# Improving the molecular basis for paleoclimate reconstruction

## Better living through quantum chemistry

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Office of Basic Energy Sciences
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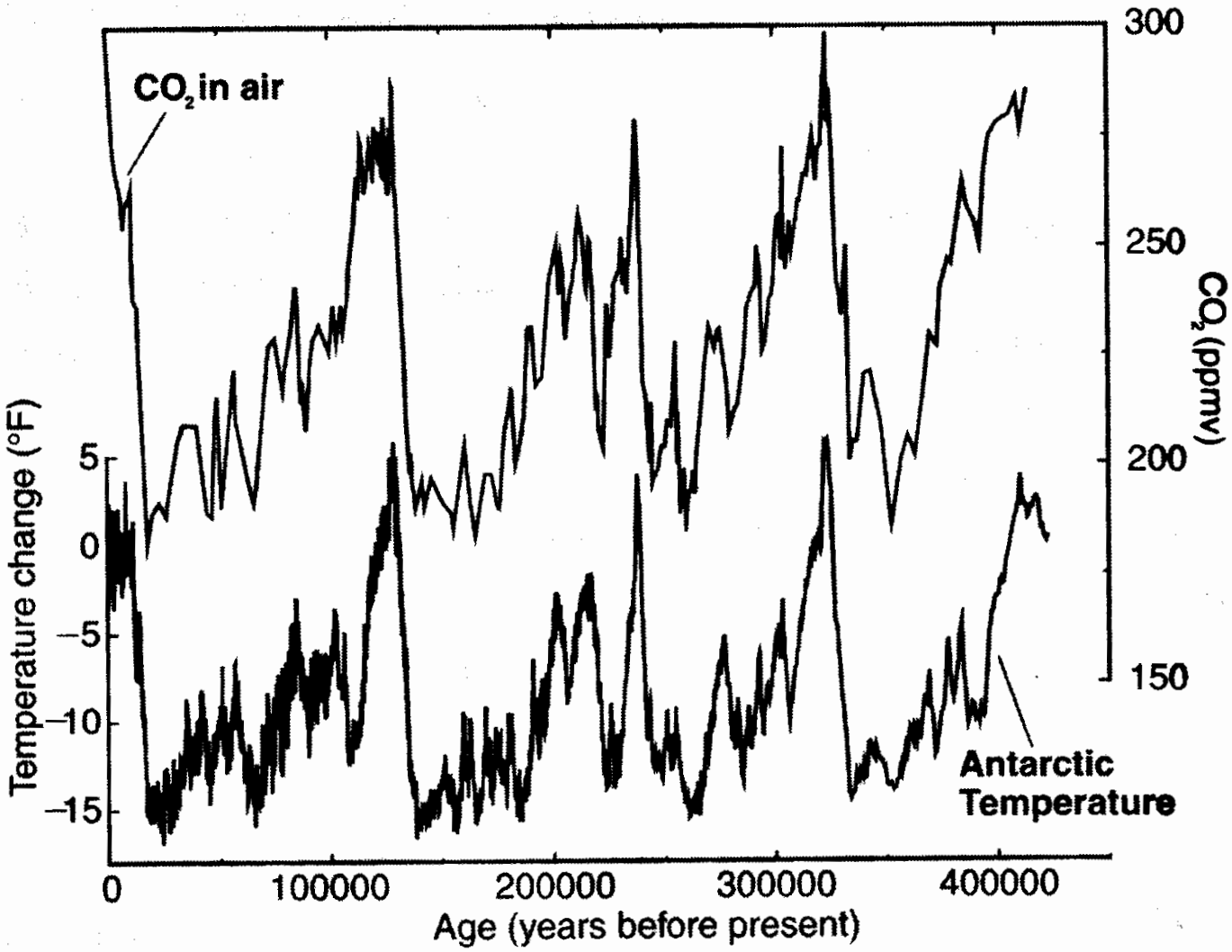
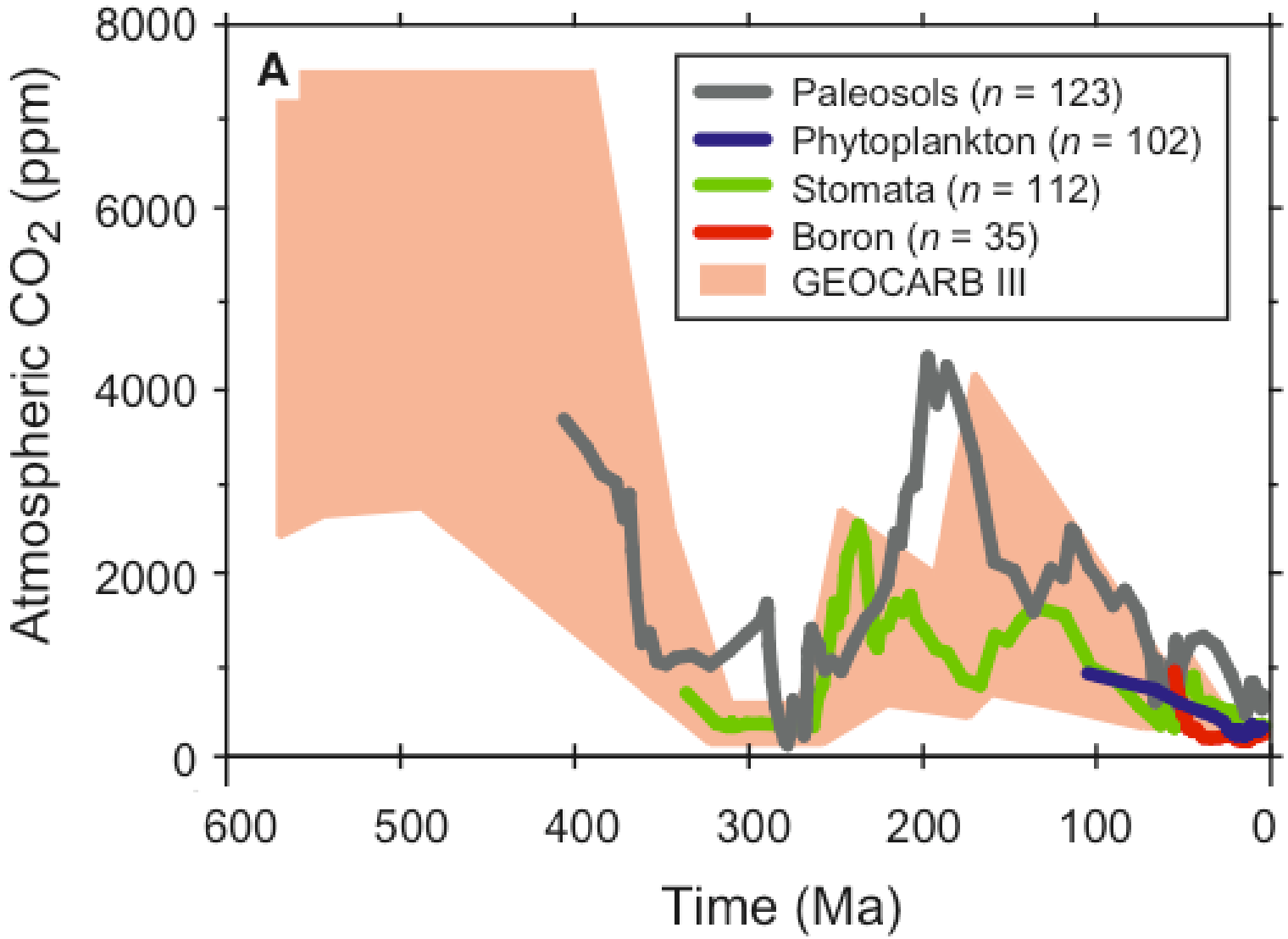
# Vostok Ice Core



