Redox-controlled selenide mineralization in the Upper Old Red Sandstone

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Synopsis

Selenium concentrations occur in organic-rich lithologies such as coal, and as secondary accumulations from the oxidative mobilization, migration and subsequent concentration upon encountering reductants such as organic matter or H2S. Here we assess the redox mineralization of copper and lead selenide phases in the cores of reduction spheroids in Devonian sedimentary red beds. We propose that the selenide mineralization occurred as descending meteoric fluids, supplied with selenium from Carboniferous coal seams, migrated through a major fault plane into underlying sandstones where localized, microbially-induced reducing conditions prevailed. These findings and other occurrences of selenide mineralization between Devonian and Carboniferous strata on the British Isles suggest a widespread selenide mineralization system between strata of that age.

Supplementary material: Detailed quantitative methodologies and supplementary data are available at http://www.geolsoc.org.uk/SUP18770.

Introduction

In sedimentary rocks, the concentration of selenium occurs in lithologies rich in organic matter, such as coals, and as secondary mineralization following mobilization from a seleniferous host rock (Raask 1985; Coleman et al. 1993; Yudovich & Ketris 2006). In near-surface environments, secondary selenium mineralization is highly redox-controlled, as selenate is mobile in oxidizing conditions and is reduced to metal selenide phases or native selenium in the presence of a reductant. Such environments include sandstone-hosted roll-front-type uranium deposits (Northrop & Goldhaber 1990; Simon et al. 1997) and reduction spheroids in sedimentary red beds (Hofmann 1990). The mineralization of selenium in anoxic environments has been attributed to biogenically-induced reduction processes, and in the light of increasing evidence for a microbially-mediated formation mechanism of reduction spheroids (Spinks et al. 2010), the concentration of selenium in reduction spheroid cores deserves scrutiny. Here we report the occurrence of metal selenide-bearing reduction spheroid cores within Upper Devonian (Upper Old Red Sandstone) red beds on the island of Great Cumbrae, and discuss the implications for selenium mineralization and selenium sources.

Regional geology

The Midland Valley Terrane of Scotland is characterized by predominantly Late Palaeozoic strata, bounded in the north by the Highland Boundary Fault Zone and in the south by the Southern Upland Fault (Fig. 1). The Late Palaeozoic sedimentary fill of the Midland Valley consists primarily of Devonian fluviatile facies of the Old Red Sandstone (Mykura 1991; Bluck 2000; Trewhil & Thirwall 2002) and overlying Carboniferous sedimentary and volcanic strata (Read et al. 2002; Waters et al. 2007) summarized in Figure 2. The Upper Old Red Sandstone (UORS), of Late Devonian age (Famennian 372–358 Ma; House 2000), of the western Midland Valley is attributed to the Stratheden Group (Fig. 2) (Paterson & Hall 1986) and unconformably overlies Lower Old Red Sandstone strata (Bluck 2000). Sedimentation in the region was structurally controlled and occurred in small fault-bound sub-basins (Mykura 1991; Caldwell & Young 2013). West of the Largs-Hunterston Fault Zone (LHFZ) (Fig. 1), the lowest stratigraphic unit of the Stratheden Group is the Wemyss Bay Sandstone Formation (Bluck 1978) which was deposited in alluvial fans and braided rivers sourced from the north and NE (Paterson et al. 1990; Mykura 1991). The overlying conformable Kelly Burn Sandstone Formation (KBF), which again only crops out west of the LHFZ, consists of red and brown medium-grained sandstones with pebble lenses. The KBF facies are trough cross-bedded with crudely defined fining-upward packages (Monro 1999) and, at over 1000 m, the formation is the thickest stratigraphic unit within the UORS in the area (Browne et al. 2002).

Carboniferous strata account for relatively little of the exposed geology on Great Cumbrae; however, the nearby
Fig. 1. (A) Location and geological map of the Midland Valley Terrane of Scotland showing the major Devonian and Carboniferous exposures between the Highland Boundary Fault (HBF) and the Southern Upland Fault (SUF). Selenide (Se) mineralization close to faults on the junction between Devonian and Carboniferous strata is shown on Great Cumbrae (Se1) and in Stirlingshire (Se2). (B) Geological map of Great Cumbrae and the surrounding area of the Firth of Clyde. Selenide mineralization occurs in the Kelly Burn Sandstone Formation within the cores of reduction spheroids on the eastern shores of Kames Bay, close to the Great Cumbrae Fault, west of the Largs-Hunterston Fault Zone (LHFZ). Data from Monro et al. (1999); Young & Caldwell (2011a, b); Caldwell & Young (2013).
and inferred overlying younger Carboniferous strata are of importance to this study, requiring a brief overview of the regional Carboniferous stratigraphy.

