

Adsorption of Cr(VI) on hydrous manganese oxide

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Hexavalent chromium is used in a variety of industrial processes. When released into the environment, it can be quite mobile and is highly toxic. Understanding and accurately predicting Cr(VI) speciation and transport is key to remediating contaminated sites. Cr(VI) forms chromate (CrO_4^{2-}) and bichromate (HCrO_4^-) anions in natural systems, which adsorb to various substrates at low pH and desorb at high pH. The goal of this study is to investigate sorption of Cr(VI) on hydrous manganese oxide (HMO) as a function of ionic strength, pH and $p\text{CO}_2$.

Hydrous manganese oxide was synthesized by alkametric titration and subsequently stored under 0 $p\text{CO}_2$ conditions. HMO was confirmed by XRD, and N_2 -BET indicated a surface area of $\sim 230 \text{ m}^2/\text{g}$. Experiments were conducted by adding 20 g/L HMO to a solution of NaNO_3 (0.001, 0.01 or 0.1 M) containing 10^{-5} M Cr(VI). The batch solution was titrated to an initial pH of 3, and by small additions of NaOH was titrated upwards to pH 10 with ~ 10 mL aliquots drawn off at ~ 0.8 pH intervals. These aliquots were further equilibrated for 24 hrs under varying $p\text{CO}_2$ (0, atmospheric or 2.5%), then centrifuged and the supernatant filtered and tested for Cr(VI) concentrations using UV-vis spectrophotometry or total Cr by ICP-OES.

Cr(VI) sorption decreases as pH increases, from nearly 95% (0.1 M NaNO_3) or 75% (0.001 M NaNO_3) sorbed at pH 3 to 0% sorbed at pH > 7 . Cr(VI) sorption depends strongly on ionic strength, with $\sim 50\%$ of the Cr(VI) sorbed at pH ~ 6 in 0.1 M NaNO_3 , compared to ~ 4 in 0.001 M NaNO_3 experiments. In contrast, Cr(VI) sorption on HMO was nearly identical for a given ionic strength under atmospheric compared to elevated (2.5%) $p\text{CO}_2$ conditions.

Future work will focus on investigating possible competitive sorption interactions between carbonate and chromate at $p\text{CO}_2$ levels $\geq 5\%$, and on Cr(VI) adsorption under other Cr(VI) loadings and ionic strength conditions. The data will be used to parameterize a surface complexation model, so that results can be readily incorporated into reactive transport models. This will further advance our predictive understanding of Cr(VI) mobility and speciation in natural environments.

Fractionation of HSE in the Tonga arc: Flux melting of a depleted source

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Highly siderophile element concentrations (Os, Ir, Ru, Pt, Pd, Re) have been determined for a suite of fresh, submarine mafic lavas from the Tonga arc front and the nascent Fonualei backarc spreading centre (FSC). The highly depleted Tongan mantle wedge combined with a high fluid flux is thought to have produced boninitic magmas at several arc and FSC locations. As such, this arc system provides an opportunity to assess the fluid mobility of PGE and to investigate the effects of fluid-induced melting and prior melt depletion on PGE behaviour during both mantle melting and magma evolution.

Tongan lavas display extreme fractionation of the platinum-group PGE (P-PGE) from the iridium-group PGE (I-PGE) which is inherited at source and is significantly greater than MORB. All of the PGE display low bulk compatibility during magma evolution, reflecting sulphide undersaturation. Rather than source PPGE enrichment by slab fluids, the fractionation of the PPGE from the IPGE can be explained by relatively low-temperature yet high-degree melting of fluid-fluxed depleted mantle. Prior melt depletion increases the likelihood of complete consumption of sulphide in the source during melting, which typically produces melts with high concentrations of all the PGE. In the Tonga arc, however, the high PPGE contents can be explained by the exhaustion of sulphide liquid in the source [e.g. 1], while the retention of the IPGE requires residual monosulphide solid solution (mss) or platinum-group minerals. Complete sulphide exhaustion is likely given high aggregate degrees of partial melting ($\geq 25\%$) of a DMM source which is sufficiently hot to melt mss. If so, the presence of laurite (Ru-Os-Ir) sulphide or IPGE alloys may explain the retention of IPGE in the source residue.

Flux-melting investigated here and a previously proposed PGE flux from the slab indicate that subduction zones are undoubtedly an environment where significant fractionation of Re and Pt from Os occurs, further indicating that the core contribution hypothesis to explain the coupled enrichments of ^{186}Os and ^{187}Os may be non-unique.

[1] Mungall *et al.* (2005) *GCA* **69**(17), 4349–4360.