Chemical Geology 337-338 (2013) 88–98

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

# Assessing the control on the effective kinetic Cr isotope fractionation factor: A reactive transport modeling approach

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ARTICLE INFO

*Article history:*
Received 4 April 2012
Received in revised form 2 November 2012
Accepted 17 November 2012
Available online 27 November 2012

Editor: B. Sherwood Lollar

*Keywords:*
Cr(VI) reduction
Cr isotope fractionation
Cr isotope fractionation factor
Reactive transport modeling
Transport limitations
Reaction mechanism

ABSTRACT

The fractionation of stable Cr isotopes is a well-accepted proxy for demonstrating Cr(VI) reduction occurring in geological systems. Published values for experimentally determined effective kinetic Cr isotope enrichment factors ($\varepsilon_{kin}$) vary over the range of 0.4–5.0‰. Most published studies propose a variation in Cr(VI) reduction mechanisms as being responsible for the wide range of $\varepsilon_{kin}$. Alternatively, varying reaction rates and/or transport limitations have been addressed. In this study the different contributions on $\varepsilon_{kin}$ were quantitatively addressed by performing a series of reactive transport model simulations. The proposed reaction network is based on a novel multi-continuum approach and expressing isotope fractionation through the formation of a $^{53}Cr(OH)_{3(s)}$–$^{52}Cr(OH)_{3(s)}$ solid solution as the product of Cr(VI) reduction. In doing so, Cr(VI) reduction was considered to occur at solid surfaces and Cr isotope fractionation was modeled by defining an equilibrium enrichment factor.

Simulating Cr(VI) reduction occurring along a 1D flow path suggested that for a given reaction mechanism $\varepsilon_{kin}$ can vary over a large range. According to our simulations the upper range of $\varepsilon_{kin}$ is defined by a reaction mechanism's theoretical equilibrium enrichment factor. In contrast, high reduction rate and/or transport limitations can shift $\varepsilon_{kin}$ to very low values. In a second model simulation our modeling approach was used to propose an alternative kinetic interpretation for the low $\varepsilon_{kin}$ observed in Fe(II)–Cr(VI) reduction experiment by others. Our simulations suggest that the individual contributions of reaction rates, transport limitations and reaction mechanisms should be addressed more carefully when interpreting experimentally determined kinetic Cr isotope enrichment factors and Cr isotope data derived from field sites. Reactive transport modeling is a powerful tool, which should be more commonly used to quantitatively assess these individual contributions in experimental systems.

## 1. Introduction

In nature, Cr mostly occurs in two stable oxidation states. The highly toxic and very soluble oxidized form Cr(VI) is primarily derived from anthropogenic activities such as leather tanning, wood impregnation, galvanization of metal surfaces and cement clinker. Cr(VI) occurs as the chromate oxyanions $CrO_4^{2-}$, $HCrO_4^-$ and $Cr_2O_7^{2-}$ and can lead to health problems such as lung cancer and dermatitis (Kotas and Stasicka, 2000). Naturally occurring chromium occurs mostly in the reduced form Cr(III), which is an essential nutrient, less soluble, adsorbs strongly on solid surfaces and co-precipitates with Fe(III) hydroxides (Rai et al., 1987; Davis and Olsen, 1995). Exceptions are some rare naturally occurring Cr(VI) minerals such as the lead chromate crocoite ($PbCrO_4$) (Frost, 2004) and Cr(VI) bearing groundwater systems naturally occurring in arid regions (Izbicki et al., 2008).

Significant fractionation of the four stable Cr isotopes ($^{50}Cr$, $^{52}Cr$, $^{53}Cr$ and $^{54}Cr$) has been reported for a series of Cr(VI) reduction experiments (Ellis et al., 2002; Sikora et al., 2008; Berna et al., 2010; Zink et al., 2010; Dossing et al., 2011; Basu and Johnson, 2012; Han et al., 2012; Jamieson-Hanes et al., 2012; Kitchen et al., 2012). These experiments showed a general trend of accumulating heavier Cr isotopes in the unreacted Cr(VI) species and an accumulation of the lighter ones in the produced Cr(III) species. In contrast, Cr(III) species did not undergo rapid isotopic exchange during a Cr(III) oxidation experiment (Zink et al., 2010). Variation in Cr isotope composition is, therefore, an accepted proxy for demonstrating that Cr(VI) reduction is occurring in geological systems. Tracking of Cr(VI) reduction is especially powerful when dealing with subsoil Cr(VI) contamination and related remediation actions. A series of case studies demonstrating naturally occurring Cr(VI) reduction has been described recently (Izbicki et al., 2008; Berna et al., 2010; Wanner et al., 2012a,b,c). Tracking Cr(VI) reduction has also been used for unraveling redox conditions throughout Earth's history (e.g., Frei et al., 2009). In this context, observed Cr isotope fractionation was used to unravel the fluctuations in the Precambrian atmospheric oxygenation (Frei et al., 2009) and to evaluate the redox evolution of hydrothermal systems (Schoenberg et al., 2008).

