

Application of X-ray absorption spectroscopy to characterize metal(loid) removal in passive treatment systems

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Introduction

Monitoring of the relative changes in dissolved metal concentrations and aqueous speciation modeling frequently are employed to evaluate the effectiveness of passive treatment systems for metal(loid) removal in mining environments. However, these methods do not provide mechanistic information on metal(loid) removal. Synchrotron-based X-ray absorption spectroscopy can provide information regarding the oxidation state and local coordination environment of the metal(loid) of interest on the reactive media, which can be used to determine if the metal(loid) removal mechanism involves sorption, oxidation/reduction, or precipitation reactions. This information is important for assessing treatment efficacy and the long-term stability of reaction products.

In this study, batch experiments were employed to evaluate the efficacy of different types of reactive media to induce removal of aqueous Se and Hg. For the Se experiments, 300 mg L⁻¹ aqueous Se(VI) (from Na₂SeO₄) was allowed to react with granular Fe filings (GIF) and an organic carbon (OC) mixture consisting of a 1:1 (w/w) ratio of wood chips and crushed leaf mulch. For Hg, 4 mg L⁻¹ aqueous Hg(II) (from HgCl₂) was allowed to react with GIF, granular activated carbon (GAC), attapulgite clay, and attapulgite clay pre-treated with two types of thiadiazole compounds [1]. Dissolved concentrations of Se and Hg were monitored over time, and X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy methods were used to characterize the forms of metal(loid)s on the reactive media.

Results and Conclusion

After 5 days of reaction, Se(VI) removal was observed to be >90% in the presence of GIF and 15% with OC. Analysis with XANES spectroscopy suggested that removal in the presence of GIF was due to reduction of Se(VI) to insoluble Se(0), whereas removal with OC was due primarily to sorption of Se(VI). For Hg, treatment efficiency varied between the reactive media, ranging from 25% removal on untreated clay after 8 days of reaction to >99% removal on clay treated with 2,5-dimercapto-1,3,4-thiadiazole. Analysis with EXAFS spectroscopy indicated the presence of Hg-O bonding on GIF and GAC, suggesting Hg removal was due to binding with Fe corrosion products or to water sorbed to the surface of activated carbon. The presence of Hg-S bonding was observed in the presence of thiadiazole compounds, suggesting Hg was bound to thiol-functional groups on these compounds.

[1] Gibson *et al.* (2011), *Environ. Sci. Technol.* **45**, 10415-10421.

The mid-Cretaceous Canadian Cordillera: Paired orogenic belts or an Altiplano-esque Plateau deflated by deep crustal flow?

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The current configuration of the central and southern Canadian Cordillera clearly shows a pairing of highstanding orogenic welts, the Coast belt to the west and the Omineca belt to the east, separated by the intervening subdued topography of the Intermontane belt. How closely this reflects the Mesozoic orogenic architecture for the southern Canadian Cordillera is debatable, but it does bring to mind some important questions regarding the orogenic processes that shaped the southern Canadian Cordillera.

The last major orogen-wide compressional event within the southern Canadian Cordillera occurred in the mid- to Late Cretaceous time, coinciding with the final closure of a marginal basin and attendant accretion of the Insular terranes. Plutons, contractional deformation and high-grade metamorphism that attest to this orogenic event are most obviously manifest in the southern Coast and Omineca belts, and provide evidence for crustal thicknesses on the order of 55-65 km, similar to the average thickness of the Altiplano plateau. So, was there a continuous, high-standing (~4-5 km above sea level) plateau across the width of the southern Canadian Cordillera, or was there an intervening low-lying area of subdued topography much like there is today, which might suggest a paired-system of orogenic belts inherited from Mesozoic orogeny? If so, how would such a system operate?

The displacement along Paleogene strike-slip faults needs to be restored in order to assess the mid- to Late Cretaceous crustal architecture of the southern Canadian Cordillera. This places the Bowser basin in the intervening region with subdued topography whose crustal thickness was on the order of 40-45 km, compared to the flanking 55-65 km welts on either side of it. This implies that the crustal architecture for the mid- to Late Cretaceous time was dumb-bell shaped in cross-section, akin to lithospheric-scale boudinage. The flanking welts would represent paired-orogenic belts characterized by thick-skinned deformation, high-grade metamorphism, anatectic melting and plutonism that were separated by the Bowser basin with its classic thin-skinned Skeena fold and thrust belt. How did the stress that was driving the Coast belt orogen nearest the convergent margin transfer to the east across the width of the orogen to drive the thick-skinned deformation and substantial crustal thickening within the Omineca belt without similarly affecting the intervening crust within the Intermontane belt?

Alternatively, could there have been an Altiplano-style plateau spanning the width of the southern Canadian Cordillera? If so, could the apparent thinning of the crust within the central part of the plateau have been the result of deflation related to general non-coaxial flow within its deepest levels? In this scenario, the general non-coaxial flow, which would include a significant flattening component, effectively evacuated material out from beneath the plateau, perhaps accentuating thickening on its flanks, leaving the appearance of the paired-orogenic belts we see today.