Applying stable isotope fractionation theory to heavy elements

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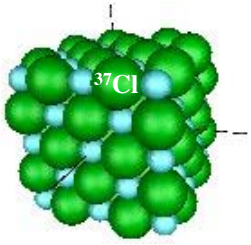

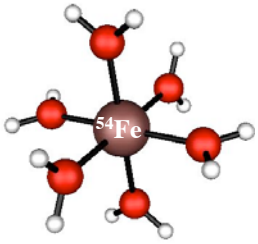

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Originally presented on May 15, 2004 at the MSA shortcourse in Montréal, Canada. This presentation is intended to summarize and complement Chapter 3 of the Reviews in Mineralogy and Geochemistry volume "Geochemistry of Non-Traditional Stable Isotopes" (Johnson, Beard and Albarède, eds. v. 55, p. 65-111). The original presentation contains a number of animated molecular vibrations, which show up as static images in the present format.

Please feel free to contact the author if you have any questions or comments.

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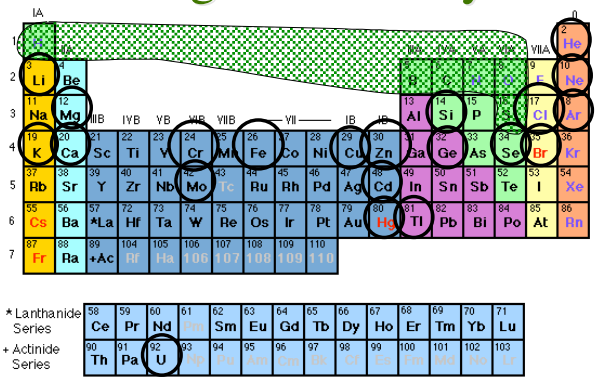
What distinguishes heavy elements?



- Terrestrial stable-isotope anomalies have been observed up to atomic #81 (Thallium).
- So far, heavy element fractionation appears to be mass dependent.

Does fractionation have the same chemical origin for all elements?

H, B, C, N, O, and S isotope variations (and to a lesser extent Li and Cl) have been studied for many years. These elements show large isotopic fractionations in many natural systems. Careful thermal-ionization mass spectrometry and the development of multiple-collector inductively-coupled mass-spectrometry have revealed that a host of other elements are fractionated as well.

δ-Notation:

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{Standard}}\right) x1000$$

$\delta^{18}O$: $R = {}^{18}O/{}^{16}O$, $R_{Standard}$ = Seawater (SMOW)

$\delta^{37}Cl$: $R = {}^{37}Cl/{}^{35}Cl$, $R_{Standard}$ = Seawater (SMOC)

$\delta^{56}Fe$: $R = {}^{56}Fe/{}^{54}Fe$, $R_{Standard}$ = IRMM14

≈ Igneous rocks, bulk Earth

Natural chemical processes tend to partially separate isotopes, but only slightly. For mathematical convenience, geochemists typically report variations in isotopic abundances in "delta units", i.e., as per mil deviations from a standard material.

Epsilon notation is also occasionally used to describe small variations in the abundances of stable isotopes of heavier elements like iron. 10 epsilon (10 ε) is equivalent to one δ.

Notation for fractionation factors:

$$\alpha_{XA\text{-}XB} = R_{XA}/R_{XB}$$

$$\delta_{XA} - \delta_{XB} \approx 1000 \bullet (\alpha_{XA\text{-}XB} - 1) \approx 1000 \bullet \ln(\alpha_{XA\text{-}XB})$$

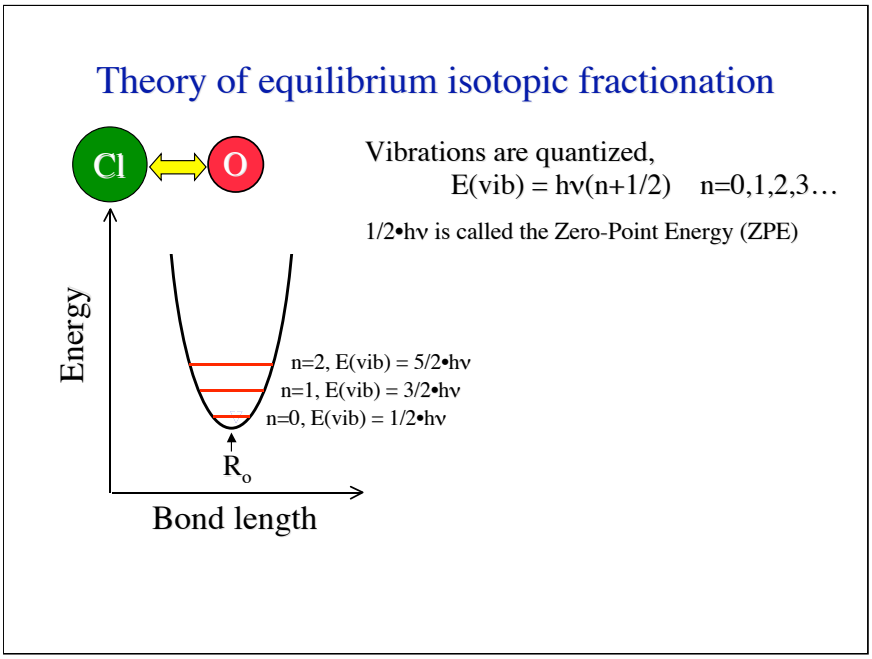
For equilibrium isotopic fractionation, α is related to the equilibrium constant of a one-atom exchange reaction:

$$^{light}XA + {}^{heavy}XB \leftrightarrow {}^{heavy}XA + {}^{light}XB$$

$$K_{eq} = \frac{[^{heavy}XA][^{light}XB]}{[^{light}XA][^{heavy}XB]} = R_{XA}\frac{1}{R_{XB}} = \alpha_{XA\text{-}XB}$$

This relationship is slightly more complicated if A or B has more than one atom of X!

The extent of isotope separation in a particular reaction is the "α". When α=1, there is no separation. α>1 indicates that the products are enriched in heavy isotopes. α<1 indicates that the products are depleted in heavy isotopes. In an equilibrium reaction, α is closely related to the equilibrium constant, though not always identical to it. The complication comes in because there will be molecules of XA and/or XB that contain a mixture of light and heavy isotopes of X. The conversion from K_{eq} to α must take those molecules into account as well.

