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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 concentrated during diagenesis, in rocks that had not experienced regional temperatures above 100°C. These occurrences add to other evidence of a role for red beds in the genesis of gold mineralization.

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There is a growing awareness that sedimentary red beds (continental successions dominated by coarse siliciclastic sediments) play a role in the cycling of gold in the upper crust. In Europe, Permo-Triassic red beds in particular have been proposed as a source of gold-mineralizing fluids (Stanley *et al.* 1990; Leake *et al.* 1997; Shepherd *et al.* 2005). Continental Devono-Carboniferous rocks, the Old Red Sandstone *sensu lato*, have received less attention in this respect. However, gold-bearing grains in modern streams cutting through Devonian red beds in Scotland (Chapman *et al.* 2009) and the proven availability of gold to the Devonian surface environment in the Rhynie hot spring system, Scotland (Rice *et al.* 1995) suggest that these red beds merit investigation for evidence of gold concentration. This study reports the low-temperature occurrence of native gold in Devono-Carboniferous red beds in Scotland.

Methods of study. The study focused at the stratigraphic top of the Old Red Sandstone, where red beds attributed to the uppermost Devonian pass into a mixed sequence of red beds, calcretes and other shallow-water limestones, including marine limestones, of the lowermost Carboniferous. The Carboniferous rocks are the traditional Calciferous Sandstone, now Clyde Sandstone Formation in Scotland and Holywood Group in Northern Ireland. Both Devonian and Carboniferous red beds exhibit widespread reduction features, especially reduction spheroids. Concentrations of metals and semi-metals are associated with the redox contrasts (Spinks *et al.* 2014). The cores of reduction spheroids are typically mineralized by roscoelite (vanadian mica), and a diversity of selenide, arsenide, oxide and native element minerals (Hofmann 2011). Samples from Millport, Isle of Cumbrae (Fig. 1; context described by Young & Caldwell 2011*a*,*b*), previously the subject of a study of selenide mineralization (Spinks *et al.* 2014), were examined for mineralogy using an ISI ABT-55 scanning electron microscope. Compositions were measured using gold, silver and vanadium pure elemental standards. Samples from North Berwick, Millport and Cultra, representing over 200 km width of Lower Carboniferous continental red bed outcrops across northern Britain (Fig. 1), were examined for trace element concentrations using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Analysis was performed using a UP213 LA system (New Wave, Freemont, CA) coupled to an Agilent (Wokingham, UK) 7500ce ICP-MS system. LA-ICP-MS was tuned for maximum sensitivity and stability using standard SRM 612 for trace elements in glass (NIST, Gaithersburg MD), optimizing the energy fluence to about 2 J cm^{-2}. A semi-quantitative calibration was provided using MASS-1 Synthetic Polymetal Sulfide (USGS, Reston, VA). Samples and the standard were analysed using a 100 µm diameter round spot moving in a straight line at 50 µm s^{-1}. A 15 s laser warm-up preceded 30 s of ablation (1.5 mm) and 15 s delay. ^{82}Se and ^{125}Te 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.

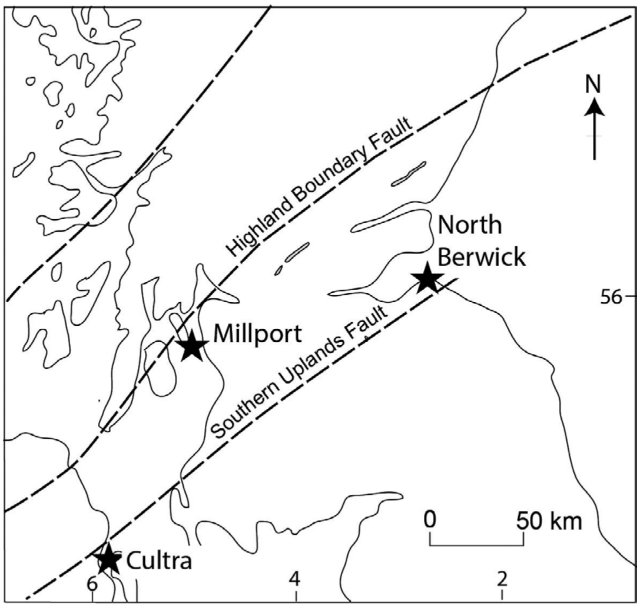

Fig. 1. Map of northern Britain and Ireland showing locations of red bed-hosted samples examined in this study.

