How do we express differences in stable isotope abundance?

UNIT 2

Fractionation Factor

$$a = \frac{R_2}{R_1}$$

The Fractionation Factor a describes the relative reaction rates for the two isotopes.

Fractionation Factor

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For example:

R_1 = Ca Isotope Ratio of calcium carbonate precipitated in water
R_2 = Ca Isotope Ratio of the Water

Fractionation Factor

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For example:

$$a = \frac{\left(\frac{^{44}Ca}{^{40}Ca}\right)_{Calcit}}{\left(\frac{^{44}Ca}{^{40}Ca}\right)_{Water}}$$

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<u>For example</u>:

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Fractionation Factor

$$\alpha_{Calcit-Water} = \frac{(^{44}Ca/^{40}Ca)_{Calcit}}{(^{44}Ca/^{40}Ca)_{Water}}$$

- Phase Transition
- direction, liquid to solid
- Incomplete chemical reaction

α is a small number, usual change occurs on the 2nd and 3rd place behind the dezimal point!

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Fractionation Factor

Heavy isotope above light isotope!

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Fractionation Factor

Stable isotope composition is expressed in d (delta) notation:

$$\delta R \text{ in } ‰ = \left[\frac{R_{sample}}{R_{standard}} - 1 \right] \times 1000$$

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R is

- the isotope ratio of the HEAVY / LIGHT isotopes in either your sample or a standard i.e. $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{44}Ca/^{40}Ca$, $^{88}Sr/^{86}Sr$
- a very small number

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Because R_{sample} never deviates much from $R_{standard}$ (natural variation in isotope ratios is limited), $[(R_{sample} / R_{standard})-1]$ is a small number.

In order to make the variation more apparent, one multiplies the value by 1000, thereby expressing the value in per mil (parts per thousand; ‰) notation.

Fractionation Factor

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Delta notation indicates the isotope ratio in your sample relative to a standard.

If the isotope ratio in your sample equals the standard, $R_{sample}/R_{standard} = 1$ and $dR = 0‰$

The International Atomic Energy Association (IAEA) maintains a set of standards used for stable isotope measurements.

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- are available to everybody in sufficient amounts

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- are homogenous in concentration and compositon

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- avoid contamination during sample processing

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Standards …

- are available to everybody in sufficient amounts
- are homogenous in concentration and compositon
- have no alteration during storage
- avoid contamination during sample processing
- work with internal lab standards calibrated to an international standard

Notation

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$$\delta^{26}Mg = \left(\frac{{}^{26}Mg/{}^{24}Mg_{sample}}{{}^{26}Mg/{}^{24}Mg_{standard}} - 1 \right) * 1000$$

$$\delta^{44/40}Ca = \left(\frac{{}^{44}Ca/{}^{40}Ca_{sample}}{{}^{44}Ca/{}^{40}Ca_{standard}} - 1 \right) * 1000$$

$$\delta^{88/86}Sr = \left(\frac{{}^{88}Sr/{}^{86}Sr_{sample}}{{}^{88}Sr/{}^{86}Sr_{standard}} - 1 \right) * 1000$$

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$\delta^{44/40}Ca$ = 0:

Sample and standard are equal.

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The heavy isotope (^{44}Ca) is enriched in the sample relative to the standard.

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$\delta^{44/40}Ca < 0$:

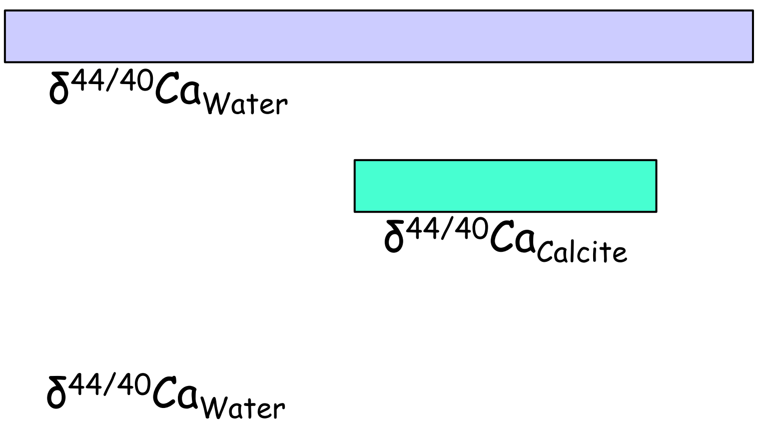
The light Isotope (^{40}Ca) is enriched in the sample relative to the standard.

