Biogeochemistry and the Geologic Record Chemical signatures for identifying life in the geological record

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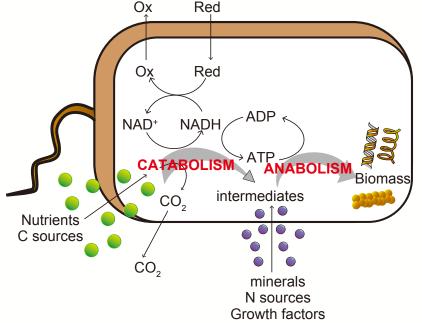
 How to use the signatures for identifying lives from Earth geological records?



Biogeochemistry

The study of ...

- How chemical elements flow through living systems and their physical environments.
- Investigate the factors that influence cycles of key elements such as bioelements (C, H, N, O, S...).



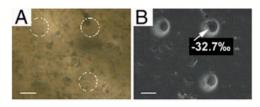


Fingerprints of life

- DNA information cannot be preserved over geologic time scale (thousands ~ million years for eukaryotes' DNA)
- Chemical and morphological signatures are utilized
- Fossils, molecular fossils
- Mineral compositions
- Isotopic signatures



Banded Iron Formation (BIF)



▲ Figure of microfossils and its C isotope ratio (Schopf et al., 2017)



▲ Rock collections with fossils at Tokyo Tech



Isotopic signatures

Isotope

variants of a particular chemical element which differ in neutron number

Radioactive isotope

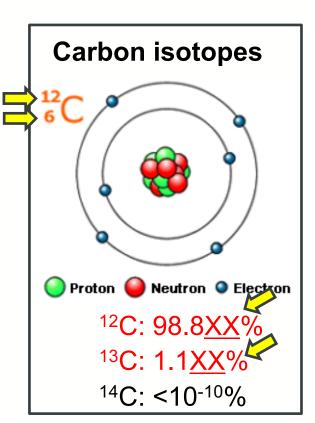
one having an unstable nucleus and which emits characteristic radiation during its decay to a stable form.

Ex: ³H, ¹⁴C...

Stable isotope

Stable. do not decay into other elements.

Behavior is slightly different by **the** mass, useful for understanding material cycle.

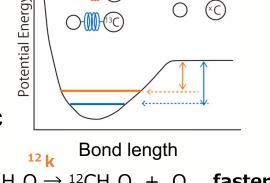




Isotopic signatures

Kinetic isotopic effect

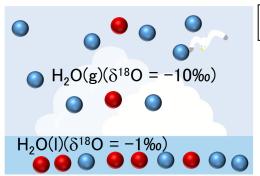
Isotope ratio is changed by kinetic reactions e.g.) the isotopic ratios are changed between substrates and products reflecting the metabolic processes



 $^{12}\text{CO}_2 + \text{H}_2\text{O} \rightarrow ^{12}\text{CH}_2\text{O} + \text{O}_2$ faster $^{13}\text{CO}_2 + \text{H}_2\text{O} \rightarrow ^{13}\text{CH}_2\text{O} + \text{O}_2$ slower

Equilibrium isotopic effect

Isotope ratio is changed by equilibrium reactions. e.g.) Temperature effect, phase (gas, liquid, solid)



¹⁸O (¹⁶O)is.. more (less) enriched in liquid than gas phase

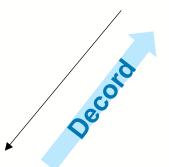


Isotopic signatures

Environmental conditions

- Temparature, pH, ORP, light intensity
- Chemical and Mineral Concentration

Field & Lab Researches









Chemical signatures

Decord

Players

- Isotopic composition of bioelements
 - -Sources
 - -Production and Consumption

Record Decord

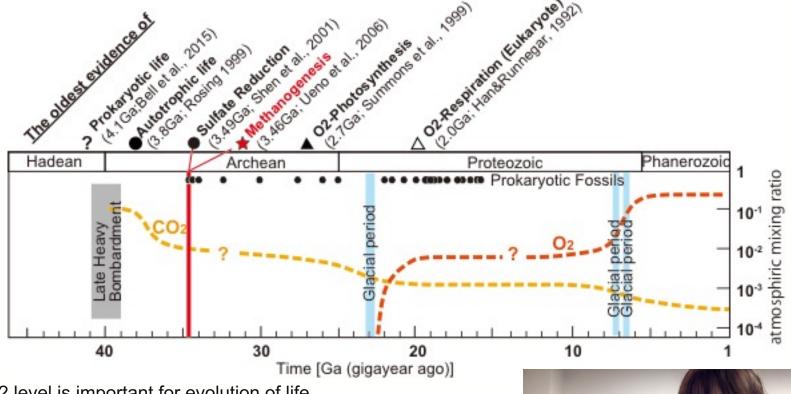
Geological records

- Microbial diversity (Molecular biology)
- Bacteria, Archaea, Virus?, ...etc.



