A seawater throttle on H_2 Production in Precambrian Serpentinizing Systems

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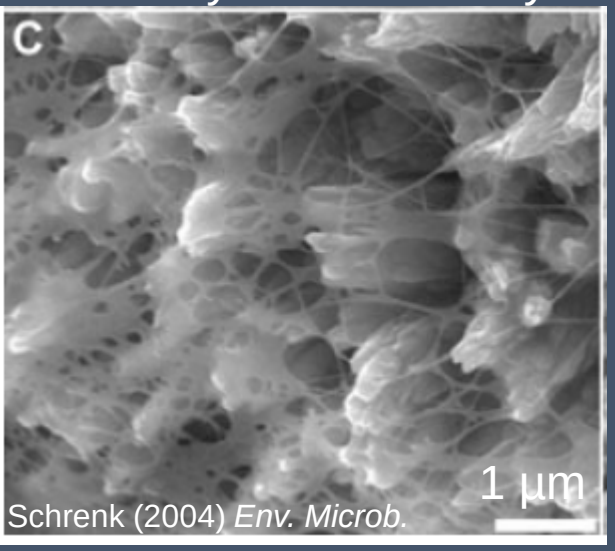
Acknowledgements

Collaborators: *Bill Seyfried (UMN), Nick Tosca (formerly Oxford, now Cambridge)*

Support:

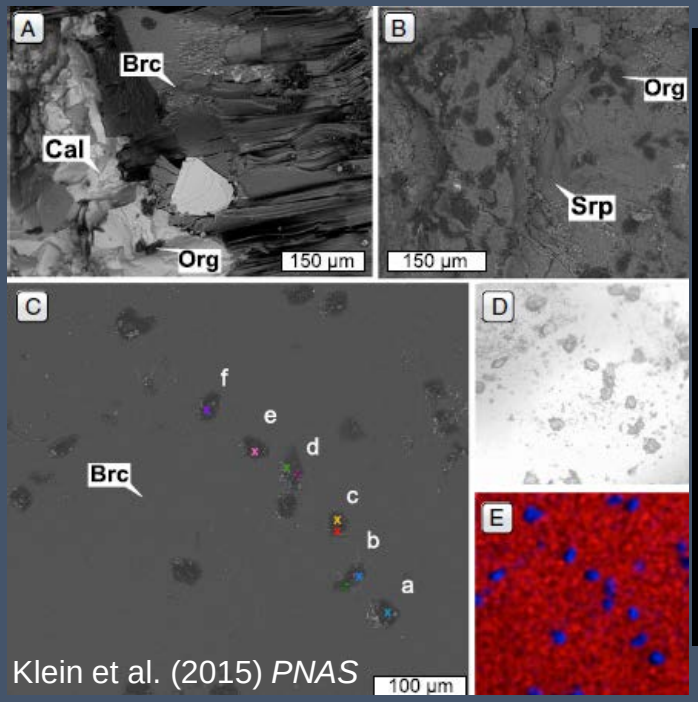
Serpentinization: Implications for life

Active System: Lost City



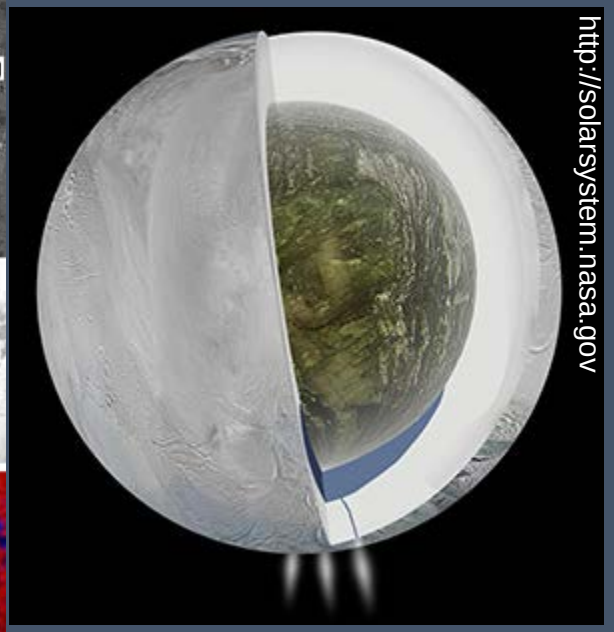
Schrenk (2004) *Env. Microb.*

Fossil System: Iberian Margin



Klein et al. (2015) *PNAS*

Saturnian moon, Enceladus



➢ *Life thrives at the interface between serpentinization fluids (H_2, hydrocarbons, high pH) and seawater*

Serpentinization: Implications for early Earth surface processes

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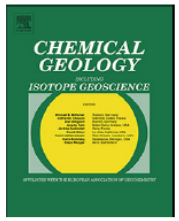

Redox states of Archean surficial environments: The importance of $H_{2,g}$ instead of $O_{2,g}$ for weathering reactions

Jihua Hao[a,*], Dimitri A. Sverjensky[a], Robert M. Hazen[b]

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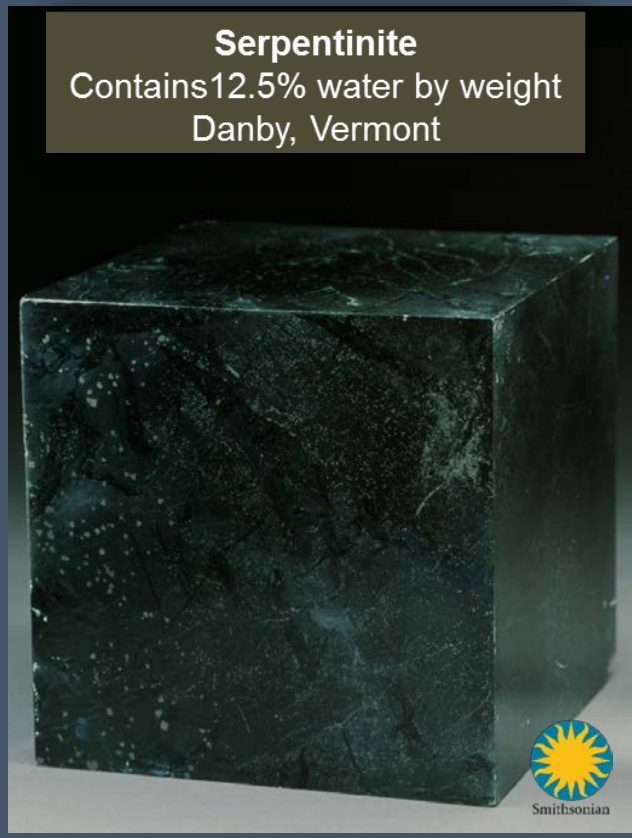
Hydrogen-Nitrogen Greenhouse Warming in Earth's Early Atmosphere