The Lower Carboniferous (Tournaisian c. 359–346 Ma) strata of the Midland Valley are assigned to the Inverclyde Group (Fig. 2), subdivided into the basal Kinneswood Formation, the Ballagan Formation and the Clyde Sandstone Formation (Paterson et al. 1990; Browne et al. 1999). The Kinneswood Formation consists of interbedded fining-upward cycles of fine- to coarse-grained, cross-bedded sandstones of varying colour; planar-bedded fine-grained sandstones; red mudstones; and concretionary carbonates (Browne et al. 1999; Young & Caldwell 2011a, b). These facies reflect fluviatile and floodplain deposition (Browne et al. 1999). The overlying Ballagan Formation represents a partial marine incursion, deposited in lacustrine or lagoonal environments (Read et al. 2002; Young & Caldwell 2011a, b). Facies include fossiliferous mudstones (Stephenson et al. 2002), siltstones, minor sandstones (Young & Caldwell 2011a), and locally brecciated minor dolomite and anhydrite beds (Browne et al. 1999). The Clyde Sandstone Formation consists of fluviatile and floodplain deposits of sandstone and calcareous silty mudstone (Browne et al. 1999; Young & Caldwell 2011a).

Unconformably overlying the Clyde Sandstone Formation in the western Midland Valley is the Clyde Plateau Volcanic Formation of the Strathclyde Group (Viséan c. 346–326 Ma) that locally overlies the Birgidale Formation on Bute, and the Laggan Cottage Mudstone Formation on Arran (Browne et al. 1999). The Clyde Plateau Volcanic Formation comprises subaerial lava flows and volcaniclastic deposits approximately 1000 m in thickness (Paterson & Hall 1986; Browne et al. 1999; Young & Caldwell 2011a). The Birgidale Formation underlies and is interbedded with the lavas on Bute and NE Arran (Young & Caldwell 2011a), and comprises mudstones rich in organic matter, pebbly sandstones, seat earths and coal beds (Browne et al. 1999; Young & Caldwell 2011b). The Laggan Cottage Mudstone Formation beneath the Clyde Plateau Volcanic Formation on Arran, also includes coal beds (Young 2008) and organic-rich mudstones (Gunn et al. 1903; Browne et al. 1999). These minor coal-bearing sedimentary units, which underlie volcanic facies, were likely deposited in small fault-bounded basins (Young 2008).

Geology of Great Cumbrae

Great Cumbrae lies c. 2 km west of Largs in the Firth of Clyde, and stretches c. 5 km N–S and a maximum of 3 km E–W (Fig. 1). The geology of Great Cumbrae and the surrounding area was first described in detail by Gunn et al. (1903) and subsequently by several other surveys (Monro 1999 and references therein). More recently, concise descriptions of the stratigraphy of the area have been detailed in Paterson et al. (1990), Monro (1999) and Young & Caldwell (2011b). The geology of the island is dominated by KBF sandstone, with the overlying younger Lower Carboniferous strata on the SW of the island. Two distinct sets of dykes transect the island: ENE–WSW-trending doleritic and tholeiitic dykes of late Carboniferous age, and NW–SE-trending Palaeogene basaltic–andesitic dykes related to the Mull Dyke Swarm (Monro 1999). Several minor faults occur on Great Cumbrae, and the major Great Cumbrae Fault (GCF) runs approximately NNE–SSW through the centre of the island (Fig. 1). Zones of secondary reduction and reduction spheroids containing mineralized dark cores occur within the KBF (Fig. 3), close to the GCF on the east coast of Kames Bay [NS 172 546]. Samples of
the reduction spheroids with mineralized cores were collected for analysis and are the focus of this study. The GCF has a complex history with several episodes of reactivation and repeated sinistral and dextral strike-slip displacements (Caldwell & Young 2013) that are important to this study and will be discussed in later sections.

The Carboniferous strata that occur on Great Cumbrae are restricted to the Kinnesswood Formation and Clyde Sandstone Formation, exposed on the SW of the island around Kames Bay (Fig. 1). Reduction spheroids occur in the red siltstones and fine-grained sandstones and siltstone of the Millport Member (Paterson & Hall 1986) on the north and NW shores of Kames Bay (Fig. 1). Here the reduction spheroids appear greenish-grey within the red sediment; however, mineralized cores are lacking. Comprehensive descriptions of the lithologies exposed at outcrop are presented by Young & Caldwell (2011b) and thus will not be covered here in detail.

### Analyses and results

#### Petrography

Analyses of the cores of reduction spheroids present within the KBF red beds close to the GCF were performed using petrographic and quantitative Backscattered Electron (BSE) & Energy Dispersive X-Ray Spectroscopy (EDS) methods with a Scanning Electron Microscope (SEM). Details on the methodology used are available in the Supplementary material.

Reduction spheroids that occur in the Kelly Burn Sandstone Formation at Kames Bay on Great Cumbrae vary from millimetres to several centimetres in diameter (Fig. 3). The reduction haloes are commonly coalesced into patchy reduced zones (Fig. 3a, b), but many reduction spheroids appear isolated and are surrounded by several centimetres of unaffected (non-reduced) sediment. The reduction haloes are spherical to spheroidal in shape and show little evidence of vertical shortening due to compaction. Mineralized cores within the reduction spheroids also vary from millimetres to over 1 cm in diameter, and locally show zoned mineralization, with densely mineralized cores surrounded by less-mineralized haloes (Fig. 3c).