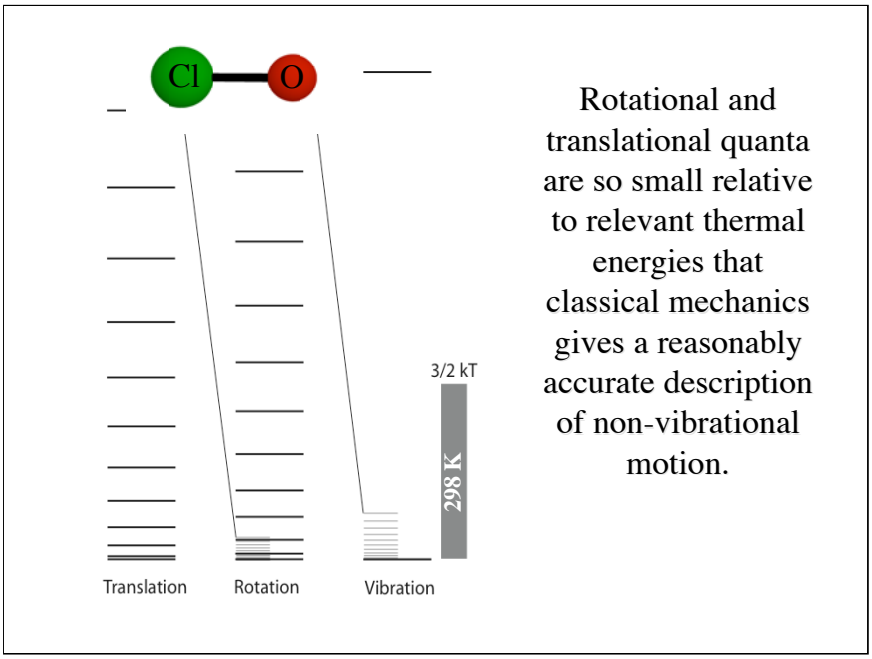


Equilibrium isotope separation is driven mainly by zero-point energy (ZPE), the quantum mechanical requirement that molecules vibrate with a half-quantum of energy even when they are in their ground states. In the figure, R_0 is the minimum of the potential energy of the bond -- this would be the equilibrium bond length if there was no atomic motion. The quantum mechanical solution assumes that the potential is shaped like a parabola, i.e. Energy = $Ar^2 + Br + C$, r = bond length. This is called a harmonic potential. Actual bond energies are usually close to harmonic near the energy minimum. What will happen to the ZPE if a heavy isotope of Cl is substituted into the ClO molecule?

Rotation and translation

Both types of motion are also quantized, but there is no zero-point energy, and the quanta are much smaller than for vibrations.
Rotational and translational quanta are much smaller than thermal energy at room temperature.

Of course vibrational motion isn't the only type subject to quantum mechanics, but it turns out to be much more important for driving isotopic fractionation.



In general, large and heavy molecules have small rotational and translational quanta, while small and light molecules have larger quanta. Vibrational quanta depend on the stiffnesses of molecular bonds and the individual masses of the vibrating atoms, rather than the size and mass of the whole molecule.

^{35}ClO $\nu = 853.72\ cm^{-1}$
$(25.59 \bullet 10^{12}\ Hz)$

$E(vib) = 1/2 \bullet h\nu$
$\approx 5106\ J/mol$

^{37}ClO $\nu = 846.45\ cm^{-1}$
$(25.38 \bullet 10^{12}\ Hz)$

$E(vib) = 1/2 \bullet h\nu$
$\approx 5063\ J/mol$

At Equilibrium, for Cl-isotope exchange between monoatomic Cl and ClO:

$$^{37}Cl + {}^{35}ClO \leftrightarrow {}^{35}Cl + {}^{37}ClO$$

$\Delta G_0 \approx \Delta E_{(vib)} = E_{(vib)}$ *products* $- E_{(vib)}$ *reactants*

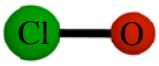
$E_{(vib)}$ *products* $= 5063\ J/mol\ (^{37}ClO)$
$E_{(vib)}$ *reactants* $= 5106\ J/mol\ (^{35}ClO)$

$\Delta E(vib) = -43\ J/mol$, driving the reaction to the right and concentrating ^{37}Cl in ClO!

Vibrational frequencies in a molecule substituted with a heavy isotope will be lighter than corresponding frequencies in an isotopically light molecule. Therefore the ZPE of an isotopically light molecule will be greater than the ZPE of an isotopically heavy molecule. A bond actually gets slightly stronger if a heavy isotope is substituted for a light one. Thus, in this simple reaction, the equilibrium tilts toward the right, in order to make the strongest (lowest-energy) bond.

Note that the energy driving this reaction is quite small, only 43 J/mol. The number of bonds on both sides of the equation are the same (one in this case). More familiar chemical reactions like oxidation or disassociation typically have energies of many 1000's of J/mol.

A rule of thumb is that 2.5 J/mol will cause a 1 per mil isotope separation at room temperature.



To get from ΔG_0 to a fractionation factor, we can use the standard thermodynamic formula:

$$\Delta G_0 = -kT \bullet \ln(K_{eq}) = -kT \bullet \ln(\alpha_{ClO\text{-}Cl})$$

$$\alpha_{ClO\text{-}Cl} = \exp(-\Delta G_0/kT)$$

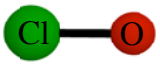
So, considering only vibrations, and if all molecules are in the ground vibrational state,

$$\alpha_{ClO\text{-}Cl} = \exp(-\Delta G_0/kT) = \exp(-\Delta E_{vib}/kT)$$

$$\approx \exp(-\{1/2 \bullet h\nu_{^{37}ClO} - 1/2 \bullet h\nu_{^{35}ClO}\}/kT)$$

$$= \exp\left(\frac{h}{2kT}\{\nu_{^{35}ClO} - \nu_{^{37}ClO}\}\right) = 1.017 \text{ at } 298 \text{ K}$$

This treatment is still incomplete, because rotations and translations are being completely ignored, along with excited vibrational states.



