

The Formation and Diagenesis of Mg-Clay Minerals in Lacustrine Carbonate Reservoirs*

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Abstract

Mg-rich clay minerals are relatively common components in modern and ancient lake systems, but are unusual in carbonate rocks. Although clays are traditionally viewed as having a negative impact on reservoir characteristics (e.g. promotion of pressure solution, localised cementation and clay seams), Mg-rich clays are prone to a series of diagenetic reactions that instead lead to the production of secondary porosity. Because of their unusual chemical composition and structure, Mg-clays are chemically more labile and wholly distinct from the more common Al-rich varieties (e.g. illite). Modern analogs and experimental syntheses show that Mg-clays act as valuable tools in constructing facies models, yet they exhibit complex and rapid responses to depositional chemistry (e.g. salinity, pH, Mg/Si ratios, temperature, detrital input and the presence of biological substrates). Once initiated, the precipitation of Mg-clays from water takes place rapidly via the formation of a poorly crystalline, viscous and extensively hydrated “gel”; an ideal substrate for the generation of spherulitic calcite. Dehydration of the gel phase is capable of releasing up to 25-30 wt. % H₂O from crystallite surfaces and interlayers, acting as an important source of diagenetic water to buried sediments. In addition to burial dehydration, Mg-clays in general, and stevensite in particular, may be prone to a number “self-initiated” acid producing reactions that lead to corrosion upon further diagenesis. Ongoing experimental work is aimed at unraveling these pathways, some of which may be uniquely attributed to the burial of Mg-rich clay structures (e.g. gel annealing and interlayer cation migration). Once destabilised, however, the distinctly Al-free chemical composition of most Mg-clays means dissolution is nearly always congruent with few secondary products beyond silica and dolomite. Our view of Mg clay diagenesis in lacustrine carbonate reservoirs is consistent with a number of sedimentary textures observed in Pre-Salt carbonates of the Santos and Campos basins. Nevertheless, understanding the interactions between Mg-clays and lacustrine carbonates is a challenging frontier for research and warrants new approaches to understanding geochemical pathways during diagenesis.

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The formation and diagenesis of Mg-clay minerals in lacustrine carbonate reservoirs

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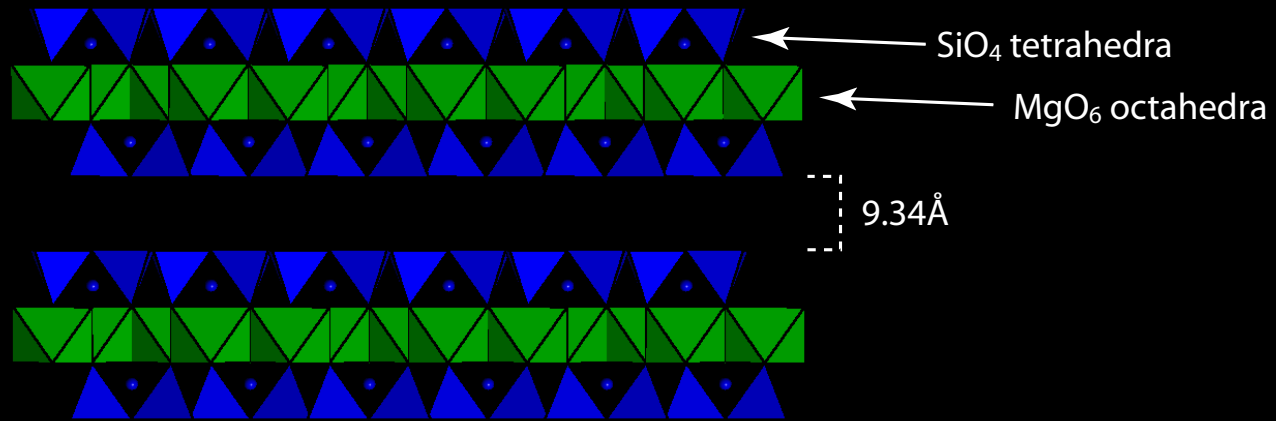