Ratio and Difference

It is $\alpha \approx \ln \alpha$ if α is sufficiently small, it can be used to determine the isotope fractionaton factor from the difference of the different reservoirs:

For example:

$$\Delta \approx 1000 \cdot \ln \alpha_{Calcite-Water} \approx \delta^{44/40}Ca_{Calcite} - \delta^{44/40}Ca_{Water}$$



The δ-Notation is like a <u>material constant</u>, alone it is not telling something about fractiontion

The Δ-Notation <u>describes the process</u> and may depend on environmental factors. It makes the proxy chacracteristics.

Isotope Fractionation Factor – Difference vs. Ratio!

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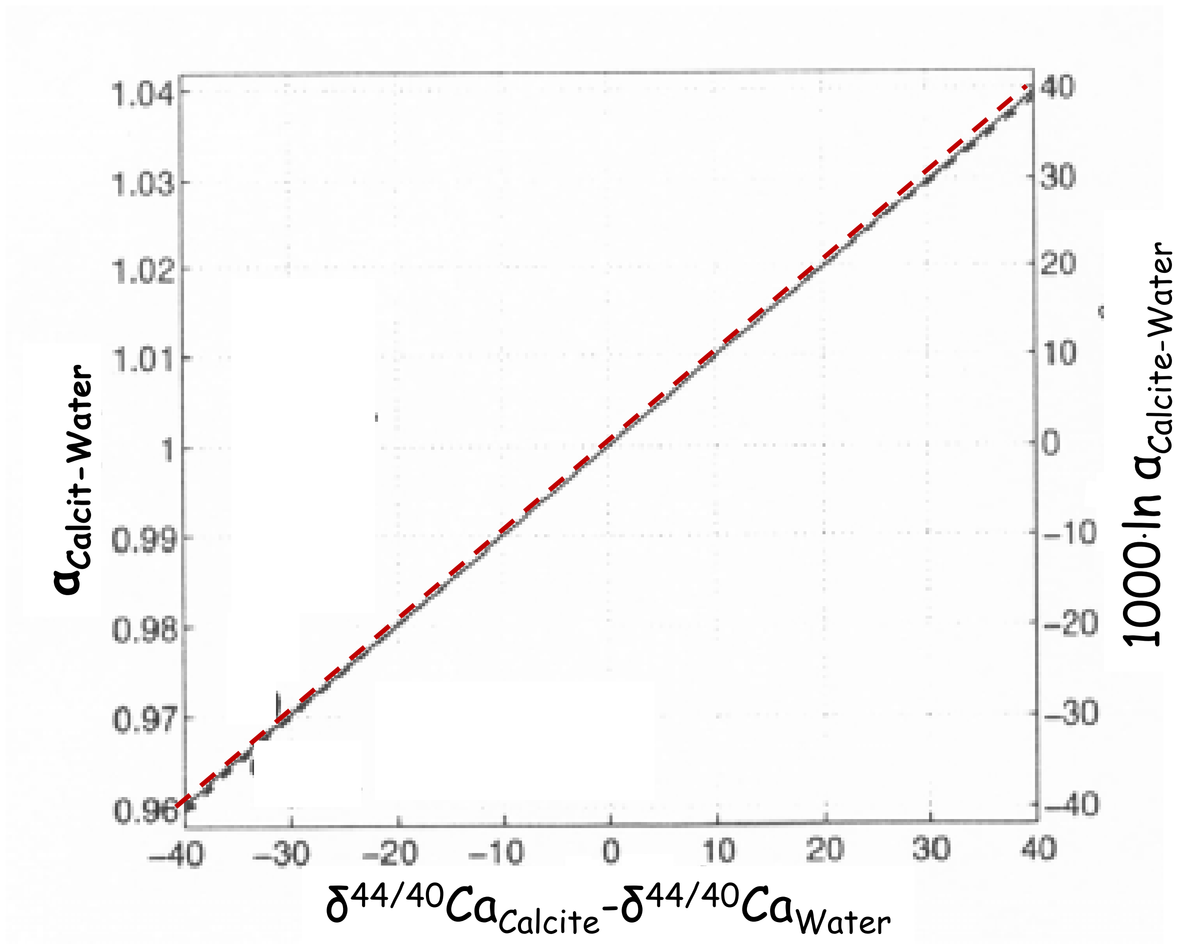