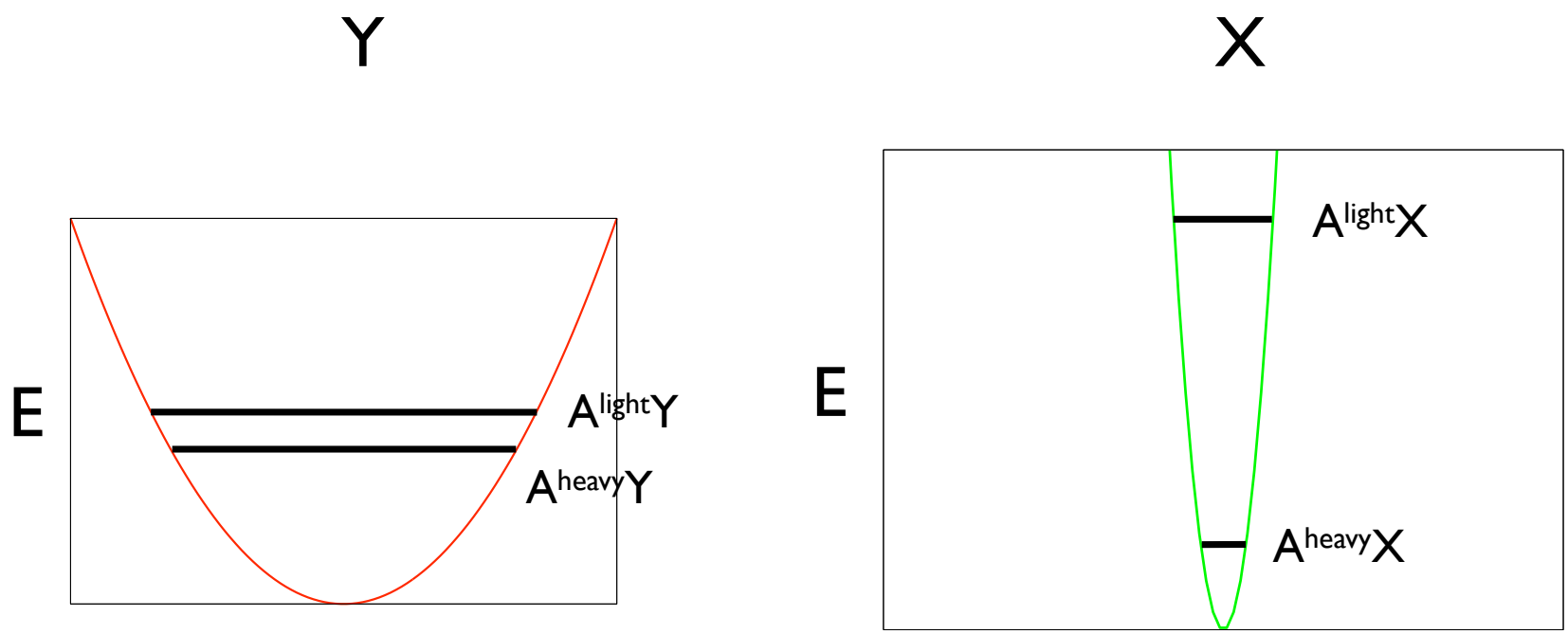

Two-mile Time Machine, Richard Alley




D. Royer et al, GSA Today 2004

# Outline

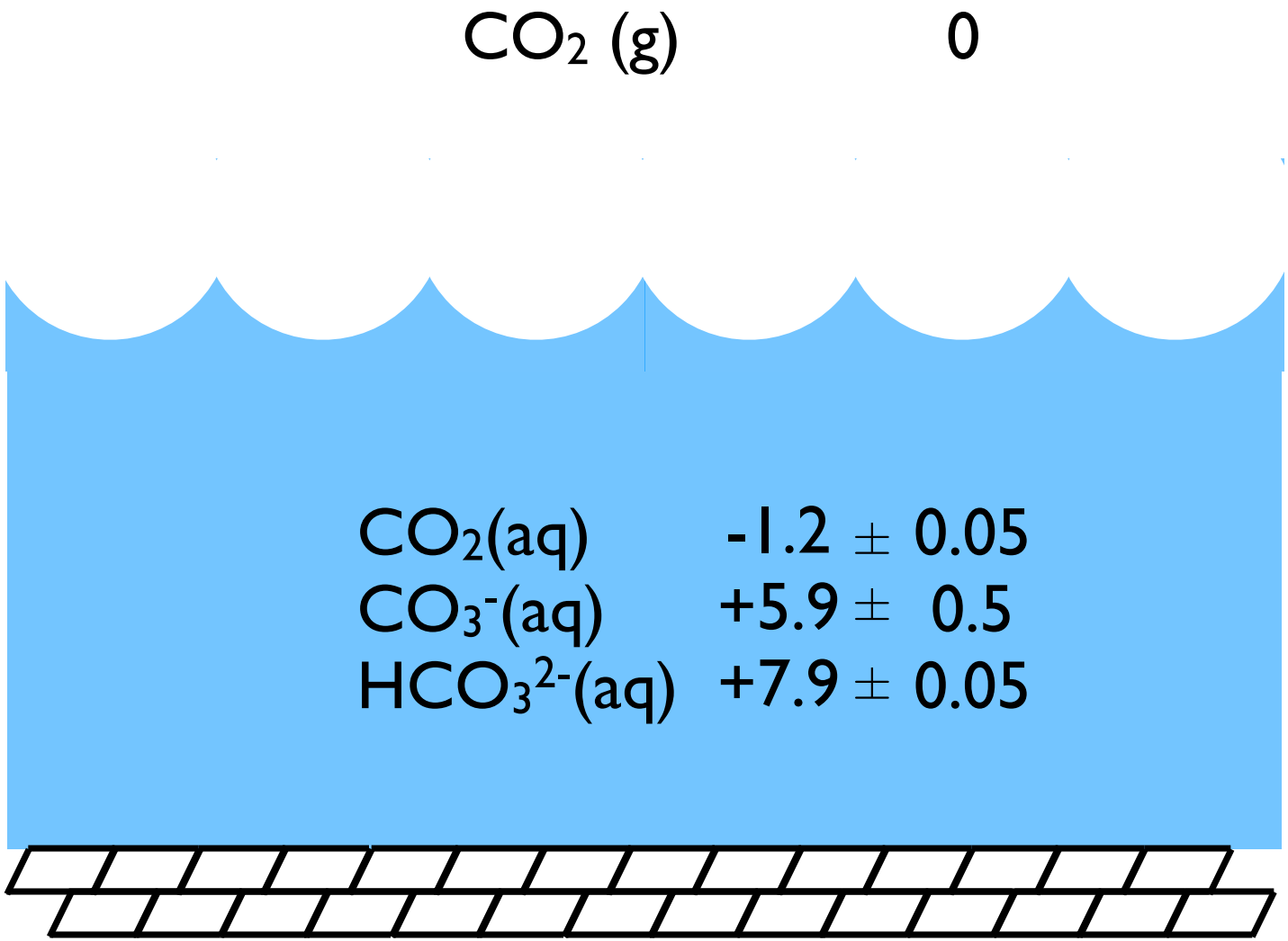
- Basics of stable isotope fractionation
- $^{12,13}C$ in atmosphere, seawater, carbonate minerals
- $^{10,11}B$ in seawater
- Heavy Istopes $^{44,40}Ca$




