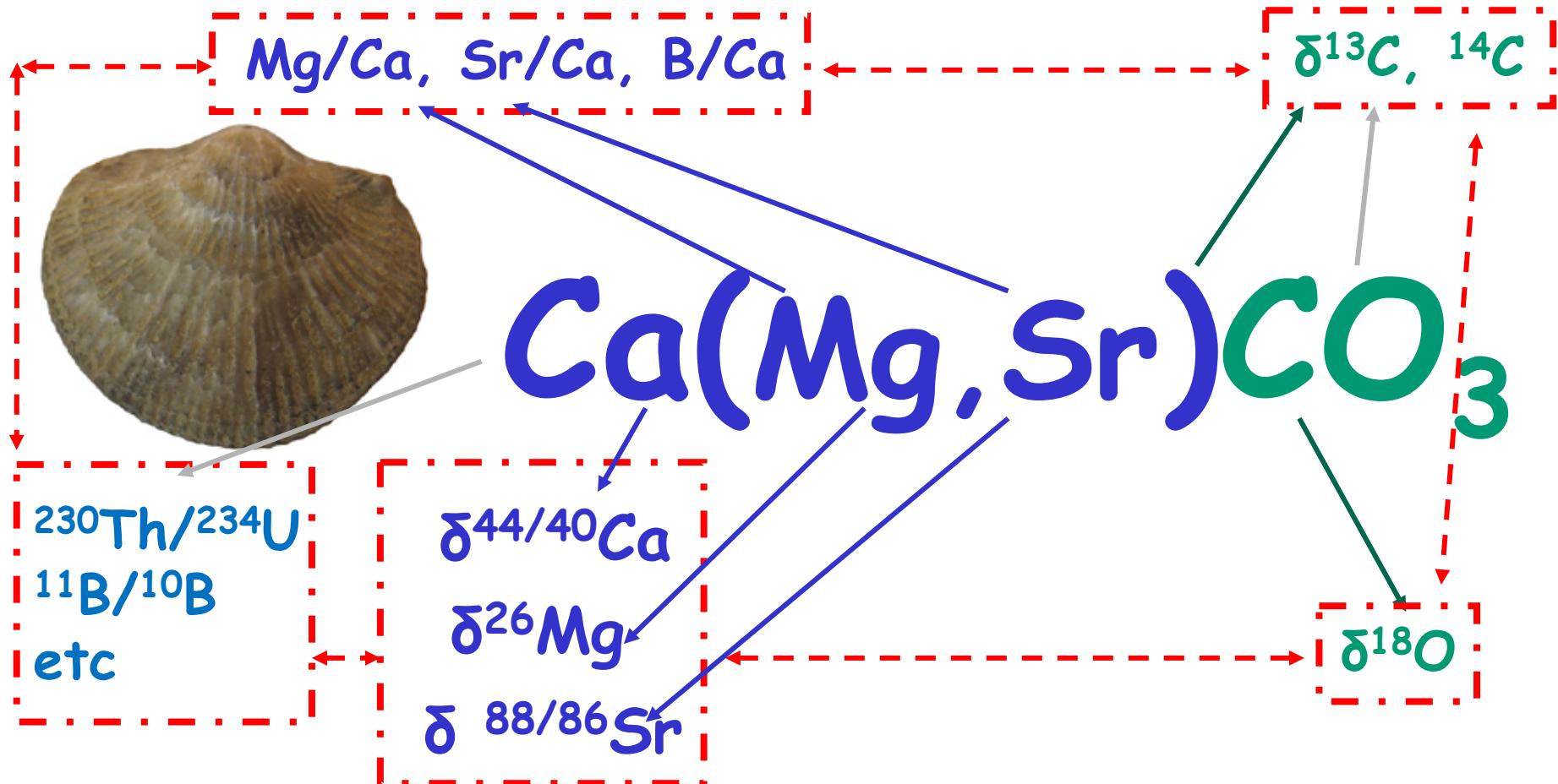


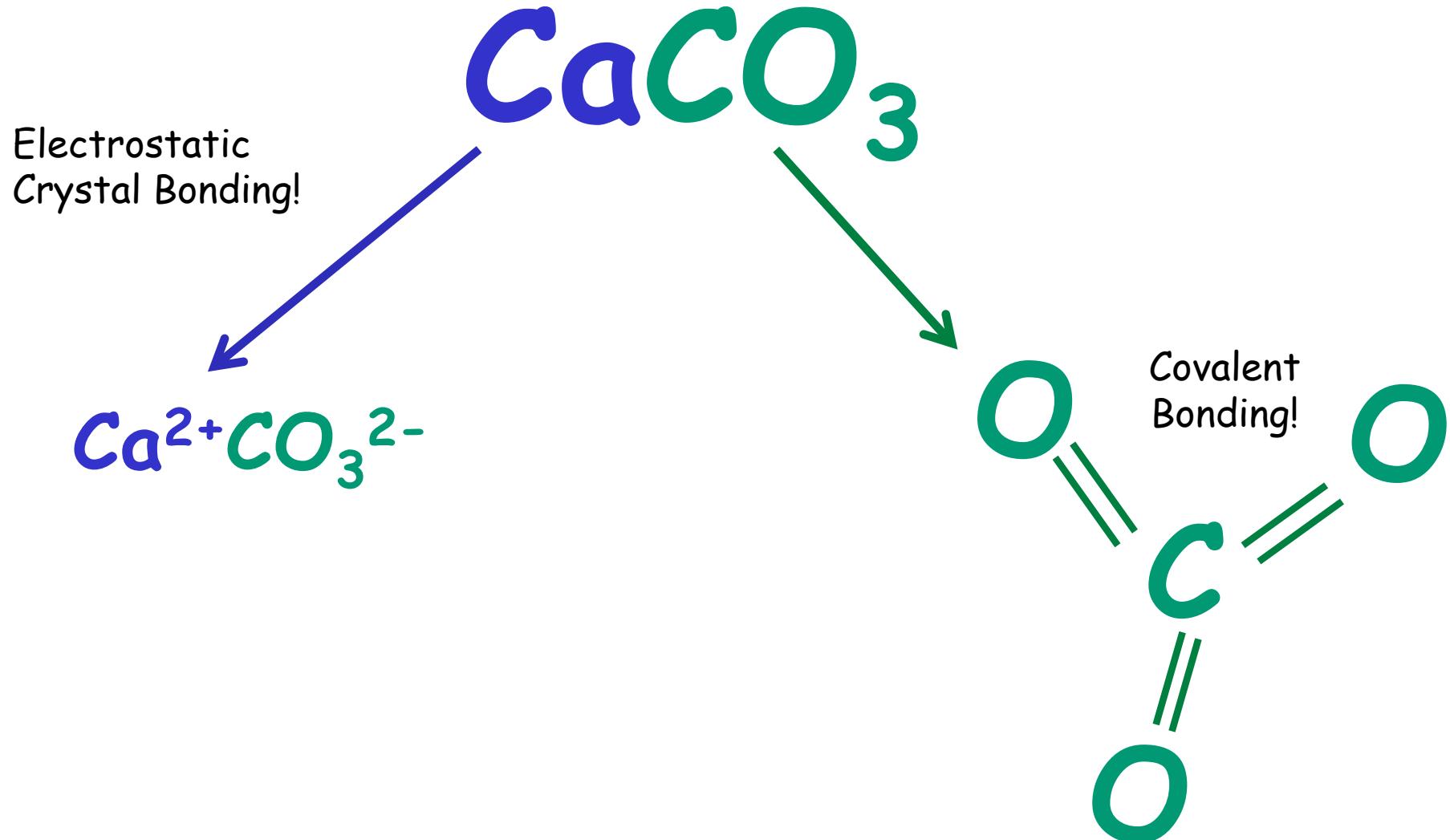
Application of isotope fractionation?

