and Baker 2001; Baker et al. 2005), although minor sulphur and/or gold may be sourced from country rocks of sedimentary origin via the processes of selective assimilation and fractional crystallization (Yang et al. 2004; Yang and Lentz 2010; Kontak and Kyser 2011).

Experimental data show that the minerals forming an immiscible sulphide melt that has separated from a silicate melt (liquation), are the most likely candidates to host gold and copper in granitoid rocks or magmas (Cygan and Candela 1995; Jugo et al. 1999; Simon et al. 2000), although the gold mainly occurs independently, either in the form of free gold or as micro-inclusions and solid solution in sulphide minerals (Kesler et al. 2002). Empirical observations of gold partitioning between magmatic sulphide minerals and granitoid melts also reveal that gold is closely associated with, and prefers to partition into, sulphide minerals. Sulphide saturation and segregation into a monosulphide solid solution that immiscibly separates and subsequently crystallizes from a melt, will result in gold and copper sequestration in sulphide minerals, and depletion of gold (which is compatible during sulphide segregation) in the silicate melt (Halter et al. 2005; Yang et al., 2006). Therefore, hydrothermal fluids (supercritical or subcritical fluids) subse-

quently released from such evolved (sulphur and copper–gold depleted) silicate magmas as a result of decompression (first boiling) and/or crystallization of anhydrous phases (second boiling), are unable to generate significant gold and copper mineralization within or proximal to the intrusions. It is noted that a small to moderate amount of pyrrhotite crystallization may not totally negate a potentially ore-forming system (Candela and Holland 1986). However, it has been learned that dissolving, resorption and decomposition of early magmatic sulphide minerals as a result of degassing and reaction with late-stage hydrothermal fluids, may liberate and release gold and copper from sequestered sulphide minerals into the exsolving fluids (Keith et al. 1997; Halter et al. 2002; Stavast et al. 2006). If this occurs, then intrusion-related gold deposits may form if such fluids are subsequently focused along or into favourable structures, such as shear zones (Lin 2001; Yang et al. 2006).

In contrast to the above scenario, if a granitic melt is undersaturated in sulphide, gold will not be segregated into a sulphide phase, and subsequent magmatic–hydrothermal evolution may result in gold partitioning into exsolving magmatic fluids. Given a suitable geological environment and favourable physiochemical conditions, intrusion-related gold deposits may then form either within the pluton or in the surrounding country rock, where they are controlled by structures such as shear zones and hydrofracture systems; in this case, gold mineralization is directly related to magmatic fluids emanating from a progressively cooling granitoid intrusion. This review paper examines the controlling factors of sulphur solubility in granitic magmas, and briefly discusses the significance of these factors and the role of sulphide saturation in the genesis of intrusion-related gold deposits.

SULPHUR SOURCES

The source of sulphur is considered an essential controlling factor for the ultimate state of sulphide saturation in felsic magmas. The amount of sulphur in a granitic magma depends on the sulphur content in the source rocks, the degree of partial melting, and the bulk sulphur partition coefficient, if the magma is generated by batch partial melting. However, the actual processes involved in felsic melt generation are more complicated (see Whitney 1989), and felsic magmas generated in different tectonic environments may have very different sulphur concentrations (e.g. Pearce et al. 1984; Ague and Brimhall 1988; Pearce 1996; Chappell and White 2001; Ishihara 2004). The initial sulphur content of a melt will determine, to some extent, whether sulphur saturation takes place during magmatic evolution; however, assimilation of sulphur from country rocks can also play an important part in sulphur behaviour during magmatic evolution and emplacement. Currently, the best method for identification of the sulphur source is the $\delta^{34}S$ values of magmatic sulphide minerals; the problem is how to distinguish magmatic sulphide from hydrothermal sulphide minerals that may also be present in granitoid rocks, and this problem may sometimes result in equivocal interpretations for sulphur sources (Ohmoto and Goldhaber 1997; Yang and Lentz 2010).

If a granitic melt is <u>not</u> saturated with sulphide under liquidus or supersolidus conditions, magmatic sulphide minerals will not crystallize from the melt; in this case, sulphur sources may theoretically be identified by determining $\delta^{34}S$ values of ferromagnesian minerals, unaltered whole rocks, or the SO_4^{2-} component in apatite (Ohmoto and Goldhaber 1997; Yang and Lentz 2010). Alternatively, the 'Kiba reagent' technique (Kiba et al. 1955; Ueda and Sakai 1984) has been suggested for the analysis of sulphur isotopes in sulphur-bearing magmatic systems regardless of their valence, to help ascertain $\delta^{34}S_{sulphate}$ and/or $\delta^{34}S_{sulphide}$ ratios; the relevant redox conditions may also be estimated in this way (Yang and Lentz 2009, 2010). It is worthy of note that some felsic volcanic rocks are known to contain magmatic pyrrhotite (Whitney 1984), suggesting that the related magmas are saturated with respect to sulphide. This primary pyrrhotite may be taken as a sulphur isotope standard in future studies to discriminate magmatic sulphides from hydrothermal sulphides without any ambiguity, because sulphur isotope fractionation in sulphide minerals under magmatic conditions, is very minor.

Granitic magmas are most likely to originate from continental crust; however, mafic melts sourced from the upper mantle could be added to the granite source region (e.g. volcanic arc granites; Pearce et al. 1984) and thus enhance partial melting of crustal rocks, which tend to have higher sulphur abundances than the upper mantle (McDonough and Sun 1995; Lentz 2003). Therefore, it is not uncommon for granitic magmas to be saturated in sulphide minerals, which are manifested by the presence of tiny primary sulphide inclusions in ferromagnesian and iron-oxide minerals, and rarely in feldspars (Keith et al. 1997, 1998; Halter et al. 2002, 2005; Yang et al. 2006). Crystallization of ferrous-iron minerals from felsic melts is likely to trigger local sulphide saturation, owing to the siderophile nature of sulphur atoms and/or ionic complexes. However, the magma chamber dynamics of voluminous granitic melts (e.g. convection cells) may result in homogeneity of sulphur distribution in resultant granitic plutons.

Marine sedimentary rocks and some other host rock sequences display variable, but generally high abundances of sulphur (and gold) (Ohmoto and Goldhaber 1997; Lentz 2003; Tomkins et al. 2009; Large et al. 2011) that could be introduced into granitoid intrusions through selective assimilation, as indicated by sulphur isotope signatures (Poulson et al. 1991; Ohmoto and Goldhaber 1997; Yang and Lentz 2010). The driving force behind this incorporation of sulphur is the presence of a sulphur concentration gradient between the intrusion and the country rocks, which allows sulphur (especially in sedimentary rocks) to transfer to the intrusion without the requirement of bulk melting (Poulson et al. 1991). It is likely that these processes facilitate sulphide saturation of originally sulphur-undersaturated granitoid magmas during emplacement into, or while passing through, sulphur-enriched sedimentary rocks. Nevertheless, unlike nickel sulphide mineralizing systems, which require a significant input of external sulphur to initiate sulphide saturation (Keays and Lightfoot 2010), gold-associated felsic sys-

tems do not appear to be controlled by the absence (or presence) of an external sulphur source, although the degree of sulphide saturation may control the style of gold mineralization (see below).