In reality, some molecules will be vibrationally excited:

$$\alpha_{ClO\text{-}Cl} = exp(-\Delta G_0/kT) = exp(-\Delta E_{vib}/kT)$$

$$E_{vib} = -kT\ln(Q_{vib})$$

$$Q_{vib} = \Sigma_{n=0}^{\infty} exp(-E_n/kT)$$

$$Q_{vib} = \Sigma_{n=0}^{\infty} exp(-h\nu(n+1/2)/kT)$$

$$= \Sigma_{n=0}^{\infty} exp(-h\nu/2kT) \bullet exp(-h\nu n/kT)$$

$$= exp(-h\nu/2kT) \bullet \Sigma_{n=0}^{\infty} exp(-h\nu/kT)^n$$

$\Sigma_{n=0}^{\infty} y^n = 1/(1-y)$

$$= exp(-h\nu/2kT) \bullet 1/\{1-exp(-h\nu/kT)\}$$

ZPE Excited states

Recall that it was assumed that the molecule vibrates harmonically.

So by including excited vibrational states,

$$\alpha_{ClO\text{-}Cl} = \frac{exp(-h\nu_{^{37}ClO}/2kT)/\{1-exp(-h\nu_{^{37}ClO}/kT)\}}{exp(-h\nu_{^{35}ClO}/2kT)/\{1-exp(-h\nu_{^{35}ClO}/kT)\}}$$

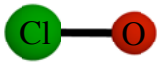
Now to add rotations and translation.

The final step is to include a simplified accounting for rotational and translational energies,

$$\alpha_{ClO\text{-}Cl} = \frac{\nu_{^{37}ClO}}{\nu_{^{35}ClO}} \frac{exp(-h\nu_{^{37}ClO}/2kT)/\{1-exp(-h\nu_{^{37}ClO}/kT)\}}{exp(-h\nu_{^{35}ClO}/2kT)/\{1-exp(-h\nu_{^{35}ClO}/kT)\}}$$

Rotation and translation

The effect of isotopic substitution on rotational and translational energies can be expressed in terms of vibrational frequencies!



$\alpha_{ClO\text{-}Cl} = 1.0096$ *at 298 K*

(the difference is due mainly to excited rotation & translation)

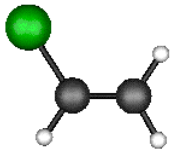
A mathematically simple accounting for rotation and translation by using a ratio of vibrational frequencies is possible because of the Redlich-Teller Product Rule, which relates ratios of vibrational frequencies to the moments of inertia and total masses of isotopically substituted molecules.

After all the accounting, the extent of isotopic separation is not quite as large as when only zero-point energies are considered. In general, the driving energy is smaller than the zero-point energy difference at finite temperatures. The higher the temperature, the smaller the driving energy becomes.

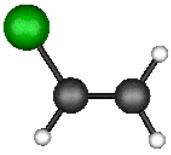
It is necessary to know vibrational frequencies of all relevant isotopic forms of a molecule or mineral (i.e. $Na^{35}Cl$ *and* $Na^{37}Cl$).

Generally, vibrational frequencies have not been measured or are incomplete for rare isotopic forms.

Predicting equilibrium isotope fractionations requires us to predict unknown vibrational frequencies.



93.53 THz w/^{35}Cl, no shift when ^{37}Cl is substituted



11.78 THz w/^{35}Cl, 0.07 THz shift when ^{37}Cl is substituted

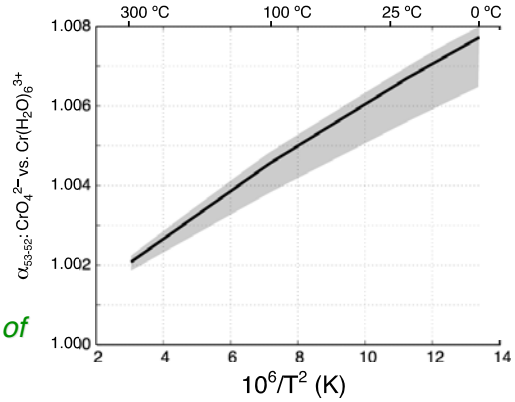
In general, the vibrational spectroscopic data for rare isotopic forms of most molecules are not known. For minerals and dissolved species the situation is even worse: often there aren't complete spectra for any isotopic forms!

The problem of predicting unknown vibrational frequencies and their sensitivity to isotopic substitution is very similar to trying to figure out what the vibrations look like. If an atom doesn't move much in a particular vibration, isotopic substitution of that atom won't affect the vibrational frequency much (as with the green Cl atom in the high-frequency vinyl chloride vibrational mode at left). If the atom moves a lot in a particular vibration (as in the molecule at right), isotopic substitution will affect the vibrational freuquency more strongly.

Qualitative rules governing equilibrium isotope fractionation, and their applicability to heavy **elements**:

1. *Fractionations are largest at low T-- scaling roughly as $1/T^2$*

- *Theory can be particularly useful for extending the temperature-range of experiments*



2. *Fractionations are largest for low mass elements -- scaling roughly as $(m_{heavy}–m_{light})/m^2$*

The figure shows a calculated fractionation between dissolved Cr^{6+} and Cr^{3+}. This calculation is discussed in more detail later in the talk.