Key points

- Evaporation is most effective means of initiating Mg-silicate nucleation ($\text{pH} > 9.5$)
- Identity of the Mg-silicate is controlled by pH, Mg/Si, salinity & presence of detrital material
- Mg-silicates initially precipitate as an aggregate of hydrated nano-particles (a gel) acting as favourable physical & chemical substrate for spherulitic calcite growth
- Mg-silicates highly sensitive to pH / P_{CO_2} fluctuations early in diagenesis and dissolve faster than calcite due to high surface area
- Mg-silicate accumulation likely concentrated in shallow to sub-littoral zones devoid of detrital flux or physical re-working
- Organic matter diagenesis (e.g., methanogenesis) in deeper/profundal sediments drove Mg-silicate dissolution & limited accumulation

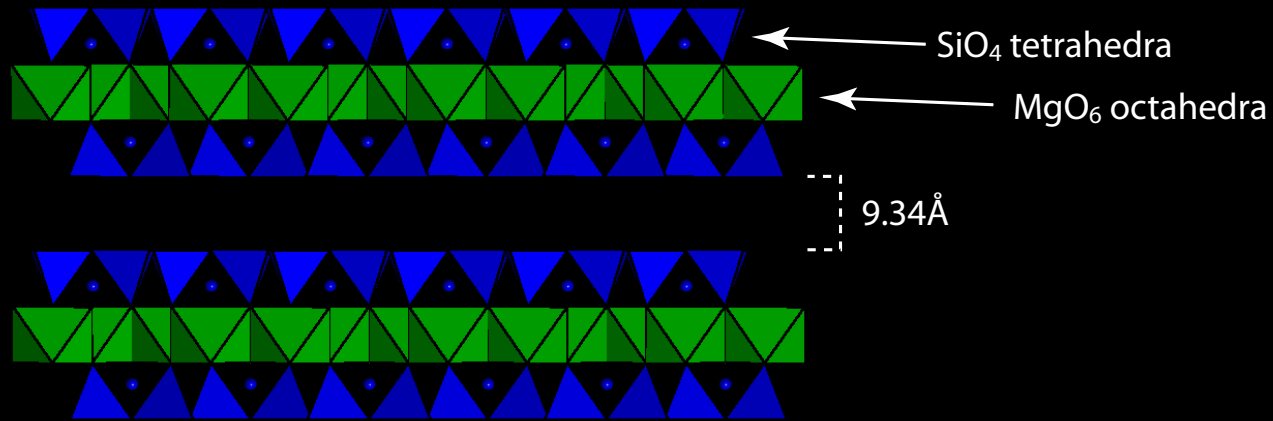
What are we dealing with?

