Stable Isotope Fractionation during Chromium(III) Oxidation by δ-MnO$_2$

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INTRODUCTION

- Hexavalent chromium (Cr) is a highly mobile anthropogenic pollutant in ground and surface waters, and reduction of Cr(VI) to the less-soluble Cr(III) is the most important natural process involved in attenuation. Progress has been made toward developing stable isotopes of Cr as indicators of attenuation.

- Previous studies have observed a preferential reduction of lighter Cr stable isotopes, attributed to a kinetically-controlled mechanism [1]. Isotope exchange between dissolved Cr(III) and Cr(VI) appears to be negligible over a period of days to weeks [2].

- Further development requires an understanding of isotopic fractionation during Cr oxidation by manganese oxides (the primary mechanism of environmental Cr(VI) formation). Previous studies on oxidation by pyrolusite (ß-MnO$_2$) have reported initial $\delta^{53/52}$Cr ratios of up to +1.1‰ in the Cr(VI) product, suggesting equilibrium isotope fractionation controlled by complex electron transfer mechanisms [3]. Laboratory investigations of fractionation during Cr(III) oxidation by birnessite (δ-MnO$_2$) have been inconclusive, and oxidation mechanisms remain unclear.

- Here, we present the latest measurements of Cr stable isotope ratio changes during Cr(III) oxidation on birnessite.

PREVIOUS WORK

Isotopic fractionation during Cr(III) oxidation by pyrolusite (ß-MnO$_2$) was measured previously [4]. Results from experiments conducted in nitrate matrix at pH 3 (Figure 1) show initial enrichment in ^{53}Cr of up to +1.3‰ in the Cr(VI) product. Similar behavior was observed in chloride matrix and at pH 4.
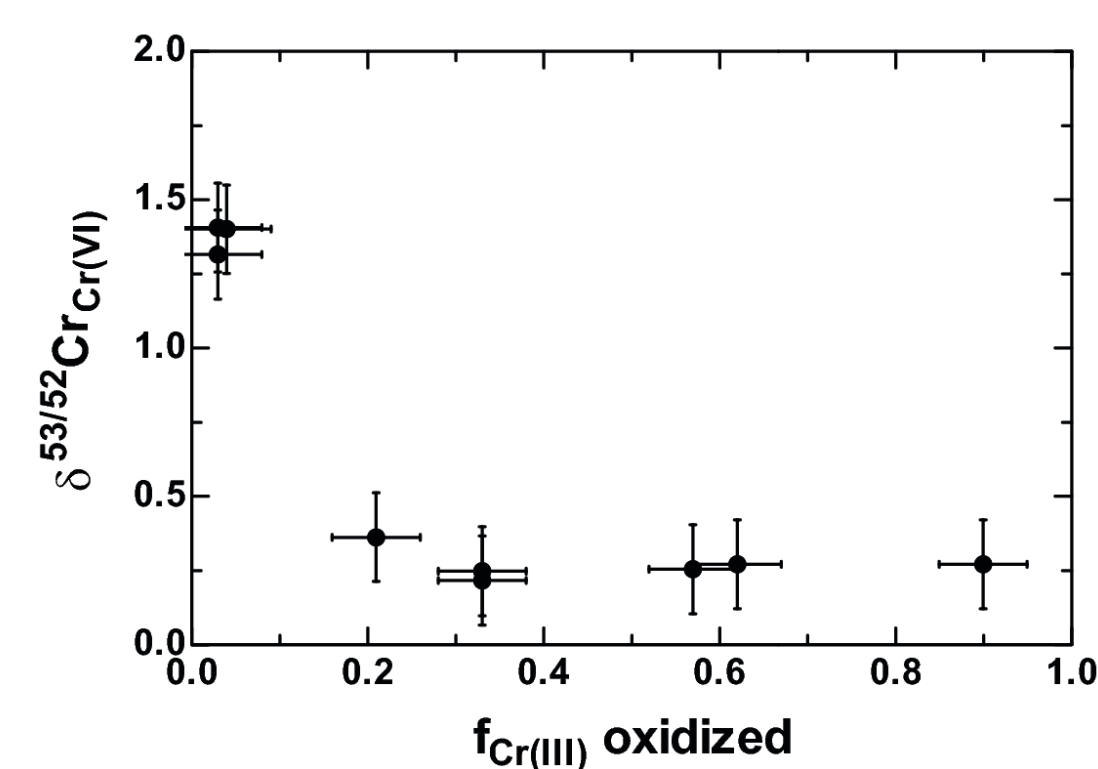

Figure 1. Isotopic fractionation during Cr(III) oxidation on pyrolusite [4]. Cr(NO$_3$)$_3$ (10.0 mg/L in Cr) was reacted with synthetic ß-MnO$_2$ (100 mg/L) in 0.1 M sodium nitrate at room temperature and controlled pH of 3.0. Data from replicate experiments are plotted.