$$(A^{heavy}/A)_X > (A^{heavy}/A)_Y$$

**Heavy isotopes accumulate into strong bonds**

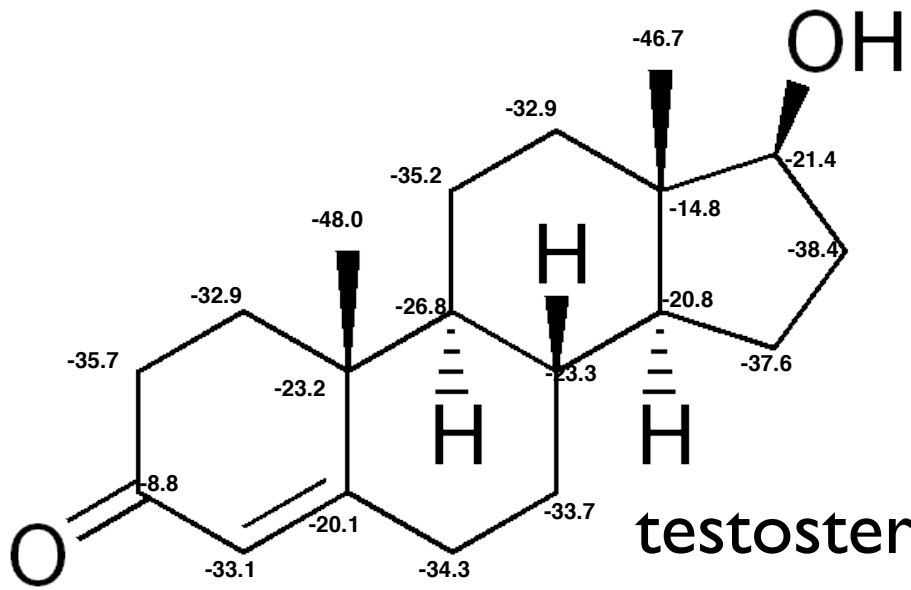
# Fractionation relative to $CO_2$(g) ‰



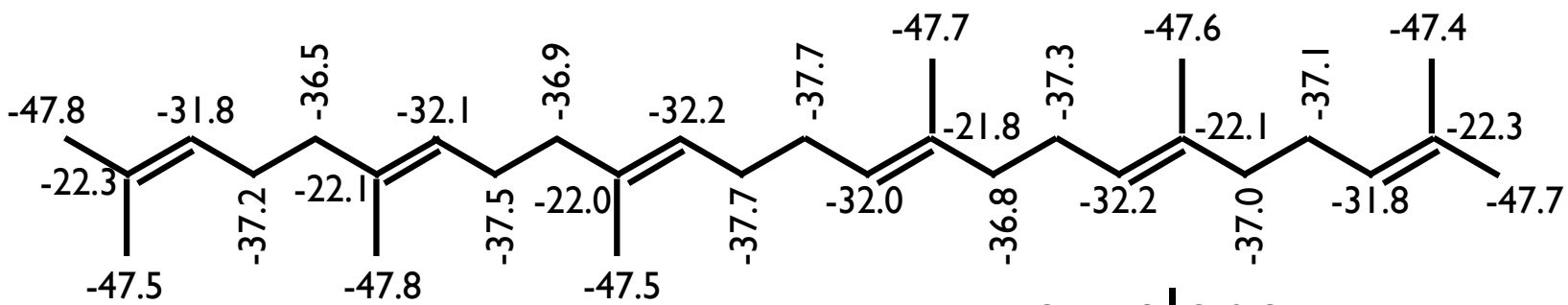
# Biomarkers

organic matter is $^{13}C$ depleted per mil wrt $CO_2(g)$

steranes
hopanes




testosterone




squalene

# Aqueous Systems

- Fluctuating coordination environment
- Dynamic chemical speciation (ion pairs, etc)
- Hydrogen bonding
- Dispersion
- Anharmonicity

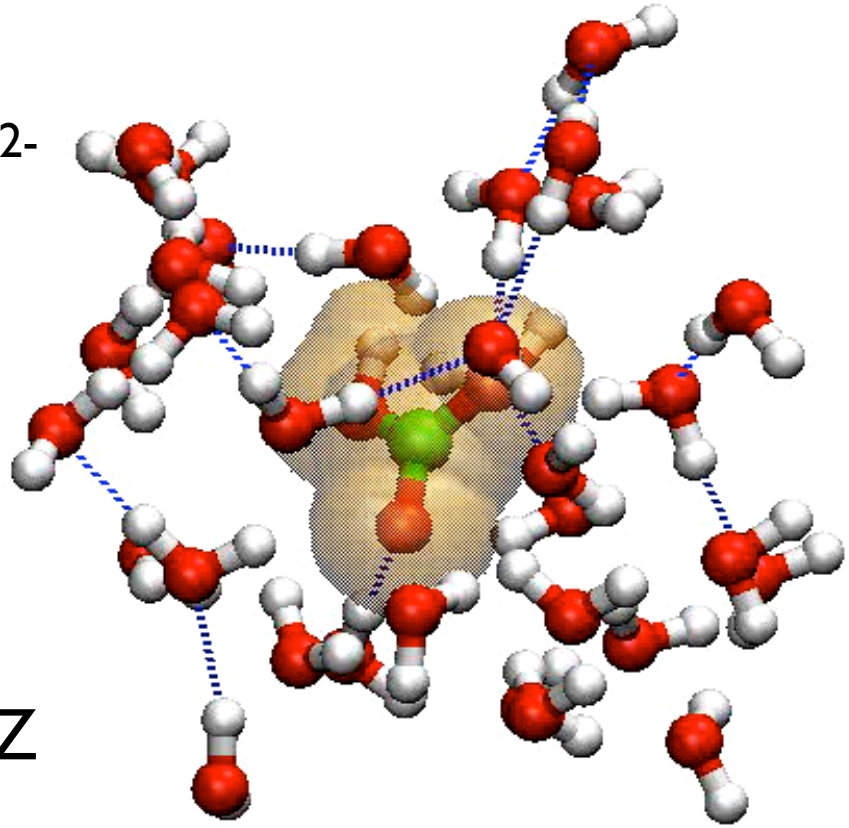
# Carbonate System Computational Approach

