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Using $\delta^{98/95}$Mo as a tracer to identify process-affected waters in the Athabasca Oil Sands Region

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Summary

Isotopic tracers can be used to differentiate oil sands process-affected waters (OSPW) from natural waters in the Athabasca Oil Sands Region (AOSR) and are useful in applications such as identifying and quantifying tailings pond seepages. Until recently, the low natural concentrations and heavy mass of molybdenum (Mo) have made Mo isotopic measurement challenging, however with recent advances in non-traditional stable isotope analysis $\delta^{98/95}$Mo fingerprinting of natural waters is now more practical. In this study, Mo concentrations and $\delta^{98/95}$Mo isotopic compositions of samples from tailings ponds, coarse tailings porewater, natural groundwater, SAGD steam condensate and SAGD disposal fluid were measured to evaluate whether $\delta^{98/95}$Mo signatures of OSPW are distinct from natural groundwaters in the AOSR. The results suggest that $\delta^{98/95}$Mo compositions of tailings pond water are not unique from natural waters and that $\delta^{98/95}$Mo may not be an effective isotopic tracer of OSPW, however Mo isotopic fingerprinting of waters is in its infancy and the results are based on a limited sample set. Differences in $\delta^{98/95}$Mo signatures between end-of-pipe coarse tailings porewater and tailings pond water collected from the free water zone suggest that biogeochemical processes within tailings ponds promote $\delta^{98/95}$Mo fractionation and Mo isotopes could provide a useful tool for investigating these processes.

Introduction

The extration of bitumen from the AOSR in northern Alberta, Canada, produces large volumes of OSPW containing fine silts, residual bitumen, metals and soluble organic compounds. Managing OSPW is a major environmental challenge and current enviornmental regulations stipulate a zero-discharge policy for OSPW. Therefore, all produced water is held on-site in large tailings ponds. Due to the toxicity of some compounds present in OSPW, accidental release of process-affected waters from tailings ponds to natural waters is a concern. For this reason, identifying locations and volumes of potential OSPW seepages from tailings ponds is critical for assessing the risk to aquatic ecosystems downstream from oil sands operations.

Identifying locations of OSPW discharge is often challenging because natural sources of groundwater and surface water interact with oil sands deposits resulting in high-salinity natural groundwater seepages that are difficicult to differentiate from natural sources (Gibson et al., 2013). Isotopic fingerprinting of OSPW is a potential method for characterizing the fate and transport of OSPW through natural surface and groundwater systems, however further work is required to develop a suite of isotopic tracers capable of identifying OSPW.

Mo concentrations in natural waters are typically very low, however a study to characterize the geochemical and isotopic signatures of waters within the AOSR identified Mo in OSPW at concentrations one to two orders of magnitude higher than in natural waters (Gibson et al., 2011). In this study, $\delta^{98/95}$Mo compositions of natual groundwaters and process-affected waters from the AOSR were measured to evaluate how natural $\delta^{98/95}$Mo signatures differ from those of OSPW.

Theory and/or Method

Archived samples of coarse tailings porewater, tailings pond water, groundwater, Athabasca River water, SAGD steam condensate and SAGD produced water were analyzed for Mo concentrations and $\delta^{98/95}$Mo isotopic ratios. Groundwater, surface water and solid samples were collected during previous investigations from the northern and Southern Athabasca Oil Sand Region, as well as from a steam assisted gravity drainage (SAGD) circuit. Solid samples of tailings sands and bitumen were digested for total metal concentrations.

Isotopic analyses were conducted at the University of Calgary. Under clean room conditions, an ion exchange proceedure was used to separate Mo from the water followed byisotope dilution mass spectrometry analysis using a Thermo Fisher Scientific Netpune Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). Dissolved Mo concentrations were determind using ICP-MS.

Examples

A total of 25 samples were anlayzed for $\delta^{98/95}$Mo, however due to the low Mo concentrations in some of the groundwater samples, results from 16 samples were determined. The $\delta^{98/95}$Mo values from the tailings pond water samples had similar signatures. Groundwaters from the McMurray Formation and Quaternary sediments also showed $\delta^{98/95}$Mo signatures similar to the tailings ponds. The coarse tailings porewater samples were significantly enriched in contrast to the tailings pond water and natural groundwater samples. The steam condensate sample from the SAGD circuit showed a similar $\delta^{98/95}$Mo enrichment signature as the coarse tailings poewater samples. The SAGD disposal fluid was depleted in $\delta^{98/95}$Mo relative to the tailings ponds and natural groundwater samples.

The $\delta^{98/95}$Mo fractionation between end-of-pipe coarse tailings porewater tailings pond water collected from the free water zone suggests that biogeochemical processes affecting Mo occur within tailings ponds. Mo concentrations in tailings pond water were also found to be higher than concentrations in coarse tailngs suggesting adsorption or precipitation of Mo during contact with aquifer materials which may also influence Mo isotope fractionation.

Conclusions

Dissolved Mo concentrations in the tailings ponds were higher than in natural waters, however the $\delta^{98/95}$Mo signature resembled that of natural groundwaters from the McMurray and Quaternary Formations. Conversely, coarse tailings porewater showed Mo concentrations lower than those observed in the tailings ponds but had an enriched $\delta^{98/95}$Mo signature. This shfit in $\delta^{98/95}$Mo signatures between end-of-pipe coarse tailings and tailings ponds collected from the free water zone of the ponds suggests that Mo fractionation may be affected by biogeochemical processes and adsorption within tailings ponds. As this is an early investigation into $\delta^{98/95}$Mo fingerprinting of OSPW, further research is requiried to understand the processes affecting Mo fractionation within tailings ponds and evaluate whether $\delta^{98/95}$Mo signatures can provide a useful tracer for fingerprinting OSPW.

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