Talc

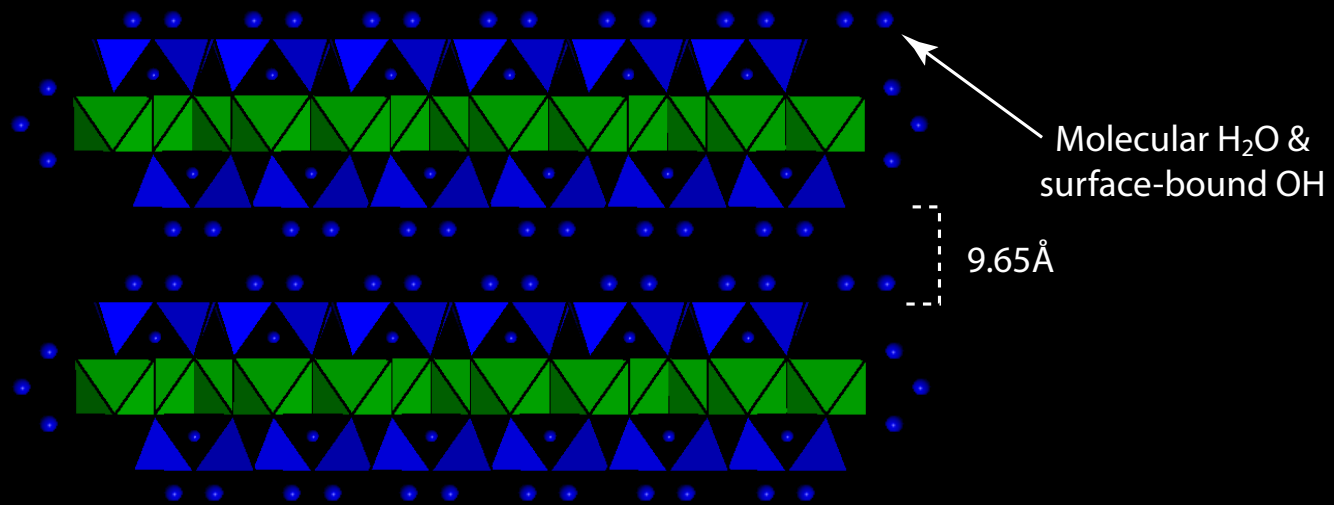


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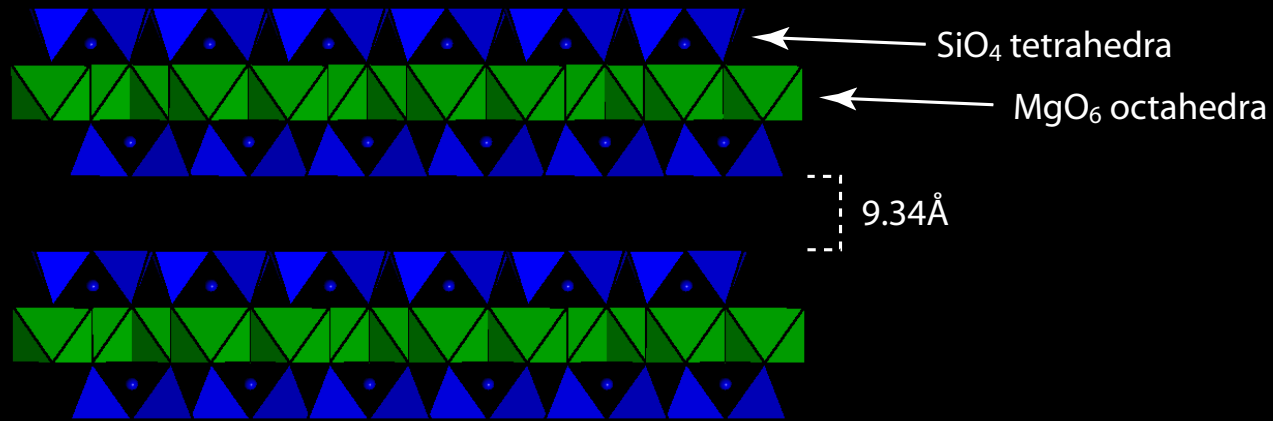