UNIT 4

Multi-Proxy Approach

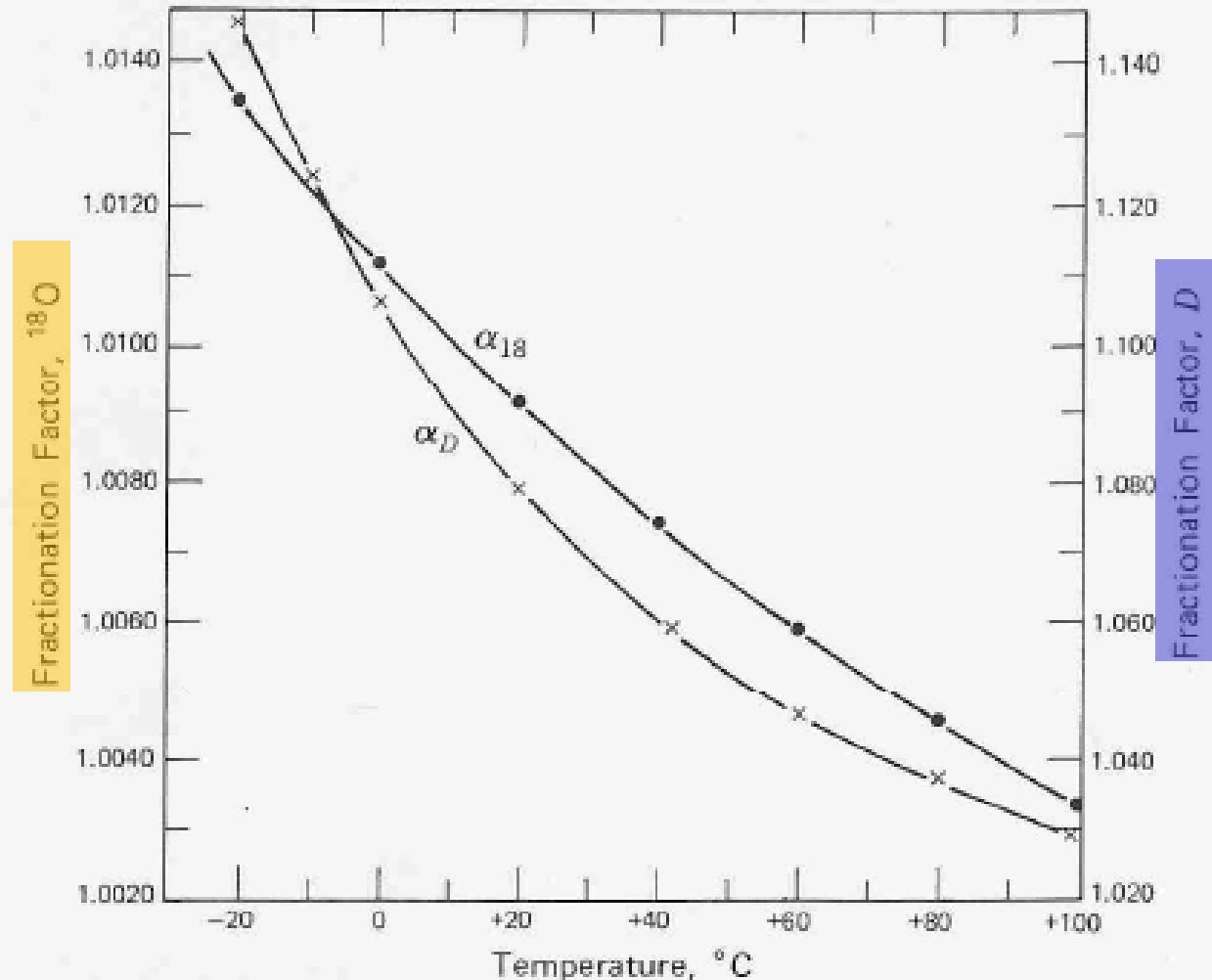


Type of bonding matters



Example

Temperature Isotope Fractionation of Hydrogen and Oxygen Isotopes in Calcite



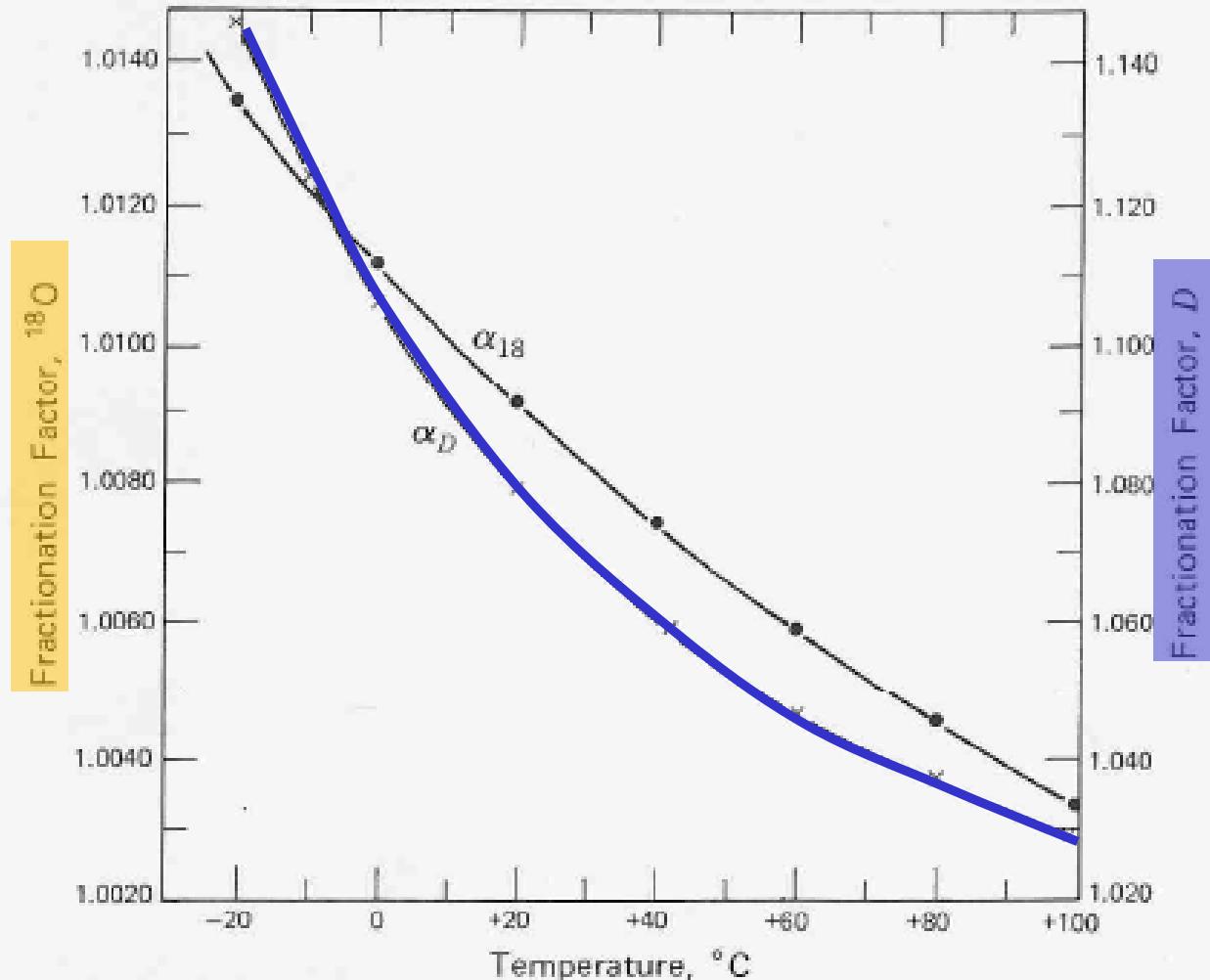
$$\alpha(^{\circ}\text{C}) = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{Calcit}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{Water}}}$$

Temperature Dependence!!!

The higher the water temperature the calcite precipitated from, the lower is the Fractionation factor!

Example

Temperature Isotope Fractionation of Hydrogen and Oxygen Isotopes in Calcite



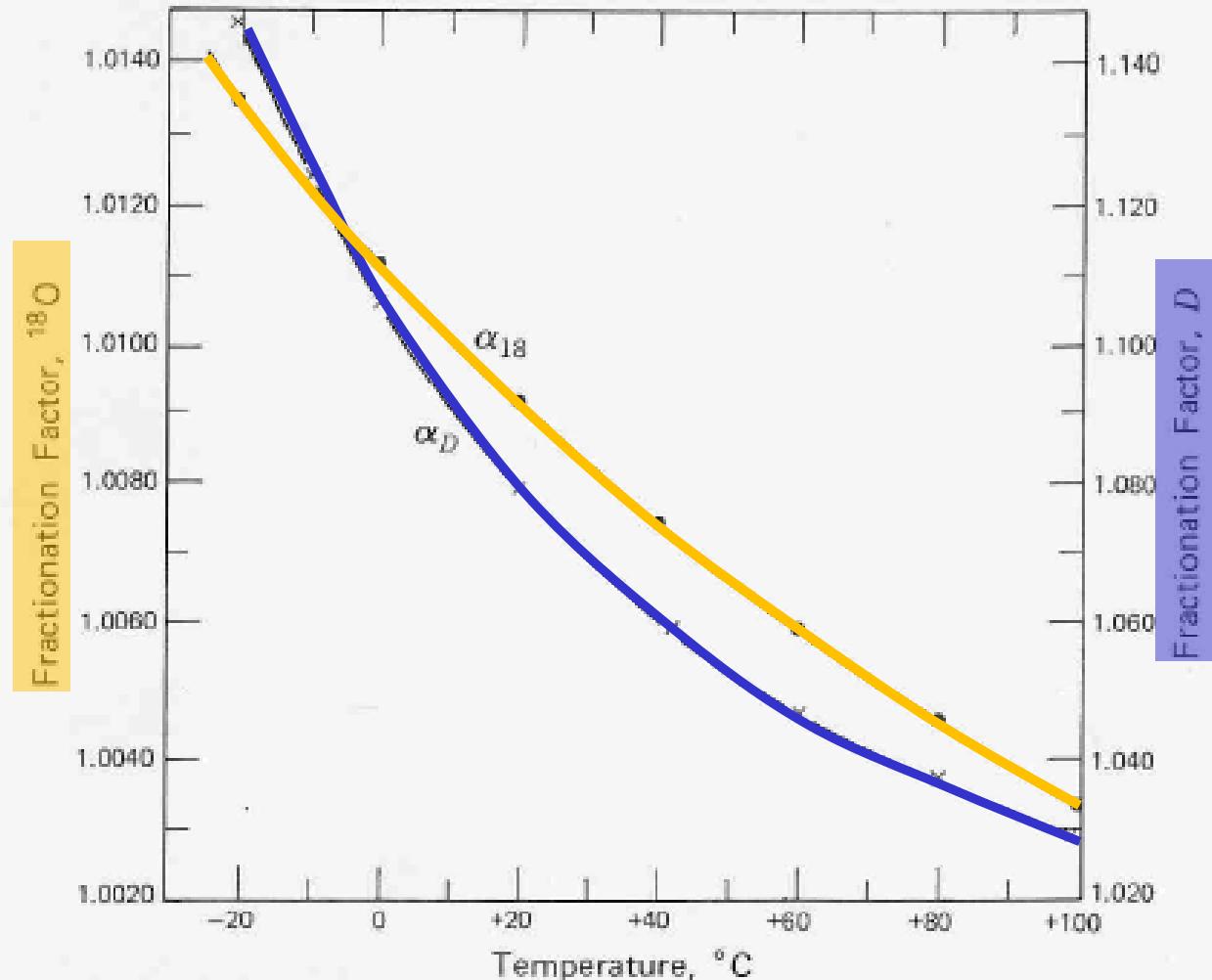
$$\alpha(\text{°C}) = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{Calcit}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{Water}}}$$