The composition and sedimentary fabric of the reduction spheroid host sandstone, together with those of the cement, secondary pore-filling and mineralization were established using BSE and EDS analyses. The host sandstone is moderately well-sorted, medium- to coarse-grained, composed mostly of quartz grains (quartz: >90%, k-feldspar and heavy minerals: <10%) that show varying degrees of roundness and sphericity. The larger grains (c. 500 μm diameter) are generally well-rounded, whereas the smaller grains are predominantly angular (Fig. 4a), suggesting mixed sediment-source areas. The primary pore-filling mineral in the host sandstone is calcite. However, within the cores of the reduction spheroids calcite has been partially replaced by the vanadium mica roscoelite and by vanadium oxide phases (Fig. 4b, c). Locally, feldspars have also undergone partial or complete replacement by roscoelite (K(V3+,Al)2(AlSi3O10)(OH)2). Within the reduction spheroid cores, there are also two metal selenide phases, and uraniferous phases (Fig. 4c).

Copper and lead selenide crystals up to c. 10 μm in diameter occur around the margins of detrital quartz grains, and locally within calcite cement (Fig. 3b, c). Uranium oxide (uraninite) and polymetallic uranium-bearing phases occur in clusters of crystals c. 6 μm in diameter as replacement phases of the calcite cement (Fig. 4c). There is no evidence for detrital organic matter present within, or close to, the reduction spheroids or mineralized cores.

Quantitative EDS-SEM analyses of the copper and lead selenide phases were performed using elemental standards for copper, selenium and silver, a crocoite (PbCrO4) standard for lead, and wollastonite (CaSiO3) for calcium and silicon. A copper selenide-bearing sample containing umangite (Cu2Se) from the type locality at Sierra de Umango, Argentina (Paar et al. 2002) was also quantitatively analysed as a control; the results are available in the Supplementary material.

Analyses of the copper selenide phases (Table 1) show average ratios of copper to selenium close to 2, similar to those of berzelianite/bellidoite (Cu2Se).

| Cu Selenide | Cu Selenide | Cu Selenide | Cu Selenide | Cu Selenide | Cu Selenide |
|-------------|-------------|-------------|-------------|-------------|-------------|
| Pt.1        | Pt.1A       | Pt.2        | Pt.3        | Pt.4        | Mean        |
| Cu          | 59.292      | 58.014      | 60.4        | 59.508      | 57.053      | 58.853      |
| Se          | 41.648      | 44.892      | 38.8        | 39.979      | 38.729      | 40.810      |
| S           | 0.111       | 0.188       | 0           | 0           | 0           | 0           |
| Total       | 101.051     | 103.094     | 99.2        | 99.487      | 95.782      |             |

Formula (based on total of 3 atoms)

| Cu          | Se          | S           |
|-------------|-------------|-------------|
| 1.912       | 1.841       | 1.978       |
| 1.081       | 1.147       | 1.022       |
| 0.007       | 0.012       | N/A         |

Cu/Se ratios are close to 2, similar to those of berzelianite/bellidoite (Cu2Se)
disregarded as a component of the selenide phase. The copper selenides present in the analysed reduction spheroid cores are berzelianite and/or bellidoite (Cu₂Se).

Quantitative analyses of the lead selenides in the mineralized cores yielded lead/selenium ratios close to 1 (Supplementary material), similar to those of clausthalite (PbSe). EDS analyses of the lead selenide phases also detected minor background peaks of Si (Supplementary material), that are again likely due to the size of the selenide crystals.

Uranium-bearing phases (Fig. 4e) occur either as homogeneous uranium oxides, which show solitary uranium peaks within EDS spectra, or as Ca-, Pb-, Se-, Si- and V-bearing polymetallic phases. The presence or absence of these elements varies in different crystals in the reduction spheroid cores. The small uranium-phase crystals occur exclusively within the calcite cement, but are closely associated with roscoelite mineralization. Thus, the presence of Ca, Si and V within some EDS spectra may reflect background detection of the main pore-filling minerals.

**Discussion**

**Reduction spheroid formation in red beds**

The presence of reduction spheroids in continental red beds is common throughout the geological record. Occurrences range from the mid-Proterozoic (Spinks et al. 2010) and throughout the Phanerozoic, but they are widely present in Permo-Triassic sandstones (Hofmann 1990, 1991). In Scotland there are several documented examples of red beds containing reduction spheroids: in the Mesoproterozoic Stoer Group of Stoer Bay (Spinks et al. 2010); the Neoproterozoic Torridon Group of Rubha Réidh north of Gairloch (Spinks 2012); the Devonian Lower Old Red Sandstone of Gamrie (Van Panhuys-Sigler et al. 1996) and Easter Ross (Parnell 1985; Parnell & Eakin 1987); the Carboniferous of North Berwick (Hofmann 1993); and the Triassic of Gruinard Bay (Evans 1982; Spinks 2012).

Reduction spheroids form in red beds as a result of secondary reduction of the haematite or goethite which coats the clastic grains. They occur with variable morphology but often appear as ‘spots’, which are in fact geometrically spherical or spheroidal features within the sediment. Dark metallic cores within the reduction spheroids are common, but are not ubiquitous. Detailed descriptions of the morphology of reduction spheroids are given in Hofmann (1990).

