Theoretical estimates of equilibrium chromium-isotope fractionations

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Introduction

We report equilibrium Cr-isotope ($^{53}Cr/^{52}Cr$) fractionations calculated for complexes, crystals, and $Cr(CO)_6$. Calculations are based on published vibrational spectra and a combination of empirical and *ab initio* force-field modeling. This goal of this study is to understand the natural processes that control variations in the stable isotope abundances of transition elements (Cr, Fe, Cu, etc.). Chromium-isotope fractionations are of particular interest because of their potential use in tracking Cr^{6+} pollution in groundwater. Recent studies have shown that light isotopes of chromium are preferentially reduced during partial reduction of dissolved Cr^{6+} to environmentally benign Cr^{3+} species, causing progressive fractionation of the remaining Cr^{6+} [1].

Equilibrium stable-isotope fractionation is driven by differences in the vibrational energies of isotopically light and heavy substances. To calculate fractionations from vibrational spectra, it is necessary to know frequencies for at least two isotopic forms. However, published spectra are usually only complete for substances containing the natural mixture of Cr-isotopes (dominated by ^{52}Cr). Force-field models are used to predict unknown frequencies for the ^{53}Cr-bearing equivalents. We use Modified Urey-Bradley force-fields and lattice-dynamics force-fields fit to the observed ^{52}Cr-dominated vibrational frequencies. *Ab initio* force-fields are also used to model $[Cr(H_2O)_6]^{+3}$, $[CrO_4]^{-2}$, and $Cr(CO)_6$.

Results

Large (> 1‰) fractionations are predicted between coexisting species with different oxidation states or bond partners. $[Cr^{6+}O_4]^{-2}$ will tend to concentrate ^{53}Cr when in equilibrium with compounds containing Cr^{3+} or Cr^0. Substances containing chromium bonded to strongly-bonding ligands like CO will concentrate ^{53}Cr relative to compounds with weaker bonds, like $[CrCl_6]^{-3}$. Substances with short Cr-ligand bonds (Cr-C in $Cr(CO)_6$, Cr-O in $[Cr(H_2O)_6]^{3+}$ or $[CrO_4]^{2-}$) will also tend to concentrate ^{53}Cr relative to substances with longer Cr-ligand bonds ($[Cr(NH_3)_6]^{3+}$, $[CrCl_6]^{3-}$, Cr-metal). Similar systematics were found in an earlier study on Fe-isotope fractionation [2].

The calculated equilibrium fractionation between $[CrO_4]^{2-}$ and $[Cr(H_2O)_6]^{3+}$ (or Cr_2O_3) agrees qualitatively with the fractionation observed during experimental reduction of $[CrO_4]^{2-}$ in solution [1], although the calculated fractionation (~6-7‰ at 298 K) is significantly larger than the experimental fractionation (3.3-3.5‰). Our results suggest that inorganic Cr-isotope fractionation at the Earth's surface is driven largely by reduction and oxidation processes.

References

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Climate changes during and after Palaeozoic glaciation phases in SW-Gondwana recorded by multi proxygeochemical investigations

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Sediments investigated in this study were taken from the Karoo Basin of South Africa, the Paraná Basin (Brazil), the Kalahari Basin (Botswana) and from the Karoo Group outcrop area of south Namibia. During the Upper Carboniferous element ratios of Rb/K, V/Cr and the chemical index of alteration (CIA) (Nesbitt & Young, 1982) of the Dwyka Group, recorded sea level fluctuations in the South African Karoo Basin. Element proxies from time equivalent profiles of southern Namibia do not reflect these changes indicating a more distal sedimentary facies. δ^{13}Corg measurements reflect furthermore the cyclicity of the Dwyka deglaciation sequences, which were previously recognized by Visser (1997) and Stollhofen et al. (2000). For a better reliability of the $\delta^{13}C$ data with regard to source or climate information, C/N ratios and biomarkers were analysed for selected samples. The sudden changes of the proxy signals portray abrupt climate shift accompanied by sea level fluctuations. A forcing process considered by Stollhofen et al. (2000) could be tectonic events, which accompanied an early period of the South Atlantic break up. In parts of the Dwyka Group the cyclicity of the above mentioned proxies shows a markedly parallel evolution to the $\delta^{13}C$ curve of Veizer et al. (1999) established for Phanerozoic seawater during the observed time slice. The shifts in the global marine $\delta^{13}C$ signal can thus possibly be related to the glaciation cycles of southwestern Gondwana during the Upper Carboniferous.

The transition zone at the Dwyka-Ecca boundary is marked by a fast but not abrupt shift of the element geochemical proxies. Higher CIA and Rb/K indicating warmer climate conditions, intensive chemical weathering in the source area and a sea level rise. Positive and negative spikes of $\delta^{13}C$ from a mean value of around -22.5‰ mark the onset of the postglacial period. During postglacial sedimentation of the Ecca Group the $\delta^{13}C$ data of the organic matter do not show a comparable trend to the element geochemical proxies. Organic rich sediments of the time equivalent Whitehill (RSA) and Irati (Brazil) Formation contain more positive $\delta^{13}C$ values.

References

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