# Key equations · Stable isotopes

Sedimentary Geochemistry (MSc) · Lecture 1 · WS 2026/27 · keep this sheet for every assignment

## 1 · Ratio and δ

$$R = \text{heavy} / \text{light} \quad (D/H,\ {}^{13}C/{}^{12}C,\ {}^{18}O/{}^{16}O,\ {}^{34}S/{}^{32}S)$$

$$\delta = (R_{sample} / R_{standard} - 1) \times 1000\ [‰]$$

- δ > 0: enriched in the heavy isotope (heavier) than the standard; δ < 0: depleted (lighter)
- **−5 ‰ is heavier than −10 ‰** (more positive = heavier)
- A δ value without its standard means nothing: write **‰ VSMOW** or **‰ VPDB**. Against what?

## 2 · Standards and conversion

$$\delta^{18}O_{VSMOW} = 1.03091 \times \delta^{18}O_{VPDB} + 30.91$$

$$\delta^{18}O_{VPDB} = 0.97002 \times \delta^{18}O_{VSMOW} - 29.98$$

- VSMOW for waters; VPDB for carbonates; $\delta^{13}C$ always vs VPDB
- Never mix values from the two scales in one equation

Coplen et al. (1983) Nature 302, 236–238

## 3 · Fractionation factor and shortcuts

$$\alpha_{A-B} = R_A/R_B = (1000 + \delta_A) / (1000 + \delta_B)$$

$$\varepsilon_{A-B} = (\alpha - 1) \times 1000 \quad \Delta_{A-B} = \delta_A - \delta_B$$

- Small fractionations, δ near 0 ‰: $\Delta \approx \varepsilon \approx 10^3 \ln \alpha$
- In general $\Delta \approx \varepsilon\ (1 + \delta_B/1000)$; at 20–30 ‰ use the exact equations
- Order matters: $\alpha_{water–calcite} = 1 / \alpha_{calcite–water}$

## 4 · Calcite–water thermometer

$$10^3 \ln \alpha_{calcite-water} = 18.03\ (10^3/T) - 32.42 \quad (T \text{ in K})$$

Kim & O'Neil (1997) GCA 61, 3461–3475; calibrated 10–40 °C

Worked example, 25 °C, seawater 0 ‰ VSMOW: $10^3 \ln \alpha = 28.05 \rightarrow \alpha = \exp(28.05/1000) = 1.02845 \rightarrow \delta_{calcite} = 1.02845 \times 1000 - 1000 = +28.45$ ‰ VSMOW = **−2.38 ‰ VPDB**

## 5 · Mass balance (mixing)

$$\delta_{mix} = \Sigma\ f_i\ \delta_i, \quad f_i = V_i / \Sigma V$$

2 L at −10 ‰ + 3 L at +2 ‰ → (2×(−10) + 3×2)/5 = **−2.8 ‰** (not the simple mean, −4 ‰)

## 6 · Rayleigh distillation and meteoric waters

$$R_{vapour} = R_0 \cdot f^{(\alpha-1)} \quad \delta_{rain} = \alpha(\delta_{vapour} + 1000) - 1000$$

$$\delta^2H = 8\ \delta^{18}O + 10 \quad d = \delta^2H - 8\ \delta^{18}O$$

f = fraction of vapour remaining · global meteoric water line: Craig (1961) · deuterium excess: Dansgaard (1964)

## 7 · Sense of scale

| | |
|---|---|
| Vapour vs the water it evaporates from | ≈ 9–10 ‰ lighter in $^{18}O$ ($\alpha_{liquid–vapour}$ = 1.0098 at 20 °C; Majoube 1971) |
| Carbonate $\delta^{18}O$ and temperature | calcite ≈ 0.2 ‰ lighter per °C → 1 ‰ ≈ 4–5 °C (same water) |
| Precipitation | temperature ≈ 0.5–0.7 ‰/°C · altitude ≈ −0.15 to −0.5 ‰ per 100 m (global mean −2.8 ‰/km) · polar ice ≈ −25 to −60 ‰ |
| Analytical precision | carbonate $\delta^{18}O$ and $\delta^{13}C$: better than ≈ ±0.1 ‰ |

**Three checks before you hand in:** (1) a change is **final − initial**, keep the signs in brackets; (2) a mixture must lie **between its end-members**, closer to the larger one; (3) every number in one equation is on **the same scale** (VSMOW or VPDB), and per mil is ×1000, not ×100.

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