Various mechanisms for the formation of reduction spots have been proposed. Many workers have attributed the secondary reduction (spheroid formation) to the presence of detrital organic material within the cores (Hartmann 1963; Van De Poll & Sutherland 1976; Durrance et al. 1978; Mykura & Hampton 1984), or to migrating hydrocarbons from leaking reservoirs (Parnell & Eakin 1987). However, neither detrital organic matter nor hydrocarbons are ubiquitous in reduction spheroids. Recent studies have attributed the formation of reduction spheroids and core mineralization to the presence of microbial activity in both Proterozoic and Phanerozoic red beds (Spinks et al. 2010). The spherical geometry of the reduction spheroids and the lack of vertical shortening indicate formation post-compaction and at depth. This suggests active anaerobic microbial activity in the deep subsurface. The dark cores in spheroids commonly contain authigenic metalliferous minerals that replace both detrital grains and cement, and are often rich in trace metals and rare earths (Hofmann 1990, 1991). Typical minerals found in these cores include chalcocite, chalcopyrite, maucherite,
native copper, native silver, nickeline, pyrite, roscoelite and uraninite (e.g. Parnell 1988a; Hofmann 1990, 1991; Spinks et al. 2010). These account for the concentrations of trace metals and other metalloid elements such as As, F, S, Se, Te and U in the cores (Hofmann 1990). Less common selenide minerals also occur in the cores of some reduction spheroids (Hofmann 1990; Milodowski et al. 2002); however, little work has been conducted on them.

The vanadium mica, roscoelite, is commonly associated with reduction spheroid mineralization (Hofmann 1990; Van Panhuys-Sigler et al. 1996). The characteristics of the roscoelite within the reduction spheroids on Great Cumbrae are comparable to other occurrences in the Old Red Sandstone (Van Panhuys-Sigler et al. 1996) and other formations. However, the presence of copper and lead selenides is of interest.

Selenide mineralization in reduction spheroids

There is evidence for the microbially-mediated formation of reduction spheroids in the absence of detrital organic matter (Hofmann 1990; Spinks et al. 2010). Reduced sulphide phases present within cores of some reduction spheroids suggest sustained in situ reduction of pore-water sulphate, causing localized reduction of the otherwise oxidized sediment. Sulphate reduction is possible via both biological and non-biological means, the latter requiring high temperatures and the presence of catalytic non-biogenic hydrogen sulphide, which is unlikely in an oxidized red bed. The formation temperatures for reduction spheroids are deduced to be low/moderate temperatures (<100 °C) (Hofmann 1990; Spinks et al. 2010). At these temperatures, the only plausible sulphate-reduction mechanism is through the activity of sulphate-reducing microbes (Trudinger et al. 1985; Machel 1987). Isotopic fractionation of the sulphur species in pyritic cores of reduction spheroids in Triassic red beds indicates microbial formation (Spinks et al. 2010). Furthermore, the presence of frambooidal pyrite in the cores of some sulphide-bearing spheroids provides additional evidence for the presence of microbial colonies within the sediments (Spinks et al. 2010).

The mineralized cores on Great Cumbrae contain selenide phases, but no sulphides. In the absence of detrital organic matter within the cores and, given the evidence in previous studies, it is possible that a microbial reductant was responsible for the formation of the reduction spheroids in the KBF. If sulphate-reducing or selenate-reducing microbes were present in the sediment, acting as a local reductant, it raises the question of why mineralization of selenides occurred instead of sulphides.

Redox-controlled selenide mineralization can result from either physical or biological processes. Of the major types of redox-controlled selenide deposits (Simon et al. 1997), the most commonly observed biogenically-induced selenide mineralization occurs in sandstone-hosted roll-front-type uranium deposits (Granger & Warren 1969; Northrop & Goldhaber 1990; Simon et al. 1997; Min et al. 2005). These form as soluble uranium, and selenium oxyanions present in oxidized meteoric or basinal fluids are reduced to insoluble uranium and selenide minerals by interaction with biogenic H₂S, sulphides, micro-organisms or organic matter (Fig. 5) (Simon et al. 1997; Min et al. 2005). Roll-front deposits, however, commonly mineralize with a zoned mineralization envelope (Northrop & Goldhaber 1990; Min et al. 2005), within which selenide minerals occur in a ‘selenium band’ close to the front of the alteration envelope beyond the oxidation–reduction interface (Fig. 5; Granger & Warren 1969). Such spatially-restricted distribution of selenium mineralization may be due to the limited spatial distribution of selective anaerobic micro-organisms (Min et al. 2005), organic matter, or represent the boundary at which the migrating fluids lost most of their oxidizing potential upon interaction with a reductant, thus precipitating selenium (Granger & Warren 1969). The same processes may occur during the formation of reduction spheroids, with the common redox-controlled addition of uraniferous and vanadiferous minerals (Parnell
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Selenium oxyanions exist in four oxidation states, which are strongly redox-sensitive; selenate (Se$^{\text{VI}}$) and selenite (Se$^{\text{IV}}$) are mobile in oxidizing conditions and are reduced to elemental selenium (Se$^{0}$) and selenide (Se$^{-2}$) in anoxic or reducing conditions (Stolz & Oremland 1999; Stolz et al. 2006). Native selenium and selenide mineralization (Se$^{-2}$) in anoxic sediments has been linked to microbial selenate (Se$^{\text{VI}}$) reduction by selenate- and sulphate-reducing microbes (Stolz et al. 2006). Selenium oxyanions are chemically and physically similar to those of sulphur (Gharieb et al. 1999), and selenium commonly substitutes for or replaces sulphur in sulphide minerals when they encounter fluids of high oxygen and selenium fugacity (Simon et al. 1997; Stanley et al. 2002). High oxygen and selenium fugacities in hydrothermal fluids are one pathway for the mineralization of selenides instead of sulphides upon reduction (Stanley et al. 2002 and references therein), which in this case is probably microbially-mediated. However, it is possible that sulphide mineralization occurred within the cores of the reduction spheroids initially, as a result of microbial sulphate reduction. Following this, influx of highly oxidized fluids with high selenium concentrations caused the replacement of sulphur with selenium (Simon et al. 1997).