Robin Wordsworth* and Raymond Pierrehumbert

The Serpentinization Reaction

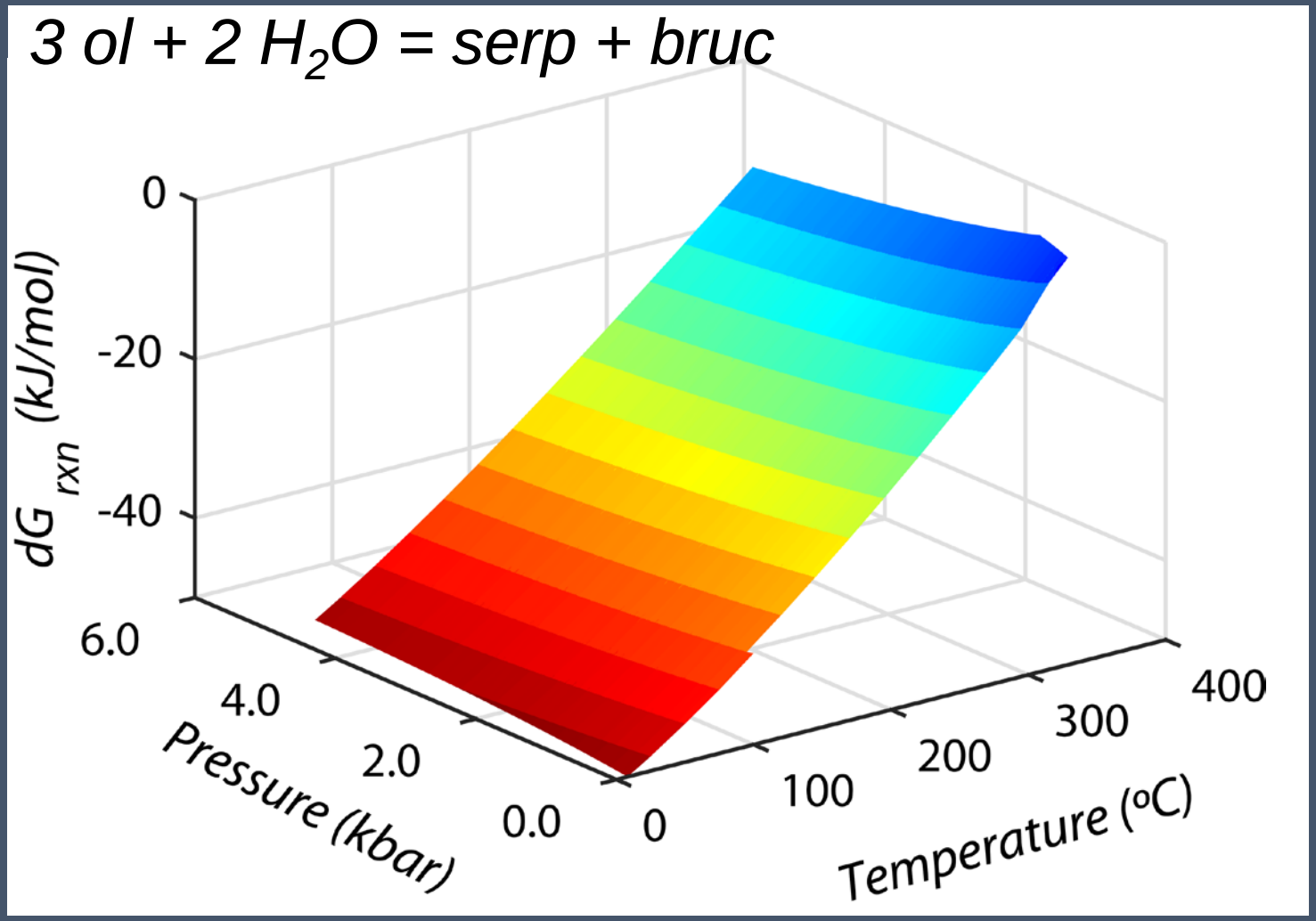
+

=

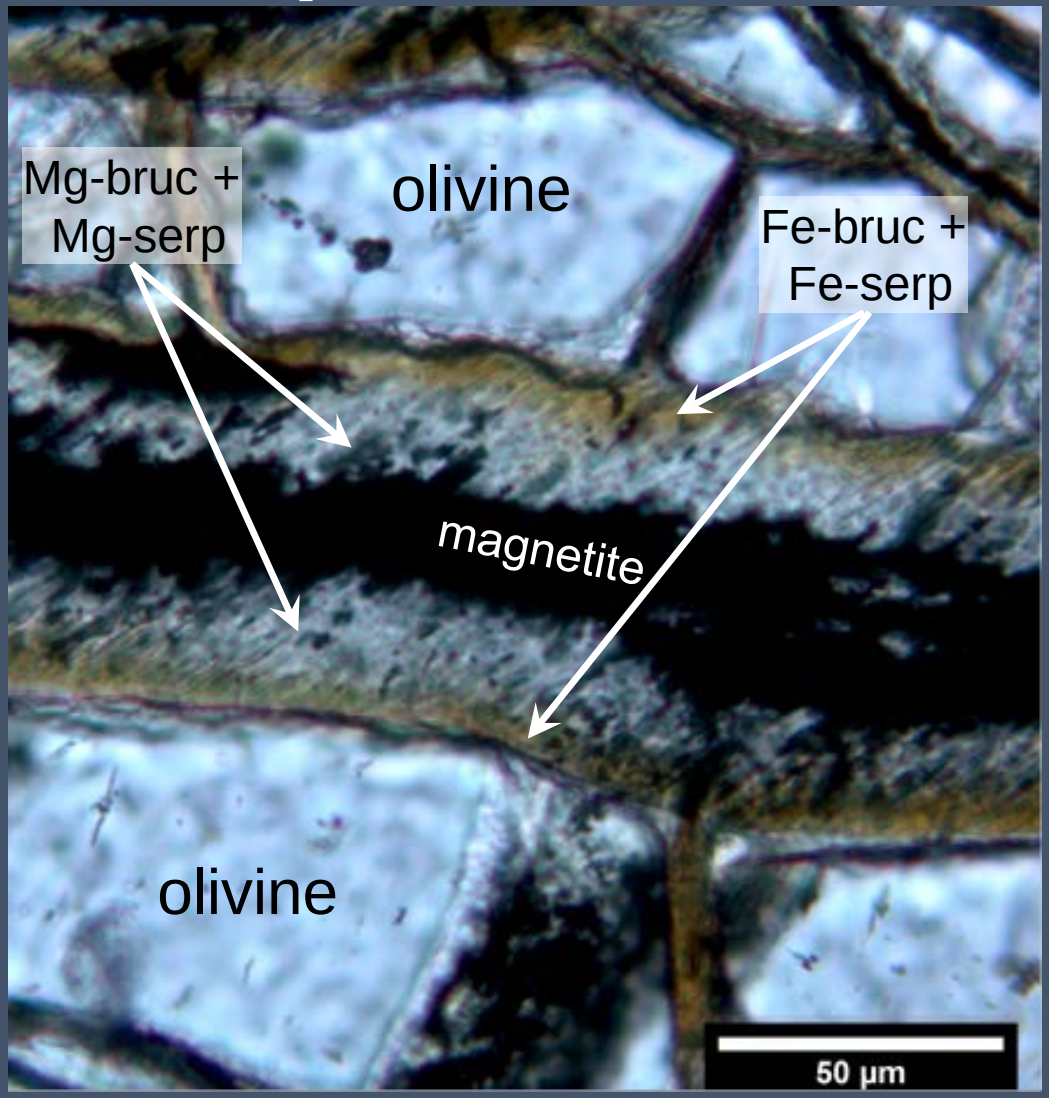


olivine + *water* = *serpentine ± brucite ± magnetite*

Olivine is extremely unstable in the presence of water

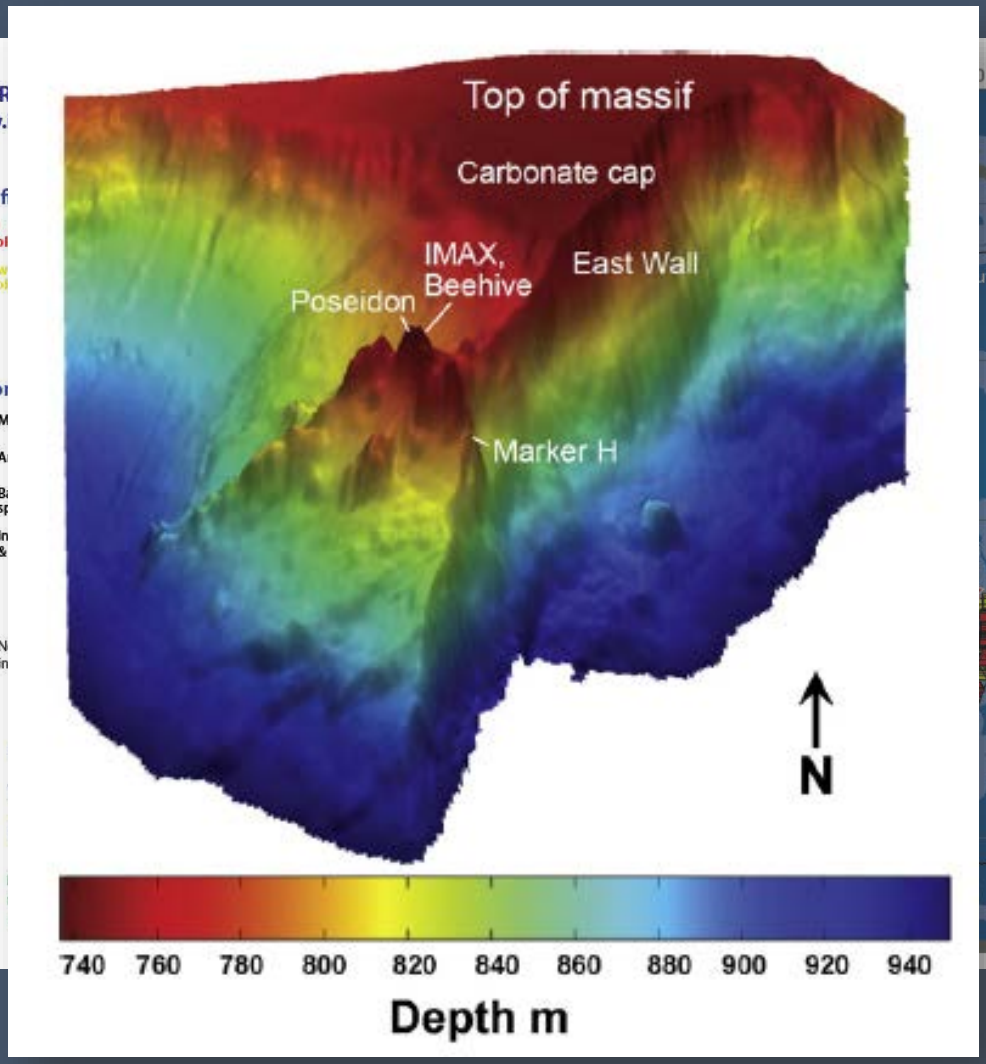


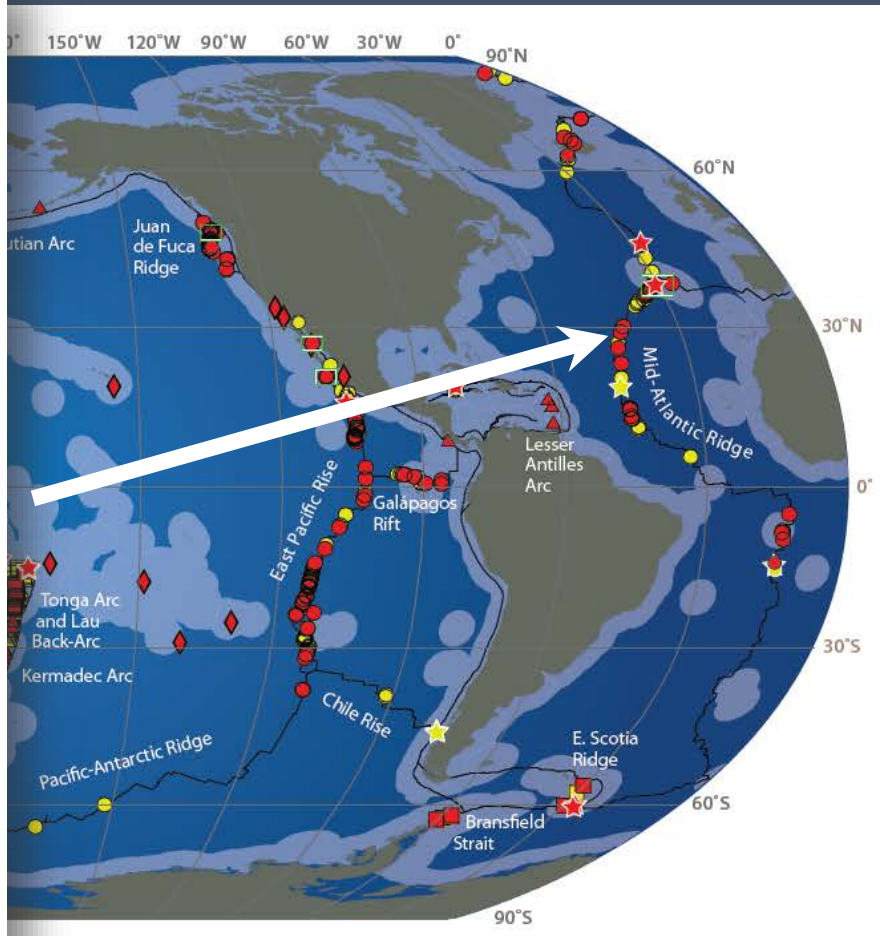
Fe partitioning and oxidation during serpentinization



