

Problem Set #8 (Stable Isotopes)  
12.104, Geochemistry, Fall 2014

This is due in class on Thursday 13 Nov 2014.

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## Problem 8.1, Rayleigh fractionation  
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Hexavalent chromium, colloquially “hex chrome”, is a major toxic contaminant in groundwaters. In the U.S., Cr(VI) contamination is often associated with leather tanning, chrome plating, and nuclear waste disposal operations.

One of the most effective ways to treat chromium(VI) contamination is to reduce the Cr(VI) (which exists as the highly-mobile chromate ion) to Cr(III), which will precipitate and become immobilized (see Eh-pH diagram below). In nature, however, manganese oxides (MnO<sub>2</sub>) are common, and can re-oxidize any Cr(III) that comes in contact with them.

Isotope measurements of Cr’s stable isotopes (50, 52, 53, 54) can be used to trace Cr(VI)-Cr(III) interconversion via redox reactions in contaminated sites. The isotope fractionation during reduction of Cr(VI) has been measured experimentally by Ellis et al. (2002) Science.

The stable isotopic composition of chromium during oxidation of Cr(III) to Cr(VI) has also been measured experimentally. Data from an experiment in which 10.0 mg/L of Cr(III) were slowly oxidized to Cr(VI) are provided in the file Problem8.1\_Data.xlsx.

## Part 8.1.1

Plot up the measured  $\delta^{53}\text{Cr}$  of both Cr redox species as a function of time.

Use the Rayleigh model and calculate the isotopic fractionation factor ( $\alpha$ ) between Cr(III) and Cr(VI) during the reaction: Cr(III)  $\rightarrow$  Cr(VI). You may wish to use SOLVER in Excel or some other fitting algorithm to fit the Rayleigh equation to this. You should have two free parameters ( $\alpha$ , or alternatively you can use  $\epsilon = \alpha - 1$ , usually expressed in permil), and the initial isotopic composition of Cr(III) [which I didn’t measure] to fit.

## Part 8.1.2

If Cr(VI) and Cr(III) are the only species in the system at any time, then the weighted average of the  $\delta^{53}\text{Cr}$  of Cr(VI) and Cr(III) should equal the initial  $\delta^{53}\text{Cr}$  of Cr(III) reactant. Use the  $\delta^{53}\text{Cr}_{\text{init}}$  you fitted above to calculate the expected  $\delta^{53}\text{Cr}$  of Cr(III) from the measured  $\delta^{53}\text{Cr}$  values of Cr(VI) alone (i.e., pretend  $\delta^{53}\text{Cr}$  of Cr(III) wasn’t measured). Do these values match the observed/modeled values?

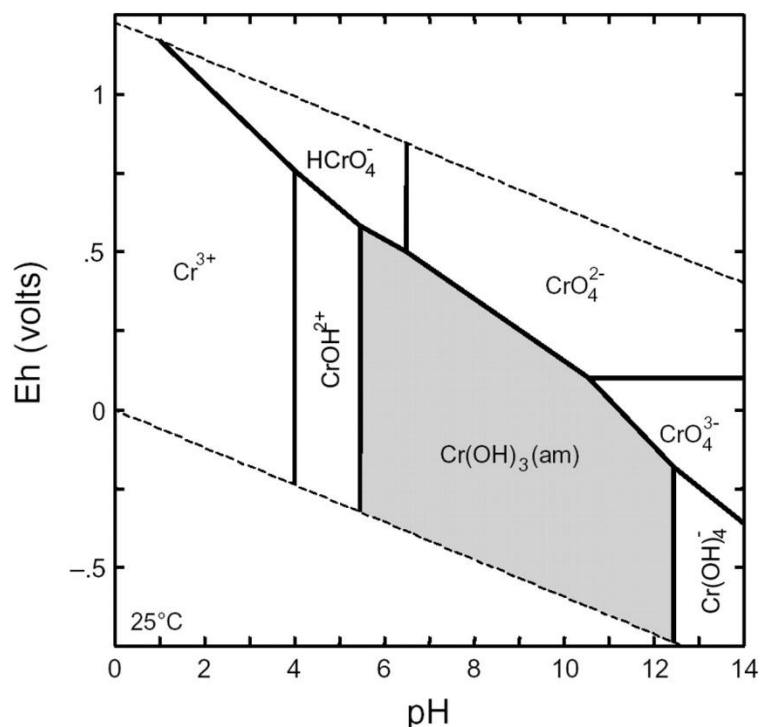


Figure 8.1. Eh-pH diagram for aqueous Cr at 25 °C. The figure is from Reeder et al. (2006) RIMG.

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## Problem 8.2, Isotope geothermometry
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In this problem you will calculate the equilibrium isotope fractionation between  $\text{CO}_2(\text{g})$  and  $\text{CH}_4(\text{g})$ , and compare it to experimental values. You'll then look at a few applications of the carbon-isotope geothermometer in natural settings.