Thus, it is likely that the reduc tant responsible for the formation of the reduction spheroids in the KBF sandstones on Great Cumbrae was generated by sulphate- or selenate-reducing microbes within pores in the sandstones, which caused either primary selenide mineralization or secondary mineralization by replacement of sulphur in primary sulphides.

Selenium migration and mineralization

A well-established type of selenium concentration occurs in lithologies rich in organic matter, such as coals, black shales and oil, and in soils overlying seleniferous deposits (Raask 1985; Coleman et al. 1993; Yudovich & Ketris 2006). Selenium concentration occurs within these as a trace isomorph in sulphides such as pyrite, or bound within organic matter (Yudovich & Ketris 2006). Secondary ‘oxidizing’ accumulations of selenium may occur in reduced selenium-bearing lithologies as products of oxidized re-mobilization and subsequent deposition by highly oxidized water (Yudovich & Ketris 2006). Processes involving highly oxidized meteoric water may also oxidize reduced selenide (Se$^{-2}$) in organic-rich lithologies to selenate (Se$^{\text{VI}}$), which can migrate and may accumulate in lithologies outside the original host rock. These supergene processes occur with both uranium and vanadium redox mineralization in tabular or roll-front-type U–V deposits. In such cases, oxidized water-borne mobilized V$^{\text{IV}}$ and U$^{\text{VI}}$ descend through porous sandstone aquifers and are subsequently reduced and mineralized by biogenic H$_2$S to V$^{\text{III}}$ and U$^{\text{IV}}$ phases, respectively (Wanty et al. 1990).

One such migration path for descending oxidized metal-rich solutions is via near-surface faults. Uraniferous reduction spheroids occur close to faults that likely acted as migration pathways for subsequent deposition by descending oxidized uranium ion-bearing fluids (Parnell & Eakin 1987; Bolonin & Gradovsky 2012). The reduction
spheroids on Great Cumbræa also occur close to a major structure the Great Cumbræa Fault (GCF) (Fig. 1), thus it is possible that this acted as a conduit for oxidized fluids bearing solubilized uranium, vanadium, selenium and copper. The GCF is part of a complex fault zone and has a long and varied history of repeated strike-slip movements with net downthrow to the west (Caldwell & Young 2013). The earliest movements of the GCF likely occurred in the Late Devonian or Early Carboniferous, with repeated recrivation on a kilometre scale up to and including the emplacement of the Hebridean Igneous Province in the Palaeogene (Young & Caldwell 2013). Selene mineralization also occurs close to faults and between the Old Red Sandstone and Carboniferous strata elsewhere in the Midland Valley. Mercury and silver-bismuth selenides are present as inclusions in pyrobitumen (Parnell 1988b) along the fault zone of the Ochil Fault between Lower Devonian volcanics and Carboniferous Coal Measures near Alva, Scotland (Hall et al. 1982).

Source of selenium

The pre-volcanic Carboniferous stratigraphy in the Firth of Clyde area is complex and is characterized by a series of fault-bound micro-basins. The Kinnnesswood Formation that overlies the mineralized reduction spheroid-bearing Upper Devonian KBF sandstone (Fig. 2) on Great Cumbræa and regionally, contains numerous beds of both dark grey organic-rich, and red mudstones (Paterson et al. 1990; Browne et al. 1999; Young & Caldwell 2011a, b). Carbon-rich shales and mudstones are thought to be the source of the selenium and accompanying metallic cations in selenide vein ores, with reddening, bleaching and Se/metal depletion occurring in shales close to the ore deposits (Stanley et al. 2002). Coal beds and seat earths of the Birgidale Formation (Paterson & Hall 1986; Young & Caldwell 2011b) are present locally beneath the Clyde Plateau Volcanic Formation on south Bute. These coals indicate a transition from the arid conditions that prevailed during deposition of the younger red bed sediments to a hot, humid climate (Young & Caldwell 2011b). Coal beds do not occur on Great Cumbræa as any inferred deposits correlating with the Birgidale Formation have been eroded. However, coal deposits might have been present in micro-basins above the surviving strata, close to the GCF on Great Cumbræa. Coal-bearing Carboniferous strata nearby on NE Arran have been reddened, likely during the Permo-Triassic, to a depth of around 180 m (Bailey 1926; Wang 1992), and some coal beds in Ayrshire on the mainland have been extensively reddened (Mykura 1960). Like the reddening of organic-rich facies close to selenide ore veins (Stanley et al. 2002), the reddening of Carboniferous strata in the Firth of Clyde area may indicate the mobilization of a source of selenium, with subsequent migration and mineralization in a reducing environment.