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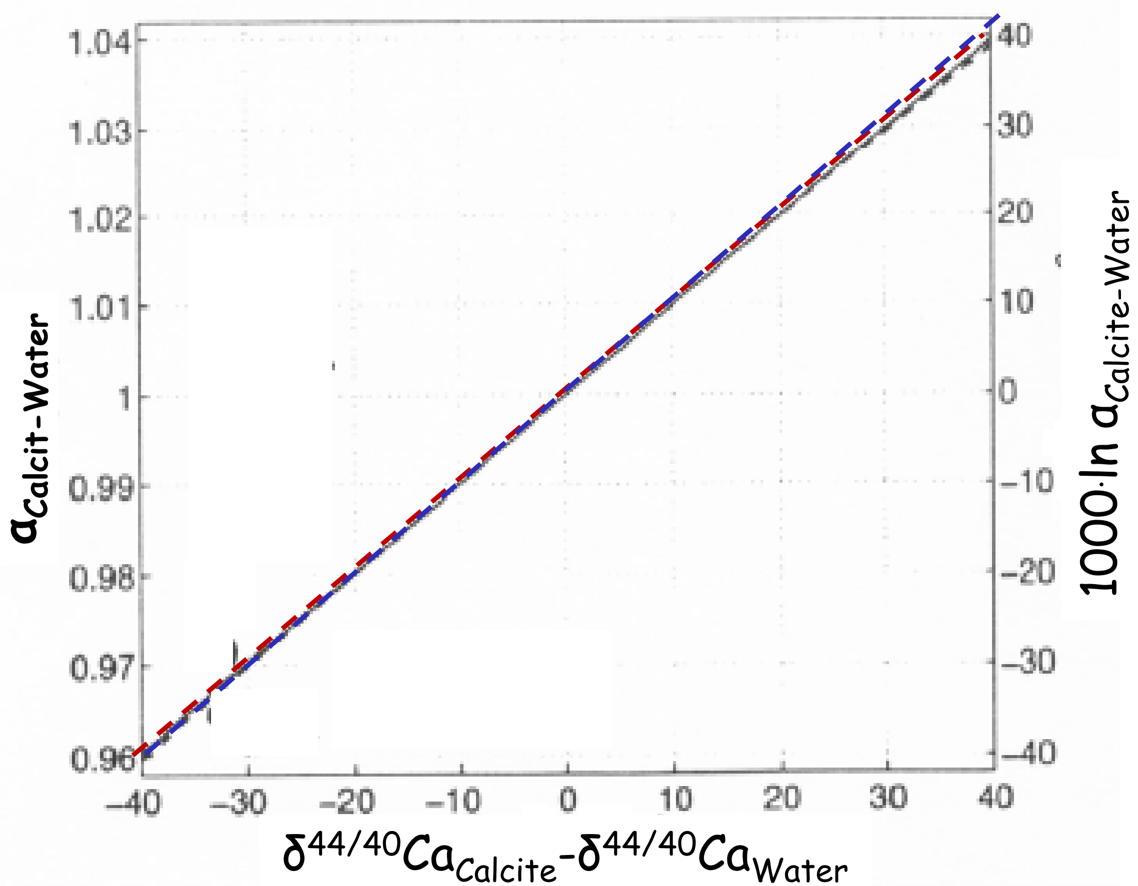