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## in GAUSSIAN - IN ATHENA
```

Put the "files for Gaussian" in some folder in your Athena account.

Run the command to launch Gaussian03 on your Athena terminal:

```
>> setup gaussian
```

Go to the directory in which you placed your files. For example,

```
>> cd ~/Documents/12.104/Gaussian/IsotopesPSet
```

Now we will call Gaussian to do calculations according to a set of input files I have provided you (the filenames for the \*.com files to be sent to Gaussian are listed in JobsQueue.txt). Run the command:

```
>> sh DoJobsGetVibs.sh JobsQueue.txt
```

After a few seconds you should see that there are now a few new directories in ~/Documents/12.104/Gaussian/IsotopesPSet/. Navigate to the directory called "resvibs":

```
>> cd ./resvibs
```

The files in here contain the vibrational frequencies you have just calculated for  $^{12}\text{CO}_2$ ,  $^{13}\text{CO}_2$ ,  $^{12}\text{CH}_4$ , and  $^{13}\text{CH}_4$ . They have extensions ".tsv", meaning "tab-separated values" file. You can open them up as text files in Excel or any other text/spreadsheet editor.

```
## in MATLAB/Excel
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Put the "files for MATLAB" in a folder somewhere on your computer. You should see two files called:

```
freqs_CarbonDioxide.csv  
freqs_Methane.csv
```

Put the vibrational frequencies you calculated into these files. I placed my calculated vibrational frequencies for  $^{12}\text{CH}_4$  and  $^{12}\text{CO}_2$  into the files already as an example. Check to see that you got similar numbers.

Run the MATLAB script:

```
CO2CH4betas.m
```

This will calculate the  $\beta$ -factors for  $^{13}\text{C}/^{12}\text{C}$  in  $\text{CO}_2$  and  $\text{CH}_4$  at various temperatures from 0 to 1000 °C, and will output the data as a CSV file, "CO2CH4betas.csv".

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## Part 8.2.1
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Using the beta-factors you obtained, calculate and plot the equilibrium isotope fractionation ( $\alpha$ ) between  $\text{CO}_2$  and  $\text{CH}_4$  as a function of temperature. In other words, the  $K_{\text{eq}}$  vs.  $T$  for the reaction:



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## Part 8.2.2
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Horita (2001) experimentally-equilibrated methane and carbon dioxide at high temperatures (200–600 °C) over catalyst.

Plot Horita's calibration (first page of his paper) on the same plot as your calculation results. Are your calculations accurate? If they are not, discuss why they might not be (hint: see Horita's paper p. 1915).

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## Part 8.2.3
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As I mentioned in recitation, marine sediments are a good place to find  $\text{CO}_2$ - $\text{CH}_4$  carbon-isotope fractionations that are near-equilibrium at low temperatures. Some published data on C-isotopes of  $\text{CO}_2$  and  $\text{CH}_4$  in marine sediments (from a core drilled offshore Vancouver) are provided in "Homework8\_Data.xlsx".

Plot the downcore d13C signatures for DIC and CH4. Comment on their general structure.

Calculate and plot the apparent isotope fractionation between CO2-CH4 downcore:  $\alpha = (^{13}\text{CH}_4/^{12}\text{CH}_4)/(^{13}\text{DIC}/^{12}\text{DIC})$ ; recall that  $\delta^{13}\text{C}_{\text{CH}_4} = (^{13}\text{CH}_4/^{12}\text{CH}_4) - 1$ , and don't forget to account for the factor of 1000 in the definition of permil (‰).

Compare these values to your/Horita's calibration for CO2(g)/CH4(g). Are the carbon isotopes of DIC and CH4 in these marine sediments close to equilibrium?\*

\*\* Note that because DIC is mostly HCO3-, the C is in a stronger bonding environment than CO2(g). So at equilibrium at ~20 °C, DIC is somewhat heavier (about 8‰) than co-existing CO2(g). This is useful because it's actually the reason why marine and terrestrial plants have about 8‰ separation in carbon isotopes, and therefore the d13C in an estuary can reflect mixing of marine and terrestrial organic matter deposition.

#### ## Part 8.2.4

Fiebig et al. (2004) measured the carbon isotopic composition of gases venting from fumaroles at Nisyros, Greece and Vesuvio, Italy:

	T <sub>vent</sub> / °C	$\delta^{13}\text{C}$ / ‰	
		CO <sub>2</sub> (g)	CH <sub>4</sub> (g)
Nisyros	100.	-1.2	-23.0
Vesuvio	100.	-0.3	-16.4

Based on Horita's calibration, calculate the equilibration temperature of CO2 and CH4 carbon isotopes in these volcanic gases. Compare this geothermometer temperature to the measured vent temperature. What does this tell you about the source of the fumarole gases?