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Remobilization and mineralization of selenium–tellurium in metamorphosed red beds: Evidence from the Munster Basin, Ireland

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ABSTRACT

Selenium and tellurium are vital elements for the ongoing development of carbon-free energy generation, but are only recovered in small volumes as by-products of base and precious metal processing. Security of supply of these commodities is of high importance as their demand is forecast to increase in the near future, thus more research is required on the varying mineralization systems where their occurrence and behavior are poorly understood, such as sedimentary basins and metasedimentary terranes.

The Munster Basin of southern Ireland is a good study area for sedimentary Se–Te in such environments as it has a regionally-high soil selenium anomaly, and is characterized by Devonian terrestrial red beds, which were metamorphosed during the Hercynian (Variscan) Orogeny. The area also contains ore-grade biogenic sediment-hosted copper and remobilized vein-hosted copper sulfides, which are prospective for chalcophile selenium and tellurium.

Quartz vein-hosted Se–Te mineralization was identified across the Munster Basin, accompanied by trace gold–silver–mercury accessory phases. New sulfur isotope data reinforces the model of sulfur and selenium remobilized from a biogenic red bed source, which reflects a wider association of selenium deposits with oxidizing environments. The co-occurrence of tellurium mineralization suggests that it too may be concentrated in oxidizing environments. Associated traces of gold add to a growing body of evidence that gold is also transported and precipitated in oxidizing conditions in continental basins.

1. Introduction

Selenium and tellurium (Se and Te) are relatively rare trace elements which do not commonly occur as mineral phases in sedimentary basins. However, they are of economic interest because they can be pathfinder elements for gold (Au) mineralization (Boyle, 1979; Ciobanu et al., 2006; Cook et al., 2009) and they are important components in advanced technologies, such as solar energy generation (Green, 2009; Moss et al., 2011). Neither selenium or tellurium are extracted as primary ore, rather they are recovered as a by-product of the processing of base metal ores such as Cu, Pb, Bi, Fe and precious metals. Both commodities are regarded among the 'critical' metals, in that their security of supply is at potential risk (Moss et al., 2011). As such, further understanding of their occurrence and behavior across diverse mineralization systems is required to continue to identify new deposits. The focus of this study is selenium and tellurium mineralization in low-temperature sedimentary basins and their subsequent surface expressions following remobilization, an area which has hitherto been poorly studied.

1.1. Overview of non-magmatic Se–Te mineralization systems

Selenium behavior in sedimentary basins is primarily redox-controlled, as selenium is mobile in strongly oxidizing conditions. This is evident in selenium-bearing redox-controlled roll-front uranium deposits in continental red beds (Reynolds and Goldhaber, 1983; Min et al., 2005), unconformity surfaces where basement rocks have been exposed to oxidative weathering (Cabral et al., 2012; Shepherd et al., 2005), unconformity-related vein deposits at subsurface redox boundaries (Johan et al., 1982; Simon et al., 1997), and gold deposits related to magmatic rock–meteoric fluid interaction (Cook et al., 2009). In roll-front deposits, zoned redox conditions cause selenides to form separately from sulfides (Granger and Warren, 1974) and in some cases native selenium marks the redox front (Nigel Cook, pers. comm.). In many of these examples, selenium is especially sequestered in, or is coeval with, iron oxides. This dependence on oxidizing environments reflects the fact that selenium can be fractionated from the chemically comparable, but much more abundant, sulfur. In relatively high-Eh conditions selenium can be immobile, while sulfur forms soluble, mobile sulfates.

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Thus selenium requires very high Eh conditions and oxygen concentrations to become mobile (Howard, 1977; Simon et al., 1997; Xiong, 2003). Most selenide minerals are precipitated at less than 150 °C (Simon et al., 1997), consistent with shallow crustal, oxidized, settings. Selenides in hydrothermal systems derived from magmatic protoliths, however, are characterized by higher temperatures of formation (Spooner, 1993).

Tellurium is much less abundant than selenium, but many tellurides are also associated with relatively low-temperature hydrothermal environments, as some telluride-rich veins are formed at temperatures below 250 °C (Afifi et al., 1988). Tellurium is not well documented in roll-front deposits, but telluride inclusions do occur in detrital gold derived from red bed successions (Chapman et al., 2009). Tellurium is much less mobile than selenium under oxidizing conditions in surface environments, largely due to the larger affinities of tellurium with iron hydroxides (Harada and Takahashi, 2009). By contrast, tellurides in greenstone terranes and metamorphic rocks are attributed to temperatures up to 400 °C, and the tellurium in many of these deposits have been assumed to be of magmatic origin (Afifi et al., 1988), though a key source of tellurium in such settings may be melting of tellurium-rich oceanic sediments (Jensen and Barton, 2000; Cook et al., 2009). Thus there is a general model of selenium mineralization derived from oxidizing brines at low temperatures, and selenium and tellurium mineralization from magmatic sources at high temperatures. However, this belies the obvious scenario in which red bed deposits become metamorphosed. We would expect the selenium and tellurium concentrated by diagenesis or deposition in oxidizing environments to be conserved, but its distribution might be modified. Questions to be addressed here are whether the selenium and tellurium, which are among the most mineralogically-diverse elements (Christy, 2015), become concentrated in metamorphic vein systems as selenide–telluride minerals; whether any such minerals also concentrate precious metals (gold, silver etc.); and how the mineral assemblages compare with those regarded as of magmatic origin.