Temperature Dependence!!!

The higher the water temperature the calcite precipitated from, the lower is the Fractionation factor!

Example

Temperature Isotope Fractionation of Hydrogen and Oxygen Isotopes in Calcite

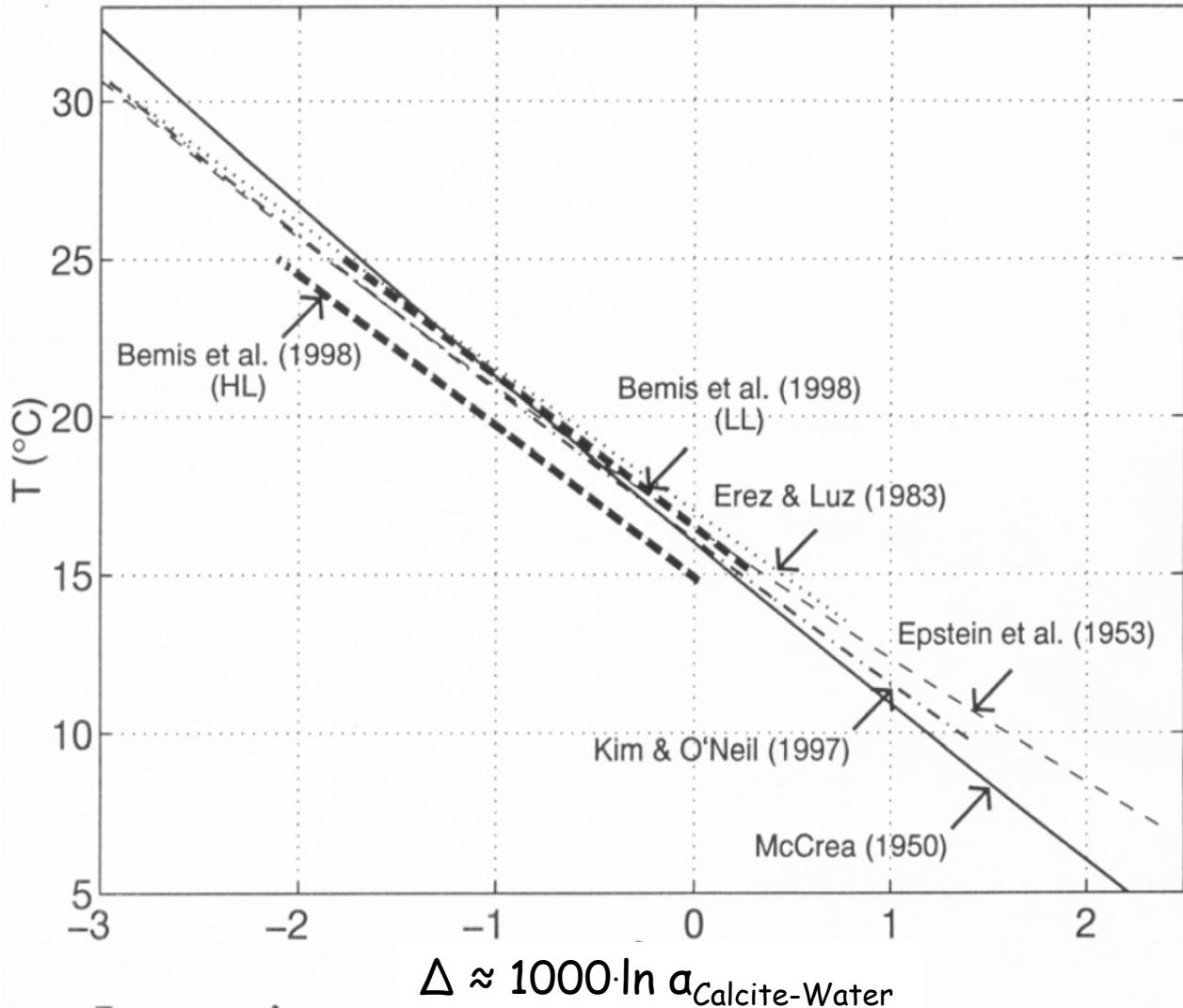


$$\alpha(^{\circ}\text{C}) = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{Calcit}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{Water}}}$$

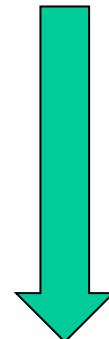
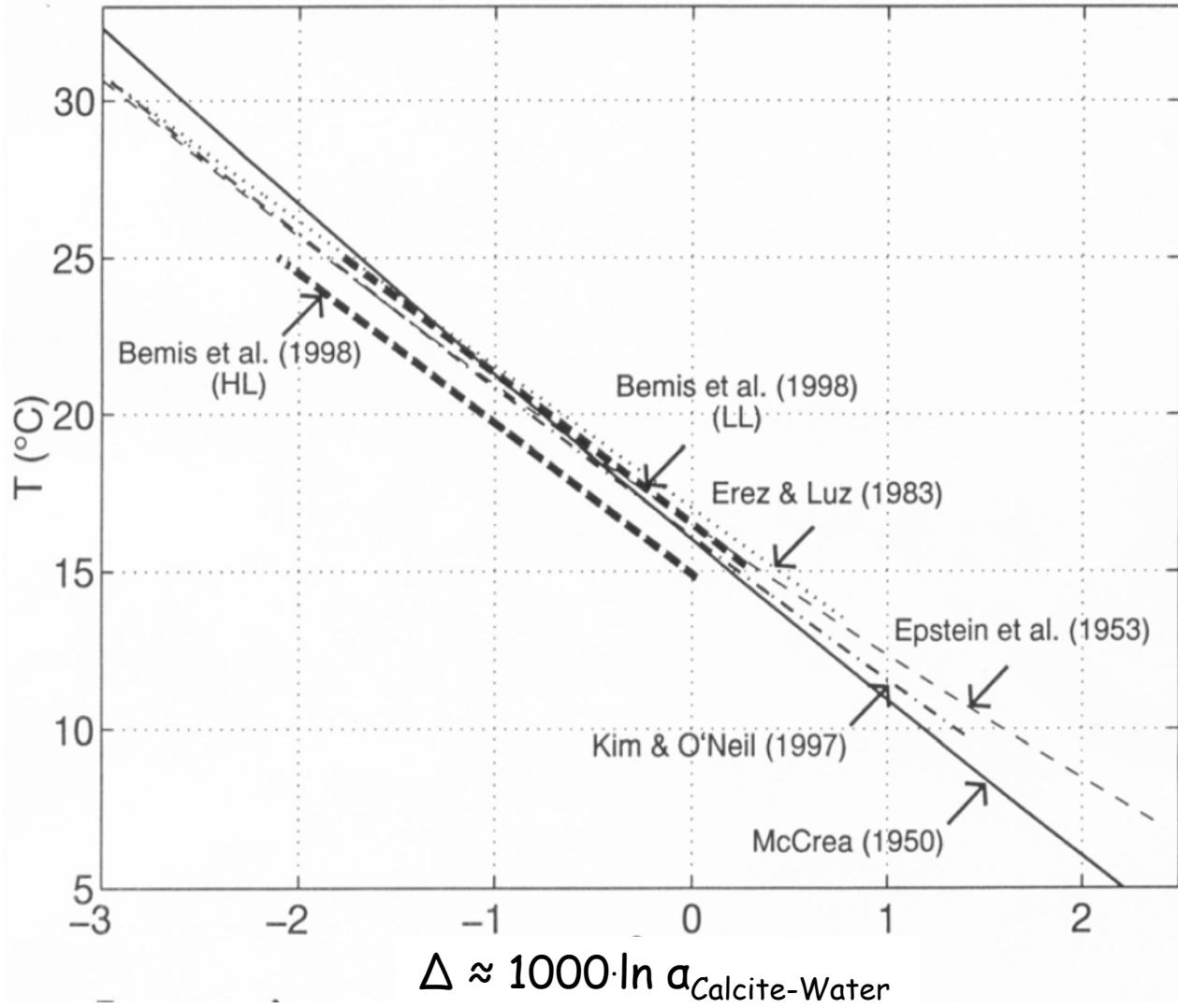
Temperature Dependence!!!

