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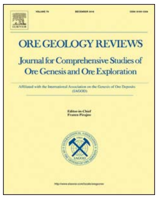

Low temperature alteration of magmatic Ni-Cu-PGE sulfides as a source for hydrothermal Ni and PGE ores: A quantitative approach using automated mineralogy

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ABSTRACT

Magmatic Ni-Cu-PGE sulfide assemblages are almost ubiquitously comprised of pyrrhotite-pentlandite-chalcopyrite(-pyrite). Sulfide alteration is common during syn- or post-magmatic fluid interaction, usually replacing sulfides with amphiboles or serpentine. However, some are altered to a low temperature (< 200 °C) hydrothermal assemblage of pyrite-millerite-chalcopyrite (PMC). An example is the Ni-Cu-PGE mineralisation in the Grasvally-Norite-Pyroxenite-Anorthosite (GNPA) Member, northern Bushveld Complex, which displays a continuum of mineralogical styles formed through progressive alteration: Style 1 primary pyrrhotite-pentlandite-chalcopyrite; which is altered to Style 2 pyrrhotite-pyrite-pentlandite-chalcopyrite; Style 3 pyrite-pentlandite-chalcopyrite; Style 4 pyrite-pentlandite-millerite-chalcopyrite; and Style 5 pyrite-millerite-chalcopyrite-cubanite. Modelling using CHILLER confirms this mineralogical sequence is thermodynamically possible at ~200 °C. Quantitative characterisation using automated Energy-Dispersive X-ray spectroscopy mapping alongside in situ laser ablation analyses determined mineral proportions, major and trace element concentrations and deportments in each style. The early loss of pyrrhotite removes over half of the bulk Fe and S during the initial stages of PMC alteration, increasing Cu, Ni and PGE tenors of the remaining sulfides significantly. As water–rock interaction progresses, pyrrhotite is replaced by pyrite and pentlandite by millerite, with concurrent losses in Fe, S and Ni. Copper is lost throughout the alteration, and is most pronounced in the more advanced stages. The fluids responsible were most likely acidic and oxidised, with metals mobilised as chloride complexes. Using Rh as an immobile normalising element, the overall mass loss in the most altered samples is calculated to be up to 90%, consistent with textural relationships that indicate 40–90% volume loss from Styles 2–5, with sulfides replaced by secondary silicates, including phlogopite, quartz, chlorite, pyroxenes and minor amphiboles. Magnetite is not a significant alteration product and thus Fe is mobilised, or incorporated into silicates. Most trace elements present in the magmatic sulfide (the IPGE, Rh and Bi) remain in the sulfide phases, and are effectively transferred to pyrite during PMC alteration, except Pd, which remains in pentlandite, and is liberated from the sulfide assemblage when pentlandite disappears. Selenium tenors increase slightly with alteration, demonstrating that alteration decreases S/Se ratios. The significant mobilisation of Ni, Cu and Pd during PMC alteration produces fluids enriched in these elements that may represent a metal source for a number of enigmatic hydrothermal Ni deposits such as Avebury, Enterprise and Talvivaara, whose metal sources remain speculative. The PMC alteration of the GNPA Member may be specifically a source for the nearby Waterberg hydrothermal Pt deposit. Furthermore, this study has implications not only for magmatic ore deposits, but also for the general implications of sulfide transformation and metal transfer in ore systems in general.

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1. Introduction

Magmatic sulfide deposits are the world's most important source of Ni and platinum-group elements (PGE) and significant associated Cu. They form following the segregation of an immiscible sulfide liquid from a mafic-ultramafic magma, with chalcophile elements being concentrated in the sulfide liquid, which accumulate into economic deposits (Naldrett, 2011). Cooling of the sulfide liquid crystallises Ni-rich monosulfide solide solution (mss) and Cu-rich intermediate solid solution (iss), which exsolve at low temperatures to give rise to the characteristic pyrrhotite–pentlandite–chalcopyrite sulfide assemblage that occurs in almost all unaltered magmatic sulfide ores (Craig and Kullurud, 1969; Kullerud et al., 1969).