Qualitative rules governing equilibrium isotope fractionation, and their applicability to heavy **elements**:

3. *Heavy isotopes prefer* **stiff** *chemical bonds. Typically this means* ***short, strong*** *bonds, correlating with*

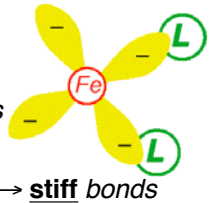
   a. *Oxidation state: high charge →* **stiff** *bonds*
   $Fe^{3+} \leftrightarrow Fe^{2+}$, $Cu^{2+} \leftrightarrow Cu^{+} \leftrightarrow Cu^{0}$, $Cr^{6+} \leftrightarrow Cr^{3+}$, $Cl^{7+} \leftrightarrow Cl^{-}$

   b. *Bond partner oxidation state: high charge →* **stiff** *bonds*
   $CCl_4 \leftrightarrow FeCl_2 \leftrightarrow NaCl$

   c. *Bond partners: "hard" anion, low atomic # →* **stiff** *bonds*
   H_2O, O_{br}, OH^-, S_2^{2-}, S^{2-}, *organic ligands*

   d. *Bond type: covalent →* **stiff** *bonds*

   e. *Low-spin electronic configuration →* **stiff** *bonds*
   3d e^- *overlap*



   f. *Coordination number: fewer bonds, smaller site →* **stiff** *bonds*
   4-fold, 6-fold, 8-fold coordination

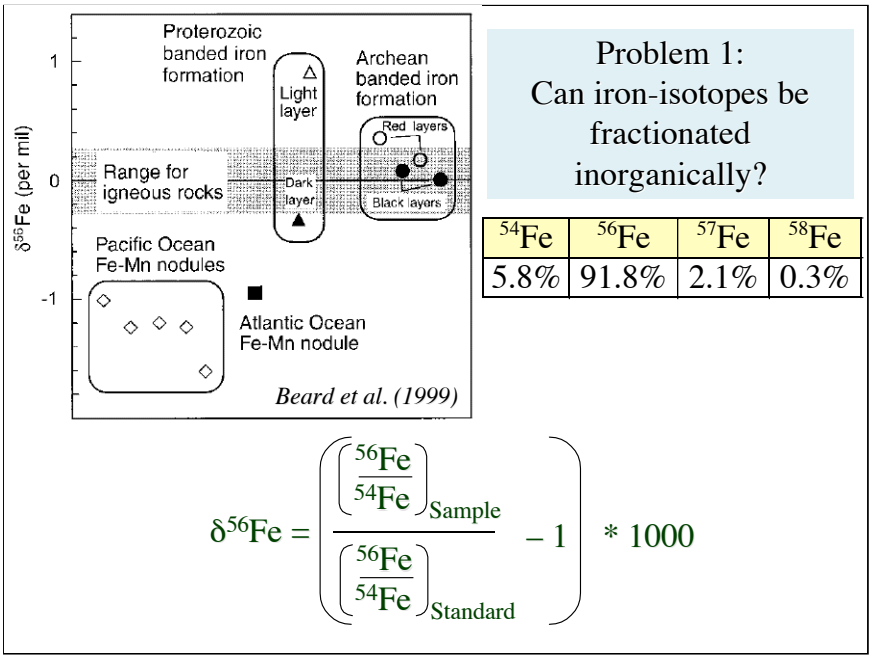
These principles should apply to all elements, but they have not been extensively tested in non-traditional stable isotope systems. In particular, it is not clear which of these rules is most important -- if two rules conflict for a particular system which will win out?

Two problems, two techniques for estimating unknown vibrational frequencies:

1. *Is there inorganic fractionation of Fe-isotopes?*
   -Empirical molecular force-fields

2. *Should Cr-isotopes track the reduction of toxic Cr^{6+} in groundwater?*
   -Ab initio force-fields

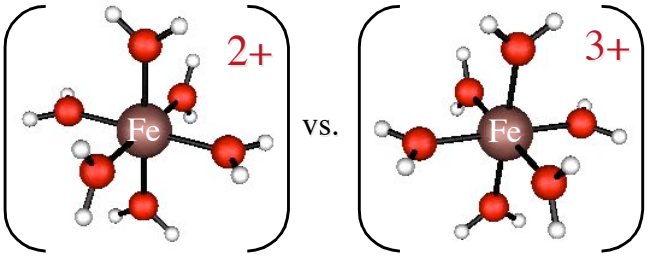
The rest of the presentation consists of two detailed case studies, highlighting techniques for quantitative estimation of isotopic separation at equilibrium for chemicals of interest in natural science.



More recent compilations of terrestrial Fe-isotope measurements are available -- this figure happens to be particularly simple. It shows that most high-temperature rocks exhibit a narrow range of Fe-isotopic compositions, while low-temperature precipitates are more heterogeneous.

The reference cited is: Beard et al. (1999) Iron isotope biosignatures. Science, v. 285, p. 1889-1892.

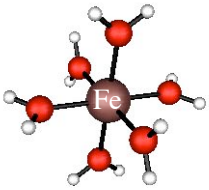
In aqueous solutions, iron bonds strongly to water molecules, typically in octahedral (6-fold) coordination. Fe^{+2} is much more soluble than Fe^{+3}.



$[Fe(H_2O)_6]^{2+}$ *reducing, soluble*

$[Fe(H_2O)_6]^{3+}$ *oxidizing, usually insoluble*

It is somewhat of a simplification to model $Fe^{3+}(aq)$ at $Fe(H_2O)_6^{3+}$. Oxidized iron has a strong tendency to form hydroxide complexes and precipitate, except at very low pH. However, little is known about the vibrational properties of molecular Fe^{3+}-hydroxyl species.



Frequencies for ^{56}Fe-dominated +2 and +3 complexes are known from Raman studies in solution, and IR and Raman studies of molecular salts.

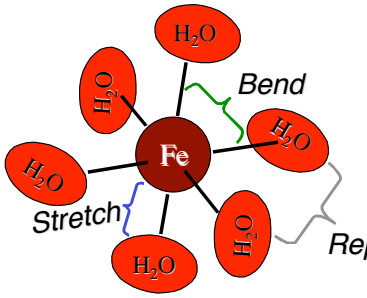
$[Fe(H_2O)_6]^{2+}$		
Vibe	w/^{56}Fe	w/^{54}Fe
1	11.39 THz	?
2	8.99 THz	?
3	11.66 THz	?
4	5.85 THz	?
5	5.76 THz	?
6	? THz	?

$[Fe(H_2O)_6]^{3+}$		
Vibe	w/^{56}Fe	w/^{54}Fe
1	15.29 THz	?
2	13.19 THz	?
3	15.14 THz	?
4	*9.11 THz*	?
5	9.59 THz	?
6	? THz	?

Symmetry arguments (Redlich-Teller) suggest that vibes 3 and 4 are sensitive to Fe-isotope substitution, because these are the only vibrations where the Fe-atom moves.

Take note of Vibe 4 for the Fe^{3+} complex. This vibration will be examined again later in the talk.