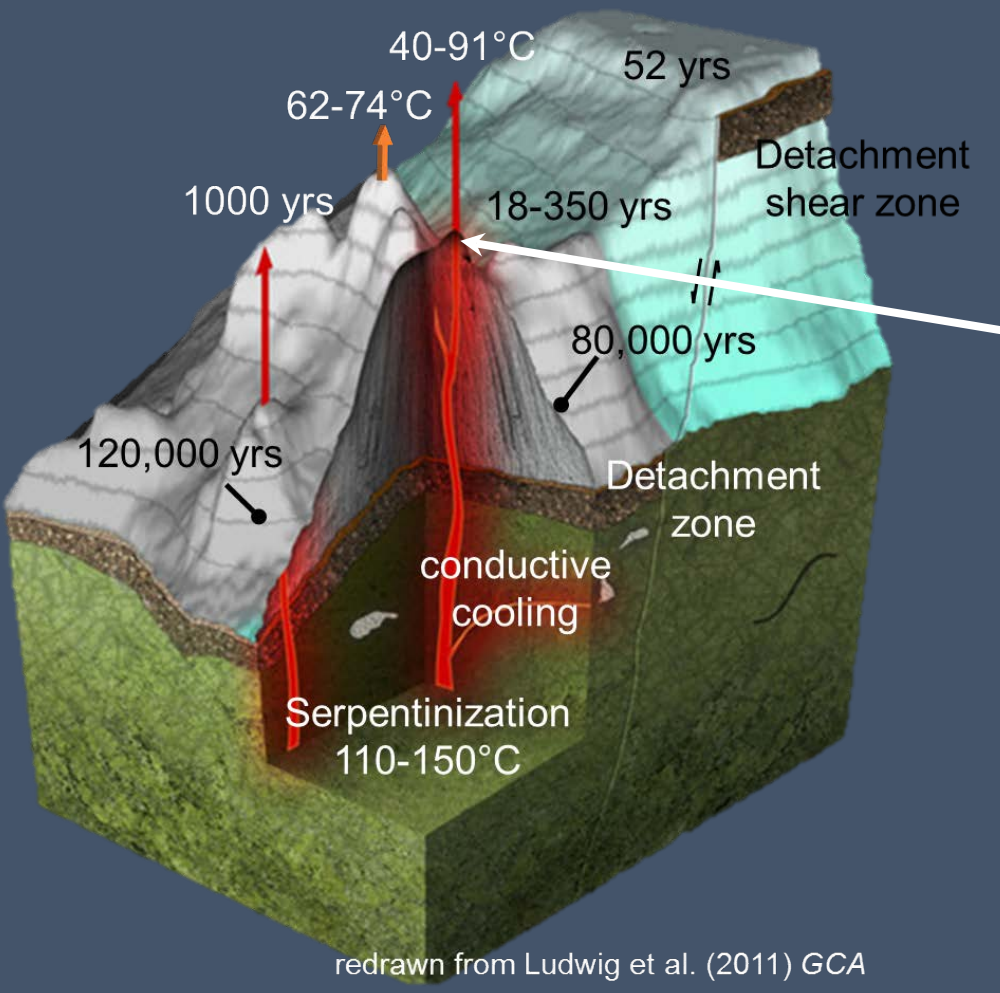
Tutolo et al. (2016) *Geology*

The Lost City Hydrothermal System

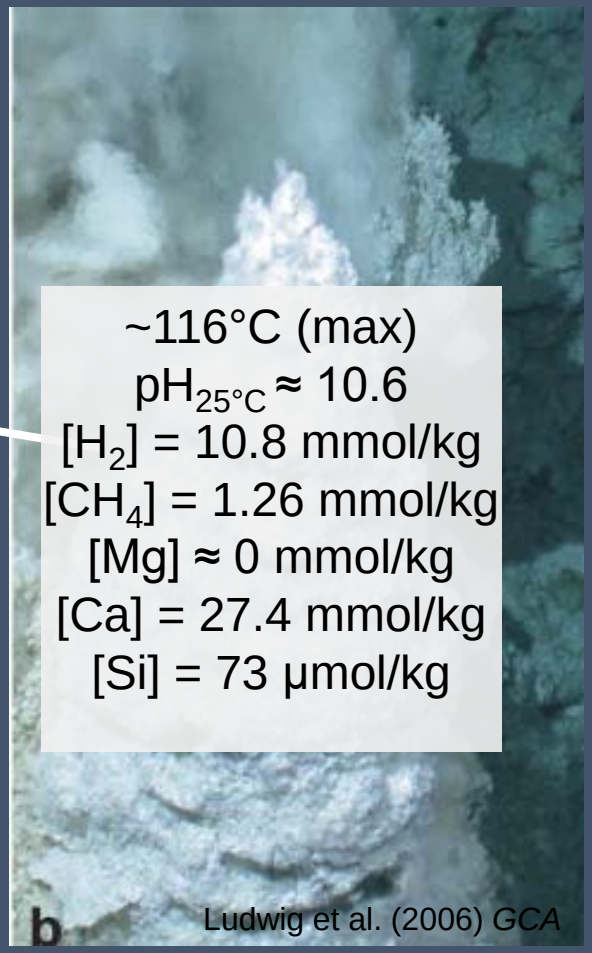




The Lost City Hydrothermal System: Vent Chemistry



redrawn from Ludwig et al. (2011) *GCA*



Ludwig et al. (2006) *GCA*

Seyfried, Pester, Tutolo and Ding (2015) *GCA*

Serpentinization and global H_2 fluxes

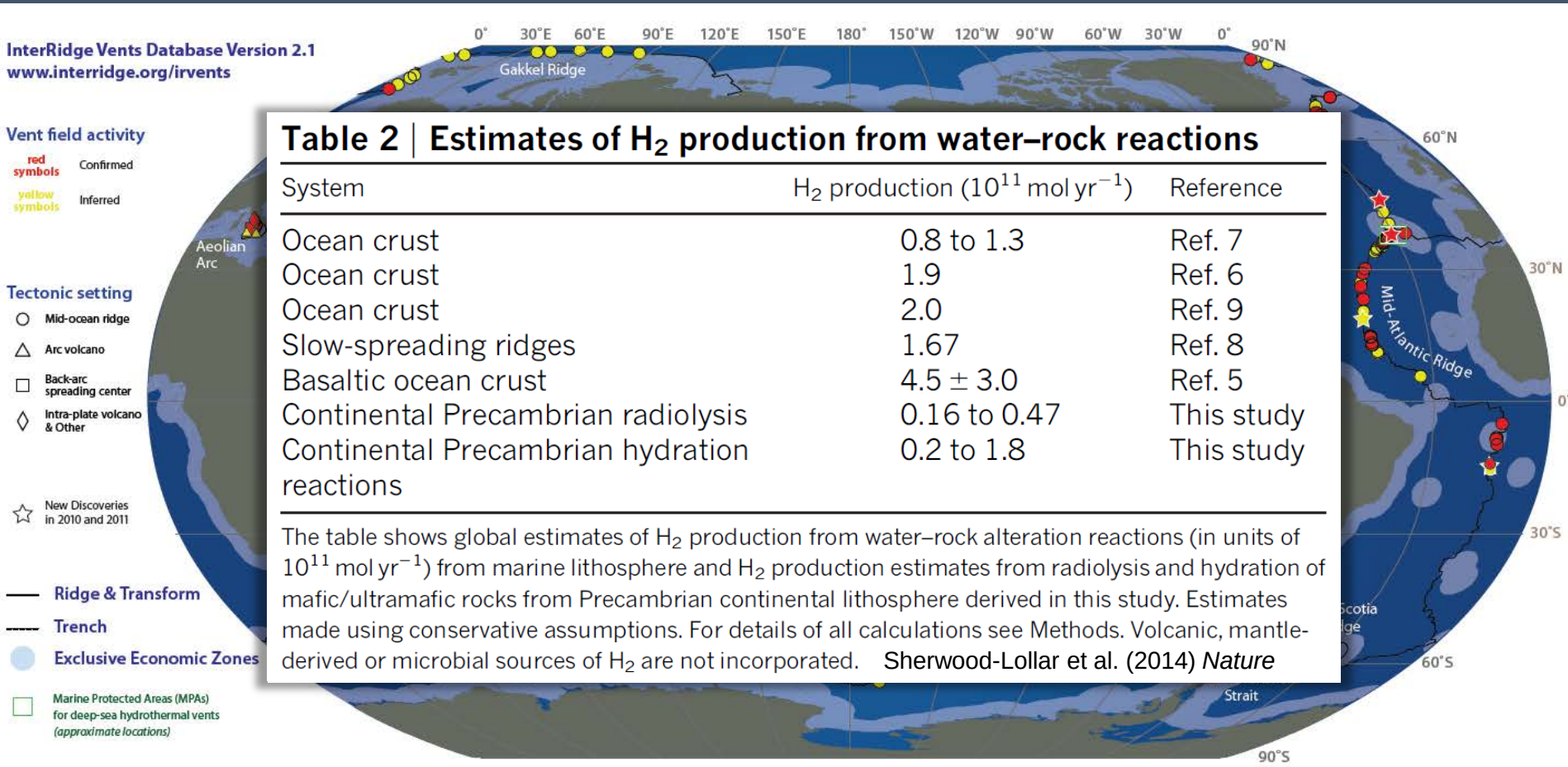


Table 2 | Estimates of H_2 production from water–rock reactions

System	H_2 production (10^{11} mol yr^{-1})	Reference
Ocean crust	0.8 to 1.3	Ref. 7
Ocean crust	1.9	Ref. 6
Ocean crust	2.0	Ref. 9
Slow-spreading ridges	1.67	Ref. 8
Basaltic ocean crust	4.5 ± 3.0	Ref. 5
Continental Precambrian radiolysis	0.16 to 0.47	This study
Continental Precambrian hydration reactions	0.2 to 1.8	This study

The table shows global estimates of H_2 production from water–rock alteration reactions (in units of 10^{11} mol yr^{-1}) from marine lithosphere and H_2 production estimates from radiolysis and hydration of mafic/ultramafic rocks from Precambrian continental lithosphere derived in this study. Estimates made using conservative assumptions. For details of all calculations see Methods. Volcanic, mantle-derived or microbial sources of H_2 are not incorporated. Sherwood-Lollar et al. (2014) *Nature*

