Isotope effects - towards isotope chemistry

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Definitions

Isotope effects

Kinetic isotope effect:
Change in chemical reaction rates when the atoms is replaced with different isotope

- Can be used to determine preferable reaction pathways for optimization
- Change is most pronounced with large differences - effect is related to vibration of the bonds

Isotope effects

Isotope fractionation:
Relative partitioning or distribution of isotopes in a natural system based on their mass

- **Mass/Kinetic**: separation is due to mass differences; in biology, organisms prefer lighter isotopic species
- **Equilibrium/Thermodynamic**: species in chemical eq.; due to reduction in vibrational energy in the substitution of a heavier isotope with a lighter one
- **Transient kinetic**: reactions do not follow first-order reaction rates
- **Mass-independent**: differences are not correlated to mass differences; non-equilibrium processes

Literature cases

Literature division

Biology

- Focus is on Ca, H/D and O
- Mostly plants, though some bacteria have been studied
- Fractionation is attributed to transfer processes

Geology/geochemistry

- Use of 'standard' samples
- Use of 'surrogates'
- Different metals are studied in the context of mineral formation

Common themes in the literature

- Lighter isotopes make weaker bonds within molecules
- 'Standards' that are used are very much not standard - its all comparative
- Too many factors that would need controls for characterization
- Processes for fractionation are not well understood in geology/geochemistry
- Use of fractionation to infer environmental conditions such as $[O_2]$

Fractionation and Wine

A study was done to use NMR techniques to perform analysis on wine.

They note some interesting things:

- Enrichment techniques had previously been used for studies of photosynthesis
- Info about the redistribution of H isotopes in the process of turning glucose and must into ethanol and water
- Constant distribution of isotope 'redistribution' matrix allowed for 'fingerprinting' for a specific region
    - Isotope ratios are of climatic significance

Word of the day:

Isotopemer: *noun* isotopic isomer; same number of each isotope with the molecule but at different positions in the structure

Martin, G. J. *et al.*. J. Agric. Food Chem. 36, 2 (1988) 316-322

Calcium

Hart and Zindler:

- Proposed that a 'mixing' process during fractionation is the cause of deviations between experiment and theory

Hindshaw *et al.*:

- Significant fractionation is observed in soil and root samples
- Age plays a factor, since nutrient uptake changes with time
- More fractionation in the roots than the stems
- Incomplete kinetic reactions favour lighter Ca isotopes

Wang *et al.*:

- The [M] has an effect on O bond lengths and may be tied to fractionation

Hart, S. R. and Zindler, A. Int. J. Mass Spectrom. Ion Pro. 89 (1989) 287-301

Hindshaw, R. S. *et al.* Biogeochemistry 112 (2013) 373-388

Wang, W. *et al.* Geochim. Cosmochim. Acta 208 (2017) 185-197

Uranium

Andersen *et al.*:

- Difference in solubility of the charge states will impact fractionation
- Heavier U isotopes favour compounds with lower oxidation states
    - Opposite to mass dependent effects, which are due to vibrations
- Studies with no U redox show limited fractionation

Yang & Liu:

- Nuclear field shift effect may decrease with temperature - also called the nuclear volume effect (?)
- Effect scales with the difference of mean-square charge radius

Andersen, M. B, Stirling, C. H. and Weyer, S. Rev. Mineral Geochem. 82 (2017) 799-850

Yang, S. and Liu, Y. Acta Geochim. 35(3) (2016) 227-239