Unknown frequencies are predicted with a simple, empirical force field model.



Three spring constants representing bond-stretching, bond-angle bending, and repulsion between non-bonded "atoms". Inertia is calculated assuming ^{56}Fe.

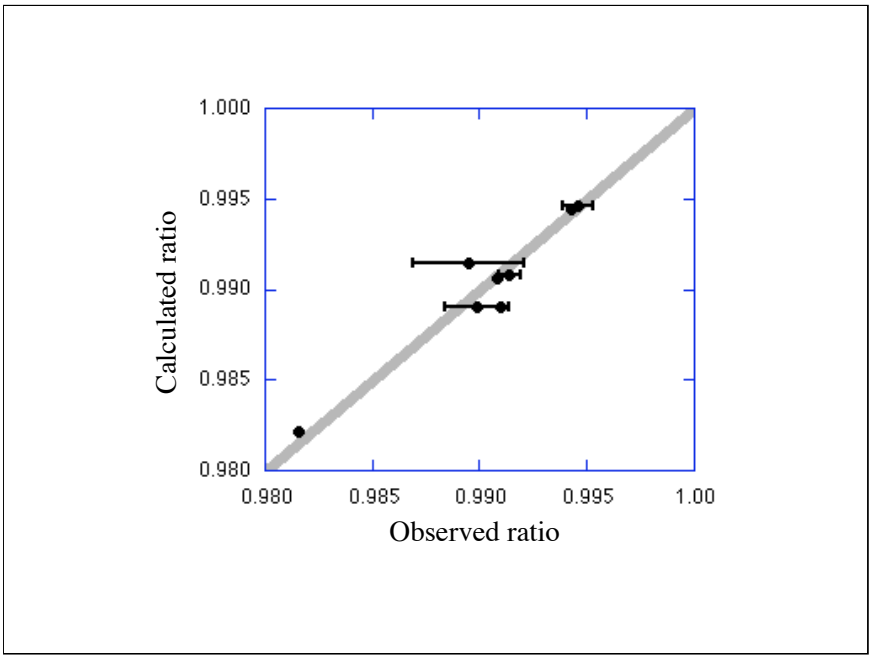
These 3 parameters are fit so that the 5 known frequencies are reproduced as accurately as possible, then the same parameters are used with ^{54}Fe.

This description corresponds to the Modified Urey-Bradley Force Field. Other empirical force field types have been proposed.

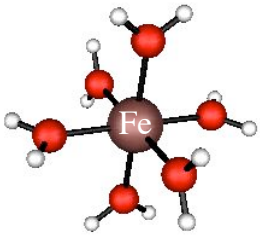
Species	*Studied Isotopes*	*Mode*	*Frequency Ratio (*ν/ν)* *Observed*	*GVFF*	*MUBFF*	*Misfit*
$SiCl_4$	^{28}Si-^{30}Si	ν_3 (F_2)	not obs.	0.9777	0.9779	
		ν_4 (F_2)	not obs.	0.9939	0.9938	
	^{35}Cl-^{37}Cl	ν_3 (F_2)	0.9908	0.9907	0.9906	–0.0002
$SnCl_4$	^{116}Sn-^{124}Sn	ν_3 (F_2)	0.9914±0.0005	0.9911	0.9908	–0.0006
		ν_4 (F_2)	not obs.	0.9909	0.9912	
RuO_4	^{96}Ru-^{102}Ru	ν_3 (F_2)	0.9943±0.0001	0.9944	0.9947	+0.0004
		ν_4 (F_2)	not obs.	0.9937	0.9934	
SF_6	^{32}S-^{34}S	ν_3 (F_{1u})	0.9816	0.9821	0.9821	+0.0005
		ν_4 (F_{1u})	0.9946±0.0007	0.9946	0.9946	Right On
$[SnCl_6]^{2-}$	^{116}Sn-^{124}Sn	ν_3 (F_{1u})	0.9895±0.0026	0.9901	0.9914	+0.0019
		ν_4 (F_{1u})	not obs.	0.9886	0.9874	
$[PdCl_6]^{2-}$	^{104}Pd-^{110}Pd	ν_3 (F_{1u})	0.9899±0.0015	0.9888	0.9890	–0.0009
		ν_4 (F_{1u})	not obs.	0.9926	0.9924	
$[Cr(H_2O)_6]^{3+}$	^{50}Cr-^{53}Cr	ν_3 (F_{1u})	0.991	——	0.989	–0.002

Another source of error is uncertainty in measured frequencies.

In order to check whether this approach is reasonable we can do the same type of calculations on other molecules and complexes where vibrational frequencies of isotopically substituted forms are known. In general, the empirical force field models reproduce measured frequency shifts pretty well, but not perfectly. For Fe, errors of the magnitude shown here suggest model errors of ~1 ‰ in calculated isotopic fractionations.



This is the data from the preceding slide plotted in graphical form. For these examples the force-field calculations usually reproduce measured frequency shifts within the measurement errors. However, there clearly are some significant differences between measured and predicted shifts.



$[Fe(H_2O)_6]^{2+}$		
Vibe	w/^{56}Fe	w/^{54}Fe
1	11.39 THz	same
2	8.99 THz	same
3	11.66 THz	11.73
4	5.85 THz	5.89
5	5.76 THz	same
6	? THz	same

$[Fe(H_2O)_6]^{3+}$		
Vibe	w/^{56}Fe	w/^{54}Fe
1	15.29 THz	same
2	13.19 THz	same
3	15.14 THz	15.24
4	*9.11 THz*	9.16
5	9.59 THz	same
6	? THz	same

Accounting for excited vibrational states at 25ºC, $\Delta E(vib) \approx -14$ J/mol for the exchange reaction:

$$[^{56}Fe(H_2O)_6]^{2+} + [^{54}Fe(H_2O)_6]^{3+} \leftrightarrow [^{54}Fe(H_2O)_6]^{2+} + [^{56}Fe(H_2O)_6]^{3+}$$

At equilibrium, $^{56}Fe/^{54}Fe$ will be about 5 ‰ higher in the Fe^{3+} complex -- suggesting that significant inorganic fractionations can occur during reduction/oxidation at low temperatures.