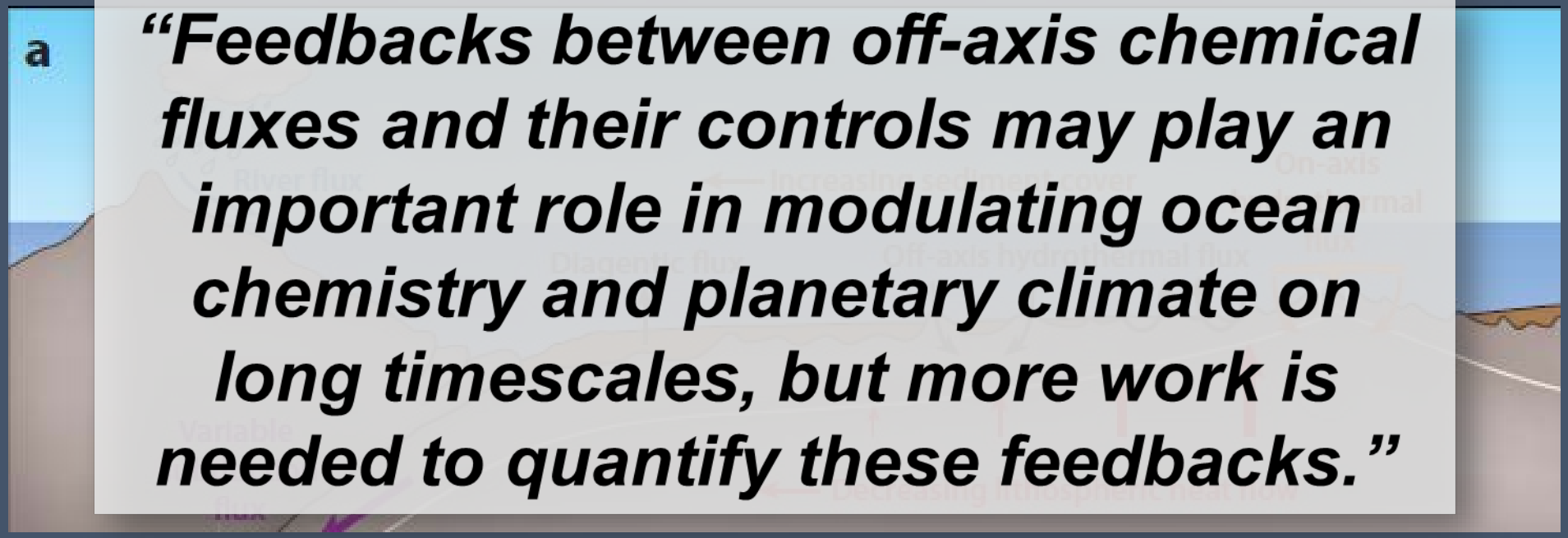
This picture would have looked very different in deep time.

Hydrothermal Processes in the Early Oceans

Fundamental research question:
Is our understanding of serpentinization-driven H_2 fluxes biased by our modern experience?

Gladstone and Diemert *When Planet Earth was New*

Low-temperature hydrothermal systems



"Feedbacks between off-axis chemical fluxes and their controls may play an important role in modulating ocean chemistry and planetary climate on long timescales, but more work is needed to quantify these feedbacks."

Coogan and Gillis (2018) *Ann. Rev. Earth and Planet. Sci*

How is H_2 generated during low-temperature serpentinization?

Low-temperature serpentinization

Magnetite in seafloor serpentinite—Some like it hot

Frieder Klein[1]*, Wolfgang Bach[2], Susan E. Humphris[1], Wolf-Achim Kahl[2], Niels Jöns[2], Bruce Moskowitz[3], and Thelma S. Berquó[4]

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[3]Department of Earth Sciences, and Institute for Rock Magnetism, University of Minnesota, Minneapolis, Minnesota 55455, USA

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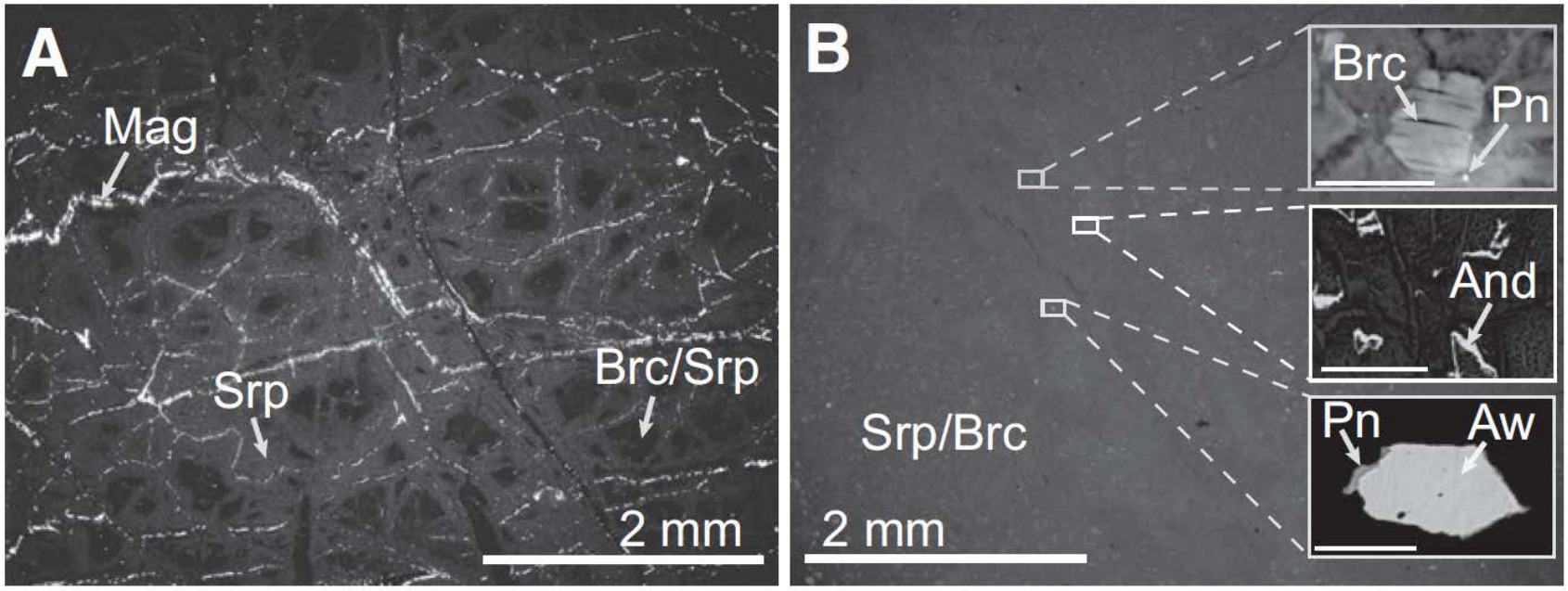
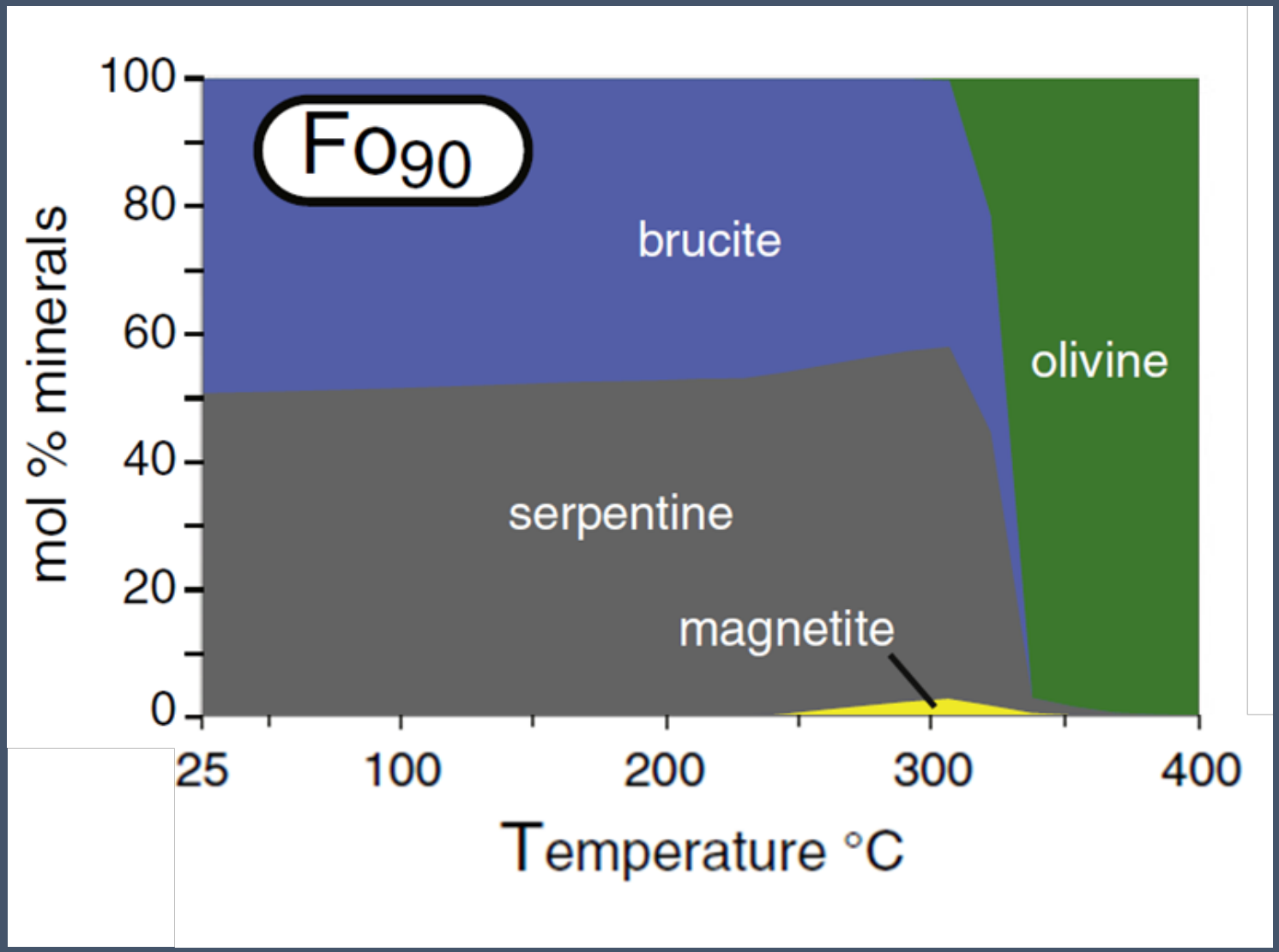


