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Gold mobility during Palaeoarchaean submarine alteration

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ABSTRACT

Seafloor alteration provides large amounts of solutes to the hydrosphere. In order to investigate gold mobility during water-rock interaction prior to 3-billion-years ago, low detection limit analysis of Au concentrations was carried out on rocks from marine alteration zones. Stratiform zones recording low-temperature (≤150 °C) seafloor alteration are a characteristic feature of greenstone belts older than 3.0 Ga. Hydrothermal processes were operating on, and immediately below, the seafloor, giving rise to extensive silicification of sub-seafloor volcanic rocks and silicification of seafloor sediments. In order to investigate gold mobility during silicification, unaltered and variably silicified volcanic rocks and associated cherts from Palaeoarchaean greenstone successions (c. 3.4 Ga) of South Africa were analyzed. Results show mobility of gold during silicification of mafic/ultramafic rocks and transfer to the Archaean ocean. Some gold was incorporated into carbonaceous marine sediments overlying the alteration zones. A combination of pervasive silicification, rarity of black shales, and low gold content in komatiites can explain the low mineralization potential of Palaeoarchaean greenstone belts for orogenic gold deposits.

1. Introduction

Ore deposit styles have varied through time due to progressive cooling of the Earth, evolution of the global tectonic regime, atmospheric/oceanic redox state and evolution of life (Holland, 2005; Groves et al., 2005; Goldfarb et al., 2010). Considering Archaean orogenic/lode gold deposits alone, secular variation exists with abundant gold in Neoarchaean but not in Palaeoarchaean greenstone belts (Goldfarb et al., 2010). Reasons for this may be multifaceted. An obvious reason may be preservational bias due to Palaeoarchaean successions being less abundant. A second factor may be linked to variations in crustal growth rate and episodicity in mantle-plume volcanism, the latter enhanced in the Neoarchaean. Thirdly, compositional change of the gold source may also have played a role, assuming an internal (greenstone) source, where Au may have been derived from leaching of fertile source rock, such as mafic rocks or metalliferous shales (Phillips and Powell, 2010; Pitcairn et al., 2006a). In this contribution we aim to evaluate the effect of submarine low-temperature alteration processes on gold distribution and mobility in rocks older than c. 3.2 Ga. By so doing we investigate potential correlation between the relative abundance of gold deposits in Archaean rocks and specific processes of Au mobilization operating during Archaean surface processes.

2. Submarine alteration >3.2 Ga ago

Rocks at the interface with the atmosphere and hydrosphere are subjected to alteration processes that result in mechanical disaggregation and changes in mineralogy and chemical composition. Elements mobile under the physico-chemical conditions of the alteration are depleted and transferred to the hydrosphere, where they may reside or be taken up by neoformed mineral phases. Immobile elements become concentrated at the site of alteration, potentially forming enrichments of economic interest, although these may be subjected to mechanical erosion. Surface alteration processes have changed through geological time, as a result of changes in atmospheric composition, conditions of the hydrosphere, surface temperatures, and the evolution of life (Holland, 2006; Hazen et al., 2008). Interactions of rocks with the hydrosphere are best preserved at the top of oceanic crust, as cooling of modern oceanic crust is achieved by the convection of seawater, giving rise to submarine alteration of basaltic rocks. Prior to the rise of oxygen to levels c. 1–10% of present day values in the Palaeoproterozoic (Holland, 2006), submarine alteration processes operated differently as compared to more recent times, due to differences in Eh, pH, and the dissolved element load of reduced marine waters that interacted with exposed crust.

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On the seafloor, the interaction between aqueous fluids and volcanic rocks causes mineral alteration and leaching/enrichment of elements (Staudigel, 2014). Zones of seafloor alteration are common throughout Palaeoarchaean greenstone belts in general, and the Barberton greenstone belt in particular, where they are conspicuous by their intense silicification (Hofmann and Harris, 2008). The 3.55–3.30 Ga Onverwacht Group is a thick pile of submarine lava flows that erupted intermittently over a time period of c. 250 Ma. Breaks in volcanic activity resulted in the deposition of thin interflow sedimentary units characterized by tuffaceous, volcaniclastic material, carbonaceous matter and chemical precipitates (Hofmann et al., 2013a). At the same time, relatively low-temperature ($\leq 150\,^\circ$C) hydrothermal processes were operating on, and immediately below, the seafloor, giving rise to extensive silicification of sub-seafloor volcanic rocks, silicification of seafloor sediments to chert and extensive hydraulic fracturing, giving rise to cross-cutting veins filled with chert and fluid precipitates (Hofmann and Bolhar, 2007; Ledevin et al., 2014). Diffuse venting over large tracts of ocean floor is envisaged to have given rise to silicification, coupled with leaching of many metals from the volcanic substrate and their transfer to the ocean (Hofmann and Harris, 2008; Abraham et al., 2011). For example, the Palaeoarchaean ocean floor was a major source for dissolved iron and nickel transferred to the ocean by reduced seawater (Hanor and Duchac, 1990; Hofmann and Harris, 2008). These elements were incorporated into secondary phases to eventually become concentrated in marine sediments, Fe in banded iron formations and Ni in shales. These lithologies and associated shale-hosted diagenetic pyrite are also enriched in Au in the Archaean (Meyer and Saager, 1985; Saager et al., 1982; Large et al., 2015), suggesting elevated dissolved Au concentrations in the Archaean oceans. Silicification of volcanic rocks may represent the mechanism of mobilization and the source of much of this gold.