Overall reaction kinetics were approximately first-order in Cr(III). Reaction was slow (1-3 days to completion) relative to reactions of Cr(III) with birnessite.

METHODS

1. Synthetic birnessite was prepared by addition of HCl to KMnO$_4$, washing with ultrapure water, and drying in air.

2. All reactions were performed in 0.1 M NaNO$_3$ in 50 mL ultrapure water at pH ~3. The temperature of the reaction vessel was controlled at 4 or 20 °C. Manganese oxide suspensions were kept in continuous motion and periodically extracted through a 0.45 µm membrane filter. Cr(VI) concentrations in filtrate were determined colorimetrically at 540 nm using diphenylcarbazide.

3. Filtrate samples were double-spiked with ^{54}Cr & ^{50}Cr, purified via a two-step anion-exchange procedure, and analyzed via multicollector inductively-coupled plasma mass spectrometry (MC-ICP-MS) at the University of Illinois at Urbana-Champaign.

4. Isotope ratios of Cr(VI) in solution are reported as $\delta^{53/52}$Cr (relative to NIST SRM 979).

RESULTS & DISCUSSION

Reaction kinetics of Cr(III) oxidation on birnessite are overall first-order. Reaction rate is highly dependent on MnO$_2$ concentration (Figure 2), but nearly independent of Cr(III) concentration (Figure 3), consistent with literature [5]. The reaction is rapid but does not go to completion, suggesting inhibition of Cr oxidation by birnessite surface alteration.
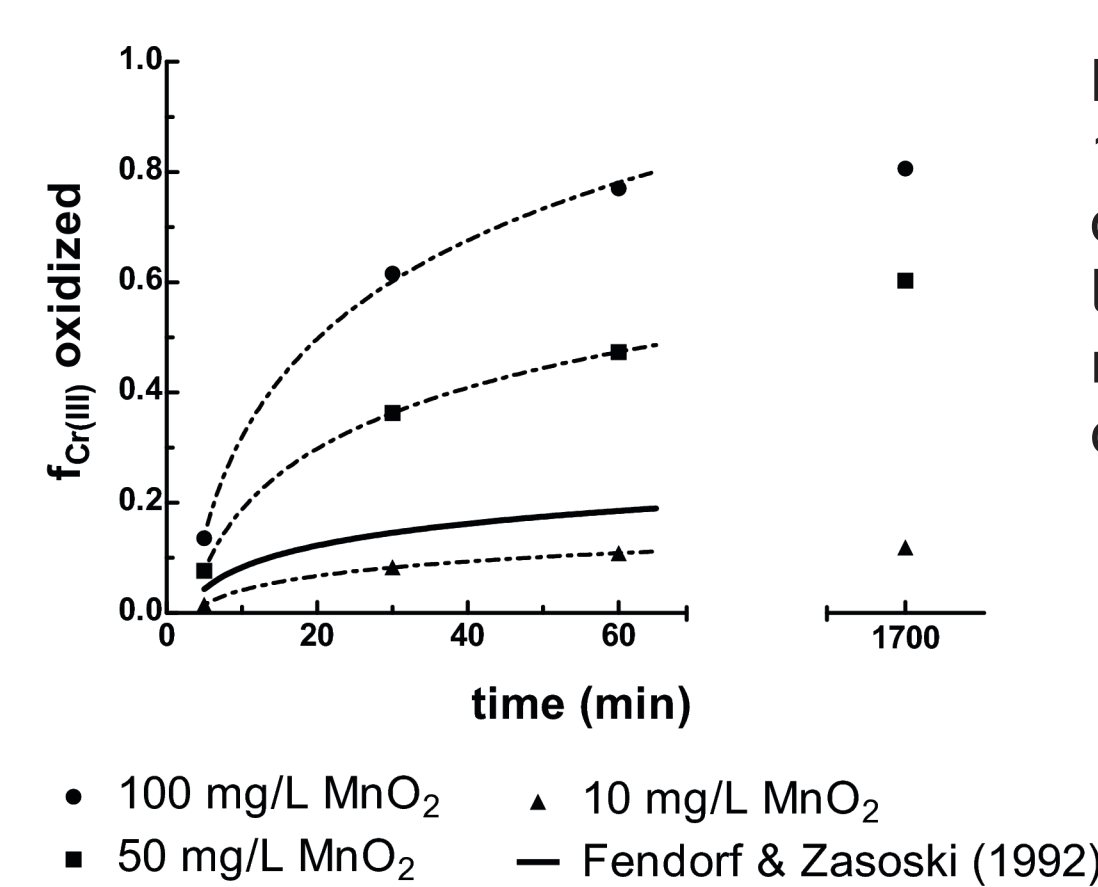