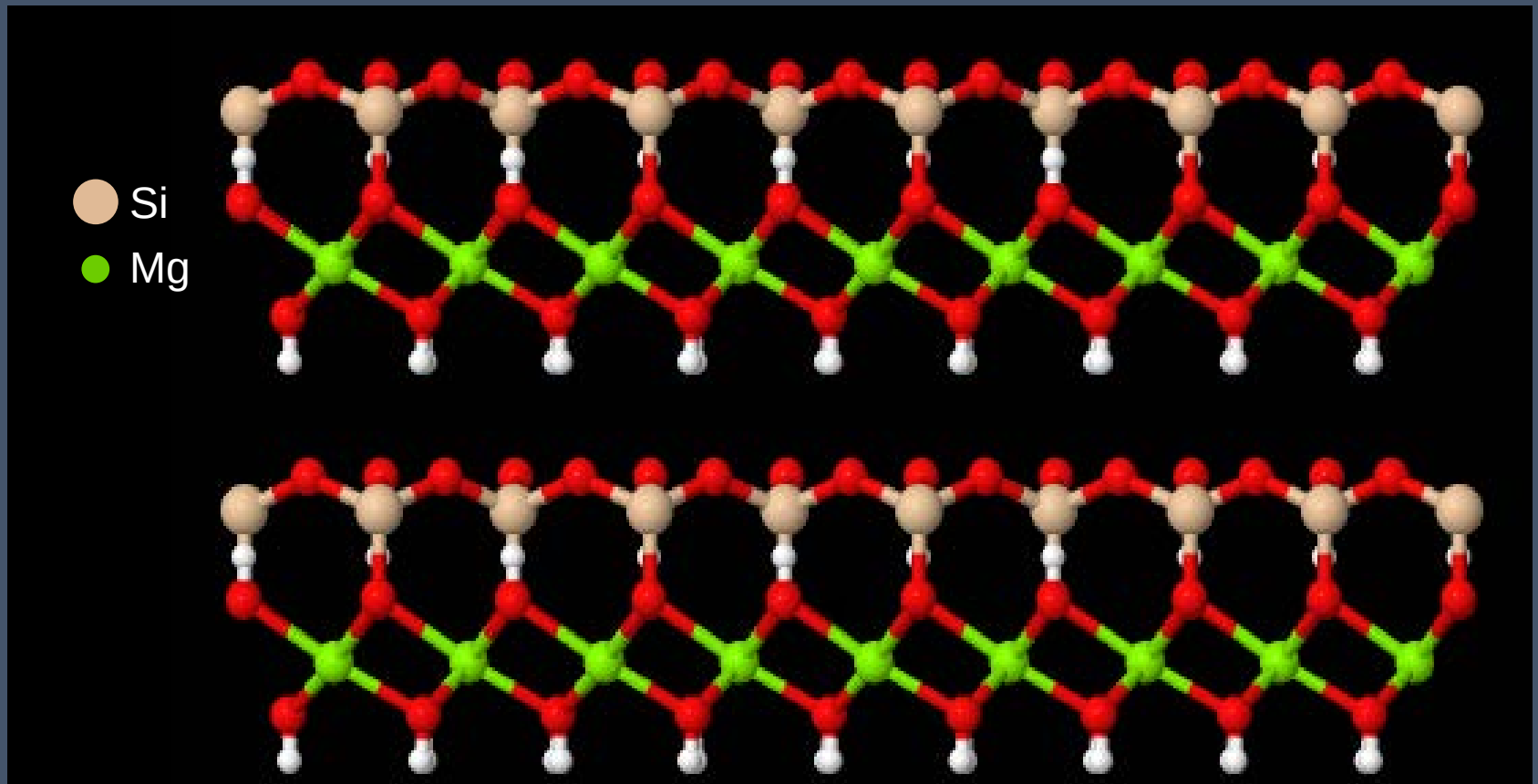
Klein et al. (2014) *Geology*

Low-temperature serpentinization



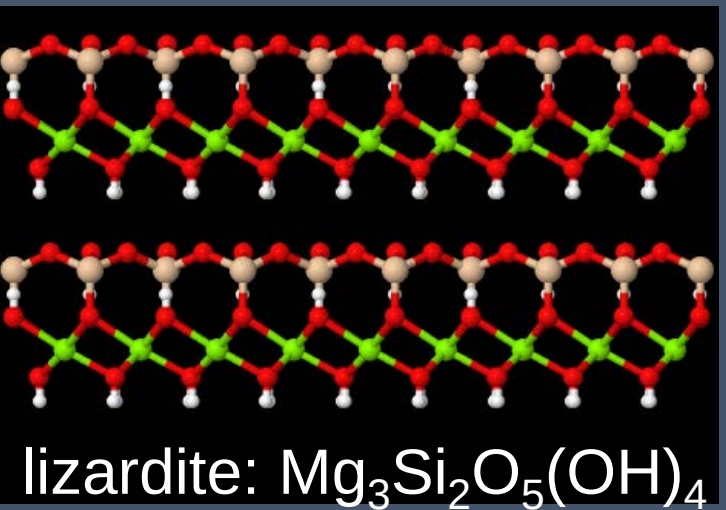
Klein et al. (2013) *Lithos*

Fe^{3+} in serpentine: Crystallographic considerations



lizardite: $Mg_3Si_2O_5(OH)_4$

Mechanisms for Fe^{3+} incorporation into serpentine (and H_2 production)



lizardite: $Mg_3Si_2O_5(OH)_4$

1. Dioctahedral substitution

2 $Fe^{3+} \leftrightarrow 3\ Mg^{2+}$, towards hisingerite:

$\square Fe^{3+}_2Si_2O_5(OH)_4$

(Tutolo et al. (2019) *Minerals*)

2. Deprotonation

$Fe^{3+} \leftrightarrow (Fe^{2+}H)$ towards "oxyserpentine":

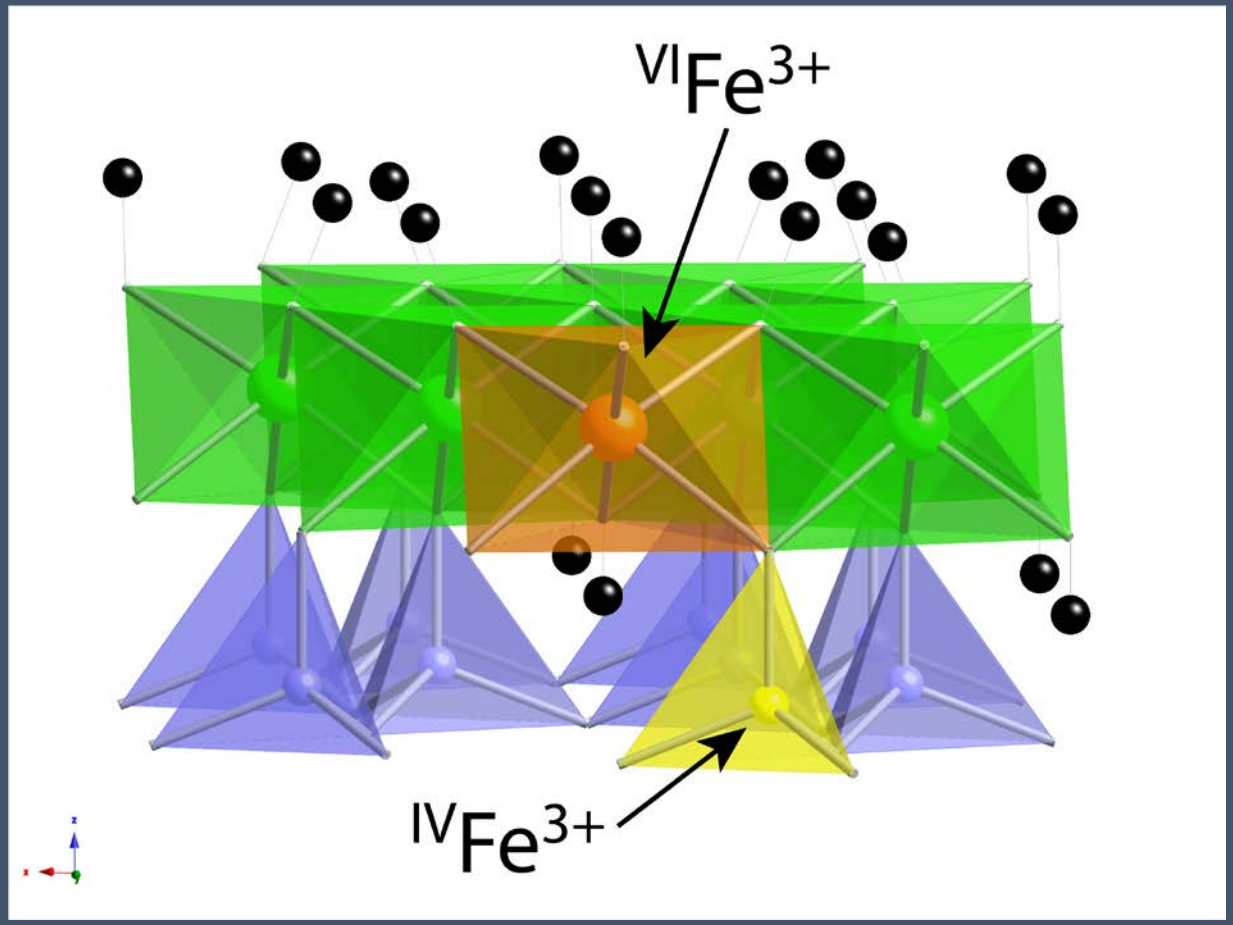
$(Mg_2Fe^{3+})Si_2O_6(OH)_3$

3. Ferri-Tschermaks

2 $Fe^{3+} \leftrightarrow (MgSi)$ towards Mg-cronstedtite:

$Mg_2Fe^{3+}_2SiO_5(OH)_4$

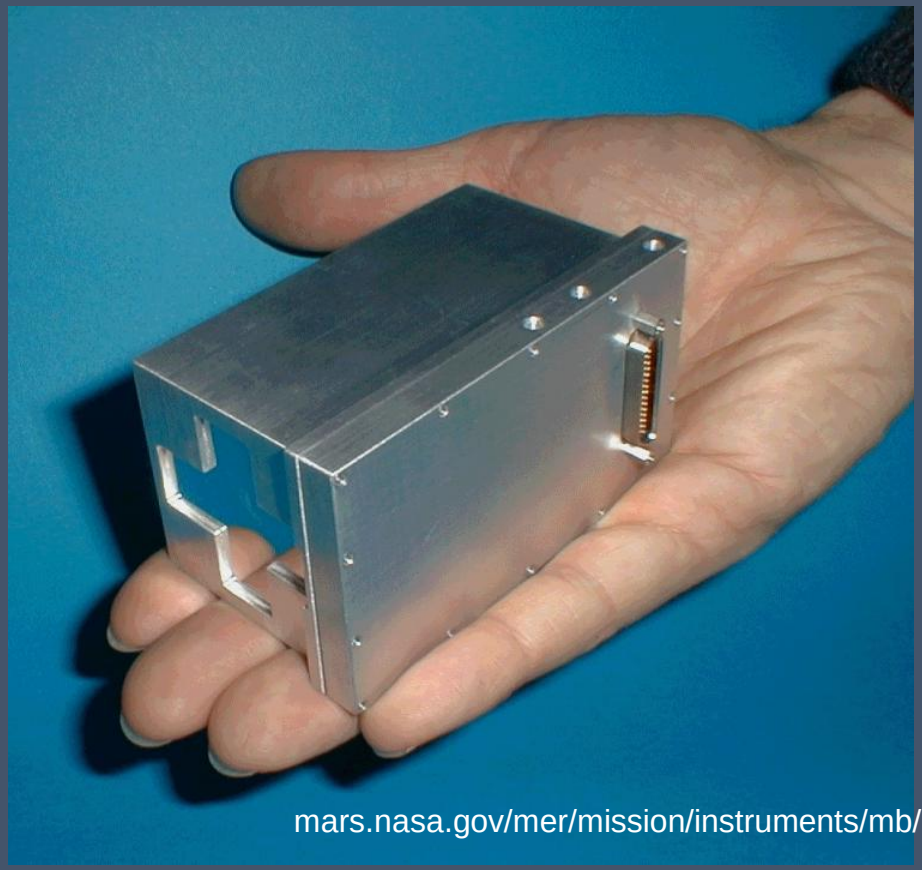
Ferri-Tschermaks Substitution



$2\ Fe^{3+} \leftrightarrow (MgSi)$ (favored at low $[SiO_2]$)

Tutolo et al (2020) *PNAS*

Fe^{3+} substitution in serpentines: Mössbauer spectroscopy



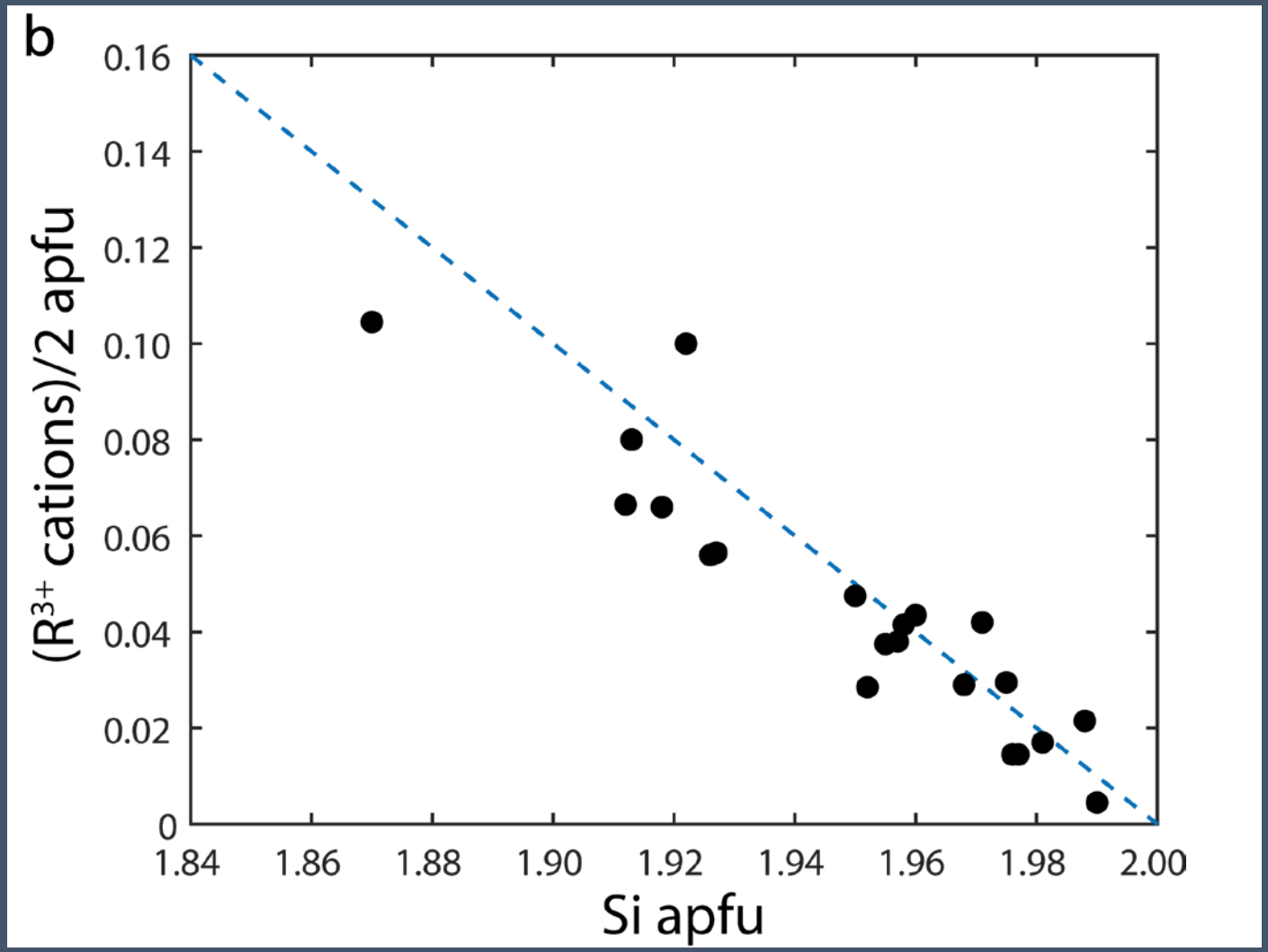
mars.nasa.gov/mer/mission/instruments/mb/

➢ *Radioactive decay of ^{57}Co interrogates **oxidation** and **coordination** state of ^{57}Fe in the sample*

$^{IV}Fe^{3+}$-for-^{IV}Si (Ferri-Tschermaks) substitution in serpentine

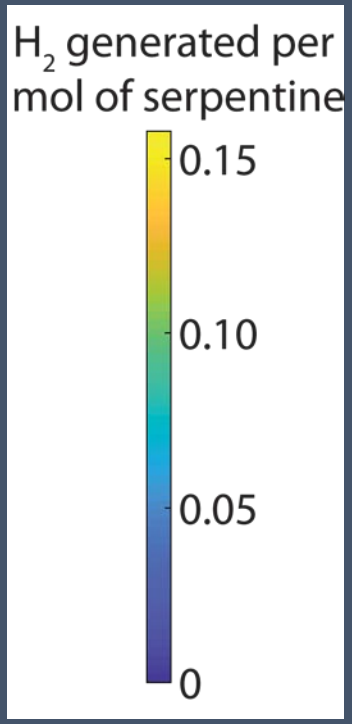
Tutolo et al *(2020) PNAS*

Analytical evidence of $^{IV}Fe^{3+}$-for-^{IV}Si substitution in serpentines



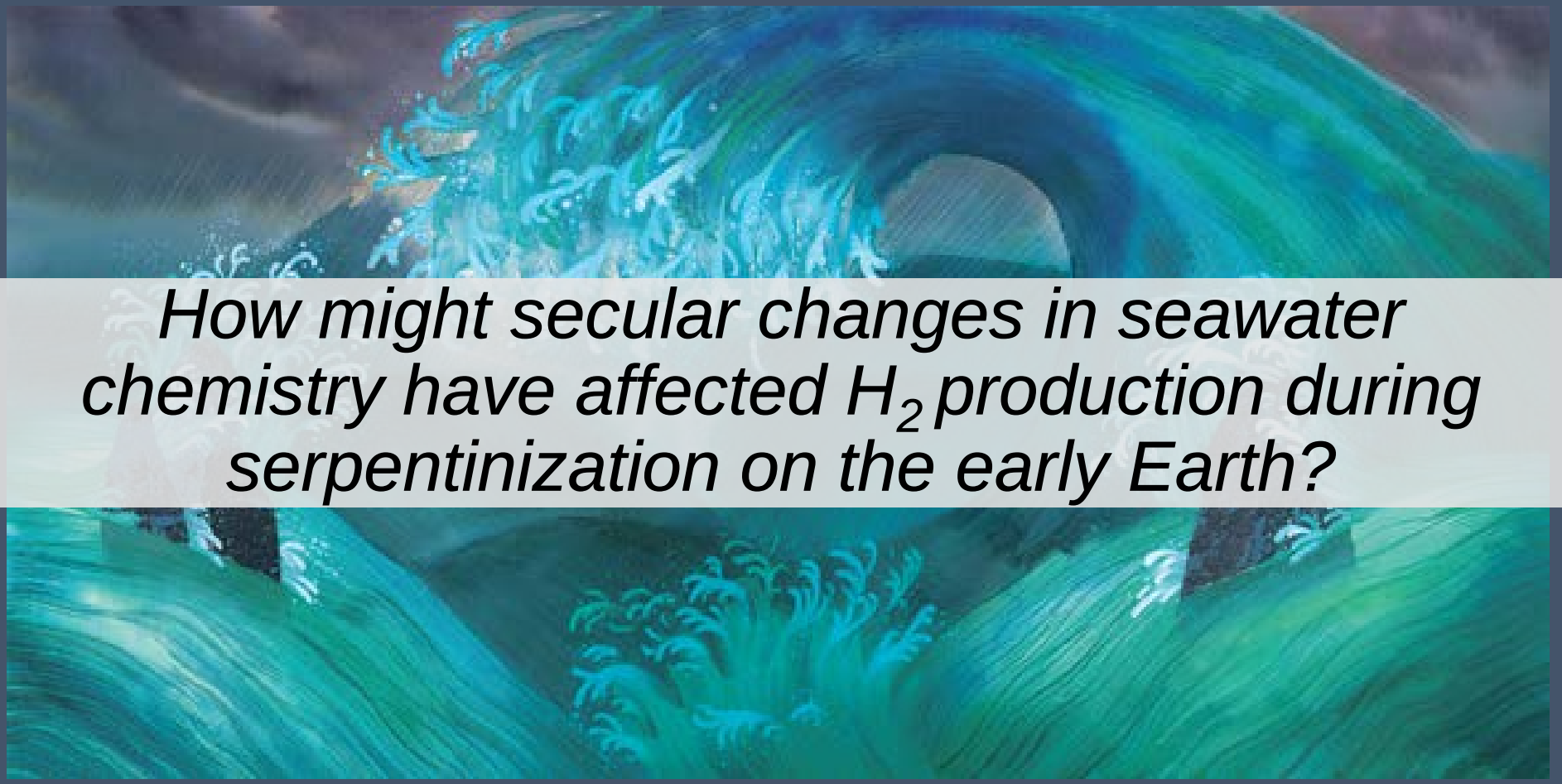
Tutolo et al. (2020) *PNAS; data from* Evans et al. (2012) *Am. Min.*