Kerolite

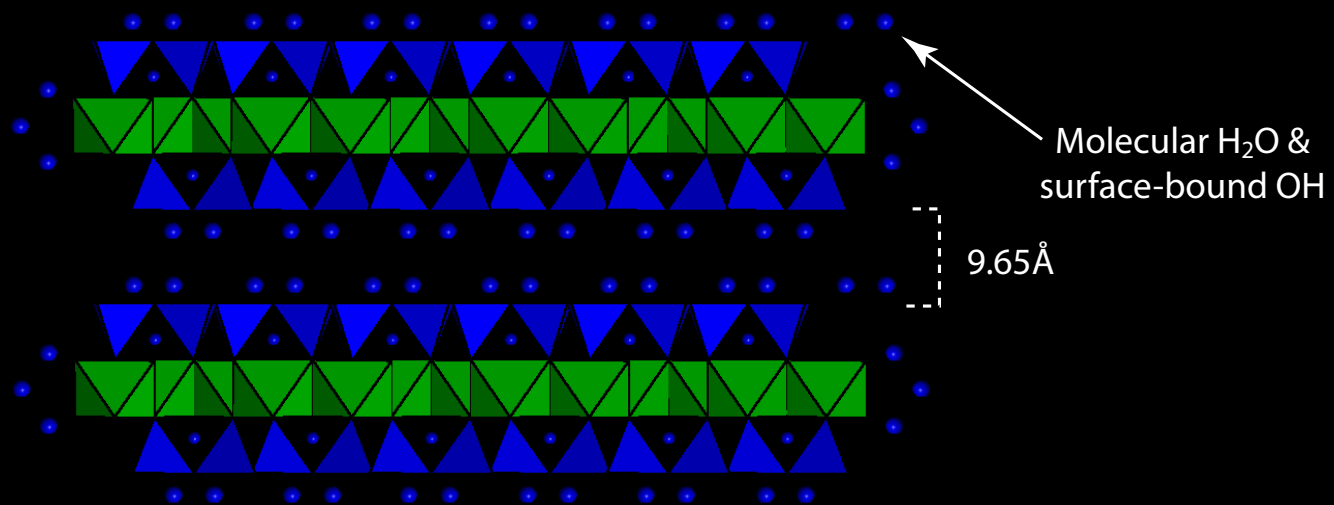


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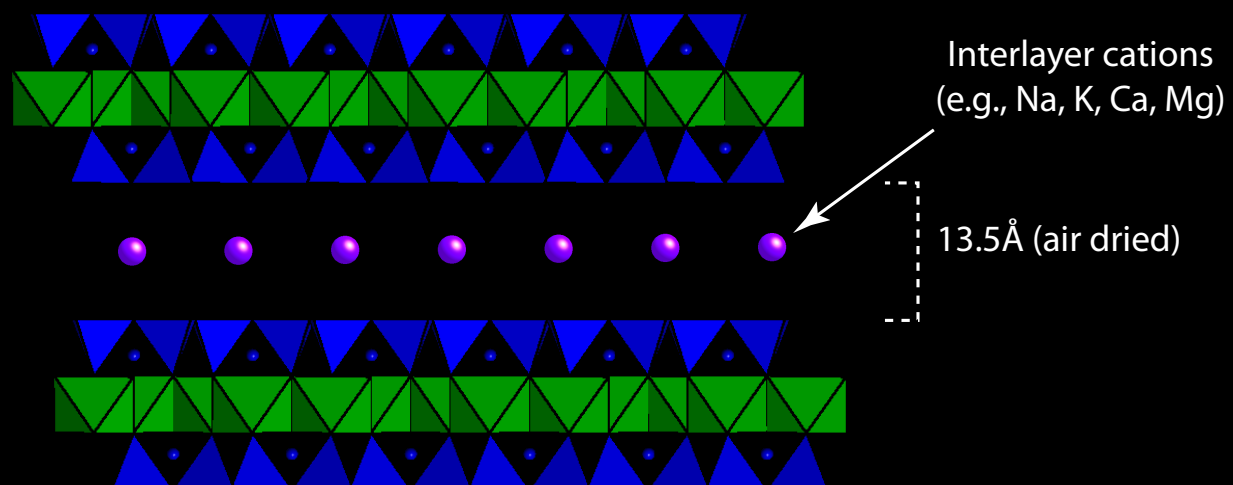
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Kerolite