An example of the effect of sulphur source on its behaviour in magma is a study carried out by de Hoog et al. (2001; Fig. 1). Their numerical modelling predicts at least 255 to 555 ppm sulphur in the magma source of the subduction-related Galunggung Volcano (Indonesia), which is up to twice the amount commonly assumed for mid-ocean ridge basalt sources and slightly higher than the primitive mantle value (McDonough and Sun 1995). This may be attributed to slab-derived excess sulphur, which is evident in ^{34}S enrichment that commonly characterizes arc magmas and gas phases (de Hoog et al. 2001). Petrographic investigations on numerous mid-ocean ridge and ocean island basalt samples indicate that these rocks may have been saturated in sulphide (Wallace and Carmichael 1992); therefore, any felsic phases such as plagiogranite that evolved from these basalts must also be saturated in sulphide, because mafic magma generally has higher sulphur solubility than felsic magma (Poulson and Ohmoto 1990). Clearly, fractionation and crustal contamination could lead to evolved magmas being saturated in sulphide. Mixing of mafic and felsic magmas may also trigger sulphide saturation in resultant hybrids, although transfer of sulphur gas to felsic magma from underplating mafic magma has been considered as a mechanism for the formation of giant auriferous base-metal porphyry deposits like Bingham, Utah (see Keith et al. 1998).

CONTROLLING FACTORS OF SULPHUR SOLUBILITY

Results from experimental studies, natural sample observations, and theoretical considerations indicate that sulphur solubility in silicate melts is controlled by temperature, pressure, bulk composition, redox conditions, and sulphur diffusion. Although these parameters usually work together and influence one another, they will be discussed separately in the following sections to illustrate and distinguish their effects

on sulphur behaviour during magmatic evolution. This is followed by a brief review of how temperature, pressure, oxygen fugacity and bulk composition together control sulphur solubility.

Temperature

Experimental data, observations from natural rock samples, and thermodynamic considerations reveal that sulphur solubility in silicate melts is correlated with temperature (Katsura and Nagashima 1974; Wendlandt 1982; Poulson and Ohmoto 1990; Carroll and Webster 1994; Mavrogenes and O'Neill, 1999; Holzheid and Grove 2002; Clemente et al. 2004; Jugo et al. 2005; Li and Ripley 2005; Liu et al. 2007; Moune et al. 2009; Baker and Morreti 2011). The general trend is that sulphur solubility in a given silicate melt increases with increasing temperature under relatively reduced conditions (i.e. $f(O_2)$ below the fayalite–magnetite–quartz (FMQ) buffer), but decreases slightly with increasing temperature under oxidizing conditions (Fig. 2). This is readily explained by the positive $\Delta f(O_2)/\Delta T$ slope of the FMQ buffer reaction. For example, if $\log f(O_2) = -8.5$ at 1200°C, raising the temperature to 1400°C is analogous to lowering $\log f(O_2)$ relative to FMQ, and sulphur solubility therefore increases (Carroll and Webster
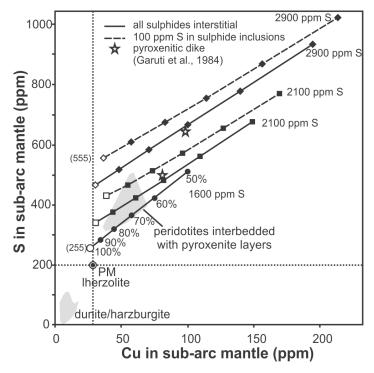

Figure 1. Variation diagram showing the amounts of sulphur and copper needed in the mantle source to produce the concentrations observed in Galunggung melt inclusions, assuming 15% melting (after de Hoog et al. 2001). The solid lines indicate model output if all mantle sulphides are interstitial, whereas the dashed lines assume that 100 ppm sulphur is present as sulphide inclusions in minerals. Sulphur concentrations in the melt inclusions have been assumed to be 2100 and 2900 ppm (minimum and maximum estimate of primary sulphur content in high-CaO melt inclusions, respectively), and 1600 ppm (maximum sulphur content of basaltic inclusions). Percentages along the solid line indicate the amount of sulphide consumed during melting. PM denotes the primitive mantle. Open symbols represent conditions at which all mantle sulphides are consumed during melting, which are the minimum concentrations needed in the sub-arc mantle to explain sulphur and copper abundances in the melt inclusions. Sulphur has to be enriched in the sub-arc mantle, whereas copper may be close to the PM value under some conditions. However, if copper has been added to the mantle, the model calculations predict even higher sulphur concentrations, and residual sulphide will be present in the mantle residue.

1994). It should be mentioned that temperature affects the sulphur solubility in mafic melts more effectively than in felsic melts, as demonstrated in studies by Katsura and Nagashima (1974), Poulson and Ohmoto (1990), Carroll and Webster (1994), and Baker and Morreti (2011), although the sulphur solubilities in those melts display similar temperature-dependant trends.

Poulson and Ohmoto (1990) attempted to simplify the relationship
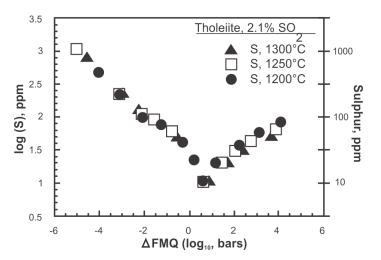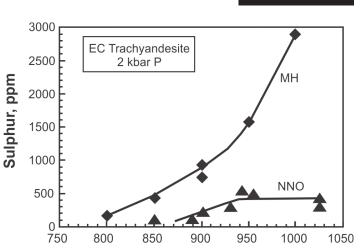
Figure 2. Sulphur solubility in a sulphur-undersaturated tholeiitic melt, 1200° to 1300°C vs. $f(O_2)$ relative to FMQ buffer (after Katsura and Nagashima 1974). ΔFMQ is in log $f(O_2)$ units relative to FMQ, e.g. ΔFMQ = 1 means $f(O_2)$ 1 log unit above FMQ. The sulphur solubility increases with increasing temperature under reduced conditions (<FMQ), whereas under oxidized conditions the solubility decreases with increasing temperature (>FMQ).