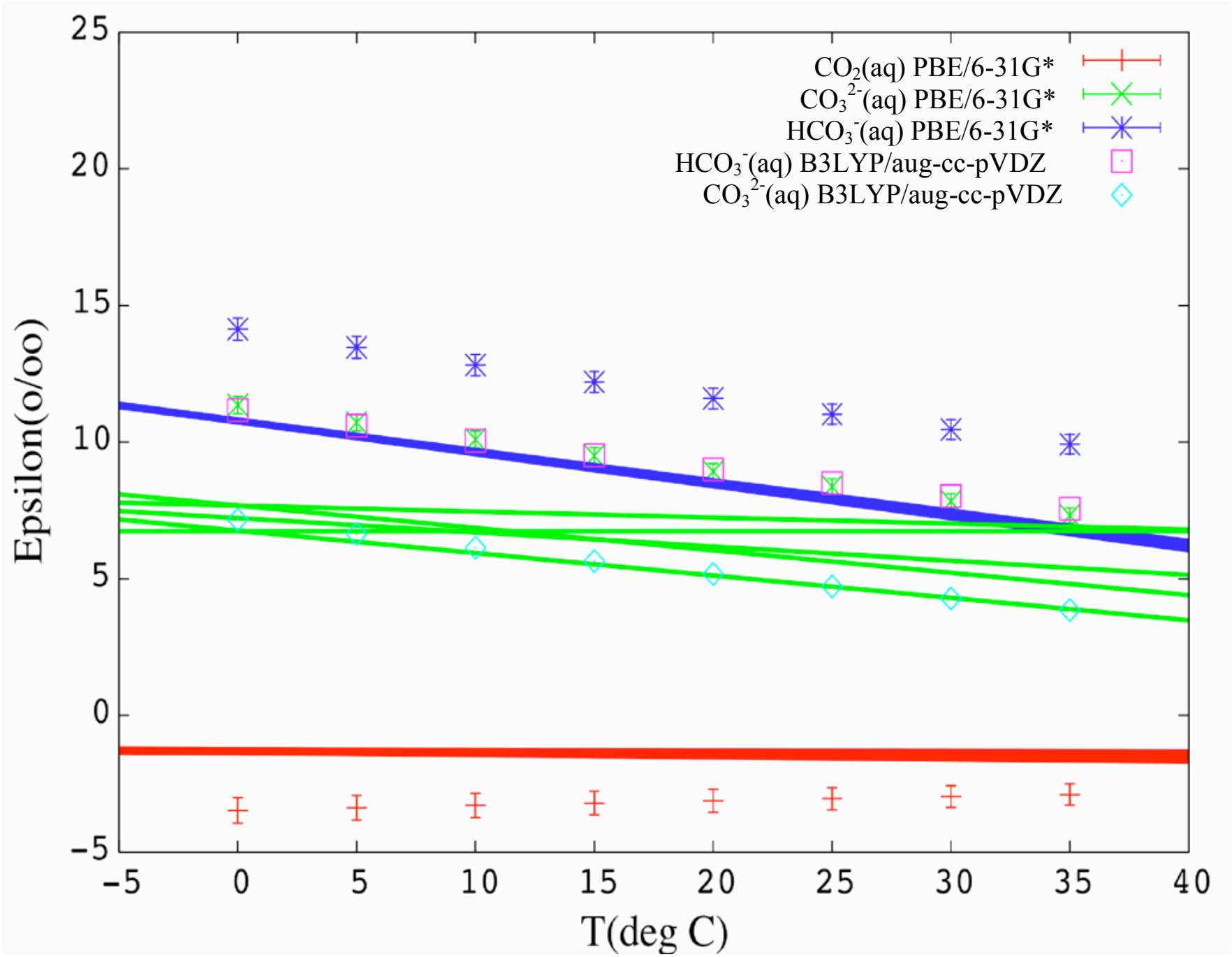
Car-Parrinello MD $HCO_3^-$ /$CO_3^{2-}$ in 32-64 waters

Harvest 10-20 "independent" configurations

Quench each configuration PBE, B3LYP, 6-31G*, aug-cc-pVDZ

Calculate harmonic vibrational partition function



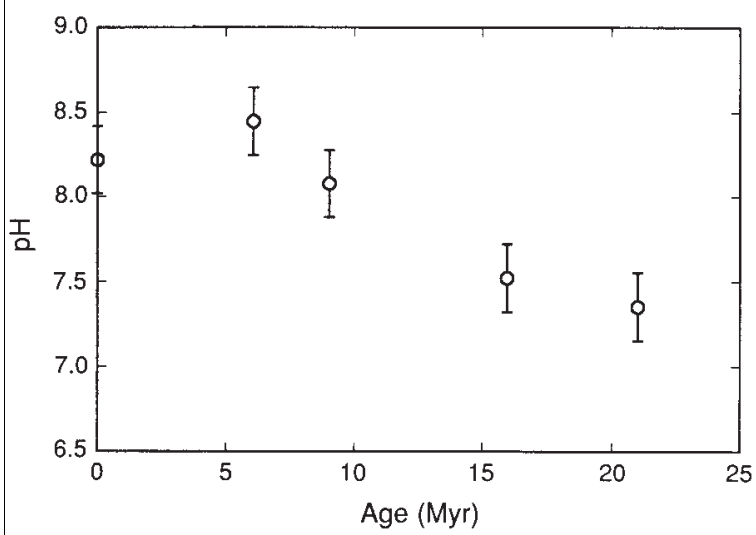

CO2(aq) PBE/6-31G*
CO3 2-(aq) PBE/6-31G*
HCO3 -(aq) PBE/6-31G*
HCO3 -(aq) B3LYP/aug-cc-pVDZ
CO3 2-(aq) B3LYP/aug-cc-pVDZ
Epsilon(o/oo)
T(deg C)
25
20
15
10
5
0
-5
-5
0
5
10
15
20
25
30
35
40