3. Analytical methods

In this study several Palaeoarchaean submarine alteration zones were analyzed for gold. Analytical results are presented in Table 1. In the context of this article we differentiate altered and non-altered rocks, with the alteration being a result of low-T hydrothermal silicification. All rocks under consideration were subjected to greenschist facies metamorphism, thus even the unaltered rocks do not preserve a primary mineral assemblage.

Gold analyses were carried out at the Department of Geological Sciences at Stockholm University using a Thermo XSeries 2 ICP-MS following the ultra-low detection limit method described in Pitcairn et al. (2006b). Analytical precision for Au analysis at Stockholm was controlled through analysis of CANMET reference material TDB1 and Rocklabs reference materials OxA71 and SE44. Multiple analyses of TDB1 ($n = 40$), OxA71 ($n = 10$), and SE44 ($n = 4$) yield values (1σ) of 6.3 ± 1.2 ppb, 80 ± 8.5 ppb, and 599 ± 64 ppb, respectively, which compare favorably with certified values of 6.3 ± 1 ppb, 85 ± 6 ppb, and 606 ± 17 ppb. The 3σ detection limit for Au analysis was ascertained using acid digested blanks and determined to be 0.03 ppb Au. The instrumental error is extremely small compared to the variability in the distribution of gold within each sample. Multiple analyses of different aliquots of the same sample show variabilities ranging from 2 to 28% with a mean variability of 10% whereas repeat analysis of the sample digest on the ICP shows a variability of less than 1% (Pitcairn et al., 2006b).

Gold concentrations are evaluated together with major and trace element abundances obtained during previous studies of the same samples (Table 2). A small set of samples of komatiites of the Mendon Formation was specifically analyzed for major and trace element contents for this study. Analytical procedures follow those outlined in Wilson (2003). A set of chert samples from the Buck Reef Chert BARB3 drill core (Hofmann et al., 2013b) recently obtained by the ICDP-funded "Barberton drilling project" was also subjected to Au analysis. For these samples we report major element contents obtained by XRF (see Agangi et al., 2015 for analytical procedure) as well as total organic carbon and sulphur contents (see Partin et al., 2013 for analytical procedure).

4. Geology of studied sections and results of Au analysis

4.1. Hooggenoeg Formation, Barberton greenstone belt

The Hooggenoeg Formation, dated between 3.47 and 3.45 Ga, consists of pillowed and massive basalt, spinifex-textured komatiitic basalt, thin interflow sedimentary horizons silicified to chert and, at the top of the sequence, dacitic to rhyolitic volcanic rocks and an epiclastic sedimentary unit overlain by the Buck Reef Chert (Lowe and Byerly, 2007). Each chert horizon is underlain by a metasomatic alteration zone (Hofmann and Harris, 2008) that is characterized by silicification and cross-cutting chert veins. The effect of Palaeoarchaean seafloor alteration on Au concentration in the Hooggenoeg Formation was investigated at two different sites.

4.1.1. Hooggenoeg Formation pillow basalt and chert

A succession of pillow and massive basalt flows, a few hundred meters thick, forms the upper part of the Hooggenoeg Formation (unit H5v, Lowe and Byerly, 2007). The basalt sequence is capped by a thin chert horizon (H5c). Commencing from ca. 50 m below the chert bed, pillow basalt becomes silicified upsection (Fig. 1). This silicification is associated with (1) replacement of igneous minerals by quartz, carbonate and sericite, (2) an increase in SiO_2, K_2O, Eu/Eu*, $\delta^{18}O$ and $\delta^{30}Si$ values, and (3) a depletion of most elements mobile during interaction with reduced water and rock, including Ni, Co, Cu, and Zn (Hofmann and Harris, 2008; Abraham et al., 2011). Silicified basalt is transected by massive carbonaceous chert veins in the uppermost few meters. Chert-veined basalt is capped by a ca. 1 m thick horizon of massive to thinly laminated black carbonaceous chert that is, in turn, overlain by grey chert containing volcaniclastic particles.

Seven samples of variably silicified pillow basalt have Au concentrations in the large range of 0.89–6.38 ppb (average of 2.89 ppb). There is a distinct trend in Au concentration relative to the stratigraphy, so that the least altered sample (deepest below the palaeo-seafloor) has the highest Au concentration (Fig. 2). There are strong correlations between the concentration of Au and a number of major and trace elements. For example CaO, which is typically depleted during Palaeoarchaean seafloor alteration, shows a strong positive correlation with Au ($R^2 = 0.89$; not shown), suggesting concomitant depletion of both Ca and Au during alteration. While silicification might have been associated with volume increase during alteration, thus lowering the average Au concentrations, this volume change must have been minor, as monitored by only slight changes in the concentration of immobile trace elements (e.g. Al, Zr). In fact, a positive correlation of CaO vs Au/Al_2O_3 ($R^2 = 0.93$; Fig. 3) indicates the mobility of gold relative to immobile Al. In contrast to decreased Au concentrations that occurred with silicification, cherts overlying the basalt are relatively enriched in Au (4.73–9.49 ppb, average 7.08 ppb; Fig. 2).

4.1.2. Hooggenoeg Formation rhyodacite and Buck Reef Chert

The Buck Reef Chert overlies a rhyodacitic igneous body, up to 2 km thick, which is interpreted as a large intrusive to extrusive lava dome and associated volcaniclastic sedimentary rocks (Lowe and Byerly, 2007; Agangi et al., 2015). The top of this unit consists of massive, feldspar- and quartz-phyric, silicified rhyodacite. Feldspar porphyroclasts are replaced by mixtures of sericite