Figure 3. Sulphur solubility vs. temperature (°C) at a constant P of 2 kb (200 MPa) for Fe_3O_4–Fe_2O_3 (MH) and Ni–NiO (NNO) buffered experiments on El Chichon trachyandesite (after Carroll and Webster 1994). All melts coexist with an H–O–S fluid phase, but MH-buffered runs are anhydrite-saturated, whereas NNO-buffered experiments contain either pyrrhotite or a Fe–S–O immiscible melt.

between temperature and sulphur solubility in silicate melts saturated with a Fe–S–O phase under various experimental conditions, and pointed out that solubility increases with increasing temperature. However, temperature has a variable effect on sulphur solubility, depending on redox conditions. This is demonstrated in Figure 3, which shows how sulphur solubility in the El Chichon trachyandesite varies with temperature at constant pressure in Fe_3O_4–Fe_2O_3 (magnetite–hematite, or MH; ≈FMQ+4.5) and Ni–NiO (NNO; ≈FMQ+0.7) buffered experiments. The MH-buffered melts are anhydrite-saturated, whereas the NNO-buffered melts are saturated with liquid or crystalline iron sulphide. At near-liquidus temperatures, the sulphur solubility in anhydrite-bearing melts is up to 5-fold greater than in the sulphide-saturated experiments, but this difference decreases with decreasing temperature. Recent experiments confirm that oxidized conditions significantly increase sulphur solubility in basaltic melts, and indicate that island-arc basalts contain higher sulphur contents than ocean-island, back-arc, and mid-ocean ridge basalts (Jugo 2009). It is noted that sulphur solubilities reported by Jugo (2009) are higher than those given in Carroll and Webster (1994) at roughly the same redox conditions. Carroll and

Webster (1994) also show that sulphur solubility increases with an increase in temperature in silicate melts ranging from 45.9 to 60.8 wt% SiO_2 (Figure 4a).

Pressure

Experimental determinations of sulphur solubility at pressures greater than 1 bar provide information about the effects of pressure on sulphur solubility in magmas. Sulphur solubility in melts of diopside (Di) and albite (Ab) were analyzed by Mysen and Popp (1980) at 15 to 30 kb and 1650°C in the presence of graphite and a C–O–S fluid phase, with $f(S_2)$ buffered by Cu–Cu$_2$S, Ag–Ag$_2$S, or Pt–PtS. Their results show that sulphur solubility increases with increasing pressure, and that sulphur solubility in a Di melt is significantly higher than in an Ab melt. This suggests that sulphur reacts preferentially with non-bridging oxygen (a non bridging-oxygen is any oxygen that is not shared by two silica tetrahedra (SiO_4) in a silicate crystal structure) in these iron-free silicate melts; the Di melt dissolves more sulphur because it contains more non-bridging oxygen than the Ab melt does. Based on the experimental conditions of Mysen and Popp (1980), most of the sulphur may occur as sulphide; it is worthy of note that the melts in these experiments do

not contain ferrous iron, which is an important factor controlling sulphur solubility (see below).

In contrast to the above study, experiments on sulphur solubility in sulphide-saturated natural melts (60% basaltic to andesitic melt and 40% sulphide) at 10 to 30 kb and 1300° to 1450°C, with a C–O–S fluid phase, reveal that the sulphur content of sulphide-saturated melts decreases with increasing pressure and increases with increasing temperature (Carroll and Webster 1994; Fig. 4).

Experiments on sulphur solubility in hydrous andesitic to dacitic melts in equilibrium with an H–O–S fluid phase were reviewed by Carroll and Webster (1994). These data are useful in defining the limits of sulphur solubility in hydrous, sulphur-saturated magmas at crustal pressures. For example, in an H–O–S vapour phase, the H_2S/SO_2 ratio increases with increasing pressure at fixed ΔFMQ; thus, high pressure magmatic gases associated with hydrous magmas will be more H_2S-rich than low pressure gases at similar temperatures and $f(O_2)$. Anhydrite may crystallize from sulphur-rich magmas at $f(O_2)$ above FMQ+2, and it may coexist with or replace iron sulphide as the major sulphur-bearing phase. These experimental results are in good agreement with values of $f(O_2)$
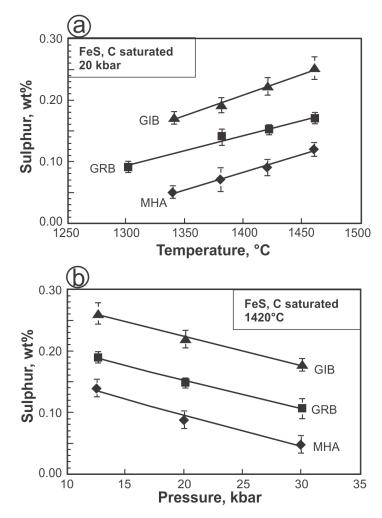
Figure 5. Sulphur contents as functions of pressure for anhydrite-saturated experiments on El Chichon trachyandesite (after Carroll and Webster 1994). Experiments with Fe_3O_4–Fe_2O_3 (MH) and MnO–Mn_3O_4 (MnH) buffers are not distinguishable, but for the highest temperature pairs of points (2 and 4 kb, 1000° and 950°C), the slightly higher sulphur contents occur in the MnH-buffered runs.

Figure 4. Effects of (a) temperature and (b) pressure on sulphur solubility in three sulphide-saturated melts (after Carroll and Webster 1994). All experiments were run in graphite capsules sealed in Pt, and equilibrated with a C–O–S gas phase with $f(O_2)$ buffered by graphite. Starting compositions include MHA (Mt. Hood andesite; 60.8 wt% SiO_2, 4 wt% FeO_{total}); GIB (Goose Island basalt; 45.9 wt% SiO_2, 14 wt% FeO_{total}); and GRB (Grande Ronde basalt; 54.4 wt% SiO_2, 11.1 wt% FeO_{total}).

estimated from natural anhydrite-bearing magmas erupted at Mt. Pinatubo, El Chichon and Lascar, Chile (Carroll and Webster 1994; de Hoog et al. 2001; Luhr and Logan 2002).

Figure 5 shows the variation in sulphur solubility with pressure for various isotherms in anhydrite-saturated melts (El Chichon trachyandesite) equilibrated with an H–O–S fluid phase at 1 to 4 kb total pressure. The anhydrite-bearing melts show a strong positive correlation of sulphur solubility with temperature, and also with pressure at T ≥ 900°C. This contrasts with sulphide-bearing melts (NNO; Fig. 3), which show little variation in