Figure 2. Kinetics of the reaction of 10.0 mg/L Cr(III) with varying concentrations of δ-MnO$_2$ at 20 °C. For comparison, the solid line represents published measurements of reaction of 40 mg/L Cr(III) with 100 mg/L δ-MnO$_2$ in 1 mM nitrate.

- 100 mg/L MnO$_2$
- 50 mg/L MnO$_2$
- 10 mg/L MnO$_2$
- Fendorf & Zasoski (1992)

Figure 3. Kinetics of the reaction of Cr(III) (varying concentrations) with 100 mg/L δ-MnO$_2$ at 4 °C.

- 50 mg/L Cr(III)
- 10 mg/L Cr(III)
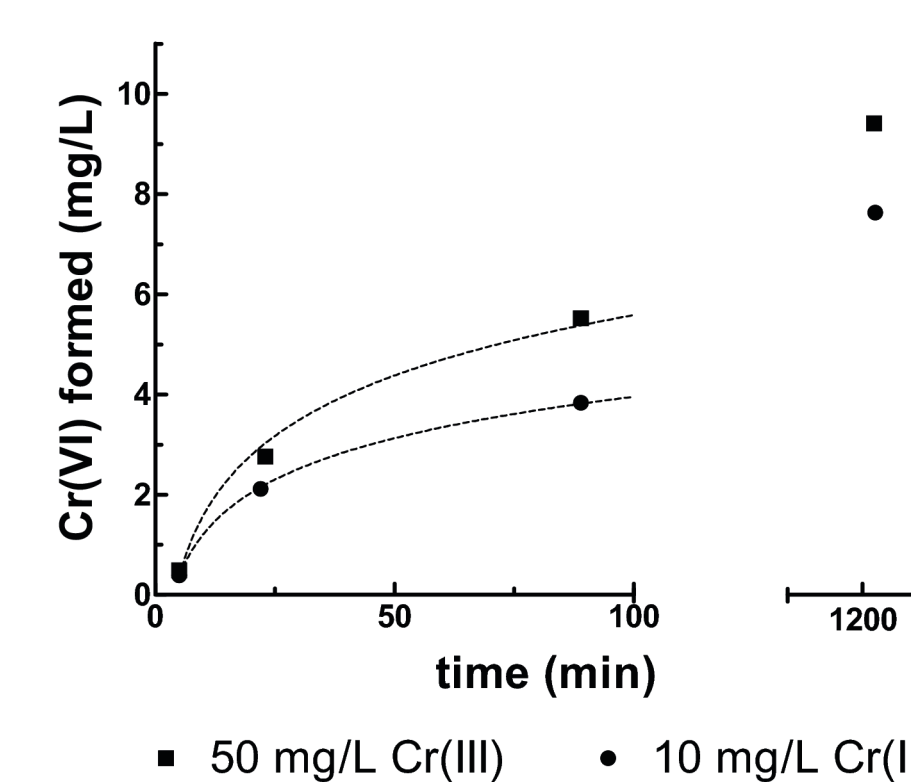
Isotope ratios in Cr(VI) during oxidation of Cr(III) on birnessite are shown in Figure 4. Greater overall fractionation is observed at 20 °C than at 4 °C.
