Stable chromium isotopes as indicators of reduction and immobilization of hexavalent chromium in groundwater

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(NOTE: I will not be extremely picky about formatting. However, this is the formatting we use in my group for submitting papers and it is fairly standard in the sciences)
Abstract

Hexavalent chromium (Cr(VI)) is a common groundwater contaminant whose mobility depends strongly on oxidation and reduction. Measurements of Cr stable isotope fractionation in laboratory experiments and natural waters show that lighter isotopes reacted preferentially during Cr(VI) reduction by magnetite and sediments. The $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of the product was $3.4 \pm 0.1\%$ less than that of the reactant. $^{53}\text{Cr}/^{52}\text{Cr}$ shifts in water samples indicate the extent of reduction, a critical process which renders toxic Cr(VI) in the environment immobile and less toxic.

1. Introduction

Chromium is a common contaminant in surface water and groundwater (BARTLETT and JAMES, 1988; ROBLES-CAMACHO and ARMIENTA, 2000) because it is used widely in electroplating and other industries and occurs naturally at high concentration in ultramafic rocks. Under oxidizing conditions, Cr is highly soluble and mobile as the Cr(VI) anions chromate ($\text{CrO}_4^{2-}$) and bichromate ($\text{HCrO}_4^-$). Cr(VI) is a suspected carcinogen (KORTENKAMP, 1996). Under reducing conditions, Cr(VI) may convert to Cr(III), which is insoluble, strongly adsorbed onto solid surfaces (LOYAUX et al., 2000), and less toxic. Cr(VI) can be removed from solution artificially via in situ reduction (BLOWES et al., 1997; LYTLE et al., 1998), or naturally by reductants such as aqueous Fe(II), dissolved humic acids, and Fe(II)-bearing minerals (BUERGE and HUG, 1997; WITTBRODT and PALMER, 1996).

Students NOTE: I have included citations in the above paragraph so you can see the formatting and usage. I will not be extremely picky about formatting, but please use a format close to this. There are fewer citations in the rest of this paper, but you should continue to cite references in this way for your entire paper.

Determining rates of reduction is thus essential in many Cr(VI) contamination cases. For example, sufficient rates of natural reduction at a given site allow use of the “monitored natural attenuation” approach, which is much less expensive and disruptive than active remediation. Determining reduction rates can be difficult; multiple rounds of groundwater sampling and analysis over several years has been required in some contaminant plumes. Reduction reactions tend to enrich products in the lighter isotopes because they preferentially react (HOEFS, 1987), and the residual reactants become progressively enriched in the heavier isotopes as reduction proceeds (BOTTCHER et al., 1990; JOHNSON et al., 1999; THODE and MONSTER, 1965). In this paper, I review the work done so far showing that Cr stable isotopes can be used to estimate the extent of reduction, which in turn can be used to estimate long-term reduction rates.
2. Methods

Cr has four stable isotopes of masses 50 (4.35%), 52 (83.8%), 53 (9.50%) and 54 (2.37%) (Rotaru et al., 1992). Ellis et al. (2002) developed a double isotope spike method for measuring mass-dependent fractionation of Cr isotopes (i.e., variations in the relative abundances of light and heavy isotopes). (NOTE: continued description of how the method works would follow)

3. Results

3.1 Laboratory determinations of Cr isotope fractionation

Ellis et al. (2002) conducted laboratory experiments to show that there is a consistent Cr isotope fractionation during Cr(VI) reduction (Fig. 1). (Continue description of results)

![Graph showing results from laboratory experiments measuring Cr isotope shifts during Cr(VI) reduction.](image_url)

Figure 1. Results from laboratory experiments measuring Cr isotope shifts during Cr(VI) reduction. f is the fraction of the original Cr(VI) remaining. Measurement uncertainties are approximately the size of the symbols. The three experiments produced identical isotopic fractionation, within the measurement uncertainties.

(Note: Figures and Tables can be embedded in the text of the paper like they are here OR they can be attached at the back of the paper. If they are attached at the back, Tables are first, then figures.)

3.2 Field Data

Only one field study has been done so far, but the results strongly suggest that the Cr isotope approach to determining Cr(VI) reduction is effective. Ellis et al. (2002) obtained groundwater samples from sites in Putnam, Connecticut and
Berkeley, California. Both are contaminated by Cr plating wastes. At the California site, groundwater flows through natural alluvium and artificial fill. On the basis of several years of data, previous workers concluded that Cr(VI) has been partially removed from solution, probably by reduction (Makdisi et al. 2003). At the Connecticut site, groundwater flows through glacial deposits which likely contain magnetite and other Fe(II)-bearing minerals.