sulphur solubility with temperature. Mavrogenes and O'Neill (1999) carried out experimental studies of sulphur content at sulphide saturation (SCSS) in basaltic and picritic melts as a function of pressure (5–90 kb) and temperature (1400°–1800°C), using three distinct regimes of $f(O_2)$. They pointed out that the SCSS shows a strong exponential decrease with increasing pressure and is insensitive to temperature for these mafic melts. The results obtained by Mavrogenes and O'Neill (1999) compare well with the observations presented in Carroll and Webster (1994) and earlier results presented by Wendlandt (1982); they are also reflect-
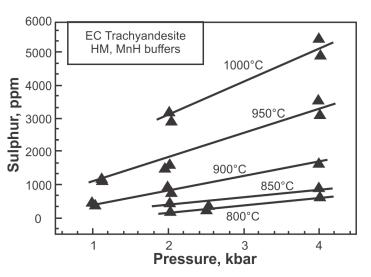
ed in numerous observations of magmatic nickel-copper sulphide mineral deposits, which require significant external sulphur to facilitate sulphide saturation, segregation, and mineralization (Keays and Lightfoot 2010) because of the negative correlation of sulphur solubility with pressure. The model established by Mavrogenes and O'Neill (1999) to illustrate the effect of pressure on SCSS in a basalt melt (Fig. 6) suggests that a magma formed in equilibrium with residual sulphide in the mantle would become undersaturated in sulphide during adiabatic ascent, thus enhancing its ability to incorporate external sulphur from country rocks (e.g. metasedimentary rocks) to the point of promoting sulphide saturation at shallow emplacement levels or even on the Earth's surface. This is consistent with empirical observations made by Keays and Lightfoot (2010) and references therein. At Noril'sk, the nickel–copper–platinum group element sulphide deposits are associated with subvolcanic intrusions emplaced into sulphur-enriched shales, marlstones, and evaporites, whereas the Deccan Trap has similar tholeiitic basalts and associated subvolcanic intrusions that have not generated any significant magmatic nickel deposits, because of the lack of sulphur-rich country rocks (Keays and
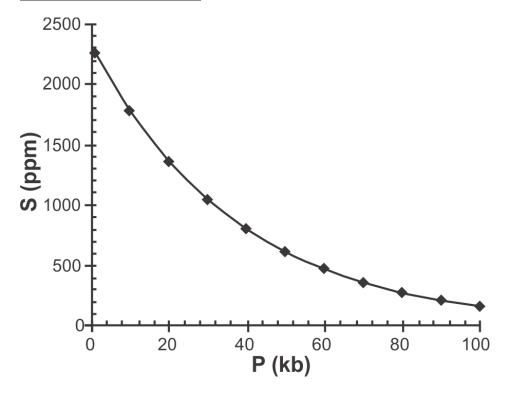
Figure 6. Diagram of sulphur content (ppm) at sulphide saturation (SCSS) vs. pressure (kb) for a basalt melt. The SCSS is calculated from the model proposed by Mavrogenes and O'Neill (1999) assuming T = 1500°C and FeS activity in sulphide liquid ($a_{FeS}^{sulphide}$) = 1.
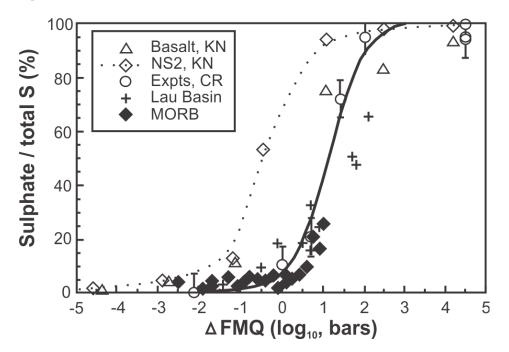

Figure 7. Sulphate as a function of $f(O_2)$, relative to the FMQ buffer (after Carroll and Webster 1994). Open triangles represent tholeiitic basalt synthesized at 1 atm, 1250°C and known $f(O_2)$; open diamonds denote $Na_2O \cdot 3SiO_2$ melts synthesized at 1 atm and controlled $f(O_2)$ and $f(S_2)$; open circles with error bars denote hydrous andesitic to dacitic melts synthesized at 1 to 2.9 kb and 920° to 1025°C. Crosses and filled diamonds correspond to submarine basaltic to andesitic glasses with determined $f(O_2)$ from measured Fe^{3+}/Fe^{2+}.

Lightfoot 2010).

It is not yet known why the experimental results of Mysen and Popp (1980) for the effect of pressure on sulphur solubility in silicate melts are different from those of Wendlandt (1982), Carroll and Webster (1994), and Mavrogenes and O'Neill (1999). Carroll and Webster (1994) pointed out that redox conditions may be related to pressure and temperature, and suggest that further work is required to resolve this apparent contradiction. Clearly, the melt compositions used in the respective experiments of Carroll and Webster (1994) and Mysen and Popp (1980) are distinctly different, and may account for the differences in the effect of pressure on sulphur solubility.

Redox Conditions

Various experiments on silicate melts demonstrate that sulphur solubility is closely linked with oxidation state, and that sulphur dissolves primarily as sulphide (reduced) and sulphate (oxidized) species (Katsura and Nagashima 1974; Poulson and Ohmoto 1990; Carroll and Webster 1994; Jugo et al. 2005; Jugo 2009). The proportions of these species in a given melt are controlled by the following equilibrium equations:

$$S^{2-}(melt) + 2O_2(gas) = SO_4^{2-}(melt)$$

The equilibrium constant of this reaction can be written as:

$$K = [SO_4^{2-}]/\{[S^{2-}] \times f(O_2)^2\}$$

where brackets refer to activities of the dissolved sulphur species in the melt. The latter equation indicates that the ratio of sulphate/sulphide will be proportional to the square of $f(O_2)$ at a fixed pressure and temperature as long as activity coefficients of the sulphur species do not vary greatly with the sulphur content in the melt. If $f(O_2)$ is below the FMQ buffer, sulphur occurs mainly as sulphide; sulphate only becomes significant (>10% of total sulphur) at $f(O_2)$ greater than 1 log $f(O_2)$ unit above the FMQ buffer (Carroll and Webster 1994).

Figure 7 shows the speciation of dissolved sulphur in quenched silicate melts as a function of $f(O_2)$. These data, both from experimental studies and from natural samples, indicate a
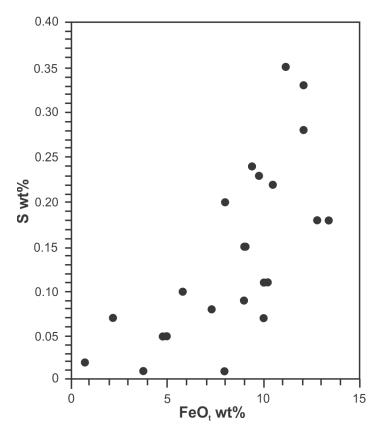
Figure 8. The relationship between sulphur and FeO_{total} in silicate glasses from inclusions in lavas and intrusive rocks from different localities worldwide (Data from Frezzotti 2001).

large increase in the proportions of sulphur dissolved as sulphate as $f(O_2)$ increases from FMQ to FMQ+2. The data illustrate the results for melt compositions ranging from dry mid-ocean ridge basalt to hydrous back-arc basalt, and experimentally synthesized dry basalt to hydrous andesitic to dacitic melts. The small variability in sulphate to total sulphur ratio over a large compositional range is consistent with temperature, pressure, and magmatic water content being of secondary importance relative to oxidation state in determining the speciation of magmatic sulphur.

