Gold in Devono-Carboniferous red beds of northern Britain

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Authigenic gold occurs in Devono-Carboniferous red beds in northern Britain. Red beds exhibit concentrations of gold and pathfinder elements for gold mineralization including tellurium and mercury, at redox boundaries. Detailed studies of samples from Millport, Isle of Cumbrae, Firth of Clyde, show particles of native gold up to 10 µm size, typically with less than 15 wt% silver. Their context indicates that the gold was

...of native gold in Devono-Carboniferous red beds in Scotland.

...traverse length at 50 µm s−1. A 15 s laser ablation preceded 30 s of ablation (1.5 mm) and 15 s delay. 82Se and 125Te were monitored for 0.1 s each. Three lines were analysed for each sample or standard. The average count signal over 20 s of the ablation was calculated for each element and subtracted by the average signal over 10 s for the initial gas blank. The standard was used to calculate the concentration (µg g−1)/counts ratio, which was multiplied by the sample counts to estimate concentration.

Results. Polished surfaces of several reduction spheroids from Millport contain grains of native gold. One spheroid was repolished twice to yield three different planes, each of which contained multiple gold grains. The grains are up to 10 µm size and approximately equidimensional (Fig. 2). They occur with a matrix of roscelite and iron oxides. Within the matrix are a large number of smaller, nanometre-scale, crystals of gold (Fig. 2). Analysis of 11 grains larger than 2 µm size showed traces of silver up to 20.5 wt% (mean 13.3 wt%), consistent with an attribution of native gold (Table 1). Vanadium occurs at up to 0.8 wt% (mean 0.6 wt%). No other trace elements were detected within the gold. Silver was...
Gold was recorded only in the reduced cores of the spheroids, and not outside the spheroids.

**Discussion.** The limitation of the gold grains to the reduction spheroids indicates that they were formed during diagenesis. Reduction spheroids form in the subsurface, and current models attribute them to microbial activity (Hofmann 2011; Zhang et al. 2014; Parnell et al. 2015b). The defining characteristic of reduction spheroids and other reduction features in otherwise red rocks is the conversion of Fe(III) to Fe(II) mineralogy; that is, from hematite to reduced iron oxides and silicates. Most of the reduction of Fe(III) in sediments is caused by Fe(III)-reducing bacteria (Lovley 1997). Where this bacterial activity is extensive, the red colour is stripped off sand grains and the sediment turns grey (Lovley 1997), and develops mottling of reduced and oxidized sediment in the subsurface. This mottling is observed in the geological record, which is thus reasoned to reflect microbial activity, distributed uniformly through the sediment (Lovley et al. 1990). The deposition of metals by reduction in the subsurface is achieved particularly through the activity of the Fe(III)-reducing bacteria. They have the potential to reduce a range of other metals and metalloids, including V, Cu, U and Se, by substituting them for Fe(III) as electron acceptors (Coates et al. 1996; Lovley 1997). These are all elements concentrated in red bed deposits, consistent with their purported microbial origin. All are present in the Millport spheroids. The elements of particular interest to us in this work, gold, tellurium and mercury, are all also concentrated from solution by Fe(III)-reducing bacteria (Kashefi et al. 2001; Kloniswka et al. 2005; Kerin et al. 2006; Kim et al. 2013), so as these bacteria will have been abundant in ancient red bed sediments they are likely to have played a role in Te, Hg and Au concentration. The particle size precipitated was smaller than that of gold found in placer deposits, so additional concentration would be required before it could be detected through panning techniques.

The metal-rich cores of the Millport spheroids are typically about 10% of the diameter, and thus 0.1% of the volume, of the whole spheroid. For an average sandstone of 3 ppb gold content (Wedepohl 1978), concentration of all the gold would produce a core of 3 ppm gold, which may be enough to explain the observed mineralization without addition of gold from outside. Quantitative data are required to explore this further.

Conodont alteration indices from Carboniferous marine rocks in the region, in both Scotland and Northern Ireland, are in the range 1–1.5, indicating temperatures not exceeding 90°C (Clayton et al. 1989; Dean 1992). These temperatures are consistent with burial of no more than 3 km, representing diagenesis rather than metamorphism. Experimental reduction of metals by Fe(III) reducers at temperatures of 60–100°C shows that microbial activity could concentrate metals in this shallow burial realm (Kashefi & Lovley 2000; Roh et al. 2002).

The association of tellurium and gold is typically encountered in magmatic, metamorphic and hydrothermal deposits (Cook & Ciobanu 2005; Ciobanu et al. 2006). Similarly, the association of mercury and gold is one normally associated with magmatic systems, metamorphic rocks and placer deposits derived from these rocks by erosion (Healy & Petruck 1990; Naumov & Osovsky 2013). The data reported here show that temperature is not a constraint, and that where tellurium and/or mercury are available, regardless of temperature, gold may be linked to them. The reduction spheroids in red beds...
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represent a diagenetic concentration of metals distinct from that in sulphides in organic-rich sediments such as black shales. Red beds as a whole represent oxidizing conditions rather than the reducing conditions of organic-rich sediments, and reduction spheroids generally lack sulphides or detrital organic matter. The spheroids more commonly contain selenides (Spinks et al. 2014). Both pyrite in black shales (Large et al. 2011, 2012) and the reduction spheroids in red beds contain diagenetic enrichments of gold, although the host mineralogy is different. Much of the gold in pyrite is in solid solution, rather than in particulate form as found in the Millport spheroids. The feasible source of the gold in continental red beds and seafloor anoxic sediments must also be different. Given that most pyrite in shales is attributed an origin through microbial sulphate reduction (Raiswell & Berner 1986), it is possible that these distinct settings share the involvement of microbial activity in metal concentration, albeit through different groups of microbes (iron reducers, sulphate reducers). However, it is the sulphide in pyrite that has a microbial origin,

Fig. 3. LA-ICP-MS map for centre of reduction spheroid, North Berwick: (a) gold; (b) mercury; (c) tellurium. Contours represent orders of magnitude, increasing towards the centre. Map widths 3 mm.

Fig. 4. LA-ICP-MS maps for centres of reduction spheroids, for (a) gold, Cultra, and (b) tellurium, Millport. Contours represent orders of magnitude, increasing towards the centre. Map widths, 3 mm.
and the combination with metals to form pyrite does not necessarily imply that the metal is microbially sequestered.

The observations made here add weight to models in which fluids passing through red beds can be potential gold ore fluids (e.g. Oszczepalski et al. 1999; Shepherd et al. 2005). Small-scale redox boundaries are critical to the distribution of gold in this case, and hence large-scale redox boundaries deserve study for possible gold concentration. The migration of hydrocarbons through red beds is a cause of extensive redox contrasts, and is a known cause of concentration of copper ore and other metals (Roberts 1980; Parnell et al. 2015a). Palaeo-oil reservoirs and migration fairways also deserve attention for their potential concentration of gold.

Conclusion

Examination of samples from reduction features in Devonian-Carboniferous red beds in northern Britain shows that they exhibit concentrations of gold. The observations have several implications, as follows.

1. Native gold was precipitated by redox-related processes at low (<100°C) temperatures in siliciclastic sediments. This may have been microbially mediated, but the present study cannot prove that.

2. A spatial relationship with pathfinder elements tellurium and mercury is expressed in this low-temperature environment.

3. Measurements at three widely spaced sites indicate that the concentrations are not exceptional, but are a normal aspect of red bed diagenesis.

4. Large-scale redox boundaries in red beds may be worth investigating for possible gold mineralization.

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