Stable isotope fractionations are caused mainly by differences in the vibrational energies of isotopically light and heavy substances

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0009-2541/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2012.11.008

(Bigeleisen and Mayer, 1947; Urey, 1947; Schauble et al., 2004). The isotopically lighter forms of any substances have a lower vibrational energy compared to the heavier ones. When substances consisting of multiple isotopic species react and the remaining reactant equilibrates with the reaction product, an unequal distribution of the isotopes is observed. Stable isotope fractionations are usually reported in terms of the isotopic fractionation factor α. For Cr isotopes, α is defined as the ratio of $^{53}$Cr/$^{52}$Cr in the two stable Cr redox states (Cr(VI) and Cr(III)). For convenience, fractionation factors are often expressed as isotopic enrichment factors ε (e.g., Schauble et al., 2004; Sikora et al., 2008):

$$\varepsilon = (\alpha - 1) \cdot 1000 \approx \ln(\alpha) \cdot 1000. \quad (1)$$

Schauble et al. (2004) determined a theoretical equilibrium Cr isotope enrichment factor $\varepsilon_{eq}$ between aqueous Cr(VI) and aqueous Cr(III) species of 6–7‰ whereas Zink et al. (2010) reported an $\varepsilon_{eq}$ of 3.5‰ for a Cr(VI) reduction experiment conducted under highly acidic conditions ($pH \ll 1$) (Table 1). In all other reported Cr(VI) reduction experiments a kinetic type isotopic fractionation behavior was observed (Ellis et al., 2002; Sikora et al., 2008; Berna et al., 2010; Zink et al., 2010; Dossing et al., 2011; Basu and Johnson, 2012; Han et al., 2012; Jamieson-Hanes et al., 2012; Kitchen et al., 2012). Applying a Rayleigh distillation model the cited Cr(VI) reduction studies determined kinetic enrichment factors $\varepsilon_{kin}$ within the range of 0.4–5.0‰ (Table 1). Kinetic isotopic fractionation is typically observed for systems undergoing a fast net reaction where the backward reaction is negligible when compared to the overall reaction rate (Young et al., 2002; Zink et al., 2010; DePaolo, 2011).

Variations in observed effective kinetic Cr isotope enrichment factors have been attributed to several causes: (i) The reaction rate of Cr(VI) reduction affects the magnitude of the kinetic Cr isotope enrichment factor such as shown for sulfur isotope fractionation (Rees, 1973; Canfield, 2001). Sikora et al. (2008) showed a kinetic dependence on the kinetic enrichment factor for microbiologically-mediated Cr(VI) reduction experiments using lactate as the electron donor. In these experiments $\varepsilon_{kin} = 1.8‰$ was observed for a high lactate concentration and a high Cr(VI) reduction rate, and $\varepsilon_{kin} = 4.0‰$ was observed for a low lactate concentration and slow Cr(VI) reduction rate (Table 1). (ii) A variation in molecular scale reduction mechanisms has been addressed as a second cause likely inducing a variation of $\varepsilon_{kin}$ (Sikora et al., 2008; Zink et al., 2010; Dossing et al., 2011). On the contrary, Zink et al. (2010) did not observe that the resulting Cr isotope fractionation factor is significantly dependent on the pH dependent speciation of Cr(VI) and Cr(III) species (Table 1). This is notable since the actual Cr(VI) reduction mechanism is also dependent on the pH value (e.g., pH = 7–9: $CrO_4^{2-} \Rightarrow Cr(OH)_2^+$; pH < 4: $HCrO_4^- \Rightarrow Cr^{3+}$). (iii) As a third cause, transport limitations, such as a limited diffusive flux towards reactive surfaces, have been reported to shift a system's effective $\varepsilon_{kin}$ to lower values (Bender, 1990; Brandes and Devol, 1997; Green et al., 2010). Even though these studies described other isotopic systems ($NO_3^-$- and $O_2$-reduction) it is assumed that transport limitations can also affect the kinetic Cr isotopic enrichment factor (Berna et al., 2010).

