River red gum biogeochemical expression of buried Broken Hill type mineralisation

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River red gums (*Eucalyptus camaldulensis*) are a tree native to Australia but now widely grown in warm and semi-arid parts of the world. In Australia, they are one of the most widely distributed tree species, especially in riparian zones of arid regions. Their distribution closely corresponds to areas where sediments and and alluvial aquifers are well developed. As such, they tend to colonise settings where the underlying bedrock geochemistry is poorly defined. These long-lived and deep-rooted trees therefore have potential to provide important biogeochemical expressions of the geochemistry of buried bedrock. This study provides an overview of multi-element (ICP-MS and XRF) analysis of leaf samples from about 500 river red gum trees from the Broken Hill region in semi-arid central Australia. Particular attention is given to the biogeochemical expression of sites of known Broken Hill type (Ag-Pb-Zn) mineralisation. It shows that biogeochemistry can provide an effective recognition of buried mineralisation, even when the overlying sediments do not contain a geochemical expression that distinctly highlights mineralisation. It also provides an indication of some of the highly elevated metal and trace element contents that can be hosted in native vegetation near the natural occurrences of ore bodies.

Samples from trees overlying mineralisation near the Pinnacles Mine and along the Broken Hill Line of Lode show highly elevated contents of Ag (max. 1.36 ppm), Pb (max. 411 ppm) and Zn (max. 338 ppm), where regional 'background' values are typically low or approaching analytical detection limits (e.g. Ag 0.01 ppm; Pb 1 ppm; and, Zn 17 ppm). Some samples from near mineralisation also contain elevated Cd, Au, In and Tl contents, however, values are variable, and these elements are best considered within the context of the major ore forming elements (e.g. In/Zn). The spatial extent of the elevated biogeochemical response depends on the size and grade of mineralisation but also the characteristics of the physical and chemical dispersion that vary in different parts of riparian zones.

Selenium adsorption and associated selenium isotope fractionation

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Riverine input is a source of selenium to the coastal oceans: between 5 and 12% of Se input consists of particulate selenium. Depending on the site, particulate organic Se is estimated to account for 40 to 100% of the particulate Se pool, suggesting that up to 60% of particulate selenium is in another form, possibly as selenium oxyanions adsorbed onto either organic matter or iron (Fe) oxides

Among the Fe oxides, goethite has been put forth as the dominant authigenic Fe(III) phase in freshwater and marine sediments. Hematite is found in association with goethite, though generally it is not as widespread. Ferryhydrite, while short lived, is a precursor to the latter phases. Thus, these ubiquitous phases are important carrier of adsorbed Se species to oceans.

Nevertheless, sorption behavior of selenate and selenite as well as the isotope fractionations associated with these reactions has not been systematically investigated. Here, we measured total Se concentrations as a function of time during the equilibration of selenate and selenite with suspensions of 2-line ferryhydrite, hematite, goethite (Table 1).

	2-line ferryhydrite	Hematite	Goethite
Selenite	50	0.5	275
Selenate	~0	~0	1

Table 1: Calculated partition coefficient (Kd; L g^{-1}) for Se sorption onto selected Fe(III) oxyhydroxide minerals.

We show that selenate does sorb onto goethite (Table 1), contrary to expectation, albeit to a much lower extent than selenite. We conclude by discussing the isotope shifts associated with these sorption reactions and the potential use of Se isotopes to fingerprint the sorption mechanism of Se removal by Fe oxides in the aquatic environment.