# What is required to get an answer accurate to 1‰?

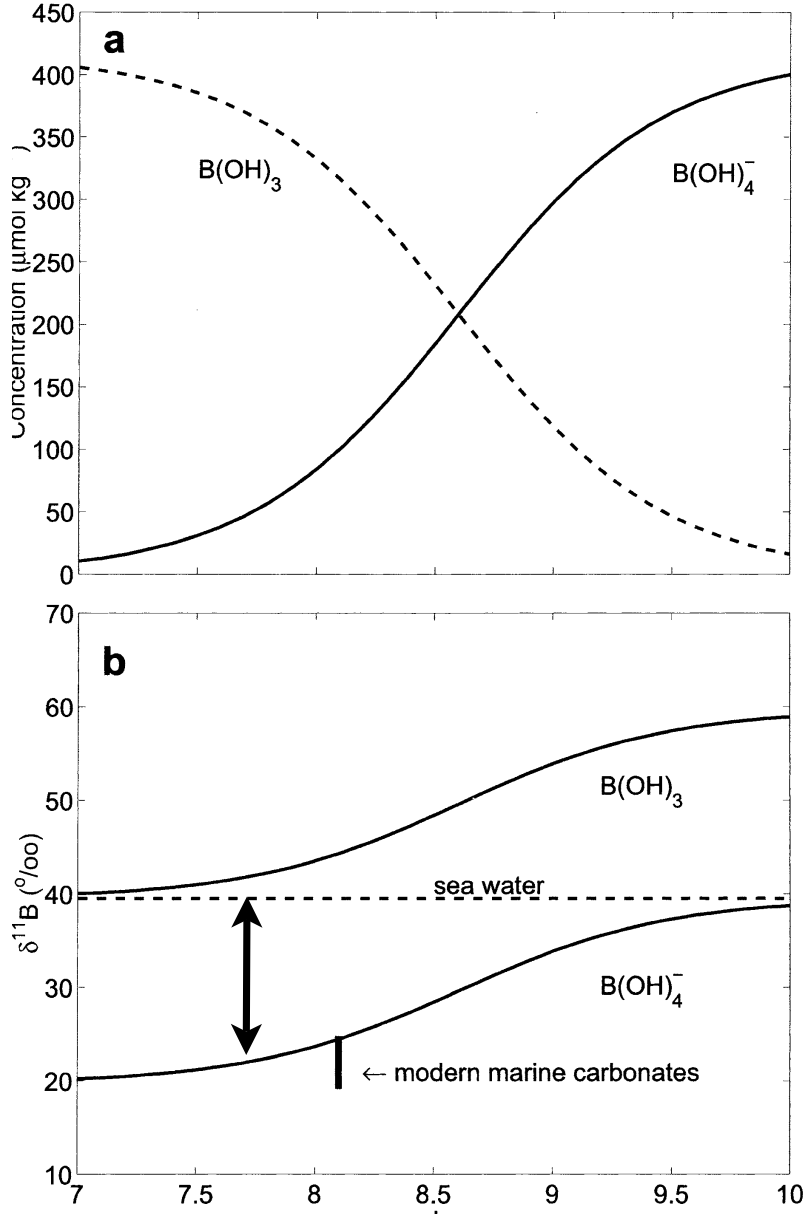
- Large systems (at least 32 water molecules)
- Continuum models qualitatively incorrect
- Some component of exact exchange (B3LYP)
- Reasonably large basis sets (aug-cc-pVDZ)
- 10-20 conformations (Baker-Pulay cluster optimization methods)
- Harmonic approximation OK at this level

# $^{10,11}B$ in Seawater

- Speciation $B(OH)_3$, $B(OH)_4$
- Assume $B(OH)_4^-$ is the only species trapped into calcite
- Assume overall $\delta^{11}B$ of oceans constant over the residence time of B in the oceans (around 10 million years)




Hemming, N.G.; Hanson, G.N. *Geochim. Cosmochim. Acta* **1991**, *55*, 537-543.




Zeebe, R.E. and Wolf-Gladrow D.A. *$CO_2$ in Seawater: Equilibrium, Kinetics, Isotopes* **2001**

J|A|C|S
COMMUNICATIONS

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# Ab Initio Calculation of Isotopic Fractionation in $B(OH)_3$(aq) and $BOH_4^-$(aq)

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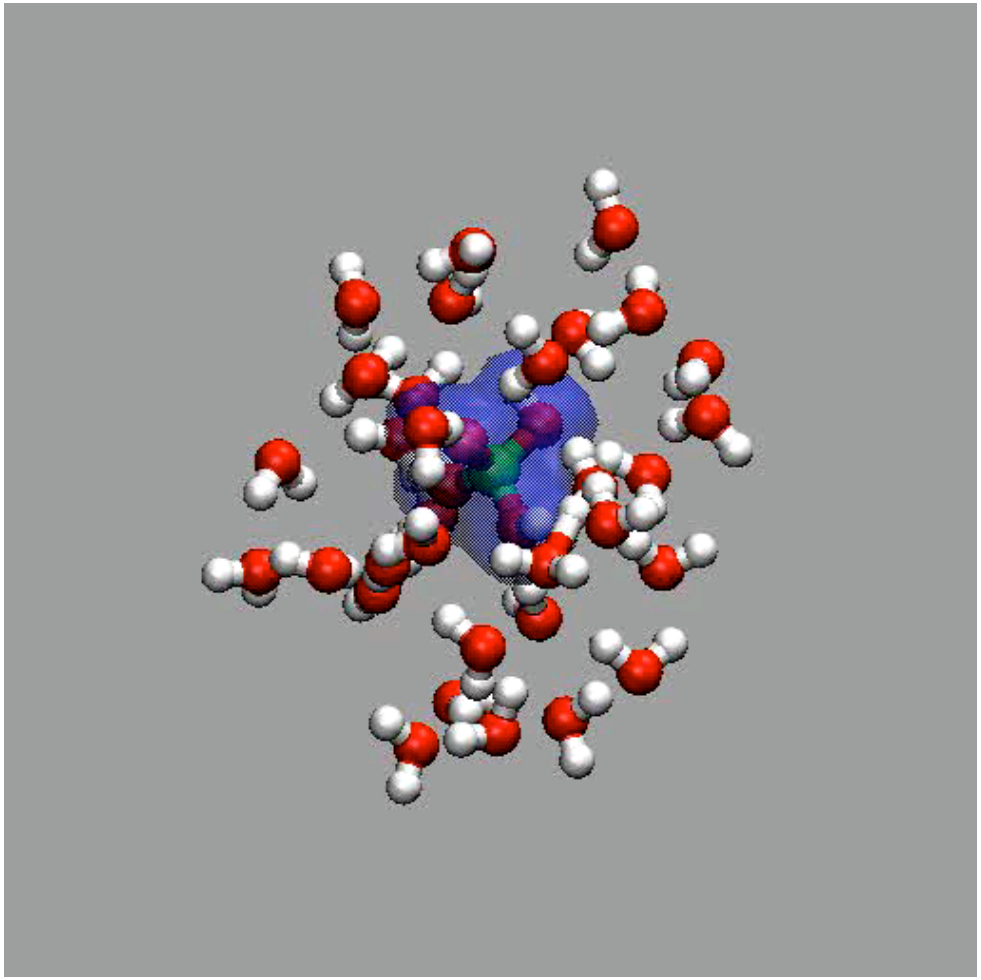
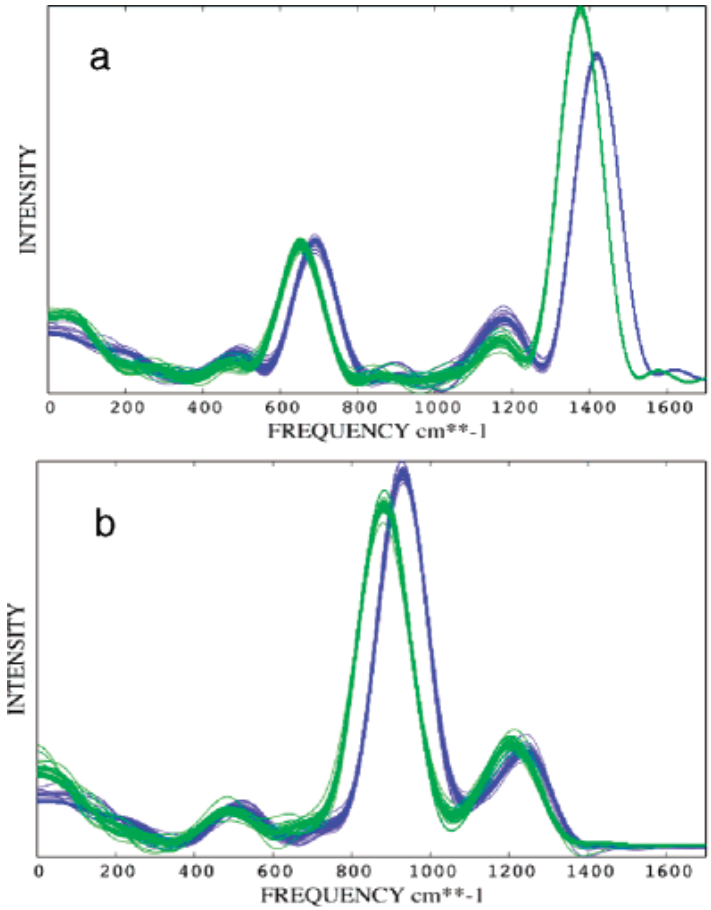