The higher the water temperature the calcite precipitated from, the lower is the Fractionation factor!

Temperature



Temperature



Future:
 Clumped isotopes: Δ_{47}
 are independent of this
 knowledge

Temperature

Condition for a reliable proxy:

Temperature

Condition for a reliable proxy:

- Primary signal (exclude diagenesis)

Temperature

Condition for a reliable proxy:

- Primary signal (exclude diagenesis)
- Sufficient and sensitive calibration

Temperature

Condition for a reliable proxy:

- Primary signal (exclude diagenesis)
- Sufficient and sensitive calibration
- Species specific calibration

Temperature

Condition for a reliable proxy:

- Primary signal (exclude diagenesis)
- Sufficient and sensitive calibration
- Species specific calibration
- Isotope composition of past seawater has to be known

Temperature

Condition for a reliable proxy:

- Primary signal (exclude diagenesis)
- Sufficient and sensitive calibration
- Species specific calibration
- Isotope composition of past seawater has to be known
- Independent of only one environmental parameter

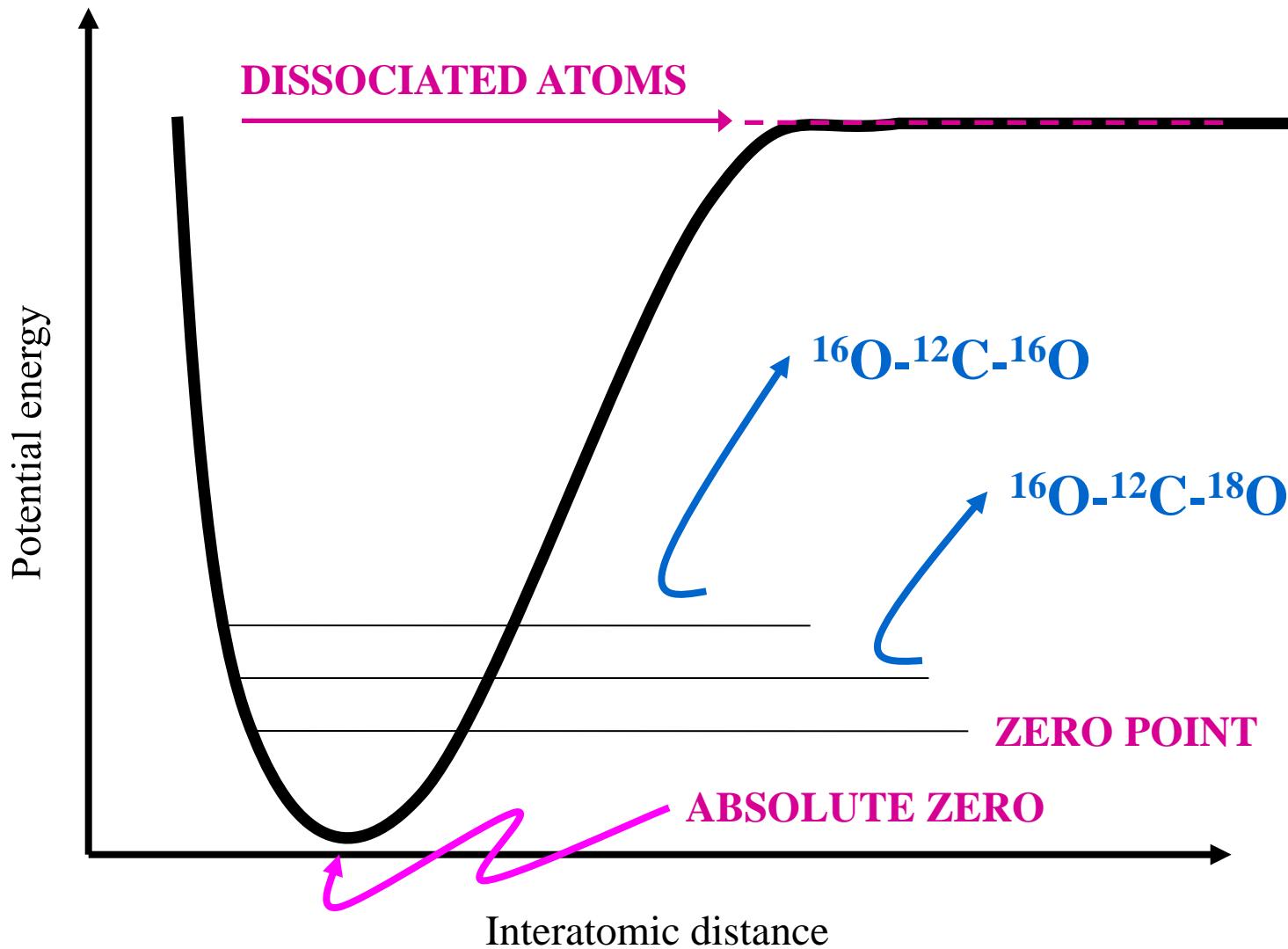
Temperature

Condition for a reliable proxy:

- Primary signal (exclude diagenesis)
- Sufficient and sensitive calibration
- Species specific calibration
- Isotope composition of past seawater has to be known
- Independent of only one environmental parameter
- Knowledge of past oxygen isotope composition

Physio - Chemical differences

Isotope effect associated with zero-point energy:



Equilibrium Fractionation

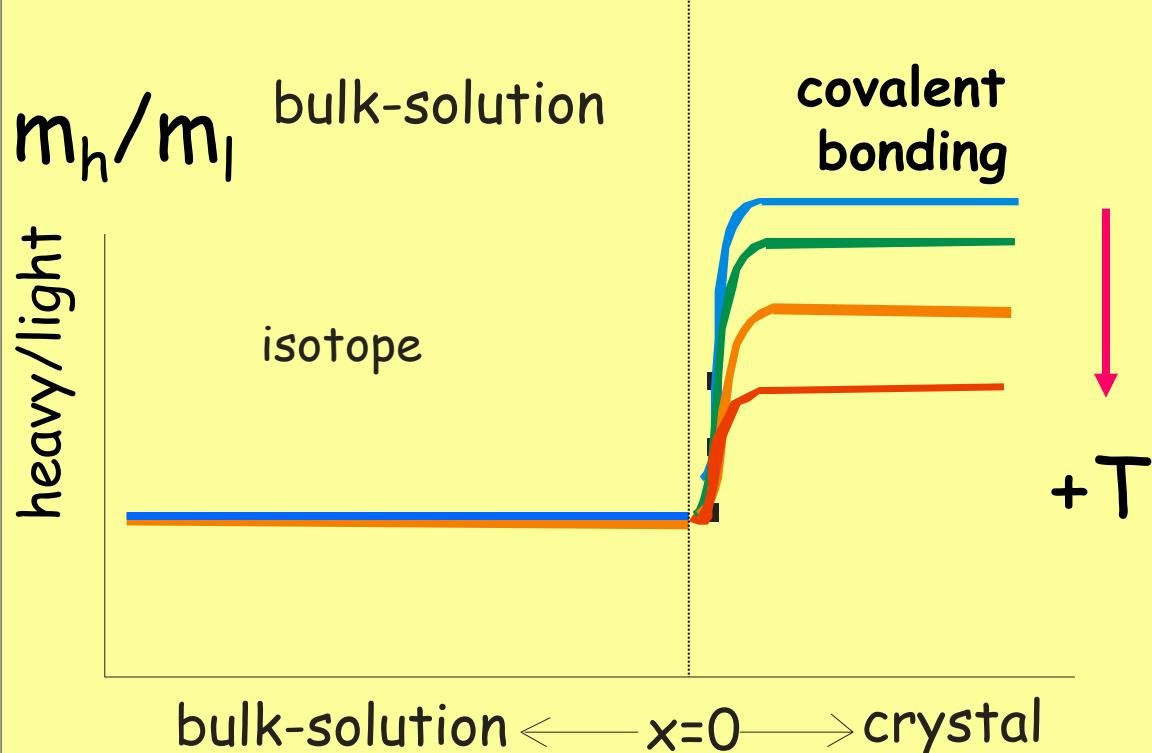
II. Understanding of Natural Dependent $^{44}\text{Ca}/^{40}\text{Ca}$ Fractionation

m_h = heavy isotope

m_l = light isotope

Equilibrium fractionation tends to enrich the **heavy** isotope with decreasing temperature!