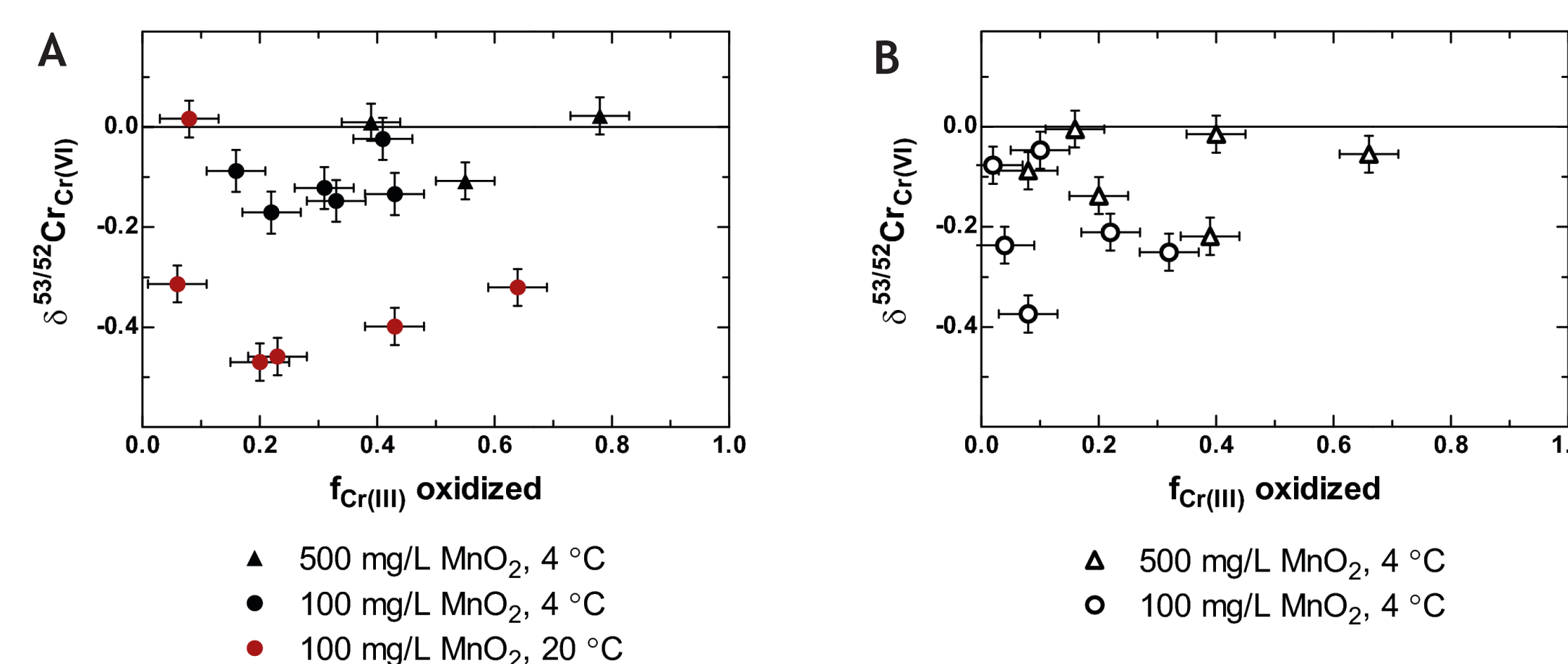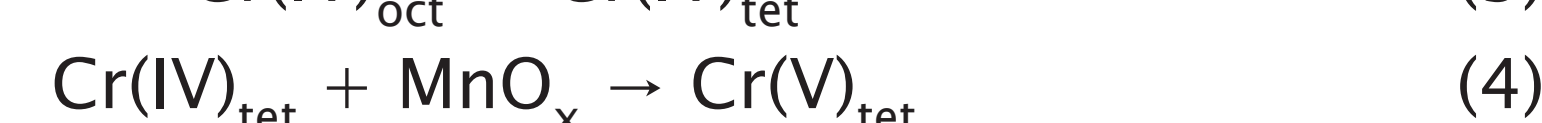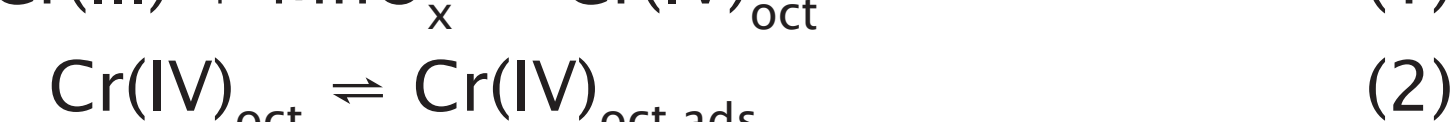

Figure 4. Isotope fractionation during oxidation of (A) 10 and (B) 50 mg/L Cr(III).

- A:
  - ▲ 500 mg/L MnO$_2$, 4 °C
  - ● 100 mg/L MnO$_2$, 4 °C
  - ● 100 mg/L MnO$_2$, 20 °C (red)
- B:
  - △ 500 mg/L MnO$_2$, 4 °C
  - ○ 100 mg/L MnO$_2$, 4 °C

These results show variation in isotope ratios of up to −0.5‰ in the Cr(VI) product. This is qualitatively consistent with a kinetic isotope effect, but the fractionation is much less than that during reduction [1].