Selenium-enriched mudstones and coals of the Lower Carboniferous may thus have provided a source of selenium and/or metallic cations to the underlying Devonian sandstones in highly oxidized surface waters, allowing mineralization of the reduction spheroid cores via microbial reduction. The selenium content of soils associated with the Old Red Sandstone in Scotland is expected to be low (Sharman 1960), emphasizing the anomalous nature of the selenium-bearing occurrence in Cumbræa. Anomalous concentrations of up to c. 1000 ppm of selenium are present in copper minerals in Devonian red beds in SW Ireland (Coghlan et al. 1963). The major selenium anomalies in the soils above these (Fay et al. 2007), and the selenide mineralization in the Ochil Fault between the Carboniferous Coal Measures and Lower Devonian volcanic rocks suggest that selenium-rich fluids migrated into the Old Red Sandstone on a regional scale. The likely source of the uranium in the reduction spheroid cores was also in the organic-rich lithologies. A plausible conduit for the descending migration of such solutions is the Great Cumbræa Fault, which was probably active both during and after the deposition of the carbonaceous strata (Fig. 6). The highly oxidizing meteoric water needed for selenium mobilization, transportation and subsequent mineralization could have been generated as a consequence of the high atmospheric oxygen concentration during the Carboniferous and Permian (Holland 2006).

Conclusions

Copper and lead selenide mineralization in the cores of reduction spheroids on Great Cumbræa occurred as a result of localized microbially-induced reducing conditions within the host sandstones, similar to those observed in roll-front uranium deposits. Organic-rich mudstones, coal beds and seat earths, present in the regionally overlying stratigraphy, likely provided a source of selenium and metal cations. The long-lived Great Cumbræa Fault, close to the reduction spheroid mineralization, could have acted as a conduit for descending seleniferous fluids. Uranium and roscoelite mineralization in these cores compares with that in other reduction spheroid occurrences that lack detrital organic matter and reinforces the model of microbial uranium–vanadium mineralization in these environments. The presence of copper and lead selenides in the cores of reduction spheroids in the Kelly Burn Sandstone Formation on Great Cumbræa has implications for potential selenium ore deposits. Microbially-induced reduction of red beds stratigraphically close to organic-rich facies, such as coals or mudstones, could potentially generate valuable reserves of selenium and related redox-sensitive minerals. The presence of selenides associated with the junction between Devonian and Carboniferous strata at several localities in the British Isles may suggest a widespread selenium mineralization system in rocks of that age.

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References

BAILEY, E.B. 1926. Subterranean penetration by a desert climate. Geological Magazine, 63, 276–280.
BLUCK, B.J. 1978. Sedimentation in a late orogenic basin: The O.R.S. of the Midland Valley of Scotland. In Bowes, D.R. & Leake, B.E. (eds) Crustal Evolution in Northwestern Britain and Adjacent Regions. Geological Journal, Special Issue, 10, 249–278.

BLUCK, B.J. 2000. Old Red Sandstone basins and alluvial systems of Midland Scotland. In Friend, P.F. (ed.) New Perspectives on the Old Red Sandstone. Geological Society, London, Special Publications, 180, 417–437.

BOLOTIN, A. & GRADOWSKY, I. 2012. Supergene processes and uranium ore formation in the Ronneburg ore field, Germany. Geology of Ore Deposits, 54, 122–131.

BROWN, M.A.E., DEAN, M.T., HALL, I.H.S., McADAM, A.D., MONRO, S.K. & CHISHOLM, J.I. 1999. A lithostatigraphical framework for the Carboniferous rocks of the Midland Valley of Scotland. British Geological Survey Research Report, RR/99/07.

BROWN, M.A.E., SMITH, R.A. & AITKIN, A.M. 2002. Stratigraphical framework for the Devonian (Old Red Sandstone) rocks of Scotland south of a line from Fort William to Aberdeen. British Geological Survey Research Report, RR/01/04.

CALDWELL, W.G.E. & YOUNG, G.M. 2013. Structural controls in the western offshore Midland Valley of Scotland: Implications for Late Palaeozoic regional tectonics. Geological Magazine, 150, 673–698.

COGHAN, H., BUTLER, J.R. & PARKER, G. 1963. Ore and Metals: A Report of the Ancient Mining and Metallurgy Committee. Royal Anthropological Institute (No. 17). Royal Anthropological Institute of Great Britain & Ireland.

COLEMAN, L., BRAGG, L.J. & FINKELMAN, R.B. 1993. Distribution and mode of occurrence of selenium in US coals. Environmental Geochemistry and Health, 15, 215–227.

DURRANCE, E.M., MEADS, R.E., BALLARD, R.R.B. & WALSH, J.N. 1978. Oxidation state of iron in the Littleham Sandstone Formation of the New Red Sandstone Series (Permian–Triassic) of southeast Devon, England. Geological Society of America Bulletin, 89, 1231–1240.