Equilibrium Fractionation



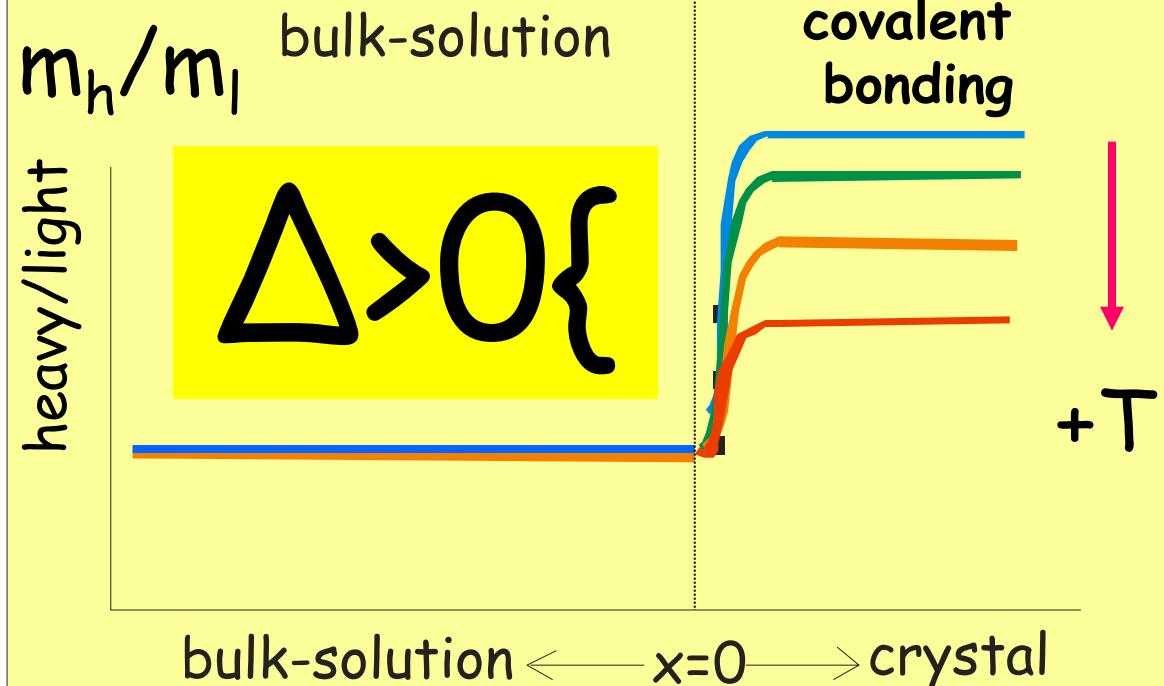
Equilibrium Fractionation

II. Understanding of Natural Dependent $^{44}\text{Ca}/^{40}\text{Ca}$ Fractionation

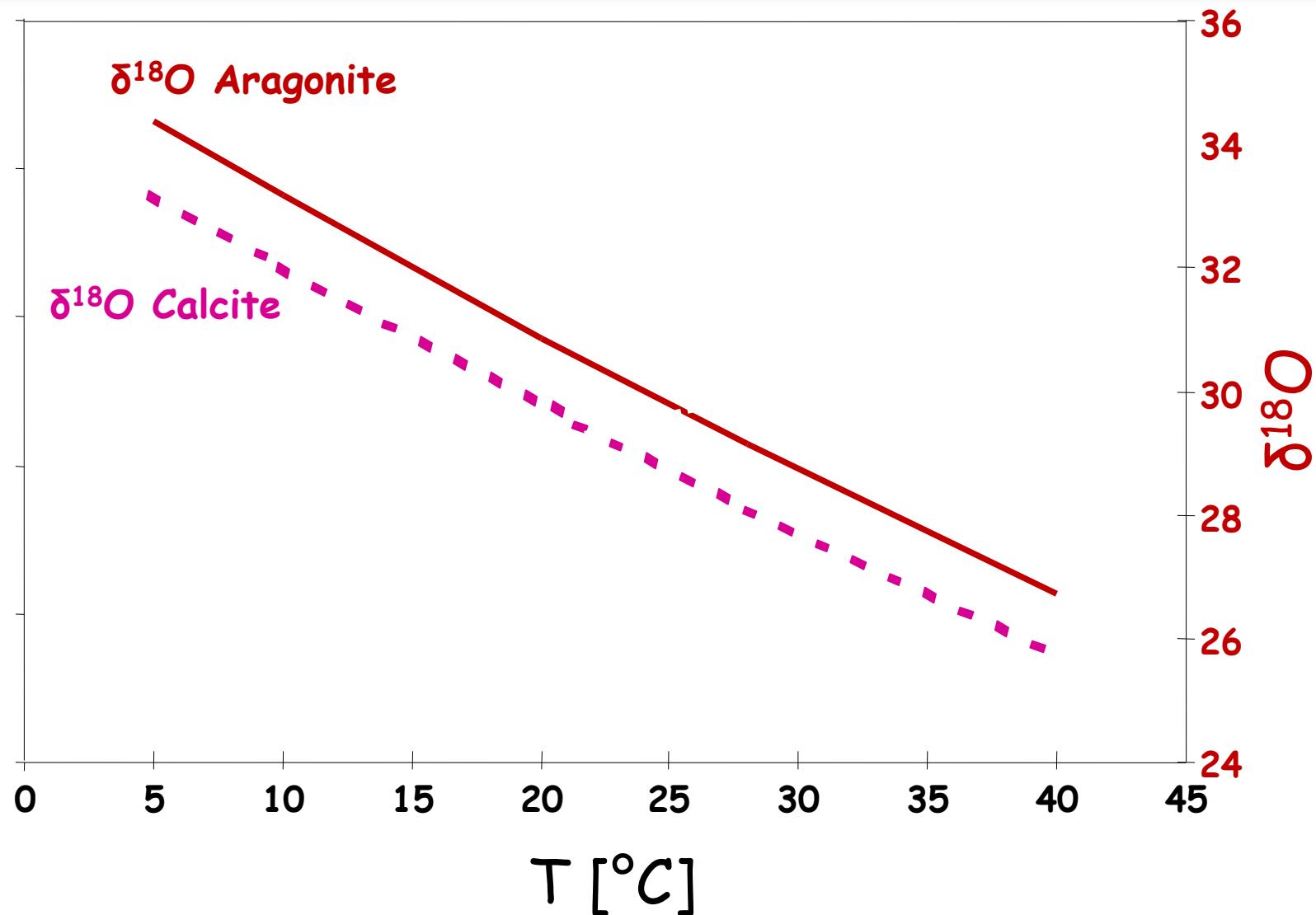
m_h = heavy isotope
 m_l = light isotope

Equilibrium fractionation
tends to enrich the **heavy**
isotope with decreasing
temperature!