H_2 generation by Ferri-Tschermaks substitution in serpentine



Tutolo et al. *(2020) PNAS*

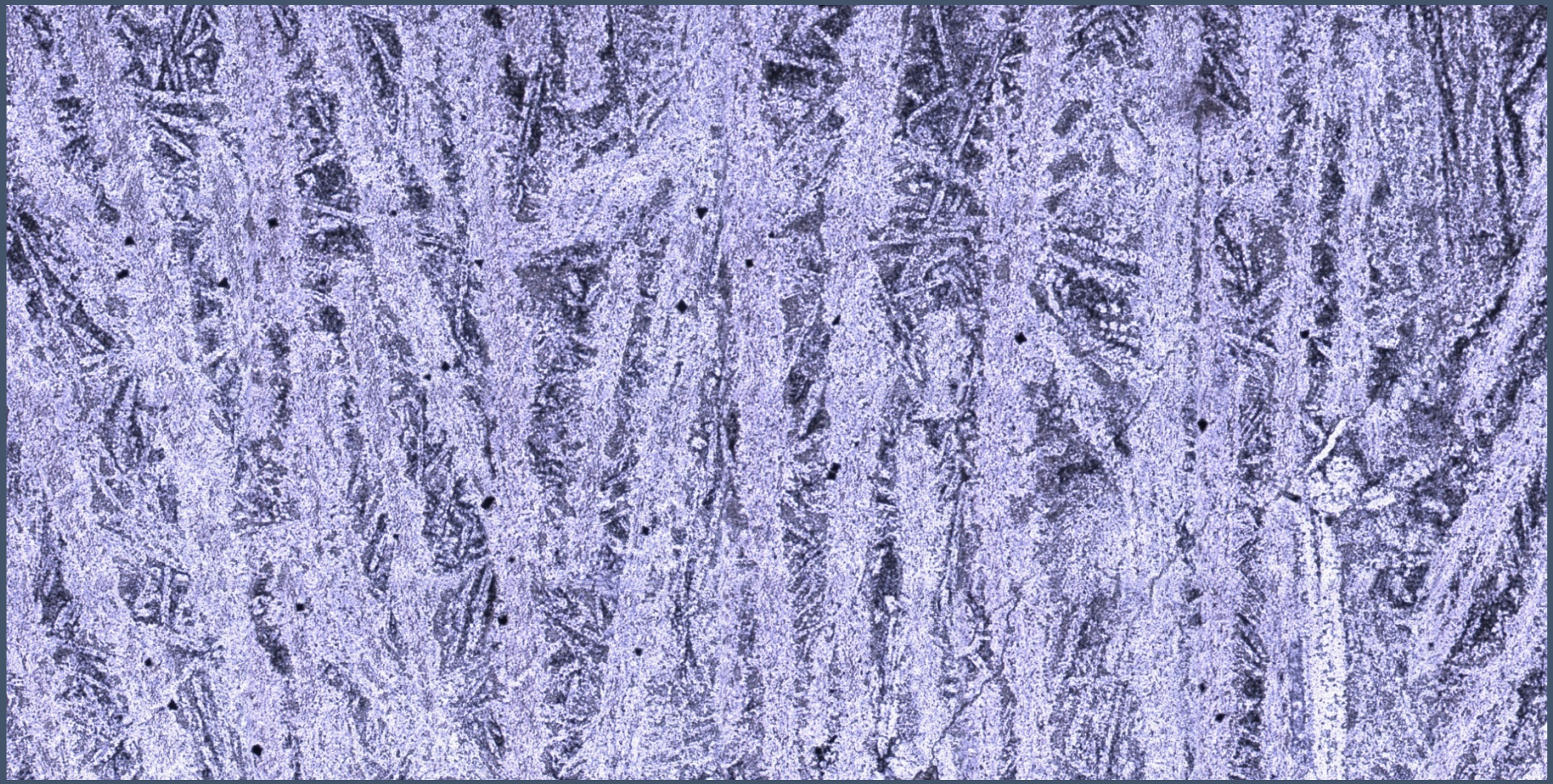
Hydrothermal Processes in the Early Oceans



How might secular changes in seawater chemistry have affected H_2 production during serpentinization on the early Earth?

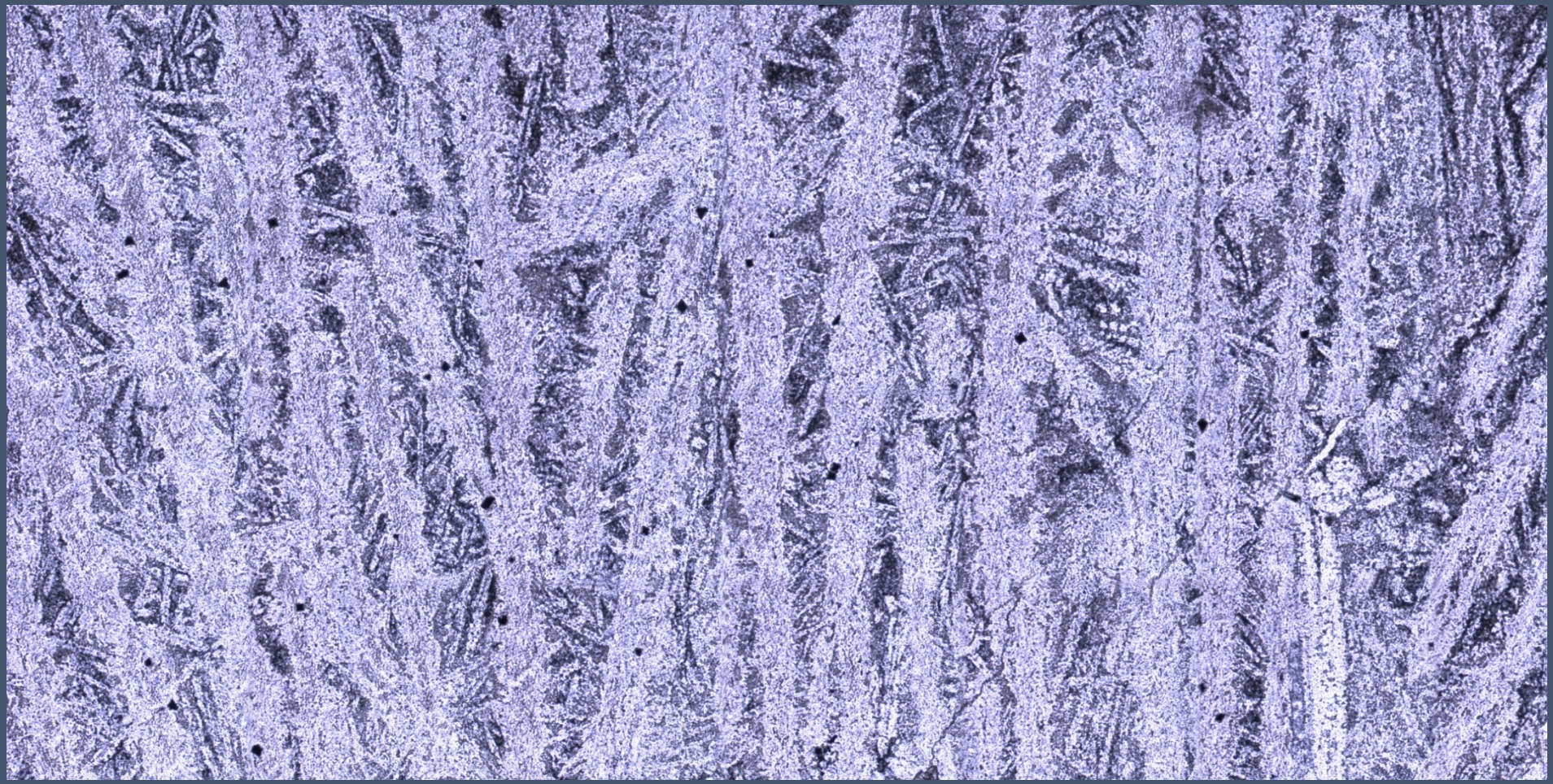
Gladstone and Diemert *When Planet Earth was New*

What is this?