EVANS, D. 1982. The Offshore Geology of Scotland in Relation to the IGS Shallow Drilling Programme. Report – Natural Environment Research Council, Institute of Geological Sciences, pp. 1970–1978.

FAY, D., KRAMERS, G., ZHANG, C., MCGRATH, D. & GRENNAN, E. 2007. Soil Geochemical Atlas of Ireland. Teagasc and the Environmental Protection Agency, Dublin.

GHARIEB, M.M., KIERANS, M. & GADD, G.M. 1999. Transformation and tolerance of tellurite by filamentous fungi: Accumulation, reduction, and volatilization. Mycological Research, 103, 299–305.

GRANGER, H.C. & WARREN, C.G. 1969. Unstable sulfur compounds and the origin of roll-type uranium deposits. Economic Geology, 64, 160–171.

GUNN, W., GEIKIE, A., PEAUGH, B.N. & HARKER, A. 1903. The Geology of North Arran, South Bute, and the Cumbreras, with parts of Ayrshire and Kintyre. Memoir of the Geological Survey, Scotland, vi + 200 pp. James Hedderwick and Sons for HMSO, Glasgow.

HALL, I.H.S., GALLAGHER, M.J., SKILTON, B.R.H. & JOHNSON, C.E. 1982. Investigation of polymetallic mineralization in Lower Devonian volcanics near Alva, central Scotland. Mineral Reconnaissance Programme Report, Institute of Geological Sciences, 53.

HARTMANN, M. 1963. Einige geochemische Untersuchungen an Sandsteinen aus Perm und Trias. Geochimica et Cosmochimica Acta, 27, 459–499.

HOFMANN, B.A. 1990. Reduction spheroids from northern Switzerland: Mineralogy, geochemistry and genetic models. Chemical Geology, 81, 55–81.

HOFMANN, B.A. 1991. Mineralogy and geochemistry of reduction spheroids in red beds. Mineralogy & Petrology, 44(1–2), 107–124.

HOFMANN, B.A. 1993. Organic matter associated with mineralized reduction spots in red beds. Bitumens in Ore Deposits, 9, 362–378.

HOLLAND, H.D. 2006. The oxygenation of the atmosphere and oceans. Philosophical Transactions of the Royal Society Series B: Biological Sciences, 361, 903–915.

HOUSE, M.R. 2000. Chronostratigraphic framework for the Devonian and Old Red Sandstone. In Friend, P.F. (ed.) New Perspectives on the Old Red Sandstone. Geological Society, London, Special Publications, 180, 23–27.

MACHEL, H.G. 1987. Some aspects of diagenetic sulphate-hydrocarbon redox reactions. In Marshall, J.D. (ed.) Diagenesis of Sedimentary Sequences. Geological Society, London, Special Publications, 36, 15–28.

MILODOWSKI, A.E., STYLES, M.T., HORSTWOOD, M.S.A. & KEMP, S.J. 2002. Alteration of uraniferous and native copper concretions in the Permian mudrocks of south Devon, United Kingdom. Technical Report, TR-02-09.

MIN, M., XU, H., CHEN, J. & FAYEK, M. 2005. Evidence of uranium biomineralization in sandstone-hosted roll-front uranium deposits, northwestern China. Chemical Geology, 26, 198–206.

MONRO, S.K. 1999. Geology of the Irvine District. 1:50 000 geological sheet 22W and part of sheet 21E (Scotland). Memoir, British Geological Survey.

MYKURA, W. 1960. The replacement of coal by limestone and the reddening of Coal Measures in the Ayrshire Coalfield. Bulletin of the Geological Survey of Great Britain, 16, 131–155.

MYKURA, W. 1991. Old Red Sandstone. In Craig, G.Y. (ed.) Geology of Scotland (3rd edn). Geological Society, London, 297–346.

MYKURA, H. & HAMPTON, B.P. 1984. On the mechanism of formation of reduction spots in the Carboniferous/Permian red beds of Warwickshire (Enville Group, England). Geological Magazine, 121, 71–74.

NORTHROP, H.R. & GOLDBACHER, M.B. 1990. Genesis of the tabular-type vanadium-uranium deposits of the Henry Basin, Utah. Economic Geology, 85, 215–269.

PAAR, W.H., ROBERTS, A.C., CRIDDLE, A.J., AMANN, G. & SUREDA, R.J. 2002. The new mineral species brotkorbite, Cu,HgS, and the associated selendite assemblage from Tuminico, Sierra de Cacho, La Rioja, Argentina. Canadian Mineralogist, 40, 225–237.

PARNELL, J. 1985. Uranium/rare earth-enriched hydrocarbons in Devonian sandstones, northern Scotland. Neues Jahrbuch fur Mineralogie, Monatshefte, 132–144.

PARNELL, J. 1988. The mineralogy of red bed uranium-vanadium mineralization in the Permo-Triassic of Belfast. Irish Journal of Earth Science, 9, 119–124.

PARNELL, J. 1988b. Mercury and silver-bismuth selenides at Alva, Scotland. Mineralogical Magazine, 52, 719–720.

PARNELL, J. & EAKIN, P. 1987. The replacement of sandstones by uraniferous hydrocarbons: Significance for petroleum migration. Mineralogical Magazine, 51, 505–515.