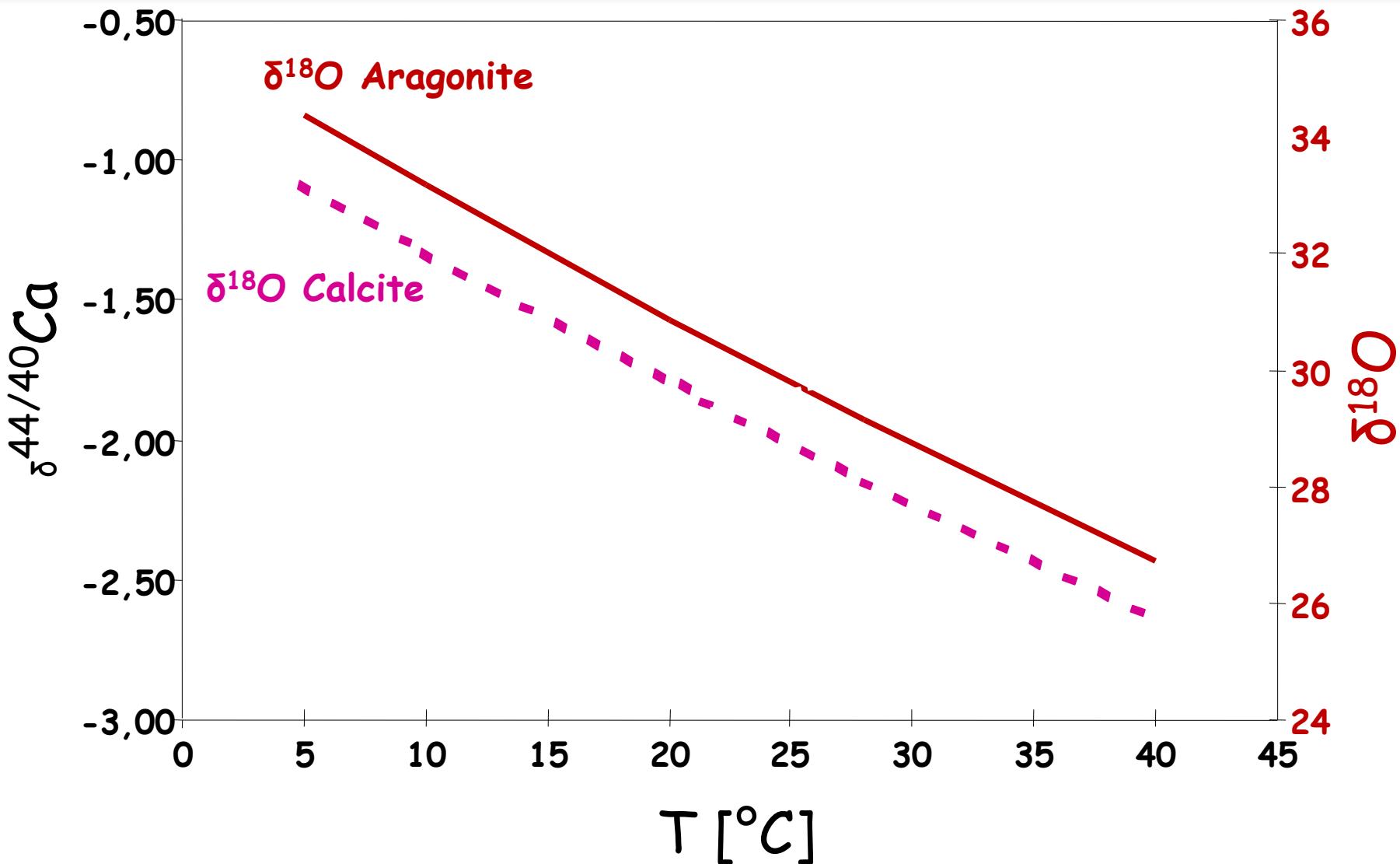
Equilibrium Fractionation



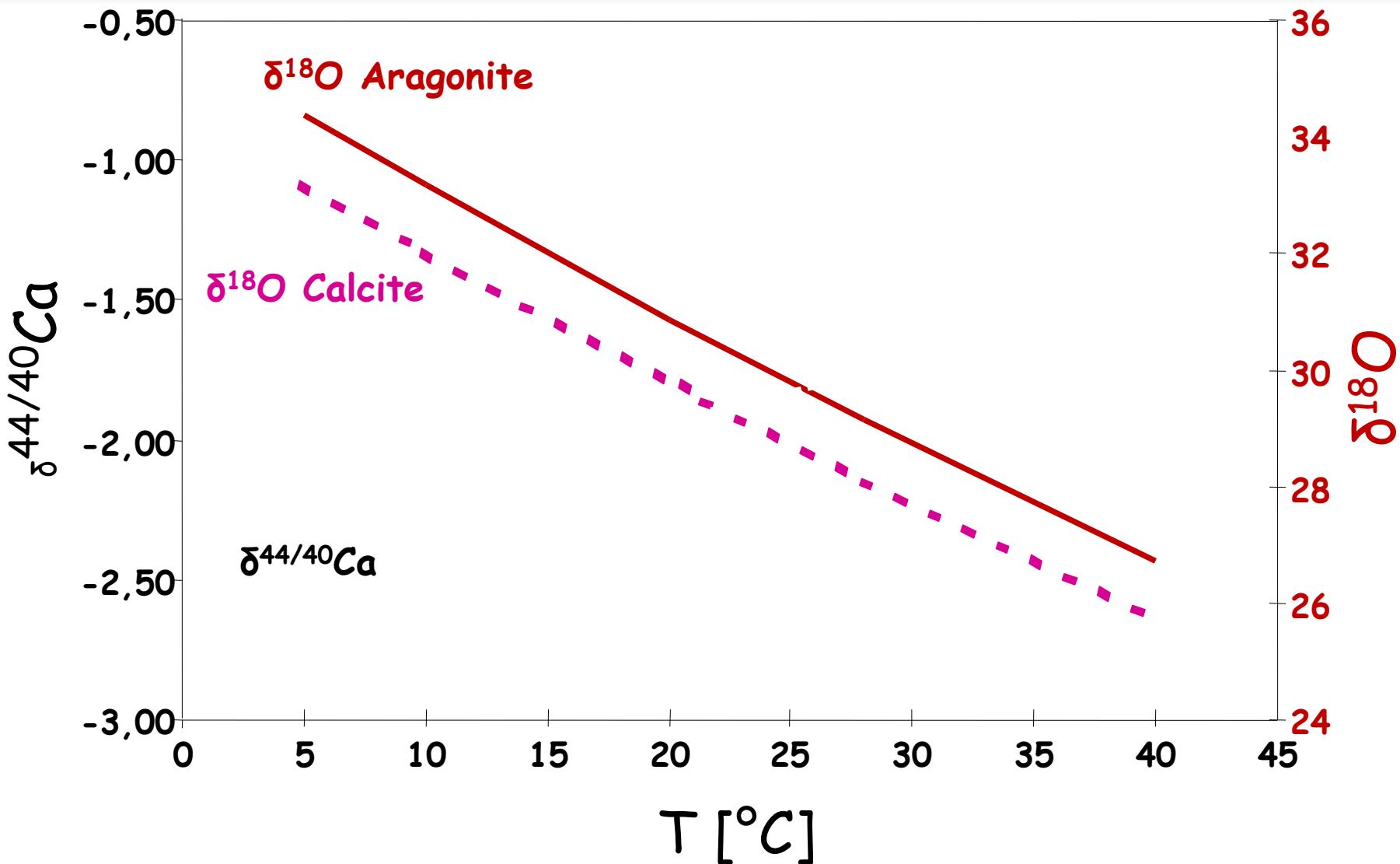
Kinetic vs. Equilibrium Fractionation



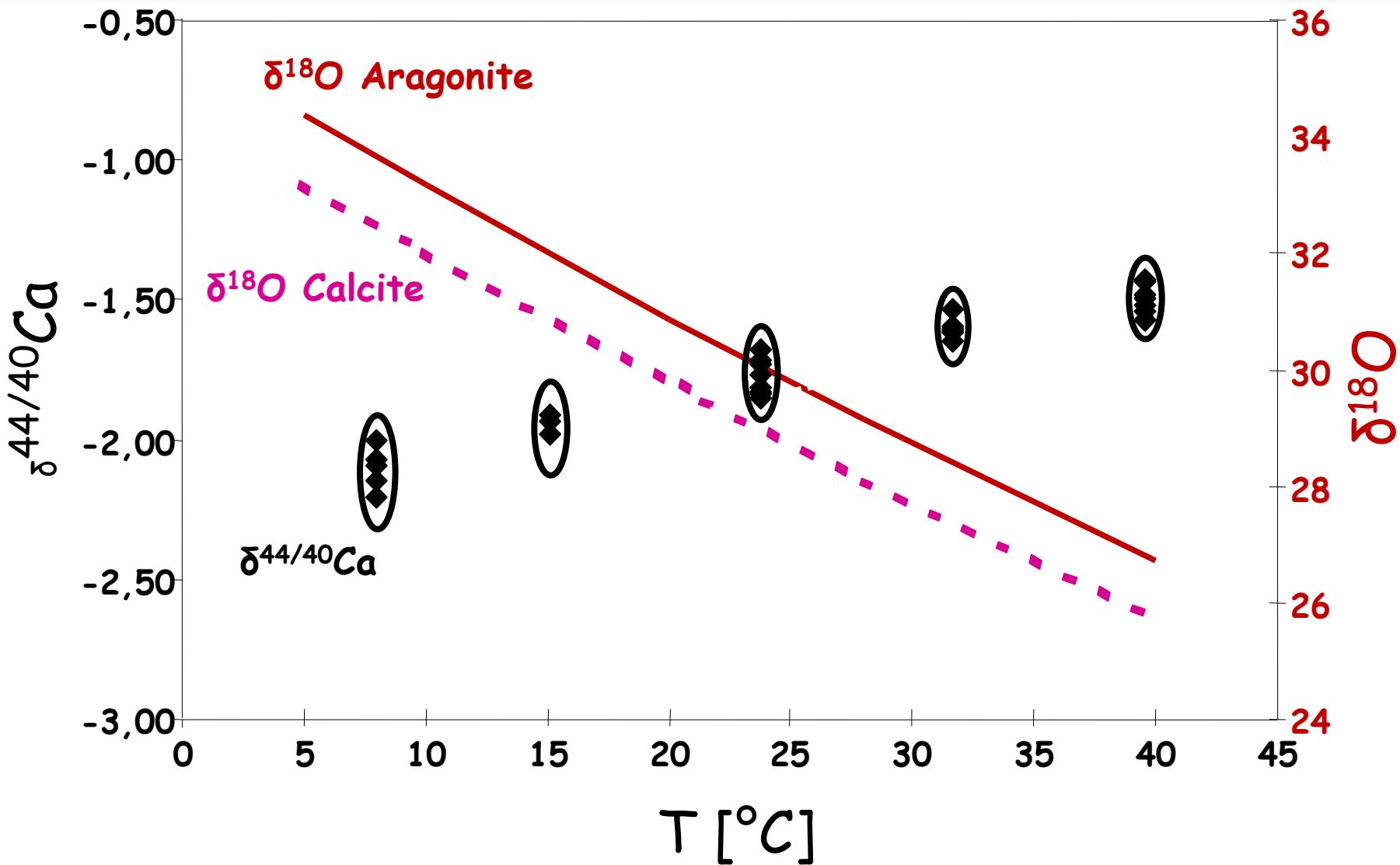
Kinetic vs. Equilibrium Fractionation



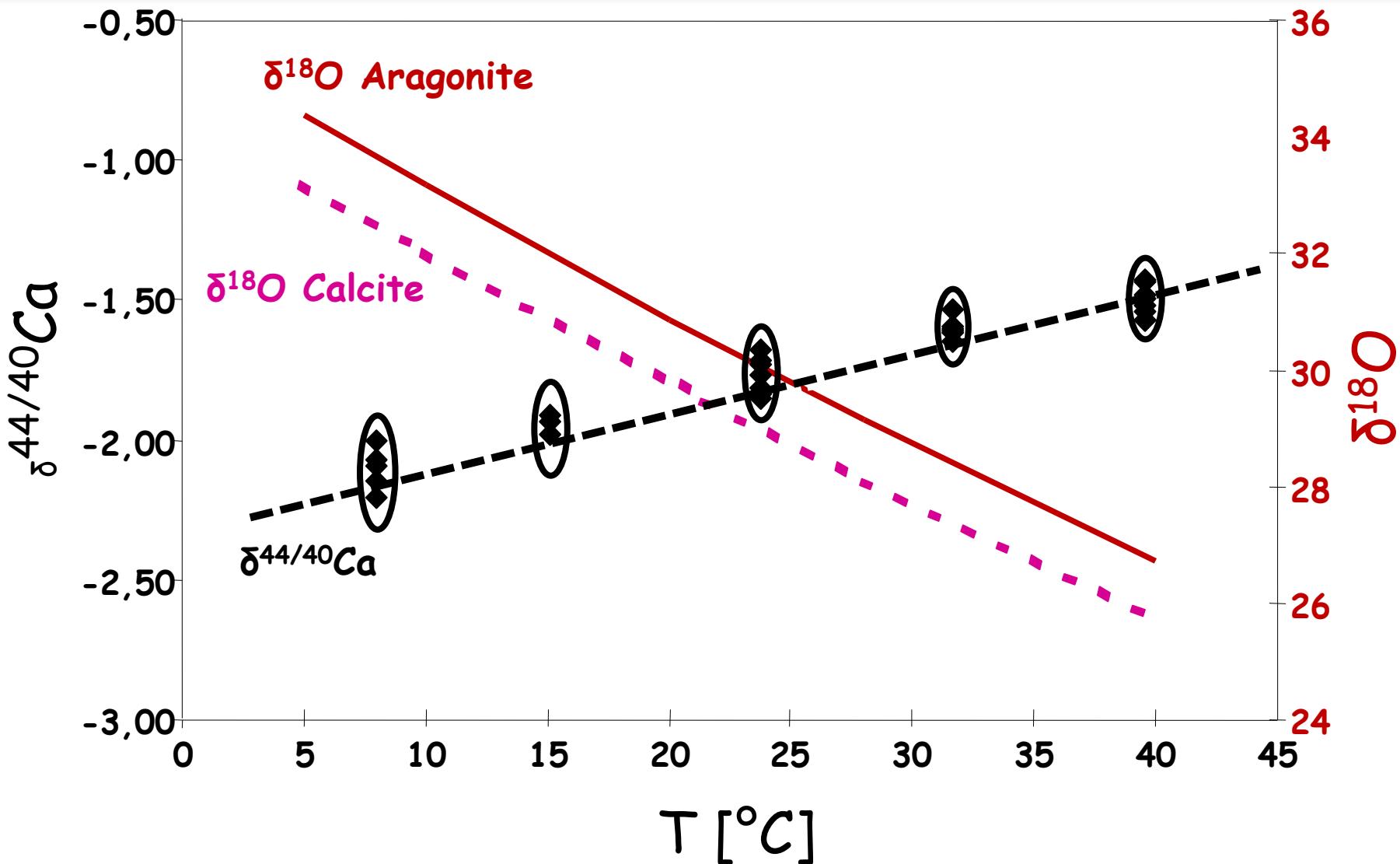
Kinetic vs. Equilibrium Fractionation



Kinetic vs. Equilibrium Fractionation



Kinetic vs. Equilibrium Fractionation



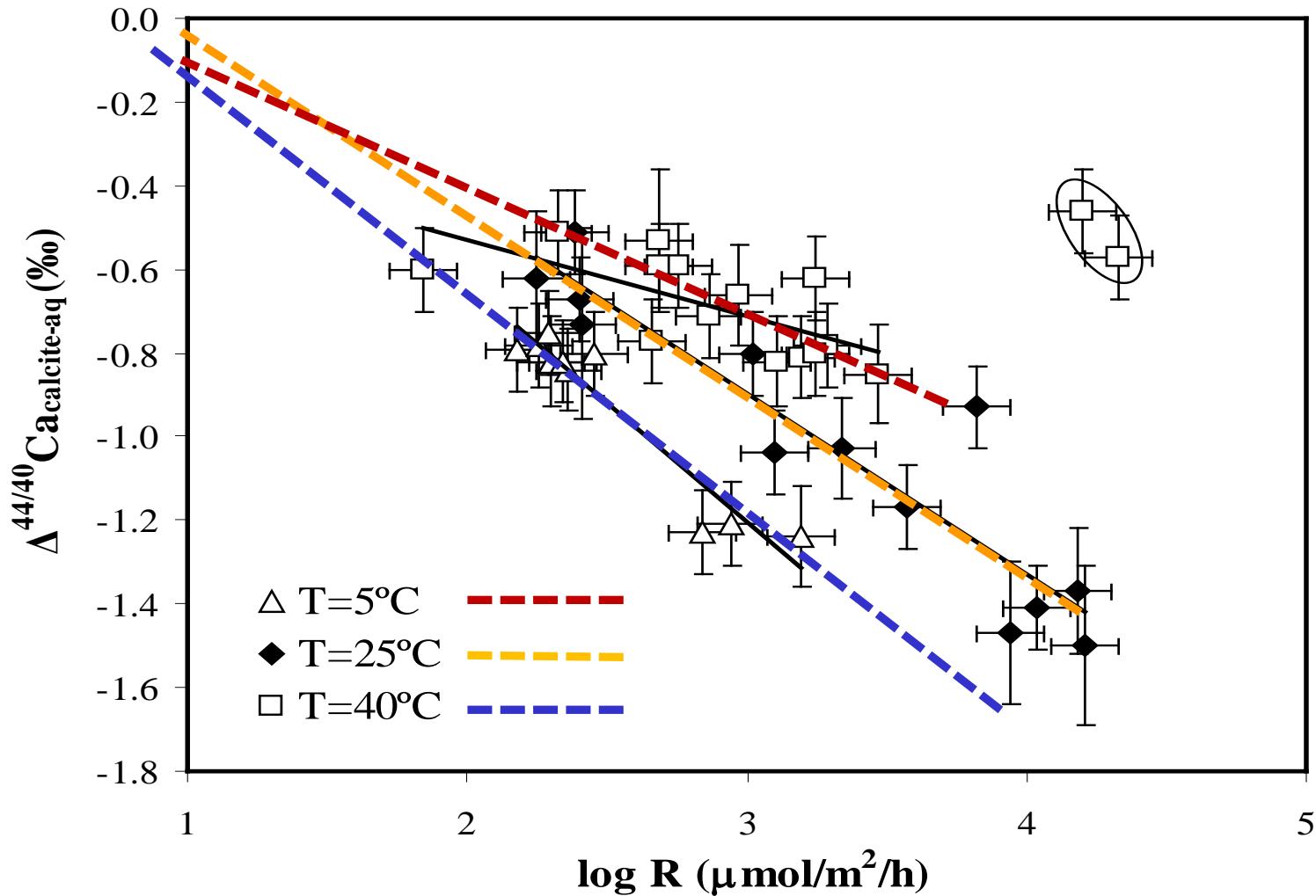
Kinetics

Isotope effect associated with Kinetic:

Because the kinetic energy for heavy and light isotopes is the same, we can write:

$$\frac{v_L}{v_H} = \sqrt{\frac{m_H}{m_L}}$$
$$\frac{v_L}{v_H} = \sqrt{\frac{28.99827}{27.994915}} = 1.0177$$

This means for $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ that regardless of the temperature, the velocity of $^{12}\text{C}^{16}\text{O}$ is 1.0177 times that of $^{13}\text{C}^{16}\text{O}$, so the lighter molecule will diffuse faster and evaporate faster.