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 roscoelite 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

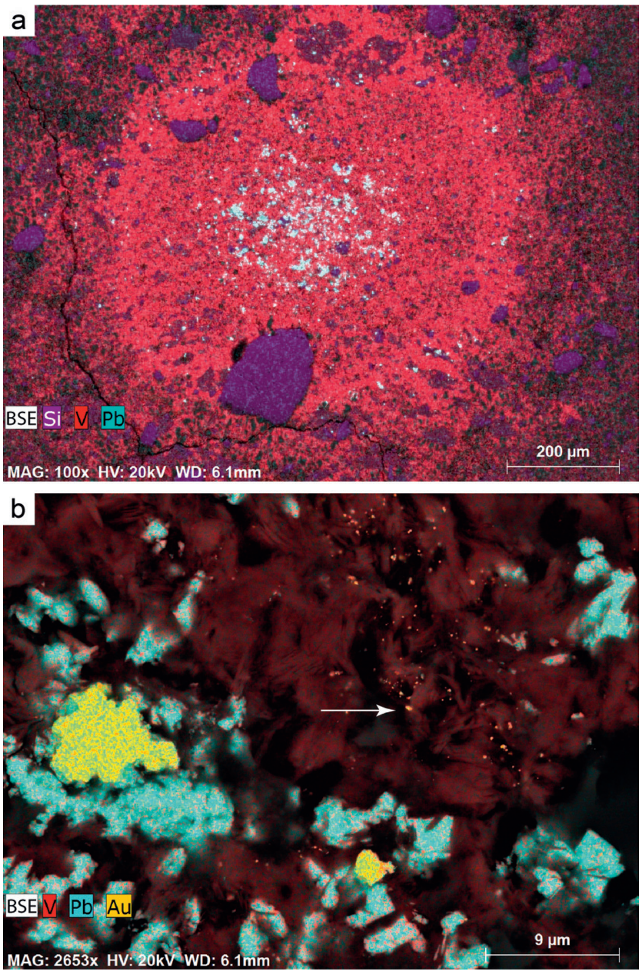

Fig. 2. Backscattered electron (BSE) micrographs of reduction spheroids containing native gold, Millport: (**a**) core of reduction spheroid, containing mixture of iron oxides and native gold (bright) in a matrix of roscoelite; (**b**) close-up of core, showing gold particle (left field, bright) and nanometre-scale gold (arrowed) within roscoelite matrix.

also recorded as a selenide without gold. Other authigenic mineral phases recorded in the spheroids include the vanadate minerals mottramite and vanadinite, the uranium silicate coffinite, and selenides of lead, bismuth, copper and iron.

Trace element concentration in the spheroids is indicated by contoured LA-ICP-MS maps made across the central mineralized portions of the spheroids. Contours by order of magnitude concentration show progressive increase in concentration of gold, and pathfinder elements for gold (mercury, tellurium), towards the centres of the spheroids. For example, mapping of a spheroid from North Berwick shows up to three orders of magnitude concentration of gold, tellurium and mercury at the spheroid centre compared with the margin (Fig. 3). Maps for spheroids from Millport and Cultra similarly show concentration of these elements (Fig. 4). Arsenic, also a pathfinder element for gold, is similarly concentrated in the spheroids.

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.* 2015*b*). 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; Klonowska *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 & Petruk 1990; Naumov & Osovetsky 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

Table 1. *Compositions (wt%) of gold crystallites, Millport, Isle of Cumbrae*

	Grain number											Mean
	1	2	3	4	5	6	7	8	9	10	11	
Au	85.98	87.21	88.12	88.98	84.30	91.02	85.86	78.95	81.07	86.43	86.58	85.86
Ag	14.34	13.67	11.97	10.97	13.73	8.42	11.40	20.54	15.76	12.05	13.32	13.29
V	0.48	0.44	0.53	0.44	0.57	0.46	0.64	0.49	0.40	0.81	0.83	0.55
Total	100.80	101.32	100.62	100.39	98.60	99.90	97.90	99.98	97.23	99.29	100.73	99.70