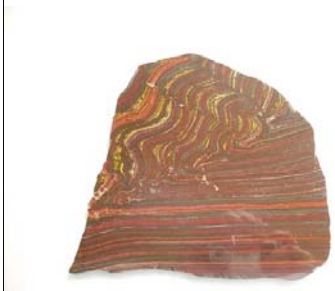
The empirical force-field models predict that only two vibrational frequencies (Vibes 3 and 4) will shift when ^{54}Fe is substituted for ^{56}Fe. We would expect, then, that these are the only two vibrations where the Fe-atom moves. Keep this in mind when we look at Cr-isotope fractionations later.

$[Fe(H_2O)_6]^{2+}$ vs. $[Fe(H_2O)_6]^{3+}$ results (25 ºC)

At Equilibrium $Fe^{3+}_{(Aq)}$ has higher $^{56}Fe/^{54}Fe$ than $Fe^{2+}_{(Aq)}$

Prediction: 5.4 ‰ ± 1 ‰ (This work)
Several ‰ (*Polyakov* -- Mössbauer)
2.5 - 3.5 ‰ (Anbar et al., in press)

Measurement: 3.0 ± 0.3 ‰ (*Johnson et al.*)

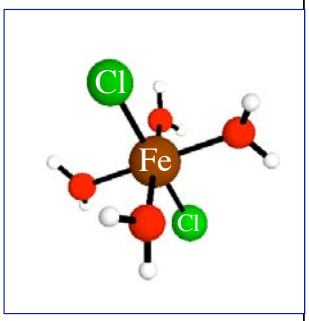


Conclusion:
For heavy elements (at least up to atomic #26, mass 56), equilibrium stable-isotope fractionations can be caused by redox reactions, changing bond-partners and coordination.

Limitations of Empirical Force Fields:

Limitations of empirical force fields

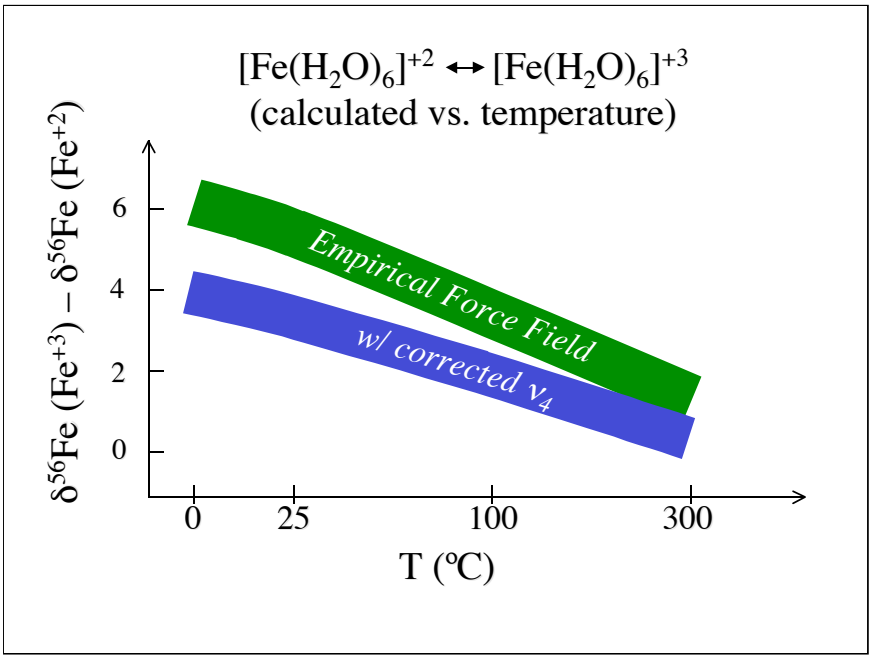
Force-field parameters must be fit to measured properties.



- There must be enough data, of high quality, for fitting.
- Independent verification of model parameters is not straightforward.
- Measurement errors cause model errors. The ν_4 bending vibration in $Fe^{3+}_{(Aq)}$ is probably at ~6 THz, not 9 THz. (Anbar et al., 2004), causing fractionation to be overestimated by 1-2 ‰

Anbar et al. created a force-field using first-principles quantum chemistry - - discussed in the next section.

The cited reference is Anbar et al. (2004) Theoretical investigation of iron isotope fractionation between $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{2+}$: Implications for iron stable isotope geochemistry. Geochimica et Cosmochimica Acta, v. 69, p. 825-837.



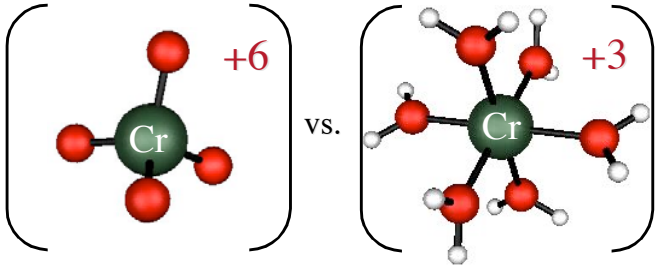
Simply using the lower vibrational frequency calculated by Anbar et al. (2004) corrects most of the apparent disagreement between measured and predicted isotopic fractionation in this system. With empirical force-fields you need good input data to get good output data!

Problem 2:

Can chromium isotopes tell us about the fate of Cr^{6+} in groundwater?

^{50}Cr	^{52}Cr	^{53}Cr	^{54}Cr
4.3%	83.8%	9.5%	2.4%

$$\delta^{53}Cr = \left(\frac{\left(\frac{^{53}Cr}{^{52}Cr}\right)_{Sample}}{\left(\frac{^{53}Cr}{^{52}Cr}\right)_{Standard}} - 1 \right) * 1000$$



$[Cr^{6+}O_4]^{2-}$ — *Oxidized, soluble, toxic(?)*

$[Cr^{3+}(H_2O)_6]^{3+}$ — *Reduced, insoluble, benign*

The Cr^{3+} complex modeled here is very similar to the $Fe^{2+/3+}$-H_2O complexes from the preceding section.