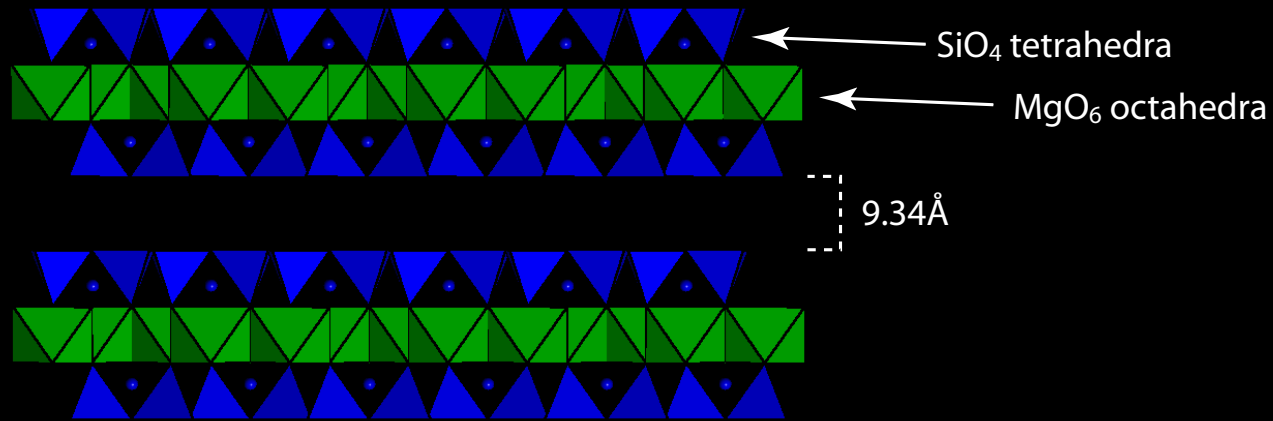


Stevensite (Mg-smectite)