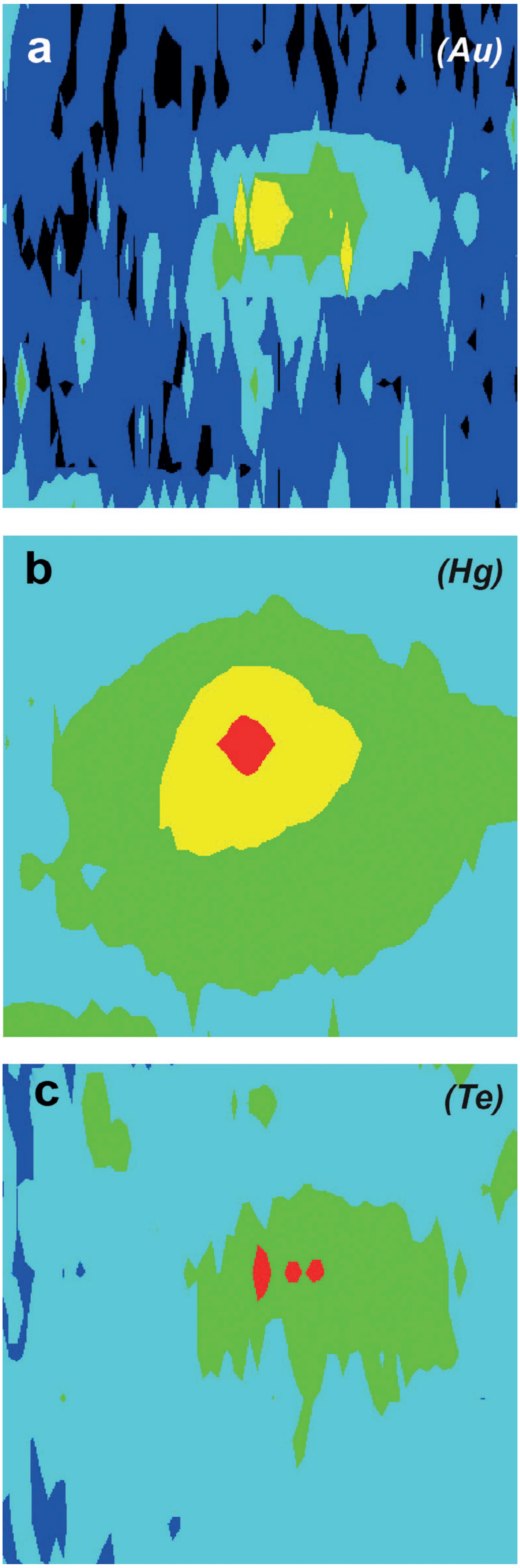

Fig. 3. LA-ICP-MS map for centre of reduction spheroid, North Berwick: (**a**) gold; (**b**) mercury; (**c**) tellurium. Contours represent orders of magnitude, increasing towards the centre. Map widths 3 mm.

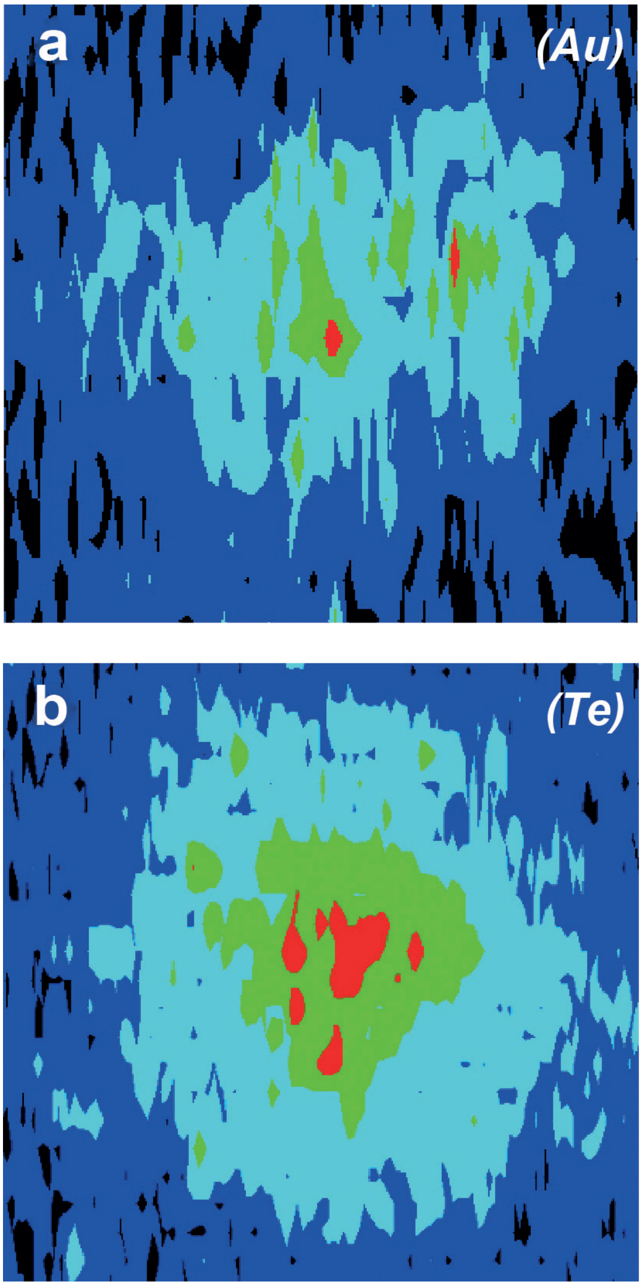

Fig. 4. LA-ICP-MS maps for centres of reduction spheroids, for (**a**) gold, Cultra, and (**b**) tellurium, Millport. Contours represent orders of magnitude, increasing towards the centre. Map widths, 3 mm.

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, 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*. 2015*a*). Palaeo-oil reservoirs and migration fairways also deserve attention for their potential concentration of gold.

Conclusion

Examination of samples from reduction features in Devono-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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