Ab initio force field

- No fitted parameters: quality can be checked by comparing model result with observed molecular structures and vibrational frequencies.
- Useful calculations are feasible for small molecules (≤ 50 atoms).
- Relatively low-level theory seems to be adequate for many molecules (at least as good as empirical FF's)

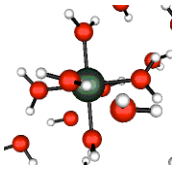
BUT:

- Only molecules and clusters only for transition elements
- Only non-magnetic minerals w/simple structures
- Systematic errors in computed frequencies

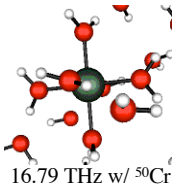
For Cr we'll use *ab initio* force-fields (B3LYP/6-31Gd) for comparison with empirical force fields.

The final caveat is particularly important -- even adequate *ab initio* methods tend to systematically over-estimate or under-estimate vibrational frequencies of most molecules. It is important to always check against measured vibrational frequencies if they are available, and apply a scale factor if necessary.

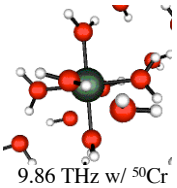
Observed frequencies vs. (ab initio) frequencies



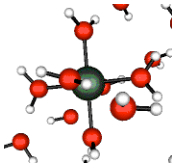
16.19 THz
(15.20 THz)



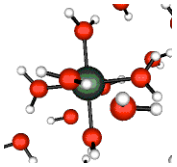
16.79 THz w/ ^{50}Cr
(16.18 THz)
shifts 0.15 THz w/ ^{53}Cr
(0.17 THz)



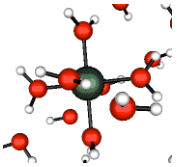
9.86 THz w/ ^{50}Cr
(9.09 THz)
shifts 0.03 THz w/ ^{53}Cr
(0.04 THz)



15.05 THz
(13.68 THz)



9.59 THz (9.26 THz)
(shifts < 0.01 THz w/ ^{53}Cr)



(6.0 THz w/ ^{50}Cr)
(shifts 0.04 THz w/ ^{53}Cr)

Notice that there are 4 vibrational modes where the Cr-atom moves, as opposed to only 2 predicted by the empirical models of Fe-H_2O complexes. This complexity may partly explain why the calculated Fe-isotope fractionations were slightly larger than measured fractionations -- but careful analysis of the models suggests that the error in the measured "Vibe 4" frequency of the Fe^{3+} complex, if real, is most important.

Results (25 °C):

$[Cr^{6+}O_4]^{2-}$ *vs.* $[Cr^{3+}(H_2O)_6]^{3+}$

$^{53}Cr/^{52}Cr$ 5 ‰ *higher in* $[Cr^{6+}O_4]^{2-}$

(Empirical FF)

$^{53}Cr/^{52}Cr$ 6-7 ‰ *higher in* $[Cr^{6+}O_4]^{2-}$

(Ab initio)

$[Cr^{6+}O_4]$ *vs.* $Cr^{3+}{}_2O_3$ *crystal*

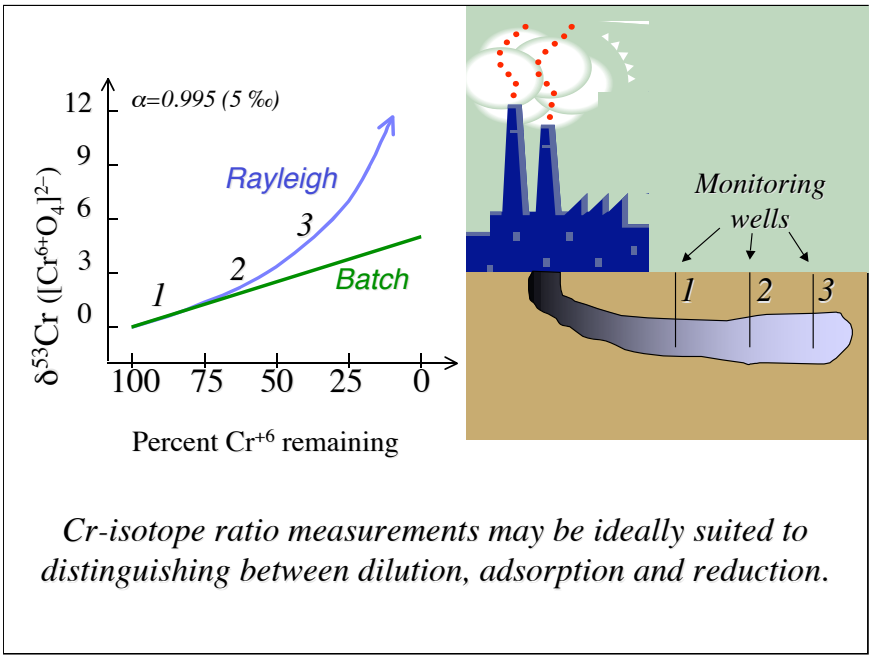
$^{53}Cr/^{52}Cr$ 6 ‰ *higher in* $[Cr^{6+}O_4]^{2-}$

(Ab initio and Empirical FF)

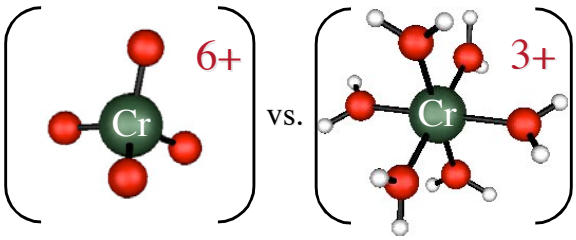
$^{53}Cr/^{52}Cr$ 5 ‰ *higher in* $[Cr^{6+}O_4]^{2-}$

(Empirical FF)

As yet there has not been an experimental calibration of the equilibrium isotope fractionation between Cr^{6+} and Cr^{3+} in solution.



This figure borrows from work by Tom Johnson and André Ellis, discussed in more detail in chapter 9 of the RiMG volume cited in the first slide.



$[Cr^{6+}O_4]^{2-}$ $[Cr^{3+}(H_2O)_6]^{3+}$

Predicted fractionation (equilibrium): 5-7 ‰	Measured fractionation (kinetic): 3.5 ‰ (Ellis et al.)