One significant implication of elevated $f(O_2)$ is an increase in the proportion of sulphate over sulphide species, thus increasing sulphur solubility; the implication is that chalcophile metals (e.g. gold, copper) remain incompatible and are retained in evolving residual melts, if $f(O_2)$ remains relatively high. With magmatic–hydrothermal evolution, these metals could be partitioned into exsolving magmatic fluids that subsequently form magmatic hydrothermal deposits (e.g. porphyry copper, copper–gold, and gold). However, empirical data suggest that reductants, such as organic carbon or graphitic country rocks are required to facilitate gold precipitation from ore fluids (Lang and Baker 2001; Chi 2002; Yang et al. 2004, 2006; Thorne et al. 2008; Kontak and Kyser 2011).

Composition of Magmas

Sulphur concentrations in silicate-melt inclusions trapped in rock-forming minerals in volcanic and intrusive rocks of different compositions may best represent the original sulphur content of their corresponding parent magmas. Data on the sulphur content of silicate-melt inclusions from various localities worldwide have been summarized by Frezzotti (2001); these data clearly indicate that sulphur concentrations are higher (up to 0.36%) in low-silica basaltic melts with high FeO, and decrease considerably (~0.07%) in felsic melts with low FeO contents. When the data are presented on a sulphur versus FeO_t diagram (Fig. 8), it can be seen that sulphur concentration positively correlates with FeO content. This is consistent with the observed natural trend in mafic to felsic rocks as reported by Katsura and Nagashima (1974), Poulson and Ohmoto (1990), and Wallace and Carmichael (1992), and reviewed by Carroll and Webster (1994). However, most melt inclusion studies reveal some degree of pre-entrapment degassing of sulphur and other volatiles (cf. Wallace and Edmonds 2011).

In basaltic melts, sulphur appears to dissolve as sulphide, as described by the following reaction (Carroll and Webster 1994):

$$2FeO(melt) + S_2(gas) = FeS(melt) + O_2(gas)$$

This equilibrium suggests a preference for S^{2-} over O^{2-} anions when ferrous iron is present.

In hydrous felsic magmas, H_2S is the dominant sulphur vapour species when $f(O_2)$ is below FMQ+1. Sulphur dissolution may be attributed to the following mechanisms (Carroll and Webster 1994):

$$H_2S(gas) + FeO(melt) + O^{2-}(melt) = FeS(melt) + 2OH^- (melt), \text{ and}$$

$$H_2S(gas) + FeO(melt) = FeS(melt) + H_2O (gas)$$

Both reactions suggest that sulphur activity in the melt is proportional to FeO activity, and is negatively correlated with water fugacity and/or water content of the melt.

Under relatively oxidizing conditions, sulphur-rich magmas contain anhydrite (Carroll and Webster 1994; Frezzotti 2001; Luhr and Logan 2002) as the predominant sulphur species. This suggests a preferential association between dissolved sulphate and Ca^{2+} in the melt. Studies of sulphate solubility in synthetic melts also show a strong correlation between sulphate solubility and the concentration of alkali metal and alkaline earth components (Jugo 2009). An increase of alkali metal and alkaline earth element concentrations would reduce the quantity of non-bridging oxygen in the melt, thus promoting dissolution of sulphur (see Mysen 1988). However, more experimental work is required to assess the effect of alkalinity on sulphur solubility. It is known that the diffusion rate of different sulphur species varies considerably (Baker and Rutherford 1996); hence, molar ratios of sulphide and sulphate in silicate melts may affect sulphur solubility, which may be estimated by using sulphur isotopes (Yang and Lentz 2009, 2010, and references therein).

Although ferrous iron is a dominant component influencing sulphur solubility, other components (e.g. Na, K, Ca, Mg, Si, Al, Fe^{3+}) in silicate

melts may also exert some control, as suggested by more complicated relationships implied by experimental and empirical data (Holzheid and Grove 2002; Li and Ripley 2005). For example, alkaline granites appear to contain more sulphur than subalkaline granites (Sillitoe 2002), because of the ability of alkali elements to influence the structure of silicate melts by reducing polymerization (Mysen 1988). Increasing the degree of polymerization, as defined by *nbo/t* (the ratio of non-bridging oxygen anions to tetrahedrally coordinated cations in the silicate melt structure; Mysen 1988), decreases sulphur solubility (Holzheid and Grove 2002). This is consistent with observations that felsic melts dissolve lower quantities of sulphur than mafic to ultramafic melts (Poulson and Ohmoto 1990; Carroll and Webster 1994; Holzheid and Grove 2002; Li and Ripley 2005), suggesting that the solubility of sulphide minerals in magmas would decrease with fractionation in a granitoid suite.
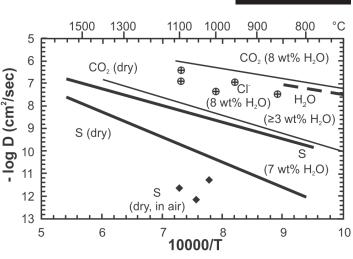
Diffusion of Sulphur in Melts

Baker and Rutherford (1996) studied sulphur diffusion in rhyolite melts experimentally at temperatures of 800°–1100°C, pressures of 1–2000 bars, water contents of 0–7.3 wt%, and $f(O_2)$ from FMQ buffer to air. In dry rhyolite melts, sulphur diffusivity can be expressed as $D_{sulphur} = 0.05exp[(-221\pm80)/RT]$, where exp stands for the exponential function, R is the gas constant, and T denotes temperature in degrees Kelvin. The results indicate that diffusivity is one to two orders of magnitude slower for sulphur than for H_2O, CO_2, and Cl^- (Fig. 9), and that diffusion of sulphur in wet melts (7 wt% dissolved water) is 1.5 to 2 orders of magnitude faster than diffusion in anhydrous melts, depending on temperature (Baker and Rutherford 1996; Fig. 9). Sulphur diffusivity appears not to be affected by $f(O_2)$ except under extreme oxidizing conditions (in air), although the proportions of S^{2-} and S^{6+} vary with $f(O_2)$ (Baker and Rutherford 1996); this suggests that diffusion of sulphur is controlled by one species over a large range in $f(O_2)$. The most likely candidate, under the experimental conditions adopted by Baker and Rutherford (1996), is the sulphide ion

(S^{2-}), even though S^{2-} is not the dominant species dissolved in the melt. At the extremely high oxidation states reached by experiments in air, the rate of sulphur diffusion drops by one to two orders of magnitude relative to less oxidized runs. It is possible that these extremely oxidized melts no longer contain significant S^{2-}, and that sulphur diffusion is controlled by some other species, e.g. SO_4^{2-}. Re-equilibration between S^{2-} and S^{6+} in oxidized melts is generally slow compared to S^{2-} diffusion (Baker and Rutherford 1996). These data find application in interpreting the evolution of a felsic magma that is undergoing degassing at a relatively shallow level, where sulphur will tend to be fractionated from other volatile species (e.g. H_2O, CO_2, and Cl^-) that diffuse more rapidly. During rapid degassing (e.g. explosive eruptions), most of the sulphur dissolved in a melt will be unable to escape from the glass before quenching (Baker and Rutherford 1996). Since sulphide (S^{2-}) diffuses faster, sulphate (S^{6+}) may remain in the melt under oxidized conditions during degassing; this is evident in cases where anhydrite is present in some igneous rocks (Baker and Rutherford 1996). It should be noted that the sulphur-degassing of felsic magmas at shallow levels may also result in sulphur isotopic fractionation, such that the composition of magmatic sulphate (i.e. anhydrite) becomes heavier (Luhr and Logan 2002), i.e. H_2S differentially exsolves with H_2O from the melt.