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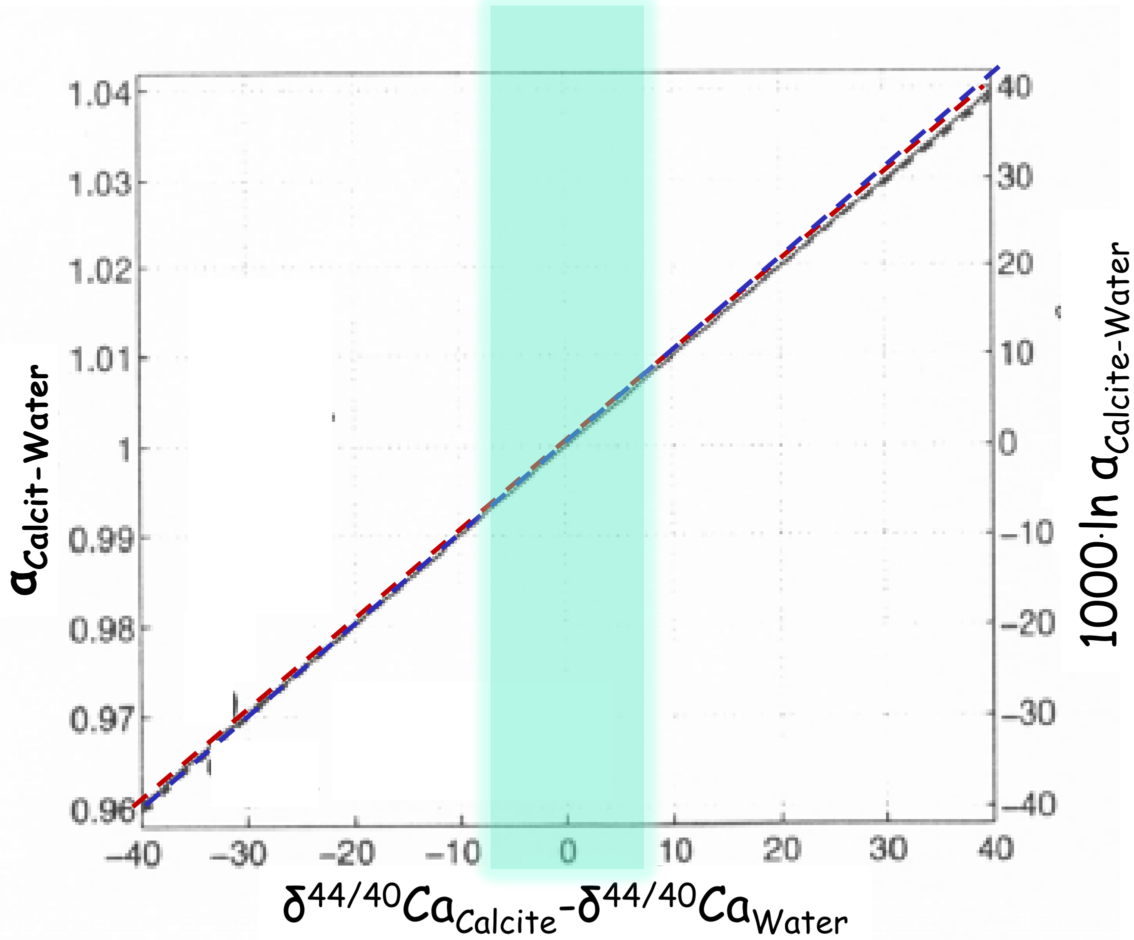

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Requirements for isotope fractionation:

1. Phase transitions

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2. Independent phase reservoirs

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2. Independent phase reservoirs
3. Incomplete chemical reactions

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