To the author's knowledge no study has yet quantitatively assessed the individual contributions of the reaction mechanism, the Cr(VI) reduction rate, and transport limitations on the effective kinetic Cr isotope enrichment factor. In this study these contributions were quantitatively addressed by performing a series of reactive transport model simulations of Cr(VI) reduction in a porous medium along a 1D flow path. In the second part, the Fe(II)-added–Cr(VI) reduction experiments performed by Dossing et al. (2011) were simulated and an alternative interpretation proposed.

## 2. Simulation of Cr(VI) reduction in porous media along a 1D flow path

### 2.1. Conceptual model

As a model simplification, it is assumed that Cr(VI) reduction occurs at solid surfaces only (Fig. 1). This assumption is based on the observation that Fe(II)-bearing minerals and solid organic matter are the most common naturally occurring Cr(VI) reducing agents (Palmer and Puls, 1994). For both cases, Cr(VI) reduction can be microbiologically-mediated if specific microorganisms are present (Sikora et al., 2008; Han et al., 2010). Most bacteria are fixed on solid surfaces and are

**Table 1**
Summary of published Cr(VI) reduction experiments.

| Reference | $e^-$-Donor | Initial Cr(VI) | Fractionation mode | Effective ε | Comment |
|---|---|---|---|---|---|
| Ellis et al. (2002) | $Fe^{2+}$ bearing minerals (magnetite) | 0.19 μM/L | Rayleigh-type | 3.3 and 3.5‰ | |
| Schauble et al. (2004) | Theoretical calculation | | Equilibrium fractionation | 6–7‰ | |
| Sikora et al. (2008) | 3.3–100 mM lactate | 5.1–9.5 μM | Rayleigh-type | 4.1–4.5‰ | Bioreduction (*Shewanella oneidensis*). Rate = $42 \cdot 10^{-18}$ mol/cell/day[a] |
| | 10,200 mM lactate | 9.5 μM | Rayleigh-type | 1.8‰ | Bioreduction (*Shewanella oneidensis*). Rate = $450 \cdot 10^{-18}$ mol/cell/day[a] |
| Zink et al. (2010) | 0.9 μM $H_2O_2$ | 0.9 μM | Rayleigh-type[b] | 4.2‰ | pH = 0.7 |
| | 0.9 μM $H_2O_2$ | 0.9 μM | Equilibrium fractionation[b] | 7.2‰ | pH = 0.7 |
| | 13.2 μM $H_2O_3$ | 0.9 μM | Rayleigh-type | 5.0‰ | pH = ca. 7 |
| | 13.2 μM $H_2O_4$ | 0.9 μM | Equilibrium fractionation | 3.5‰ | $pH \ll 1$ |
| Berna et al. (2010) | $Fe^{2+}$ bearing minerals (e.g. green rust) | 1.92 μM | Rayleigh-type | 2.4 and 3.1‰ | |
| Dossing et al. (2011) | 0.05 nM $Fe^{2+}$ (batch experiment) | 0.42 nM | Rayleigh-type | 3.1–4.5‰ | |
| | 0.03 mM $Fe^{2+}$/min (added experiment) | 0.78 μM | Rayleigh-type | 1.5‰ | |
| Han et al. (2012) | 20 mM lactate | 50 μM | Rayleigh-type | 2‰ | Bioreduction (*Pseudomonas stutzeri*); aerobic conditions |
| | 20 mM lactate | 50 μM | Rayleigh-type | 0.4‰ | Bioreduction (Pseudomonas Stutzeri); denitrifying conditions |
| Basu and Johnson (2012) | Fe(II) doped goethite | 17.7 μM | Rayleigh-type | 3.91‰ | |
| | FeS (75 μM Fe(II)) | 19 μM | Rayleigh-type | 2.11‰ | |
| | Green rust (100 μM Fe(II)) | 11 μM | Rayleigh-type | 2.65‰ | |
| | $FeCO_3$ (84.2 μM Fe(II)) | 19 μM | Rayleigh-type | 2.67‰ | |
| | 4 g of reduced sediment | 24 μM | Rayleigh-type | 3.18‰ | |
| Kitchen et al. (2012) | 60 mM $Fe^{2+}$ | 20–22 μM | Rayleigh-type | 4.20 ± 0.11‰ | pH = 4–5.3 |
| | 10 mg humic and 200 μM fulmic acid | 21 μM | Rayleigh-type | 3.11 ± 0.11‰ | pH = 4.5–5 |
| Jamieson-Hanes et al. (2012) | 7.5 g organic C (batch experiment) | 100 μM | Rayleigh-type | 3.50 ± 0.1‰ | |

[a] Rate observed during first 24 h of experiment.

[b] Fractionation mode not clear since all experiment resulted in the same extent of Cr(VI) reduction. Presented here are the two different possibilities for interpretation (equilibrium vs. kinetic fractionation).