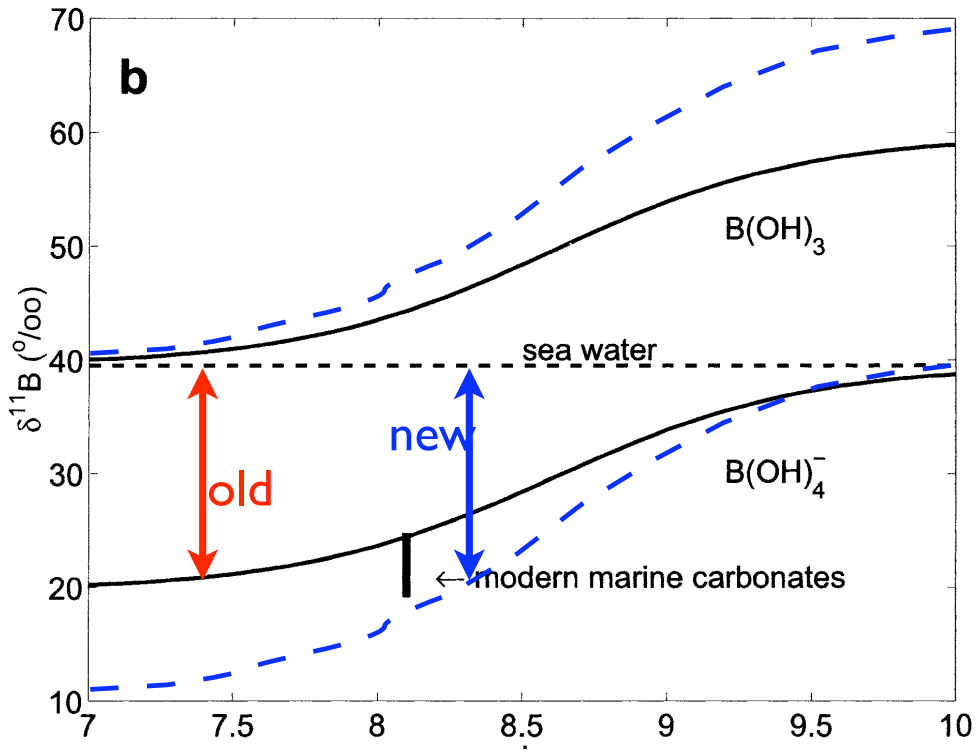


# $^{10,11}B$ in $B(OH)_3$, $B(OH)_4^-$

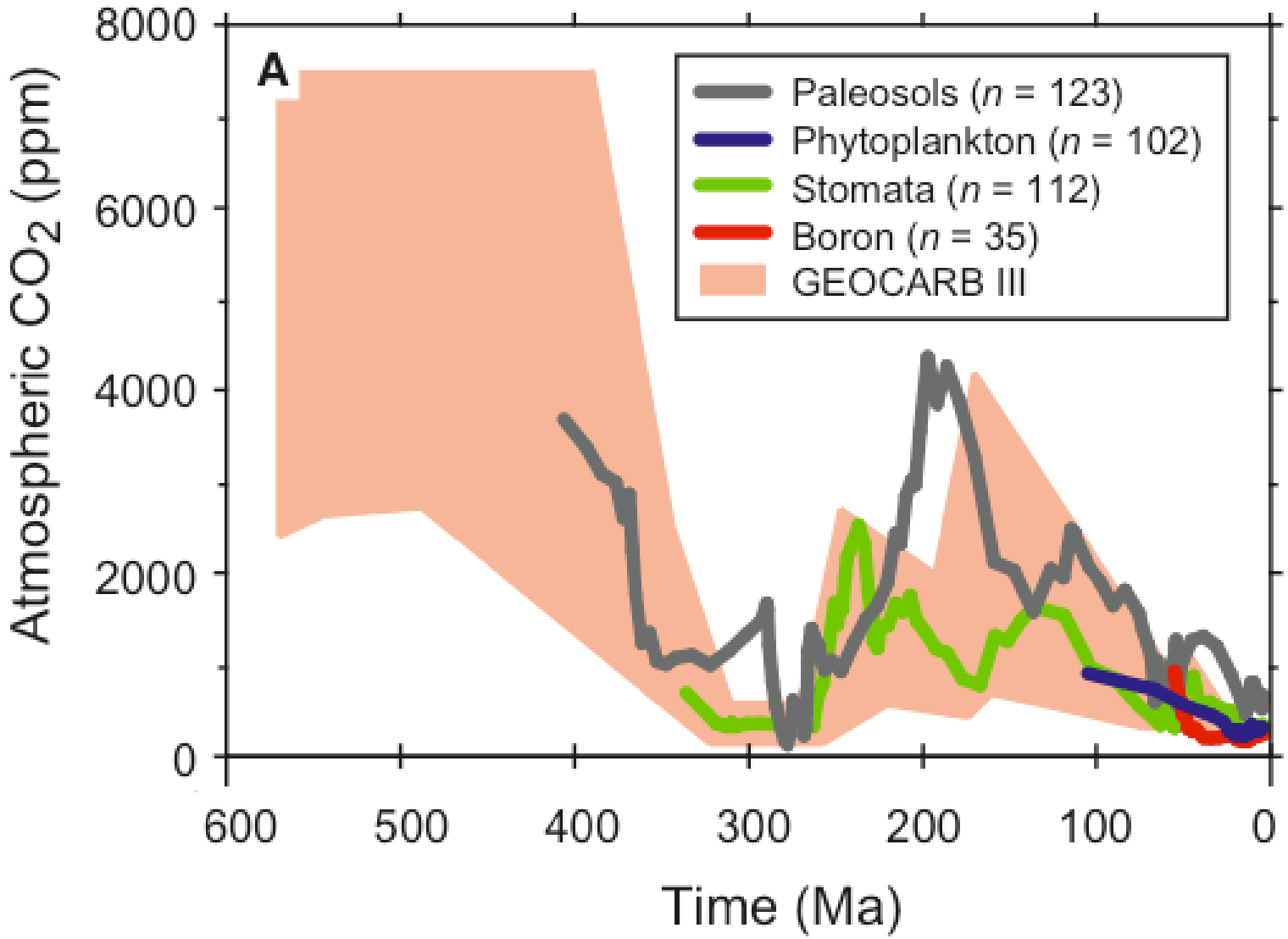
- $\alpha_{B(OH)3/B(OH)4-} = 1.028$
- old value 1.019, estimated by empirical harmonic force field with:
  - wrong mode assignments
  - wrong degeneracies
  - missing frequencies