Sulphur Solubility in Silicate Melts as a Function of P-T-X-$f(O_2)$

Experimental data and observations of natural samples confirm that sulphur solubility in silicate melts is a function of pressure, temperature, chemical composition, and redox conditions of the system in question. Diffusion of sulphur species (sulphide versus sul-

Figure 9. Diffusivities of sulphur in rhyolite melts compared with other common volatile species such as H_2O, CO_2, and Cl^- (after Baker and Rutherford 1996).

phate) in the melt may influence instant sulphur solubility prior to apparent equilibration between these species, and sulphur sources control the ultimate degree of sulphide saturation in felsic melts. A general equation of sulphur solubility in silicate melts, defined as sulphur content at sulphide saturation (SCSS), is given by Mavrogenes and O'Neill (1999):

$$ln[S\ in\ ppm]_{SCSS} = A/T + B + CP/T + ln\ a_{FeS}^{sulphide}$$

where P is pressure in bars, T is temperature in degrees Kelvin, $a_{FeS}^{sulphide}$ is the activity of FeS in sulphide liquid, and A, B, and C are parameters related to composition (X), $f(O_2)$, and $f(S_2)$ of the silicate melt. The coefficients A, B, and C may be determined by experiments at controlled P, T, X, and redox conditions (Carroll and Rutherford 1985; Poulson and Ohmoto 1990; Carroll and Webster 1994; Mavrogenes and O'Neill 1999; Holzheid and Grove 2002; Clemente et al. 2004; Jugo et al. 2005; Li and Ripley 2005; Liu et al. 2007; Moune et al. 2009). The abundance of water in the melt may also affect sulphur solubility (Carroll and Rutherford 1985; Carroll and Webster 1994; Clemente et al. 2004; Liu et al. 2007), although the degree to which it does so may be less pronounced than for the other factors.

　　Table 1 lists sulphur solubilities (as SCSS) in a granitic melt, calculated on the basis of algorithms presented in Holzheid and Grove (2002), Li and Ripley (2005), and Liu et al.

Table 1. Calculations of sulphur solubility (sulphur content at sulphide saturation, or SCSS) in granitic melt

	Granophyre[1]	Equation[2]	Equation[3]	Equation[4]
SiO_2	69.10			
TiO_2	0.89			
Al_2O_3	13.00			
Fe_2O_3	0.96			
FeO	4.90			
MgO	1.20			
CaO	1.80			
Na_2O	3.70			
K_2O	3.60			
Total	99.15			
X_{H2O}			0.01	
T (°C)		1200	1200	1200
P (kb)		1	1	1
SCSS (ppm)		192	394	802

[1] – Lightfoot et al. (2001); [2] – Li and Ripley (2005); [3] – Liu et al. (2007); [4] – Holzheid and Grove (2002). Water content in melt is considered in the equation proposed by Liu et al. (2007).
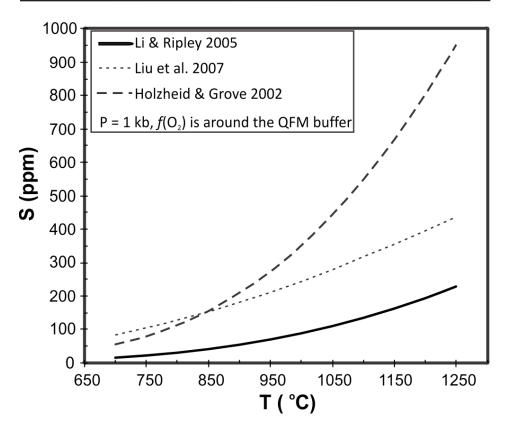

Figure 10. Modelling for the solubility of sulphur (ppm) in granitic melt in granitic melt vs. temperature (°C) at fixed pressure of 1 kb on the base of models by Li and Ripley (2005), Liu et al. (2007), and by Holzheid and Grove (2002). Oxygen fugacity is around the FMQ buffer. The composition data of granitic melt from Lightfoot et al. (2001).

(2007). The average composition of granophyre from the Sudbury Igneous Complex (Lightfoot et al. 2001) was used for the calculations (an Excel spreadsheet was created to facilitate the calculation, which is available upon request from the authors); this composition is well constrained and was selected to demonstrate the use of these algorithms. The redox conditions assumed in Table 1 are near the FQM buffer. The calculations demonstrate that the algorithm (equation) used can have significant implications for mineral exploration: the equation from Li and Ripley (2005) yields 192 ppm for sulphur solubility, lower than the 394 ppm calculated by Liu et al. (2007), and much lower than the 802 ppm calculated by Holzheid and Grove (2002). Here, no attempt is made to evaluate which equation would better approximate the actual solubility of sulphur in the granite melt, because different assumptions were made in developing the algorithms. However, the calculations indicate that sulphide saturation in the granite melt requires between 192 and 802 ppm sulphur, which implies a need for input of external sulphur to trigger sulphide saturation in some less evolved granitoid magmas. At a fixed pressure of 1 kb (100 MPa), the algorithms demonstrate that the solubility of sulphur in the granitic melt increases with increasing temperatures (Fig. 10), and that the predicted values of these models are different, particularly at higher temperatures. This indicates that the solubility of sulphur in granitic melt would decrease with fractionation.

DISCUSSION

The behaviour of sulphur in granitoid magmas is very important in understanding the metallogeny of intrusion-related gold (and copper) ore deposits. Sulphur solubility and the state of sulphide saturation in magmas are two of the most important controlling factors for the formation of intrusion-related gold deposits, such as those in the western Yukon Territory and southwestern New Brunswick (Canada), eastern Alaska (USA), and elsewhere (e.g. Newberry and McCoy 1995; McCoy et al. 1997; Thompson et al. 1999; Thompson and Newberry 2000; Lang and Baker 2001; Chi 2002; Fan et

al. 2003; Groves et al. 2003; Blevin 2004; Yang et al. 2004, 2006, 2008; Yang and Lentz 2005a,b; Hart 2007; Chi et al. 2008; Thorne et al. 2002, 2008; Kontak and Kyser 2011; McFarlane et al. 2011; Zhu et al. 2011).