PATERSON, I.B. & HALL, I.H.S. 1986. Lithostratigraphy of the late Devonian and early Carboniferous rocks in the Midland Valley of Scotland. Report of the British Geological Survey, 18(3).

PATERSON, I.B., HALL, I.H.S. & STEPHENSON, D. 1990. Geology of the Greenock District. 1:50 000 geological sheet 30W and part of sheet 29E (Scotland). Memoir, British Geological Survey.

RAASK, E. 1985. The mode of occurrence and concentration of trace elements in coal. Progress in Energy and Combustion Science, 11, 97–118.

READ, W.A., BROWNE, M.A.E., STEPHENSON, D. & UPTON, B.G.J. 2002. Carboniferous. In Trewin, N.H. (ed.) The Geology of Scotland (4th edn). Geological Society, London, 251–299.

SHARMAN, G.A.M. 1990. Selenium in animal health. Proceedings of the Nutrition Society, 19, 169–176.

SIMON, G., KESLER, S.E. & ESSENE, E.J. 1997. Phase relations among selenides, sulfides, tellurides, and oxides: II. Applications...
to selenide-bearing ore deposits. Economic Geology, 92, 468–484.

SPINKS, S.C. 2012. Geological evidence for the oxygenation of the atmosphere in the Torridonian, and contemporaneous successions. PhD Thesis, University of Aberdeen Library, Entry 001497336.

SPINKS, S.C., PARNELL, J. & BOWDEN, S.A. 2010. Reduction spots in the Mesoproterozoic age: Implications for life in the early terrestrial record. International Journal of Astrobiology, 9, 209–216.

STANLEY, C.J., CRIDDLE, A.J., FORSTER, H. & ROBERTS, A.C. 2002. Tischendorfite, Pd₈Hg₃Se₉, a new mineral species from Tilkerode, Harz Mountains, Germany. Canadian Mineralogist, 40, 739–745.

STEPHENVSON, M., WILLIAMS, M., MONAGGAN, A., ARKLEY, S. & SMITH, R. 2002. Biostratigraphy and palaeoenvironments of the Ballagan Formation (Lower Carboniferous) in Ayrshire. Scottish Journal of Geology, 38, 93–111.

STOLZ, J.F. & OREMLAND, R.S. 1999. Bacterial respiration of arsenic and selenium. FEMS Microbiology Reviews, 23, 615–627.

STOLZ, J.F., BASU, P., SANTINI, J.M. & OREMLAND, R.S. 2006. Arsenic and selenium in microbial metabolism. Annual Reviews on Microbiology, 60, 107–130.

TREWIN, N.H. & THIRWALL, M.F. 2002. Old Red Sandstone. In TREWIN, N.H. (ed.) The Geology of Scotland (4th edn). Geological Society, London, 251–299.

TRUDINGER, P.A., CHAMBERS, L.A. & SMITH, J.W. 1985. Low-temperature sulphate reduction: Biological versus abiological. Canadian Journal of Earth Sciences, 22, 1910–1918.

VAN DE POLL, H.W. & SUTHERLAND, J.K. 1976. Cupferous reduction spheres in Upper Mississippian red beds of the Hopewell Group at Dorchester Cape, New Brunswick. Canadian Journal of Earth Science, 13, 781–789.

VAN PANHUYS-SIGLER, M., TREWIN, N.H. & STILL, J. 1996. Roscoeelite associated with reduction spots in Devonian red beds, Gamrie Bay, Banffshire. Scottish Journal of Geology, 32, 127–132.

WANG, W.H. 1992. Origin of reddening and secondary porosity in Carboniferous sandstones, Northern Ireland. In Parnell, J. (ed.) Basins on the Atlantic Seaboard: Petroleum Geology, Sedimentology and Basin Evolution. Geological Society, London, Special Publications, 62, 243–254.

WANTY, R.B., GOLDHABER, M.B. & NORTHROP, H.R. 1990. Geochemistry of vanadium in an epigenetic, sandstone-hosted vanadium–uranium deposit, Henry Basin, Utah. Economic Geology, 85, 270–284.

WATERS, C.N., BROWNE, M.A.E., DEAN, M.T. & POWELL, J.H. 2007. Lithostratigraphical framework for Carboniferous successions of Great Britain (Onshore). British Geological Survey Research Report, RR/07/01.

YOUNG, G.M. 2008. Geochemical investigation of an unusual alteration profile developed at the base of a Carboniferous lava flow, Isle of Bute, Scotland. Transactions of the Royal Society of Edinburgh, Earth and Environmental Science, 99, 49–59.

YOUNG, G.M. & CALDWELL, W.G.E. 2011a. Early Carboniferous stratigraphy in the Firth of Clyde area: New information from the Isle of Bute. Scottish Journal of Geology, 47, 143–156.

YOUNG, G.M. & CALDWELL, W.G.E. 2011b. Stratigraphical context and geochemistry of Tourmaisian (pre-Clyde Plateau Volcanic Formation) tuffs, Great Cumbrae, western Midland Valley of Scotland. Scottish Journal of Geology, 47, 21–32.

YUDOVICH, Y.E. & KETRIS, M.P. 2006. Selenium in coal: A review. International Journal of Coal Geology, 67, 112–126.

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