Klochko, K.; Kaufman A. J.; Yao, W.; Byrne, R. H., Tossell, J. A. *Earth Planet Sci Lett*. **2006**, 248, 276-285

# IMPLICATIONS



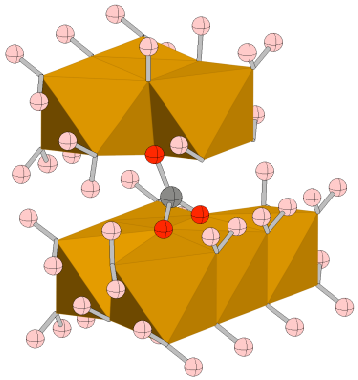

- Old estimates of fractionation constant completely erroneous
- New theoretical curve changes pH inferences by nearly a unit
- **Immediate impact of quantum chemistry on a truly global problem**

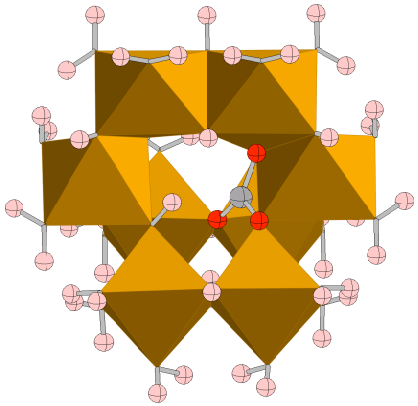



D. Royer et al, GSA Today 2004

B3LYP/m6-31G*/aug-cc-pVDZ

-19 ‰

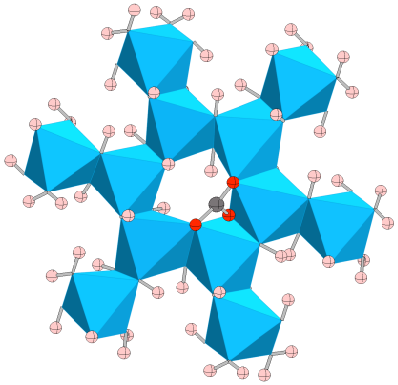


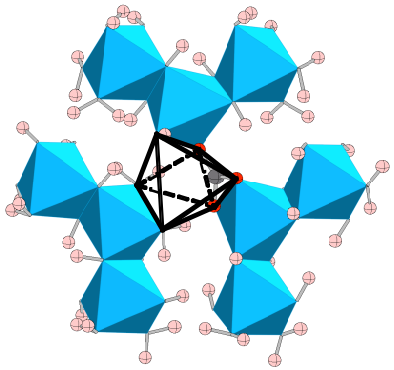


-0.6 ‰

$CO_2$(m) in Goethite FeOOH

+4 ‰



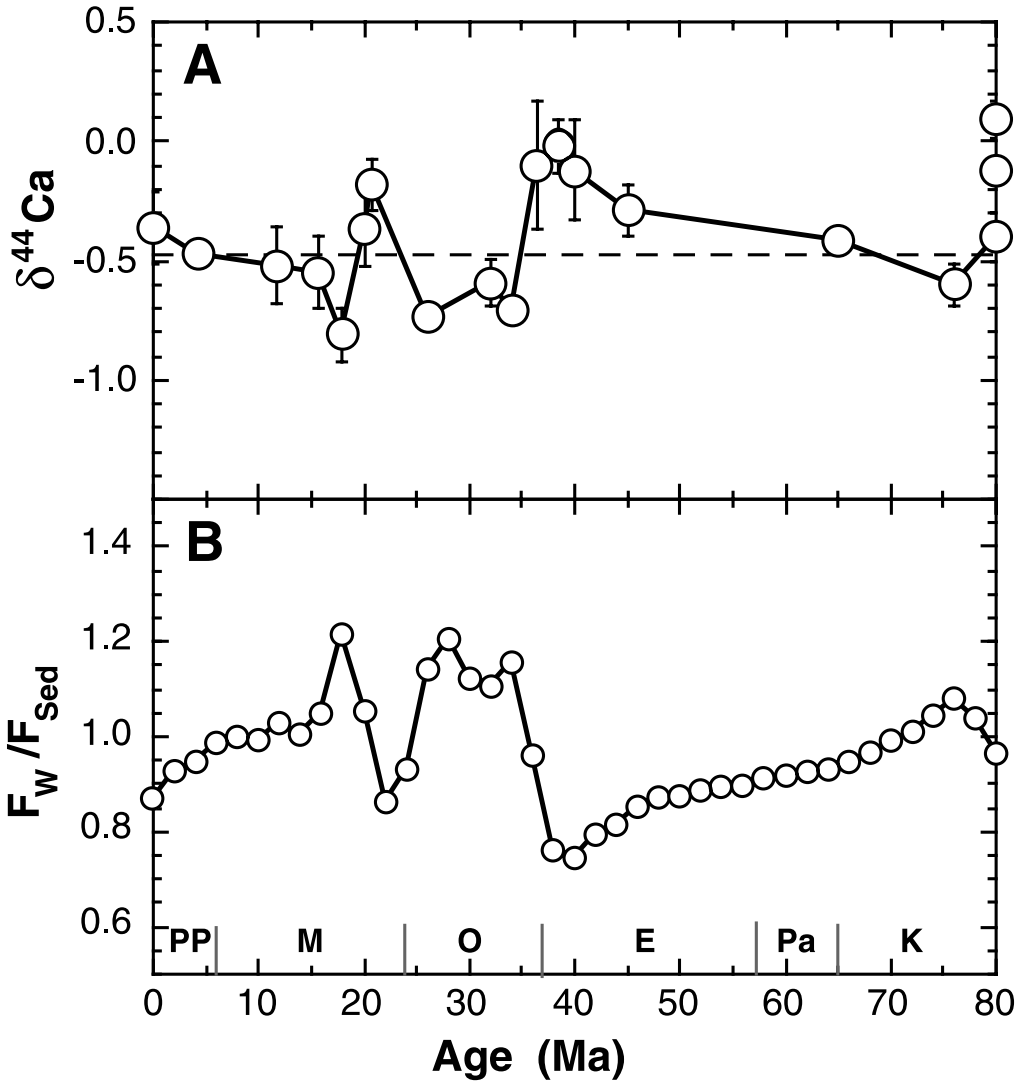


+12 ‰

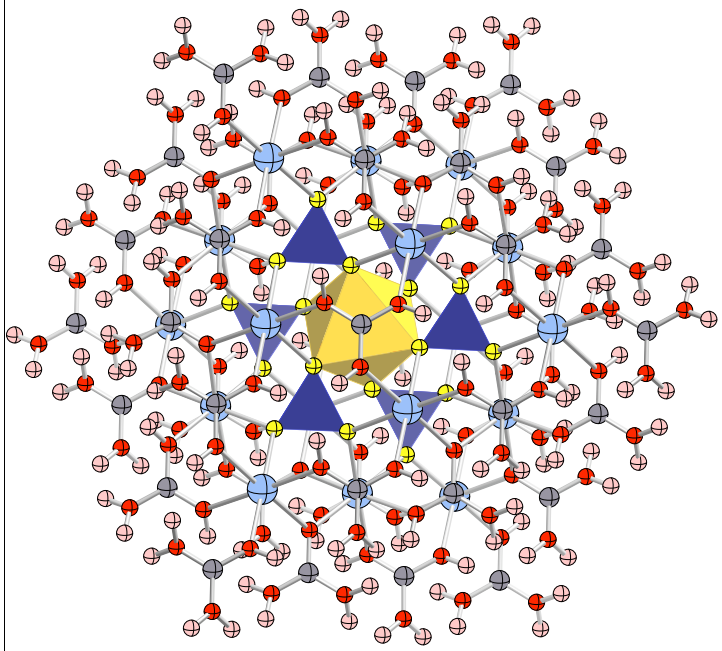
$CO_2$(m) in Gibbsite $Al(OH)_3$

# Isotopic Evidence for Variations in the Marine Calcium Cycle Over the Cenozoic

Christina L. De La Rocha[1]* and Donald J. DePaolo[1,2]