Hydrothermal deposits of Ni sulfides and PGE are much less common but do exist, with Ni deposits found in mafic-ultramafic igneous, and sedimentary host rocks (González-Álvarez et al., 2013), and epigenetic PGE deposits found in a range of settings (Wood, 2002). These enigmatic classes of deposits include some major deposits, such as the Avebury Ni deposit, Tasmania, Australia (Keays and Jowitt, 2013), the Enterprise Ni deposit in Zambia's Copperbelt (Capistrant et al., 2015), the Waterberg hydrothermal Pt deposit in northern South Africa (McDonald et al., 1995), the hydrothermally remobilised Pt-Cu-Au New Rambler deposit, Wyoming (Nyman et al., 1990), and epigenetic Pt-Au deposits in Brazil and Australia (Sener et al., 2002). The source of metals in all these deposits is very poorly constrained but the most commonly proposed theory is that the metals have been mobilised from magmatic sulfides within mafic-ultramafic rocks, though no definitive evidence has been put forward and this key aspect of ore genesis remains speculative.

Alteration of magmatic sulfides is very common, and whilst Cu and Au are relatively mobile during fluid alteration, Ni and the PGE are generally thought to be immobile under most conditions, such as serpentinisation, amphibolitisation and talc-carbonate alteration of ultramafic rocks (e.g. Barnes and Liu, 2012). However, Liu et al. (2012) showed experimentally that Ni can become mobile in certain oxidised and acidic conditions and Le Vaillant et al. (2015, 2016a) have shown that there are other hydrothermal conditions that effectively mobilise Ni, Cu and PGE, such as those involving As-rich orogenic fluids. Effective mobilisation of Ni, Cu and PGE could produce fluids that are enriched in these elements and provide a source for enigmatic hydrothermal occurrences of this element association.

Replacement of magmatic sulfides by secondary silicates is extremely common, and usually takes the form of amphiboles such as actinolite-tremolite-talc around the margins of sulfide blebs (Li et al., 2004). This process generally reduces the volume of the sulfides slightly by replacing them from the outer edges. Whilst the sulfides are affected by this alteration, platinum-group minerals (PGM) are often left unaltered as satellite grains around the reduced sulfide grains (e.g. Hutchinson and Kinnaird, 2005). Nevertheless, the assemblages of such altered ores are still overwhelmingly dominated by pentlandite-pyrrhotite-chalcopyrite. However, there are a number of cases where low-temperature hydrothermal alteration has apparently changed the mineralogy of the sulfides, with pyrrhotite being altered to pyrite, pentlandite to millerite, and chalcopyrite being partially altered to cubanite (e.g. Dare et al., 2011; Djon and Barnes, 2012; Smith et al., 2011; Piña et al., 2012). This characteristic assemblage produces a more complex mineralogy, and PGE are either mobilised into the fluid phase, taken up variably by the secondary sulfide alteration products, or recrystallized as secondary PGM. As such, pyrite and millerite in such ores can become major hosts for Pt and other PGE (e.g. Oberthür et al., 1997; Barkov et al., 1997; Gervilla and Kojonen, 2002; Djon and Barnes, 2012; Dare et al., 2011; Piña et al., 2012, 2013; Smith et al., 2014; Graham et al., 2017).

