Separation of dissolved Cr(III) organic complexes from river water for Cr isotope analysis

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An understanding of chemical speciation of trace metals in natural water is important because the effect of trace metals on ecological and biological systems are generally influenced by their chemical forms. Elderfield (1970) found from thermodynamic calculations that $Cr(VI)O_4^{2-}$ should be the predominant species in the oxygenated water. But he also showed through direct measurements that in certain cases, the concentration of Cr(III) is higher than Cr(VI). Since there is a fair amount of organic material in natural waters, which is capable of binding with Cr(III), this inconsistency in results could be caused by the presence of soluble Cr(III) organic complexes. Nakayama (1980) reported that the hydrolysed Cr(III) ion complexed with organic ligand does not co-precipitate with $Fe(OH)_3$, which had been used to separate Cr(III) from total pool of Cr in seawater. Jeandal (1984) showed that Cr recoveries could be higher if more Fe is used. The Cr(III) removed by Fe co-precipitation is compared to a measurement of the total Cr, which captures Cr(VI) and the labile pool of Cr(III), but may not capture all of the organically complexed Cr(III), depending on whether the sample was pre-treated to destroy the organic ligands or not (Cranston and Murray, 1980; Jeandel and Minster, 1987).

In order to study the dissolved Cr(III) organic complexes, we first prepared stock solutions of Cr(III) complexes using various organic acids such as humic acid, citric acid, ethylenediaminetatraacetic acid (EDTA) and Cr (III) acetylacetonate. Using the $Fe(OH)_3$ co-precipitation method, we were successful in obtaining Cr concentration and $\delta^{53}Cr$ for each organic complex and the results matched the initial Cr concentrations used at the beginning of the experiment. The functional group ‘carboxylic acid’ (-COOH), present in all the organic acids used in this experiment, play a large role in the complexation during co precipitation (Henneberry et al., 2012). It forms a strong, inner-sphere complexation with Fe hydroxide.

In this talk we will present the results of our quality assurance tests aimed at demonstrating the extent to which various pools of Cr that may exist in natural waters can be cleanly separated for Cr isotopic analysis.

[1] Cranston et al 1980. Limn Ocean. 25, 1104-1112
[2] Jeandal et al 1984. Marine Chemistry 14, 347-364

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