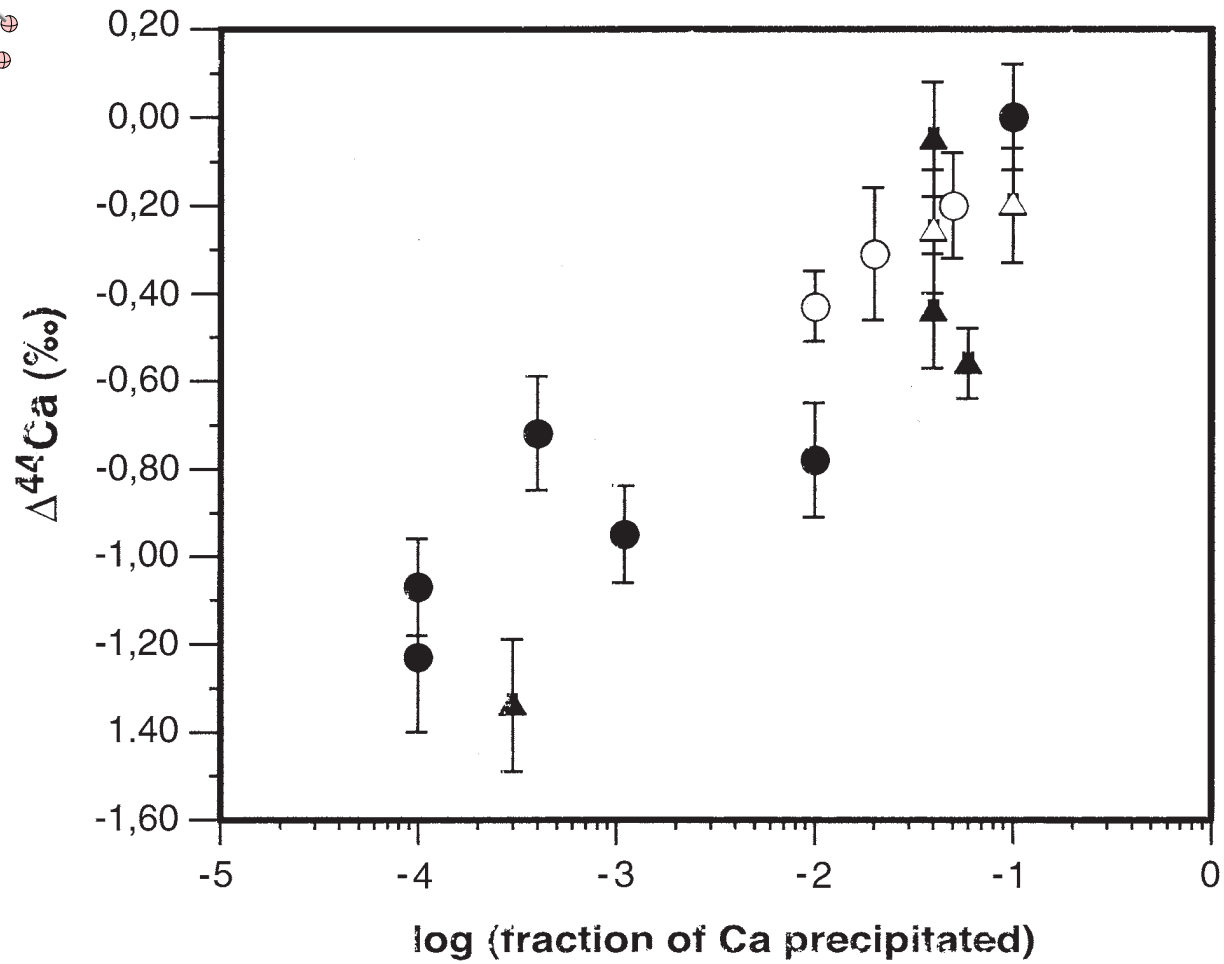


# Heavy Stable Isotopes, Ca, Fe, Hg
# Small fractionations!



**Rate-controlled calcium isotope fractionation in synthetic calcite**

D. Lemarchand,[1,*,†] G. J. Wasserburg,[1] and D. A. Papanastassiou[1,2]
[1]The Lunatic Asylum, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA
[2]Earth and Space Sciences Division, Mail Stop 183-335, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109-8099 USA




- At least aug-cc-pVDZ on coordinating carbonates
- Kills all our resources for 3 months

# What might be required for 0.1‰ accuracy?

- Go beyond DFT (great forum for large MP2 calculations)
- Larger systems (ion pairs?)
- More configurations (about 100)
- Anharmonicity?
  - Quantum Dynamics
  - Free Energy (avoid calculating partition function)