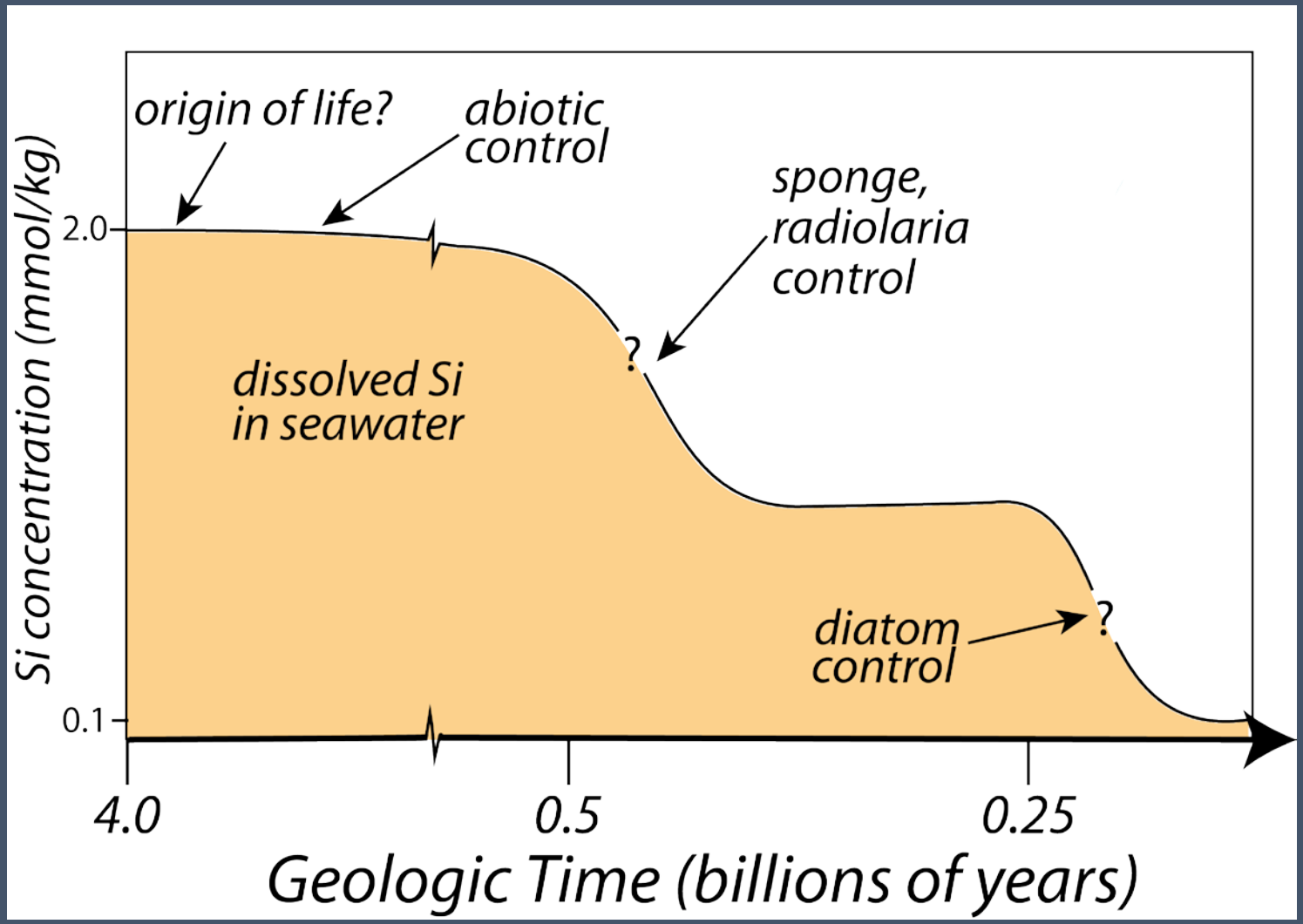
Field of view ≈ 1 cm

Silicified Komatiite from the 3.3 Ga Mendon Formation



Field of view ≈ 1 cm

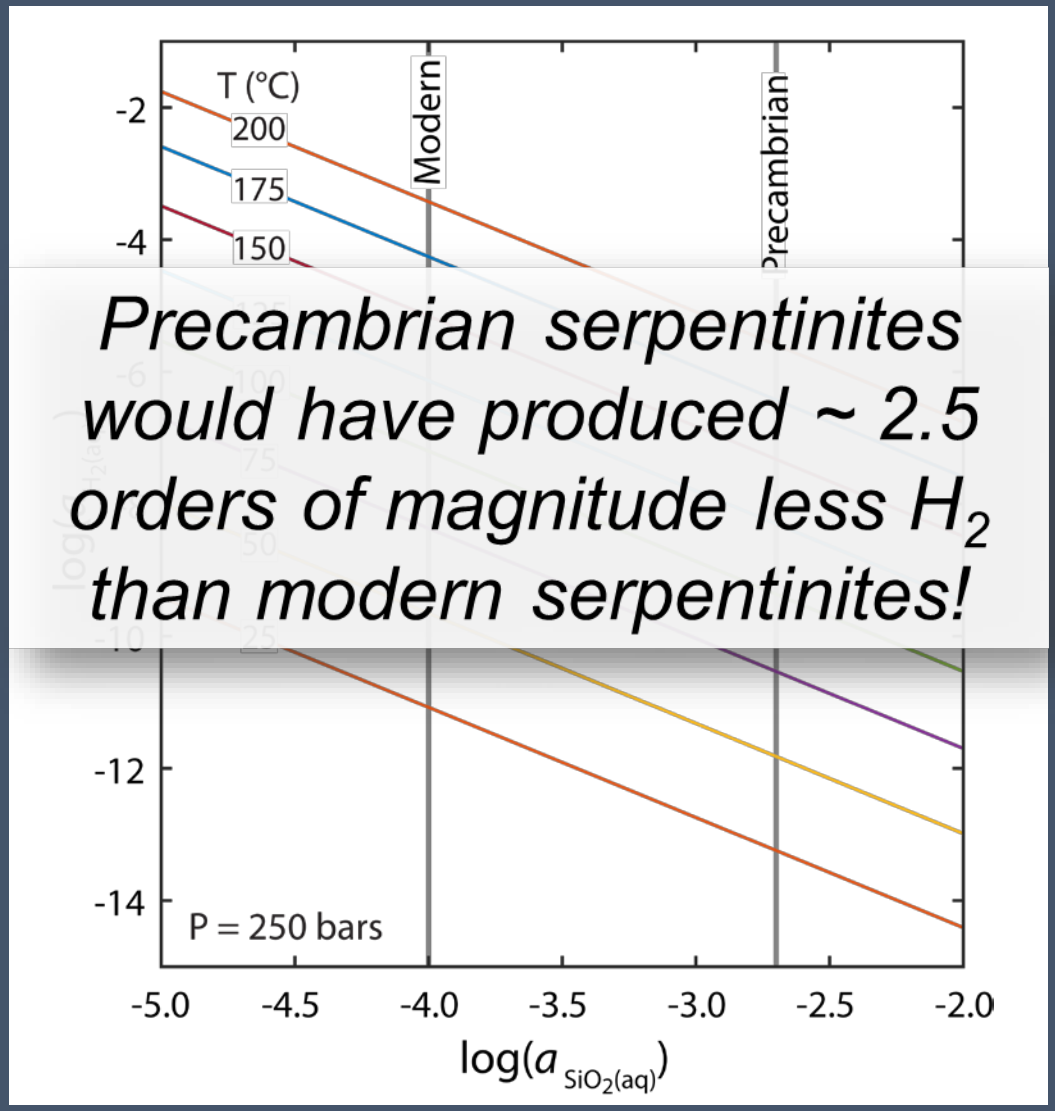
Secular change in the SiO_2 cycle



Siever et al. (1991, 1992) *GCA*, Conley et al. (2017) *Frontiers in Marine Sci.*

Fe^{2+}-Fe^{3+} equilibria in serpentine

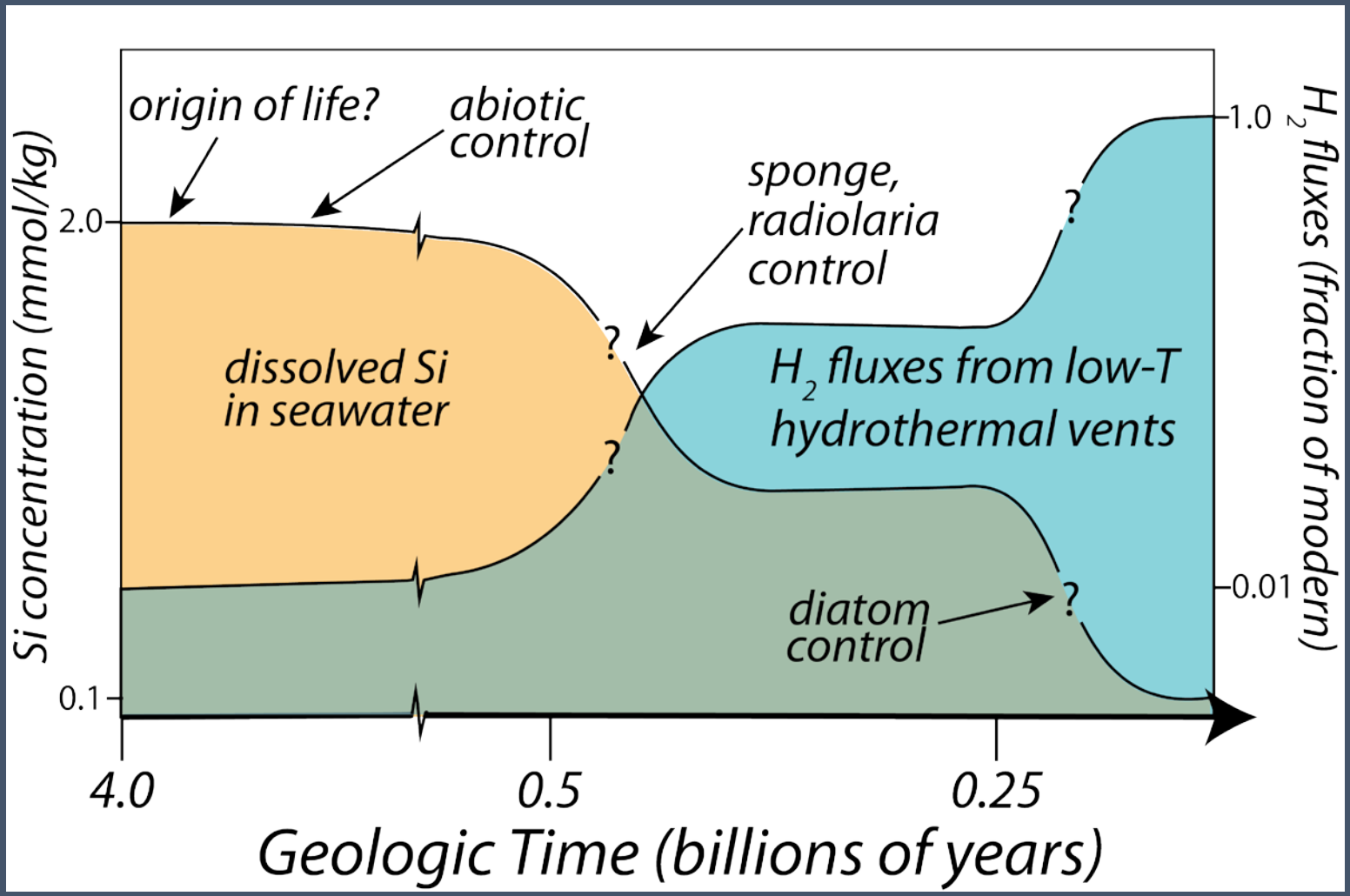
$Fe^{2+}\text{-serp}_{(XMg=0.9)} + 0.05\ H_2O \rightleftharpoons Fe^{3+}\text{-serp}_{(XMg=0.9)} + 0.25\ SiO_2(aq) + 0.15\ H_2(aq)$



Precambrian serpentinites would have produced ~ 2.5 orders of magnitude less H_2 than modern serpentinites!

Tutolo et al. *(2020) PNAS*

Hypothesized H_2 fluxes through Earth's history



Take-Home Points

- **H_2 production during low-temperature serpentinization is linked to a Si deficiency in the serpentine structure, which itself is caused by low SiO_2(aq) concentrations in fluids derived from modern seawater**

- **Elevated SiO_2 in Precambrian seawater (and the waters of other diatom-free oceans) would thus have limited the extent of H_2 production during serpentinization**

Thanks! Questions?

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