Measured groundwater $^{53}$Cr values (Table 2) ranged from 1.1 to 5.8‰ in the samples from the California site, and from 1.3 to 4.0‰ in the samples from the Connecticut site. All of the groundwater Cr(VI) analyses show enrichment in the heavy isotope relative to the plating baths. Apparently, Cr(VI) reduction has preferentially removed lighter isotopes from the groundwater. The variation in $^{53}$Cr values at each site suggests that reduction of Cr(VI) is occurring and has progressed to different degrees in different parts of the contaminant plumes. The highest $^{53}$Cr values are found in the samples with lowest Cr(VI) concentration at both sites. This result is expected, as the fringe areas of the contaminant plumes likely have greater degrees of reduction than the plume cores, where Cr concentrations are high and the reducing power of the aquifer materials has been depleted.

Students NOTE: Use of Tables and Figures is required. Some of you may have trouble finding good figures, but please try to include something, for practice.
Table 2. Cr isotope ratio determinations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Cr(VI)] (mg/L)</th>
<th>$^{53}$Cr (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent Cr, Rocks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{K}_2\text{Cr}_2\text{O}_7$ reagent</td>
<td>-</td>
<td>0.35</td>
</tr>
<tr>
<td>$\text{Cr(NO}_3\text{)}_2$ reagent</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>BIR Basalt, Iceland</td>
<td>-</td>
<td>-0.04</td>
</tr>
<tr>
<td>B H V O Basalt, Kilauea</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>J B Basalt, Japan</td>
<td>-</td>
<td>-0.04</td>
</tr>
<tr>
<td>Plating bath- R.I.</td>
<td>ca. $10^5$</td>
<td>0.37</td>
</tr>
<tr>
<td>Connecticut Site</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plating bath 1</td>
<td>ca. $10^5$</td>
<td>0.36</td>
</tr>
<tr>
<td>Plating bath 2</td>
<td>ca. $10^5$</td>
<td>0.29</td>
</tr>
<tr>
<td>CrO$_3$ supply</td>
<td>-</td>
<td>-0.07</td>
</tr>
<tr>
<td>MW-8 groundwater</td>
<td>4.5</td>
<td>2.23</td>
</tr>
<tr>
<td>MW-9 groundwater</td>
<td>8.61</td>
<td>1.28</td>
</tr>
<tr>
<td>MW-11s groundwater</td>
<td>16.1</td>
<td>1.93</td>
</tr>
<tr>
<td>MW-11 groundwater</td>
<td>0.63</td>
<td>3.62</td>
</tr>
<tr>
<td>MW-12 groundwater</td>
<td>1.63</td>
<td>3.96</td>
</tr>
<tr>
<td>California Site</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-3 groundwater</td>
<td>0.98</td>
<td>1.08</td>
</tr>
<tr>
<td>MW-10 groundwater</td>
<td>0.13</td>
<td>5.79</td>
</tr>
<tr>
<td>MW-12 groundwater</td>
<td>3.1</td>
<td>3.39</td>
</tr>
</tbody>
</table>

4. Discussion

4.1 Calculation of reduction rates from isotope data

The results of the Ellis et al. (2002) study strongly suggest that stable Cr isotope ratios can serve as indicators of the extent of Cr(VI) reduction in groundwater. Given present knowledge, one can speculatively calculate the extent of reduction. Ellis et al (2002) did this for two samples. MW-9 and MW-12, using equation 1, an assumed $\delta$ value of 0.9966 and an assumed value of 0.34‰ (the mean of the plating bath analyses) for the initial $^53$Cr of the contaminant Cr, 31% and 68% of the Cr(VI) initially present in the wells was reduced.

However, these calculations carry large uncertainties because....

4.2 Uncertainty in fractionation factors

Cr(VI) reduction by bacteria or reducing agents other than those studied here could induce greater or lesser isotopic fractionation than we observed.
4.3 Potential confounding effects of other reactions in nature

Apart from reduction, sorption, precipitation and uptake by plants and algae can also remove Cr from solution. If these processes and/or Cr(III) oxidation induce isotopic fractionation, this could complicate interpretation of $\delta^{53}$Cr measurements. However, as with S and Se isotopes, we expect that the dominant cause of Cr isotope fractionation is oxyanion reduction. Cr isotope studies may also be useful in assessing redox conditions in modern or ancient oceans.

4.3 Needed future work

Future work should concentrate on determining if the isotopic fractionations measured in the laboratory experiments apply in natural settings....

5. Conclusions

A small amount of work has been done to develop Cr isotopes and indicators of Cr(VI) reduction. (Summarize in a few sentences...)

This work strongly suggests that Cr isotope measurements can be used to determine Cr(VI) reduction rates in groundwater systems
Bibliography