1.2. Scope of study

In order to investigate selenium and tellurium mineralization in sedimentary red beds and subsequent remobilization, such mineralization was sought in the metamorphosed Devonian Munster Basin, SE Ireland (Fig. 1). The Munster Basin is a good target for study, because: (i) Unlike other Devonian red bed basins in the British Isles, it has been metamorphosed, during the Hercynian Orogeny (Fig. 2), at well documented temperature and pressure (Meere, 1995) with widespread evidence for fluid flow in the rocks during metamorphism.

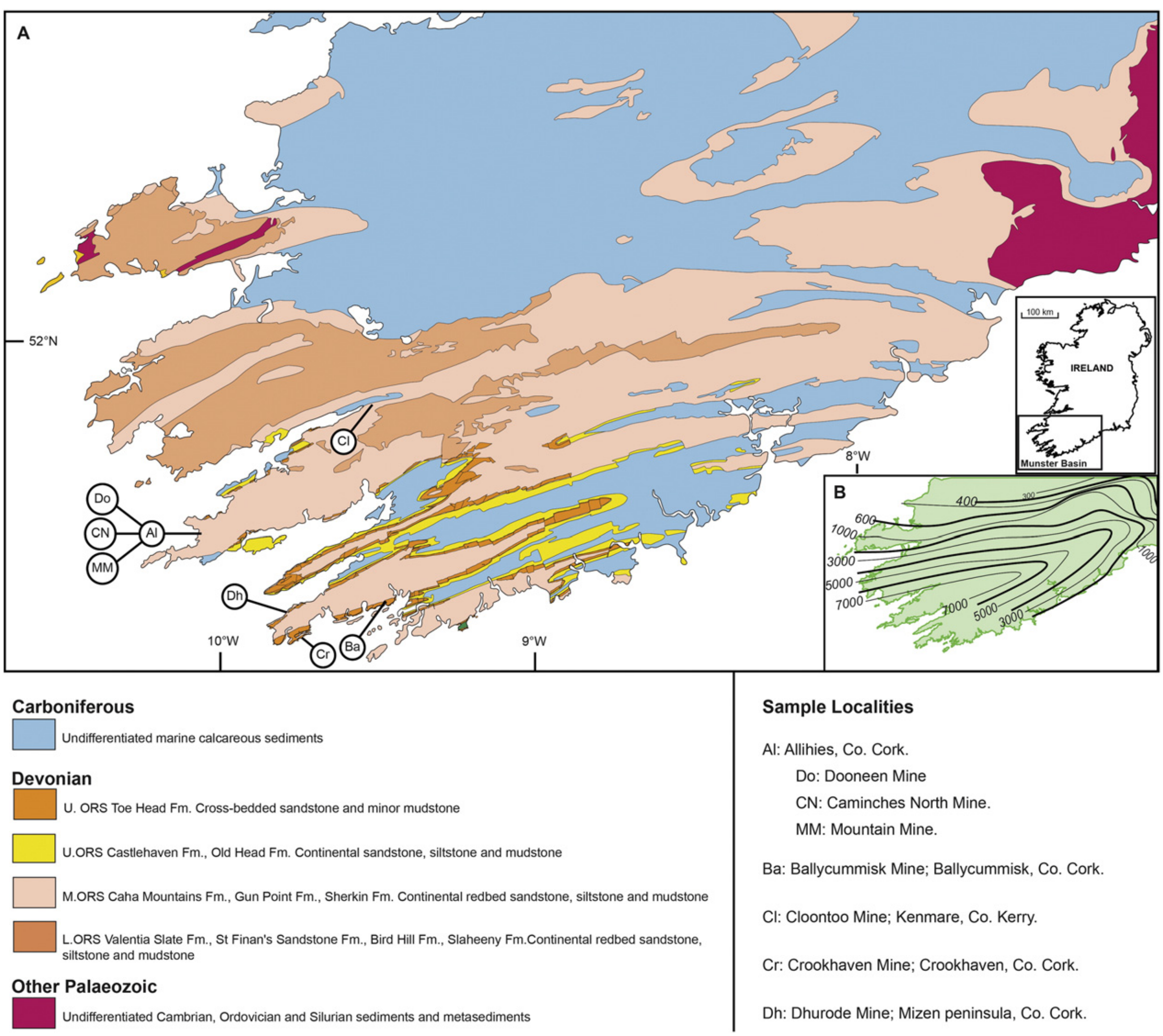

Fig. 1. A) Summary geological map of the Munster Basin showing the main Old Red Sandstone (ORS) and Lower Carboniferous Strata compiled using data from Pracht and Sleeman (2002). Sample localities are highlighted by text bubbles and are referred to in the Legend. B) Isopachs of the Devonian sediments of the Munster Basin (after MacCarthy, 1990).