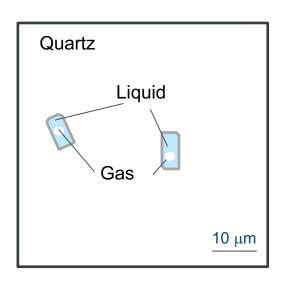
Earth's Early Environment

Earth environment interact with origin and evolution of life



- O2 level is important for evolution of life
- → the content of oxidized minerals and S isotope ratios are used for signatures of O2 level
- Small C isotope ratio (δ^{13} C) of microfossils
- \rightarrow The difference of δ^{13} C values between carbonate and organic carbon (< -30‰) indicated the possibility of Acetyl-CoA pathway and/or Calvin cycle product.

Isotopic signature for Methanogens



▲ Image of Fluid inclusion in the rock

- The sample rocks (~3.5Ga); at the Dresser Formation at the North Pole area in Pilbara craton, Western Australia (Ueno et al., 2006)
- Fluid inclusion; Tiny bubble of liquid or gas trapped inside a solid mineral-phase
- Measure C isotope ratio (δ¹³C) of CO₂ and CH₄ in fluid inclusion



Isotopic signature for Methanogens

Methane production processes (Biogenic)

Acetate Fermentation

CH₃COOH + H₂O
$$\rightarrow$$
 CH₄ + CO₂ + H₂O (δ^{13} C_{CH4} - δ^{13} C_{CH3COOH} = -22 ~ -7 %)

CO₂ reduction

$$CO_2 + 2H_2 \rightarrow CH_4 \ (\delta^{13}C_{CH4} - \delta^{13}C_{CO2} = -70 \sim -30 \%)$$

Methane production processes (Abiotic)

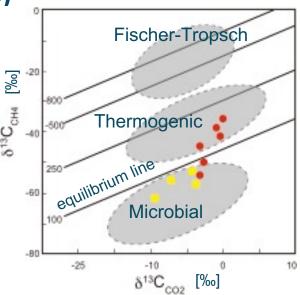
Thermogenic decomposition,

$$\cdots -C-C-C-C-\cdots \rightarrow C + C-C + C-C-C + \cdots$$
(kerogen)

Fischer-Tropsch reaction

$$H_2$$
 + CO or $CO_2 \rightarrow C$ + C-C + C-C-C +... + nH_2O





▲ Measured fluid inclusions in rocks (Figure simplified from Ueno et al., 2006)



Take-home message

Environmental conditions (Physical conditions)

Biotic & Abiotic Processes

Equilibrium / Kinetic isotope effect

Recode Decode

Geological records

Signatures of life ...

- Chemical signatures, especially <u>stable</u> <u>isotope information</u>, are important tool for identifying the biogenic signatures preserved in geological records
- To understand how to record and decode the signatures, <u>researches on modern</u> <u>earth material cycle and organisms</u> are necessary.







Suggested Reading

Isotope geochemistry

Allègre, C. (2008). Stable isotope geochemistry. In C. Sutcliffe (Trans.), Isotope Geology(pp. 358-435). Cambridge: Cambridge University Press. doi:10.1017/CBO9780511809323.008

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Sharp, Zachary. "Principles of Stee Isotope Geochemistry, 2nd Edition." (2017). doi:10.5072/FK2GB24S9F

References

- Bell et al. (2015), Potentially biogenic carbon preserved in a 4.1 billion-year-old zircon, *Proceedings of the National Academy of Sciences*, **112** (47) 14518-14521, doi: 10.1073/pnas.1517557112
- Rosing (1999), 13C-Depleted Carbon Microparticles in >3700-Ma Sea-Floor Sedimentary Rocks from West Greenland, *Science*, **283** (5402) 674-676, doi: 10.1126/science.283.5402.674
- Ueno et al. (2006) Evidence from fluid notisions for microbial methanogenesis in the early Archaean era, *Nature*, **440** (1000) 516-519, doi:10.1038/nature04584
- Shen et al. (2001), Isotopic evidence for microbial sulphate reduction in the early Archaean era, *Nature*, **410** (6824) 77-81, doi: 10.1038/35065071
- Summons et al. (1999), 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis, Nature, **400** (6744) 554-557, doi: 10.1038/23005
- Han and Runnegar (1992), Megascopic eukaryotic algae from the 2.1-billion-yearold negaunee iron-formation, Michigan, *Science*, **257** (5067) 232-235, doi: 10.1126/science.1631544