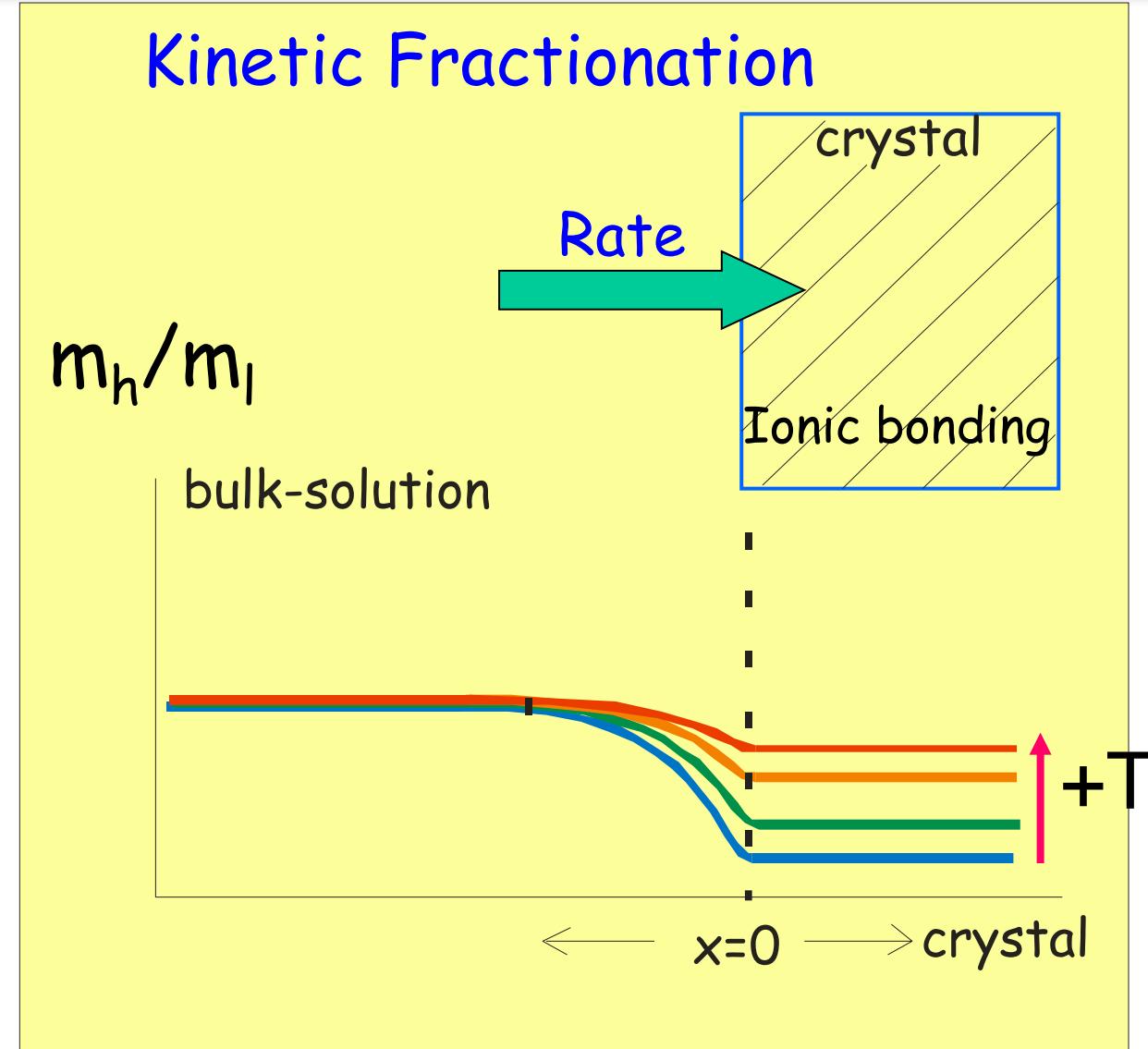
$\Delta^{44/40}\text{Ca}_{\text{calcite-aq}}$ vs. Precipitation Rate

Kinetic Fractionation

II. Understanding of
Natural Dependent
 $^{44}\text{Ca}/^{40}\text{Ca}$ Fractionation

m_h = heavy isotope
 m_l = light isotope

Kinetic fractionation
tend to enrich
the light isotope
with decreasing
temperature!

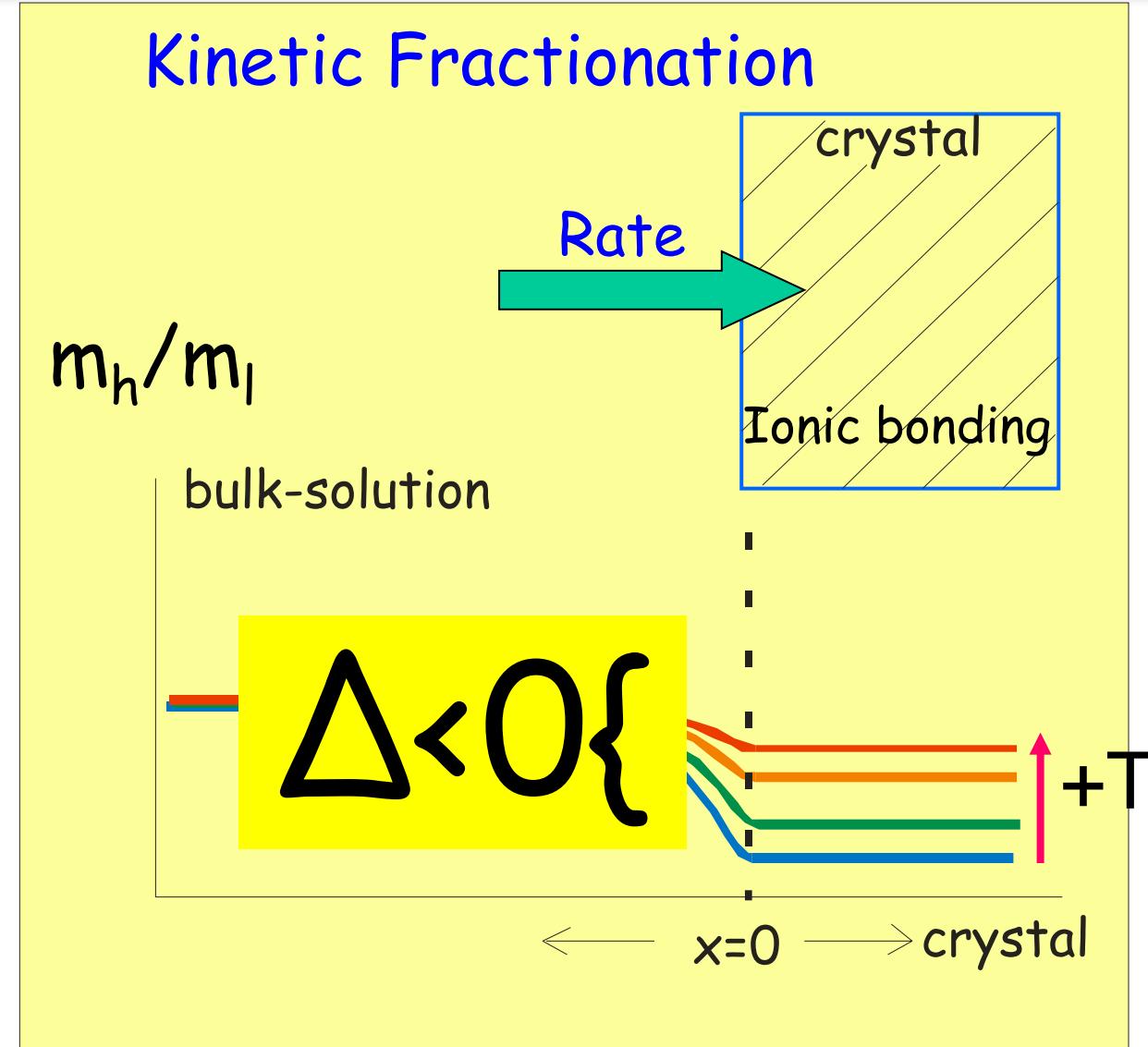


Kinetic Fractionation

II. Understanding of
Natural Dependent
 $^{44}\text{Ca}/^{40}\text{Ca}$ Fractionation

m_h = heavy isotope
 m_l = light isotope

Kinetic fractionation
tend to enrich
the light isotope
with decreasing
temperature!



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 643084