Oxygen fugacity and melt composition (especially FeO content) are important factors in controlling the behaviour of sulphur in felsic melts, and the nature of the wallrocks is particularly important in influencing the oxidization state of a melt. Subduction-related I-type magma that is originally oxidized, for example, may display features of (reduced) ilmenite-series intrusions when the magma is emplaced into organic (reduced carbon)-bearing calcareous sedimentary rocks (Ague and Brimhall 1988; Whitney 1989; Yang and Lentz 2005a). However, Ishihara (2004) emphasized that the source region composition may play a more important role in controlling the redox conditions of granitoid magma than the country rocks into which the magma is emplaced.

High copper and gold fluxes associated with sulphur-rich degassing volcanoes fed by underplating magmas, indicate that copper and gold behaviour in magmatic systems is strongly related to sulphur (e.g. Keith et al. 1997; de Hoog et al. 2001; Stavast et al. 2006; Frank et al. 2011; Wallace and Edmonds 2011). The process of sulphur-degassing may result in the release of metals from early magmatic sulphide minerals to the melt and associated magmatic fluids. Gold and associated mineralizing elements in intrusion-related gold deposits may therefore be directly derived from the intrusion, although minor amounts could be incorporated from country rocks by selective assimilation and subsequent fractional crystallization. Jugo et al. (1999) carried out experimental studies on gold and copper partitioning between pyrrhotite (Po), an intermediate solid solution (Iss) of composition $Cu_{19}Fe_{30}S_{51}$, and haplogranitic melts under conditions of 850°C, 1 kb, gas saturation ($a_{H2O} \approx 0.9$) and $\log f(O_2) = -13.2$ ($\approx$FMQ + 1.5). Their results show that gold partition coefficients for Iss and Po are, respectively, $D^{Iss/melt}$(gold) = 5.7×10^3 and $D^{Po/melt}$(gold) = 140, indicating that immiscible segregation (and subsequent crystallization) of sulphide
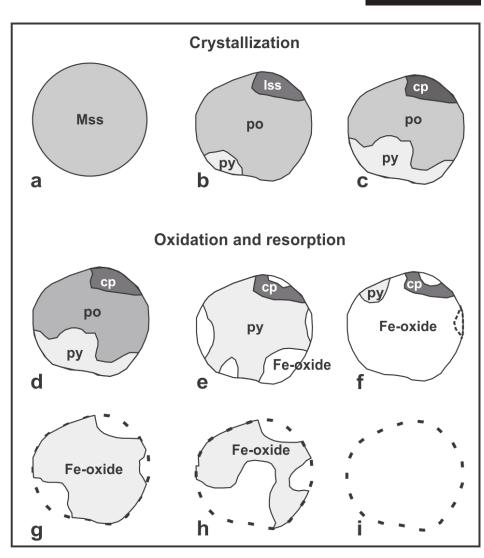

Figure 11. The processes of resorption, oxidation and decomposition of early magmatic sulphide minerals reacted with hydrothermal fluids, enriching ore materials (i.e. gold, copper, sulphur) in the fluids (after Stavast et al. 2006). Crystallization of the immiscible monosulphide solid solution (Mss) segregates from the silicate melt (a) to form pyrrhotite (po), pyrite (py), and intermediate solid solution (Iss) (b), and then chalcopyrite (cp) and po (c). Destruction of the sulphide minerals (d to g) by resorption and (or) oxidation; some resorption of the sulphide bleb back into the melt also occurs at this stage. Pyrrhotite is subsequently oxidized to pyrite and Fe oxide (d). Resorption continues and pyrite is oxidized to Fe oxide (e). Pyrite and chalcopyrite are oxidized to Fe oxide (f), leaving spongy Fe oxide remnants (g). Fe oxide also is resorbed (h). If the sulphide bleb is completely resorbed, no trace of sulphide or Fe oxide is present (i).

melt may effectively deplete a granitic melt in gold and other chalcophile metals. This result is consistent with empirical observations from natural granitoid rocks (Yang et al. 2006). Furthermore, $D^{Po/melt}$(gold) may increase greatly with increasing sulphur fugacity and decreasing $f(O_2)$ within the Po stability field. Destabilization of both magmatic Iss and Po relative to magnetite due to changes in $f(O_2)$ and $f(S_2)$

can lead to the release of gold from sulphides to the melt and/or magmatic fluids and provide a source of metals (gold, copper, and sulphur) to ore-forming fluids (Keith et al. 1997; Stavast et al. 2006; Kesler and Wilkinson 2010; Frank et al. 2011; Simon and Ripley 2011). Figure 11 illustrates the processes of resorption, oxidation and decomposition of early magmatic sulphide minerals, and liberation of gold,

copper and sulphur to hydrothermal fluids; these processes would significantly enrich the fluids in these elements.

It is known that intrusions provide at least some of the heat necessary to initiate and maintain large-scale convective hydrothermal systems (Cathles 1981) and can also be an important source of metals during the genesis of ore deposits (Candela and Holland 1986; Boomeri et al. 2009, 2010). The exsolution of a magmatic volatile phase (MVP) and the partitioning of ore metals from the melt into the MVP are important processes in concentrating metals from a dispersed state in the magma by means of the buoyancy of the less dense MVP. Where there is no immiscible sulphide melt segregation, the magma is mostly undersaturated with respect to sulphur, and gold therefore remains in the melt. During magmatic–hydrothermal evolution, gold may then prefer to partition into exsolving magmatic fluids if the physiochemical conditions and geological environment are both favourable, particularly under relatively high temperatures (e.g. Kesler et al. 2002; Heinrich et al. 2004; Frank et al. 2011). Consequently, in a suitable geological setting, a gold deposit may originate from a MVP and form within the intrusion and/or peripheral country rocks; alteration is limited, and restricted to hydrofracture systems. A gold deposit formed in this way is termed here a Type-1 intrusion-related gold deposit. For example, the gold deposits at Dublin Gulch, Clear Creek, Brewery Gulch, and Clarence Stream (Canada), and Timbarra (Australia), may belong to this category (McCoy et al. 1997; Thompson et al. 1999; Lang and Baker 2001; Thorne et al. 2002, 2008; Mustard et al. 2006).

The most important characteristic of Type-1 granite intrusion-related gold deposits is that the granite is not saturated in sulphide minerals, hence gold remains in the magma until the final stage of fractionation, at which time it partitions into the exsolving MVP to form ore fluids, i.e. no evidence of magmatic sulphides remains in the granite. Mustard et al. (2006) provide an excellent example of Type-1 intrusion-related gold deposits, namely the Timbarra gold deposit in Australia. They found that gold and associated metals (e.g. Bi, W, Sn) become enriched during fractional crystallization in a composite granite intrusion, and disseminated mineralization occurs at the final stage (in this case, a syenogranite zone that hosts the gold deposits). Disseminated ore consists of gold-bearing muscovite-chlorite-carbonate alteration zones and infill of primary miarolitic cavities within the massive leucogranite. Mustard et al. (2006) suggest that the lack of early sulphide, early Cl-bearing fluids, and prolonged crystallization together result in concentration of gold in the fluid phase during fractional crystallization. Thorne et al. (2002, 2008) also demonstrated that some fractionated phases, such as aplite–pegmatite dykes from the Clarence Stream gold deposit, New Brunswick, Canada, contain significant gold, implying that fractional crystallization could enrich gold and generate a Type-1 gold deposit, provided that the granite (in this case, the Magaguadavic granitoid suite) is undersaturated in sulphide minerals (McLeod and McCutcheon 2000; Yang et al. 2006).

