Selenium uptake in otoliths from cold-water fish species captured downstream from coal mining

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Establishing the exposure histories of wild fish to trace element contaminants within an aqueous environment is often difficult for fish species with large home ranges. Chemical analyses of muscle or visceral tissues can provide information on recent exposure, but depuration, metabolic transformation, and tissue redistributions preclude temporal resolution. Otoliths, the calcified structures in the inner ear of teleost fish, are considered to be metabolically stable and therefore may serve as continuous recorders of exposure to trace elements in the environment. Otoliths are composed of layers of aragonite in a protein matrix deposited annually throughout the lifetime of the fish, thus providing a time scale. Both the inorganic portion and protein matrix have the capacity to incorporate a wide range of trace elements, and, as such, otoliths may be used to determine a fish's history of contaminant exposure in the wild.

Otoliths from three cold water fish species from Elk River, British Columbia, Canada were examined to delineate any selenium (Se) contamination signatures contained therein relating to adjacent coal mining activity. The Elk River watershed contains elevated levels of Se owing to naturally occurring seleniferous host rock surrounding coal deposits, as well as five coal mining operations that mobilize Se from exposed host rock into the watershed. Selenium concentrations in otolith primordia tended to be low, indicating that these fish emerged in low Se areas, and moved into areas of increased Se later in life. Individuals captured from the same area had varying Se exposure profiles, indicating the fish do not move *en masse* into and out of high-Se areas. Year-to-year variability of Se exposure patterns within an otolith suggests inconsistent utilization of high- and low-Se areas by the individual. The contrasting exposure profiles for these fish, which have home ranges of tens of kilometres, indicate that soft tissue concentrations would not necessarily reflect the relative abundance of Se in their environments.

Fe(II)-induced trace element release from crystalline iron oxides

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Interfacial electron transfer and atom exchange (ET-AE) between aqueous Fe(II) and Fe(III) oxides induces surface transformations resulting from spatially separated growth and dissolution processes [1-4]. Redox-active elements are known to experience speciation changes during Fe(II)-Fe(III) ET-AE but the fate of redox-inactive elements remains poorly understood. We have recently shown [5] that aqueous Fe(II) can catalyze Ni(II) cycling through goethite and hematite by inducing adsorbed Ni to become incorporated into the mineral and pre-incorporated Ni to be released to solution. Here we examine the kinetics of Ni(II) and Zn(II) release from Ni(II)- and Zn(II)-substituted goethite and hematite when these minerals are exposed to aqueous Fe(II) solutions.

Ni and Zn release follows a 2nd order kinetic rate law and occur on a different timescale than Fe(II) adsorption but on a similar timescale as Fe isotope exhchange for goethite [2]. This suggests that the mechanism for release is not related to displacement of surface associated Ni but rather occurs during the Fe(II)-Fe(III) ET-AE process. The concentration of Fe(II) and pH strongly influence the quantity and rate of metal release. The type of metal substituent also affects reactivity; Zn release is more pronounced from hematite vs. goethite whereas the opposite trend occurs for the Ni systems. Sequential batch experiments (i.e., periodic fluid replacement to remove products while the solid remains for further reaction) display greater total Ni and Zn release than observed in single batch experiments (cf. 28% vs 9% of Ni released from goethite), demonstrating that the aqueous metal concentration is a negative feedback on release. Incorporated redox-active trivalent metals [Mn(III) and Co(III)] exhibit similar release to solution, suggesting that their release is coupled to reduction and that they may cause net Fe(II) oxidation. Our results illustrate a previously unrecognized role of Fe(II) on the release of trace elements from iron oxide minerals. Such reactions may liberate essential trace elements or cause enhanced mobility of contaminants in natural environments and engineered systems.

[1] Catalano *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 1498-1512. [2] Handler *et al.* (2009) *Environ. Sci. Technol.* **43**, 1102-1107. [3] Rosso *et al.* (2010) *Environ. Sci. Technol.* **44**, 61-67. [4] Yanina & Rosso (2008) *Science* **320**, 218–222. [5] Catalano *et al.* (2011) *Min. Mag.*, this volume.