Conclusion:
The reduction Cr^{6+} and subsequent precipitation of Cr^{3+} should leave the remaining Cr^{6+} enriched in heavy isotopes. Similar isotopic tracing of reduction is possible for $[ClO_4]^-$, organochlorides, etc..

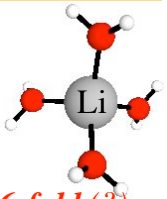
Remediation reactions of many toxic groundwater species seems to involve substantial isotopic fractionation. If these fractionations are larger relative to fractionations in adsorption, they may be ideally suited to unravelling the relative importance of reaction, adsorption, and dilution in controlling abundance variations of dissolved pollutants.

What controls lithium-isotope fractionation?

^{6}Li	^{7}Li
7.5%	92.5%

$$\delta^{7}Li = \left(\frac{\left(\frac{^{7}Li}{^{6}Li}\right)_{Sample}}{\left(\frac{^{7}Li}{^{6}Li}\right)_{Standard}} - 1 \right) * 1000$$

Seawater is highly enriched in ^{7}Li (by ~30 ‰) relative to sediments. Mantle, riverine lithium are intermediate. Li-isotopes have been used to trace fluids evolved in subduction zones, and the weathering of continents.



- *Lithium always occurs as* Li^{+},
- *is probably coordinated to* H_2O, OH^{-}, *or* O_{br} *in most minerals & dilute solutions (like seawater),*
- *has a fixed electronic structure (no d-electrons).*

•Coordination in solution 4-fold, in minerals 6-fold (?)

Qualitative analysis can be made for other elements, including Mg and Ca. These elements don't exhibit much redox chemistry in terrestrial environments, and are usually bonded to some form of oxygen (OH^{-}, H_2O, etc.). Biological molecules, however, can be more diverse -- take for example the Mg-N bonds in chlorophyll -- and may have distinctive fractionation behaviors as a result. Kinetically controlled fractionations may also be important for these elements.

What are the oceanic sinks for platinum-group elements?

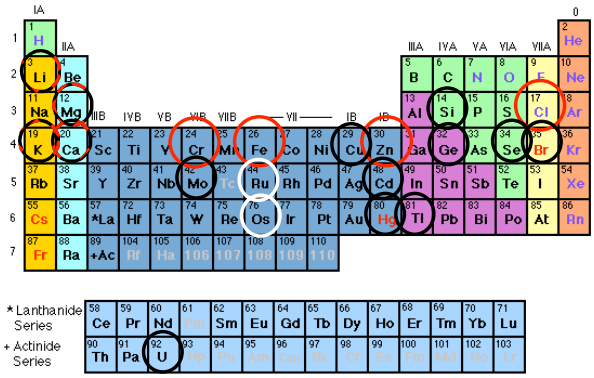
^{96}Ru	^{98}Ru	^{99}Ru	^{100}Ru	^{101}Ru	^{102}Ru	^{104}Ru
5.5%	1.9%	12.7%	12.6%	17.1%	31.6%	18.6%

^{184}Os	^{186}Os	^{187}Os	^{188}Os	^{189}Os	^{190}Os	^{192}Os
0.02%	1.6%	~2%	13.3%	16.1%	26.4%	41.0%

Produced by ^{187}Re decay

- *Ru and Os both occur naturally in a zoo of oxidation states, from 8+ (OsO_4) to 2+ (RuS_2), even 0 (Pt-alloy). Oxidized forms (≥ 6+) may be more mobile than intermediate and reduced forms.*
- *In oxidized form, commonly bonded to O, OH^- groups, Cl^- may also be an important bond partner. In reduced form, sulfides or organic molecules.*

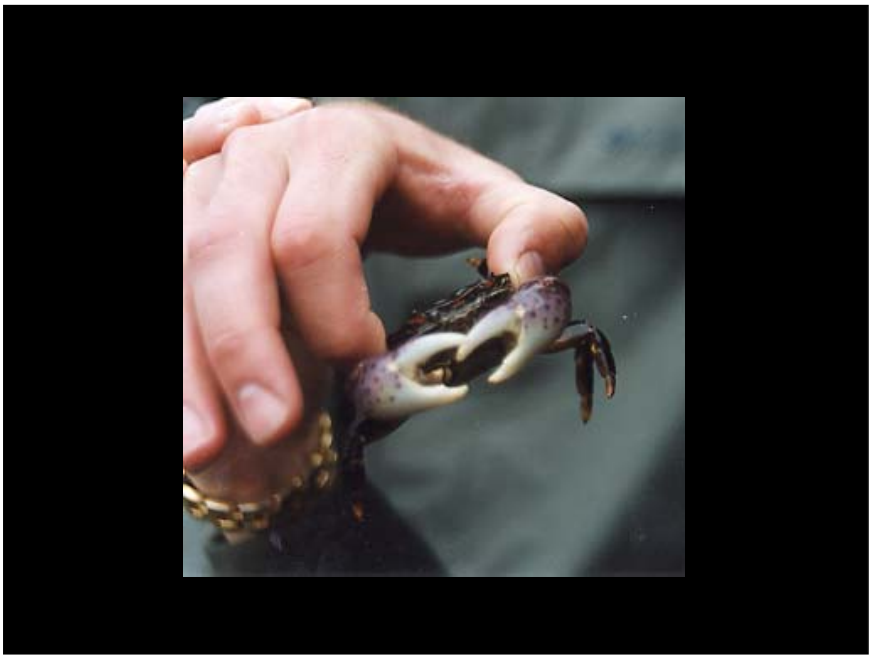
Fixation into oxidized vs. anoxic sediment, partial removal in estuaries are likely to cause significant, possibly characteristic stable-isotope fractionation, as observed for Mo (*Barling et al.*)



Conclusions:

1. Theory can provide a basic quantitative framework for understanding stable-isotope fractionations of light and intermediate-mass elements.

2. *Ab initio* force fields, where appropriate, are particularly suited to the problem of estimating unknown vibrational frequencies.



Talk given at the MSA short course on the Geochemistry of Non-traditional Stable Isotopes in Montréal on May 15, 2004.

Please feel free to contact the author if you have any questions or comments.

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