However, if a granitic magma becomes saturated in sulphide, the residual melt would be depleted in gold because of immiscible sulphide melt segregation (liquation) and incorporation of gold (and copper) into sulphide minerals. This process results in evolved magmas becoming depleted in gold and copper; release of a MVP from such magmas during decompression (first boiling) and/or crystallization of anhydrous phases (second boiling), does not generate significant gold or copper mineralization within or around the intrusions, precluding the formation of Type-1 gold deposits. Nevertheless, late stage, low pH, relatively highly oxidized and low temperature hydrothermal fluids, derived either from cooling magmas at depth or from intrusion-driven circulation of local groundwater, may preferentially leach and sequester gold (chloride complexes at T > 300 °C, and bisulphide complexes at T < 300 °C) that was incorporated in sulphide minerals during early sulphide saturation in the melt. If a significant amount of gold released in this manner is concentrated in a suitable geological structure, such as shear zones (Lin 2001) and/or hydrofracture systems, a second type of intrusion-related gold deposits, here termed a Type-2 gold deposit, may form. The Pogo, Ryan Lode, and Tin Dome gold deposits, Alaska (USA), and gold mineralization at Lake George (New Brunswick, Canada) may be categorized as Type-2 deposits (Thompson and Newberry 2000; Lang and Baker 2001; Yang et al. 2004; Leonard et al. 2006).

Type-2 granite intrusion-related gold deposits are characterized by the presence of early magmatic sulphide minerals in the intrusion. These intrusions were saturated in sulphide during magma evolution and gold is dominantly hosted in the sulphide minerals; however, the magmatic sulphide minerals are unstable, and ready to be dissolved and decomposed upon reaction with chloride- or bisulphide-bearing circulating hydrothermal fluids, either derived from sequential release of cooling magmas at depth, or from the circulation of local groundwater driven by the cooling intrusion above the brittle-ductile transition. The congruent or incongruent dissolution of gold (copper, sulphur) into those fluids would enhance the potential for mineralization if focused into favourable structures and/or chemically reactive host rocks. The Pogo deposit features gold-bearing quartz vein systems that are hosted dominantly by altered gneiss (and to a lesser extent by granite) and contain less than 3% sulphide minerals, including pyrite, pyrrhotite, loellingite, Ag–Pb–Bi–S minerals, and native gold (Thompson and Newberry 2000); low temperature mineralization and alteration overprint the early mineralization without apparent zonation (Smith et al. 1999). The Lake George deposit exhibits early tungsten–molybdenum–gold stockwork mineralization superimposed by later gold–antimony quartz vein mineralization associated with a magmatic pyrrhotite-bearing granodiorite intrusion that is contiguous with a large pluton at depth (Seal et al. 1988; Yang et al. 2004, 2006). Resorption and spongy-textured pyrrhotite and magnetite evident in the granodiorite indicate that gold was liberated from early magmatic sulphides when they interacted with low-pH, relatively low temperature hydrothermal fluids derived from

a cooling granite intrusion at depth, leading to deposit formation.

Types 1 and 2 gold deposits have many similarities, and they may not be easy to distinguish. Detailed evidence from fluid inclusions suggests that Type-1 gold deposits form at relatively higher temperatures and that the relevant mineralizing fluids have higher salinities and sulphur fugacities compared to Type-2 deposits. However, comparisons of gold partition coefficients between a MVP and silicate melt, and between a sulphide melt and silicate melt (e.g. Connors et al. 1993; Jugo et al. 1999; Harris et al. 2003; Heinrich et al. 2004; William-Jones and Heinrich 2005; Yang et al. 2006; ; Simon et al. 2007; Zezin et al. 2007; Seo et al. 2009; Frank et al. 2011) suggest that the transport of gold is much more efficient, in terms of metal budgets in the ore system, in hydrothermal fluids that reacted with early sulphide minerals to liberate gold, compared to a MVP. The relative economic importance of Type 1 vs. Type 2 intrusion-related gold deposits needs to be assessed in future studies (see also Simon and Ripley 2011). Type 2 deposits appear to exhibit more structural control, and exploration models and techniques employed in searching for these deposits should take this, and the mode of gold transport, into account. Clearly, the geochemical characters of gold-associated granitoid intrusions and the status of sulphide saturation within these intrusions may be the key to discriminating Type 1 and Type 2 intrusion-related gold deposits.

CONCLUSIONS

The behaviour of sulphur in felsic magmas is controlled by the sulphur source, temperature, pressure, melt composition, redox conditions, and sulphur diffusivity. The most important factors affecting sulphur solubility are FeO content and oxidation state; the highest sulphur solubilities are seen in the most FeO-rich melts. In other words, felsic melts with low iron content have lower sulphur solubility compared to magmas having mafic compositions. Sulphide dominates in melts under reduced conditions ($f(O_2)$) near or below FMQ buffer), whereas sulphate predominates under relatively oxidized conditions ($f(O_2)$) above FMQ

+ 2). Decrease in temperature and increase in pressure usually result in decrease of sulphur solubility at fixed $f(O_2)$; speciation of sulphur in the melt and related degassing behaviour are also controlled by its diffusivity. An essential factor controlling the ultimate sulphide content of the melt is the sulphur source, which is in turn controlled by the geodynamic processes of magma generation in a given tectonic setting, and by the mechanisms of magma emplacement and nature of country rocks. The type of intrusion-related gold deposit is determined by whether or not sulphur is saturated in the granitoid melt. Sulphur undersaturation in granitic melts indicates a higher probability of yielding Type-1 intrusion-related gold deposits, which form as a result of fractionation and partitioning of gold into a MVP. However, if gold is incorporated into sulphides during early sulphide saturation, which appears to rule out the possibility of generating Type-1 deposits, late stage hydrothermal fluids with low pH and relatively high $f(O_2)$ may leach gold and concentrate it in favourable geological structures, such as shear zones and/or hydrofracture systems, forming a Type-2 intrusion-related gold deposit. Type-1 gold deposits typically form at higher temperatures and the mineralizing fluids have higher salinities compared to Type-2 deposits. Few studies have attempted to discriminate the two types, hence their relative importance needs to be further evaluated so that improved exploration models and strategies may be formulated.

ACKNOWLEDGEMENTS

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