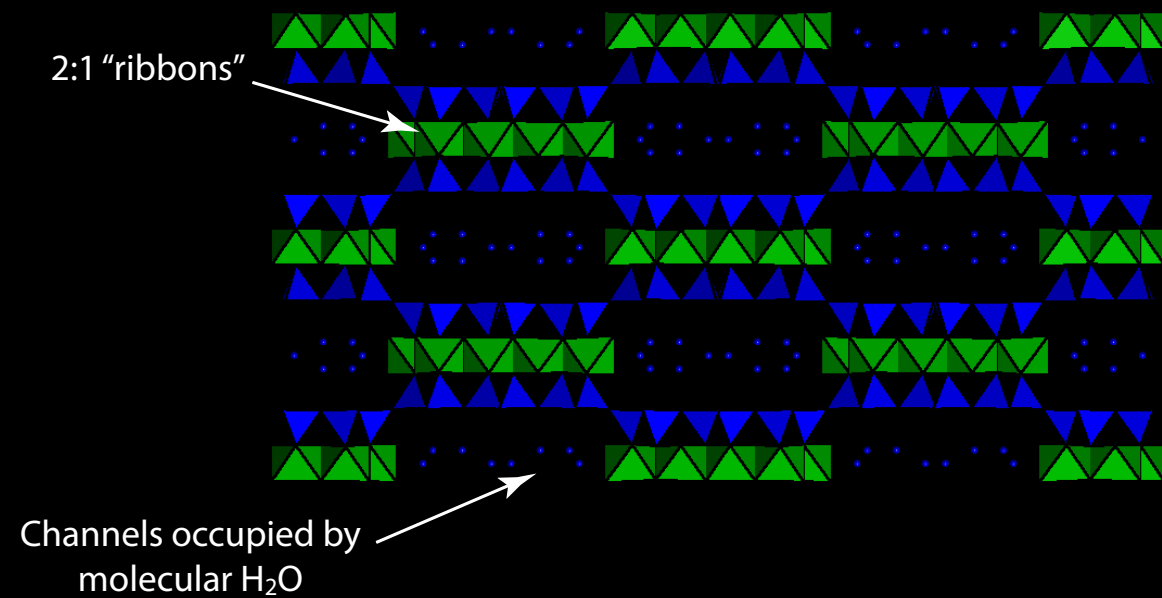


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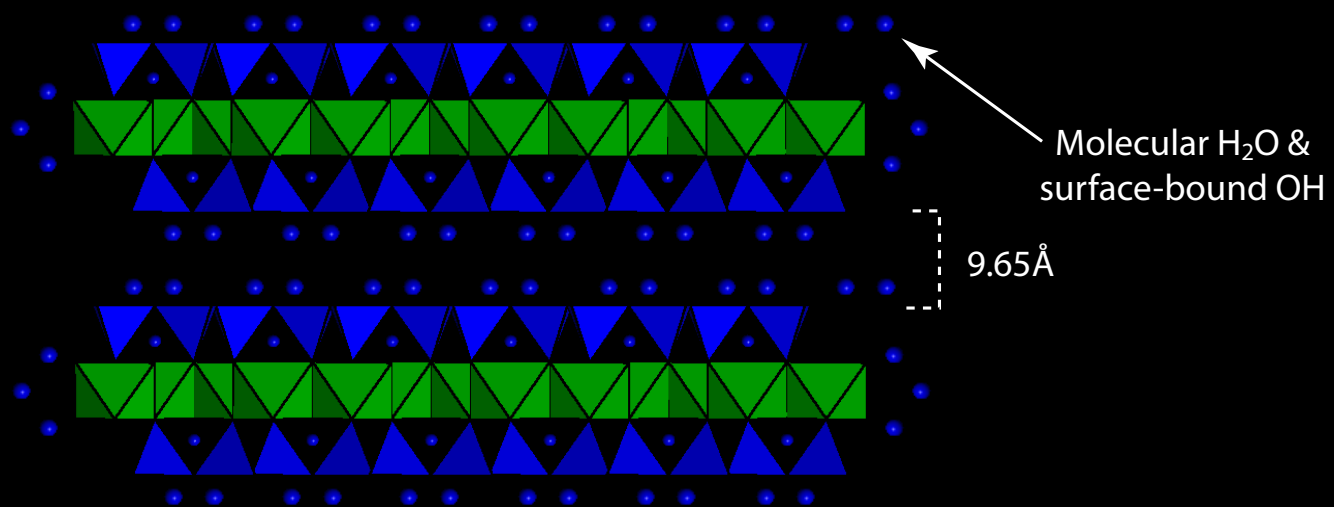
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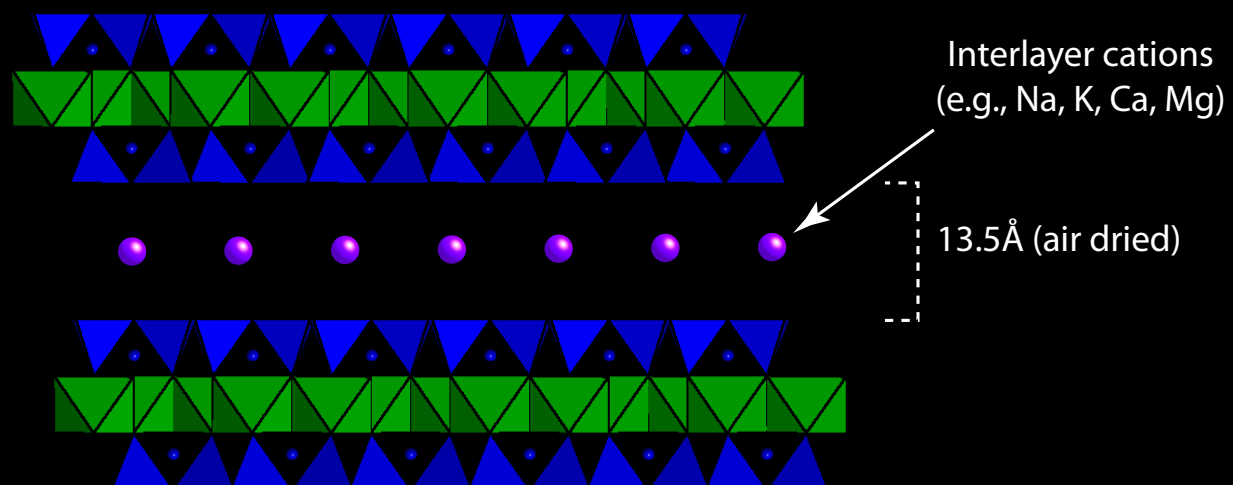
Sepiolite