Schauble et al. [6] predicted equilibrium isotope fractionations of up to +7‰ ($\Delta^{53/52}$Cr$_{Cr(VI)-Cr(III)}$). Our results suggest that oxidation of Cr on birnessite cannot be solely equilibrium-controlled.

The positive $\delta^{53/52}$Cr during oxidation of Cr(III) on ß-MnO$_2$ may be explained by greater equilibrium effects from back-reaction of Cr(VI) to Cr(III). ß-MnO$_2$ sorbs more Cr over time than does δ-MnO$_2$ [7]. This may result in greater equilibration time for rate-limiting electron transfer reactions on ß-MnO$_2$.
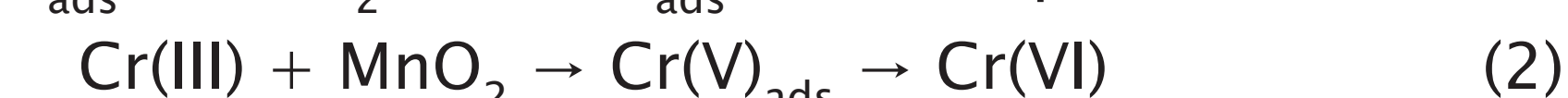
Observed isotope fractionations will depend on the rate-limiting step and back-reactions in the mechanism. Silvester et al. [8] postulated the following mechanism of Cr(III) oxidation by Na-buserite:

$$Cr(III) + MnO_x \rightarrow Cr(IV)_{oct} \quad (1)$$
$$Cr(IV)_{oct} \rightleftharpoons Cr(IV)_{oct,ads} \quad (2)$$
$$Cr(IV)_{oct} \rightarrow Cr(IV)_{tet} \quad (3)$$
$$Cr(IV)_{tet} + MnO_x \rightarrow Cr(V)_{tet} \quad (4)$$
$$Cr(V)_{tet} + MnO_x \rightarrow HCrO_4^- \quad (5)$$

According to this mechanism, step 1 is rate-limiting at low MnO$_2$ concentrations, while step 3 is rate-limiting at high MnO$_2$ concentrations. Our results do not enable identification of the rate-limiting step. However, we expect that isotope fractionation would be primarily controlled by steps 1 & 3 and associated back-reactions.

RESULTS & DISCUSSION (CONT.)

An alternative mechanism for Cr oxidation via a parallel reaction scheme [9] was proposed as follows:

$$Cr(III)_{ads} + MnO_2 \rightleftharpoons Cr(IV)_{ads} \rightarrow minor\ products \quad (1)$$
$$Cr(III) + MnO_2 \rightarrow Cr(V)_{ads} \rightarrow Cr(VI) \quad (2)$$

Reaction sequences 1 & 2 compete for Cr(III), but only pathway 2 can produce the Cr(VI) product. Cr reacts increasingly faster by sequence 1 than by sequence 2 as the reaction proceeds. By this mechanism, a back-reaction of Cr(IV) to Cr(III) (sequence 1) and subsequent formation of Cr(VI) via sequence 2 could contribute to both equilibrium and kinetic effects.

Zink et al. [2] observed non-Rayleigh fractionation of approx. +0.2‰ in the Cr(VI) product of Cr(III) oxidation by aqueous hydrogen peroxide. These results were hypothesized to reflect the formation of metastable Cr(V) intermediates during a simultaneous reduction step.

The negative values of $\delta^{53/52}$Cr in the Cr(VI) product obtained in our work may thus be attributed to differences in electron-transfer rates due to adsorption and coordination change processes at solid surfaces. We suggest that these processes involve temperature-dependent back-reaction steps that contribute less to overall fractionation than the forward steps.

CONCLUSIONS

- Structural differences between manganese oxides may contribute to variation in isotope ratios and kinetic behavior during oxidation processes. Temperature- and concentration-dependent reaction steps may contribute to observed differences in fractionation.

- Further experiments are required to identify the mechanistic source(s) of fractionation. Our results may be interpreted in light of published mechanisms of Cr oxidation by MnO$_2$.

- Isotopic fractionation during oxidation may need to be considered as a factor in the development of Cr stable isotopes as indicators of contaminant attenuation.

FUTURE WORK

- Purification method development to allow simultaneous measurement of Cr(VI) and Cr(III) isotope ratios during reaction.

- Further experiments to investigate temperature, concentration, & matrix dependence of isotope fractionation.

- Characterization of isotope effects during oxidation with synthetic manganite (γ-MnOOH).

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