Whilst this alteration of magmatic sulfides has been observed empirically, the transformation from a magmatic pentlandite-pyrrhotite-chalcopyrite assemblage to one of hydrothermal pyrite-millerite-chalcopyrite(–cubanite) has never been assessed quantitatively. The conversion of pyrrotite (Fe_7S_8) to pyrite (FeS_2) implies a relative gain of S; quite possible if a S-bearing fluid is involved in alteration. Alternatively, it could be a result of a loss of Fe, which would also be consistent with pentlandite ($(Fe,Ni)_9S_8$) converting to millerite (NiS); the latter also requiring some loss of Ni. Alteration of chalcopyrite ($CuFeS_2$) to cubanite ($CuFe_2S_3$) involves loss of Cu relative to S and Fe (possibly due to Fe gain), but also an increase in Fe relative to S. As such, the reactions in this style of alteration clearly involve significant changes in mineralogy; which will have a major impact on the ratios of the major constituents of the sulfide assemblage, the metal tenors of the sulfide, and the potential mobilisation of the base and precious metals into hydrothermal fluids. Determining whether mass loss or gain has occurred requires a quantitative approach with well-defined end members.

In this paper, we aim to quantify the hydrothermal alteration of magmatic pyrrhotite-pentlandite-chalcopyrite ores to pyrite-millerite-chalcopyrite assemblages (henceforth referred to as 'PMC alteration') by applying automated mineralogy, with supporting Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) data, to track the distribution and deportment of major and trace metals during PMC alteration. We utilise a suite of ore samples from the northern Bushveld Complex that show a continuum from unaltered, primary magmatic pentlandite-pyrrhotite-chalcopyrite to completely altered millerite-pyrite-chalcopyrite-cubanite. For the first time, we are able to quantify the process in terms of significant, but relatively variable bulk losses of Fe, Ni, Cu, PGE, Se and S from sulfide, major sulfide volume reduction, and the subsequent increase in the tenor of a number of base and precious metals. The significance of identifying effective Ni-Cu-PGE mobility and the implications of producing Ni-Cu-PGE-bearing hydrothermal fluids as a source for enigmatic hydrothermal deposits, and the wider processes of sulfide alteration and metal transfer in ore deposits, is explored.

2. Empirical and experimental studies

A number of magmatic sulfide deposits have been identified as comprising variable amounts of the low temperature assemblage of pyrite-millerite-chalcopyrite, usually as partial replacement of the primary pyrrhotite-pentlandite-chalcopyrite assemblage. These include deposits and occurrences in the northern Bushveld Complex, South Africa (Smith et al., 2011, 2014), the Lac Des Iles Complex, Canada (Djon and Barnes, 2012; Duran et al., 2015), Aguablanca, Spain (Piña et al., 2012), and the Great Dyke of Zimbabwe (Piña et al., 2016). In all of these studies, the presence of pyrite and millerite is attributed, at least in part, to low-temperature hydrothermal alteration, supported by textural relationships and the experimental evidence that the pyrite-millerite assemblage can only coexist at temperatures below around 230 °C (Naldrett and Kullerud, 1967; Naldrett et al., 1967; Craig, 1973; Misra and Fleet, 1974).

Both millerite and pyrite can however, form as a product of primary magmatic mss. In the case of millerite this is only in some cases of extremely Ni-enriched komatiite ores, in which Ni-rich mss can dissociate to assemblages of pyrite, pentlandite and millerite (Barnes et al., 2011). However, in all the cases of millerite in the more mafic systems cited above, it forms as an alteration product from pentlandite. Pyrite can also be a primary product of the cooling of mss if the S to metal ratio of the sulfide liquid is high enough (~ 40 wt% S at 600 °C), and up to 30% pyrite can be accommodated by a the breakdown of mss at temperatures below 700 °C (Naldrett et al. 1967; Kullerud et al. 1969; Craig 1973). Pyrite and pentlandite, however, cannot co-exsolve until 230 °C when the mss tie line separating pyrite and pentlandite in the Fe-Ni-S system breaks (Naldrett et al., 1967). Pyrite formed in the mss-iss-pyrite system has been shown experimentally to be enriched in a range of highly siderophile and chalcophile elements, such as the PGE, Te, Se and As (Cafagna and Jugo, 2016). However, most natural sulfide melts