Kerolite

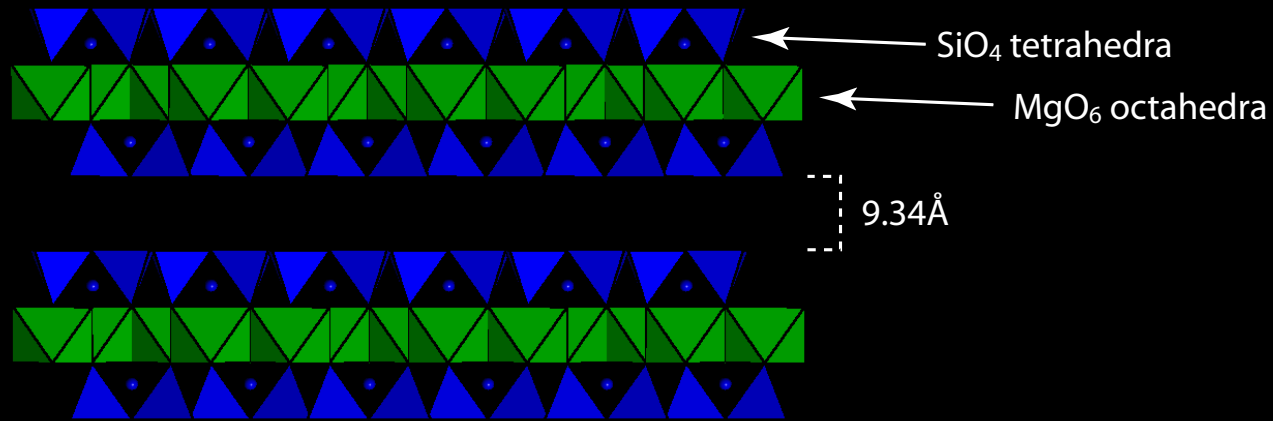


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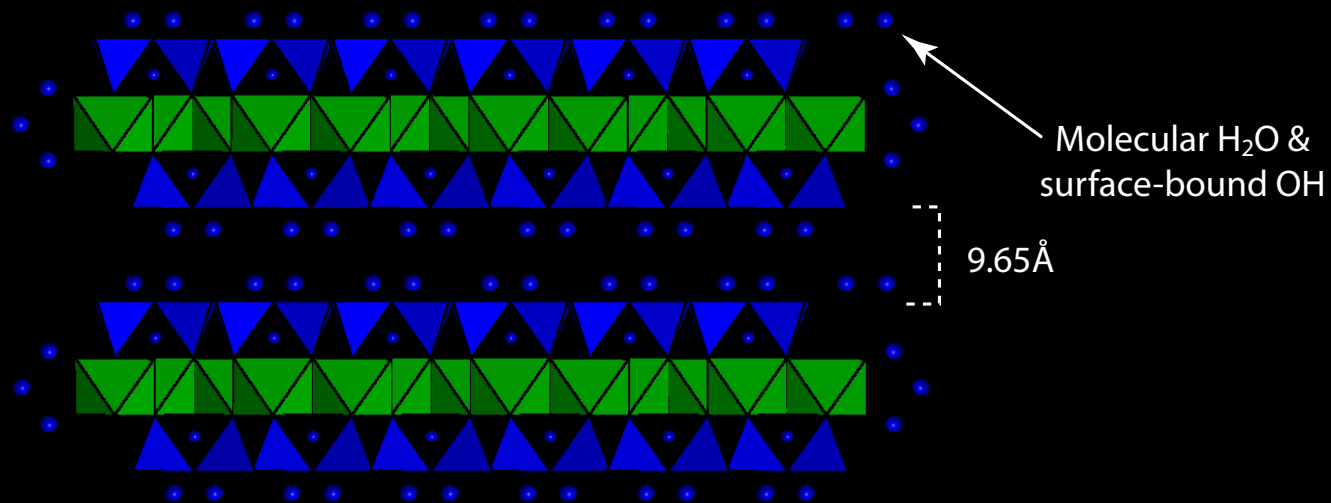


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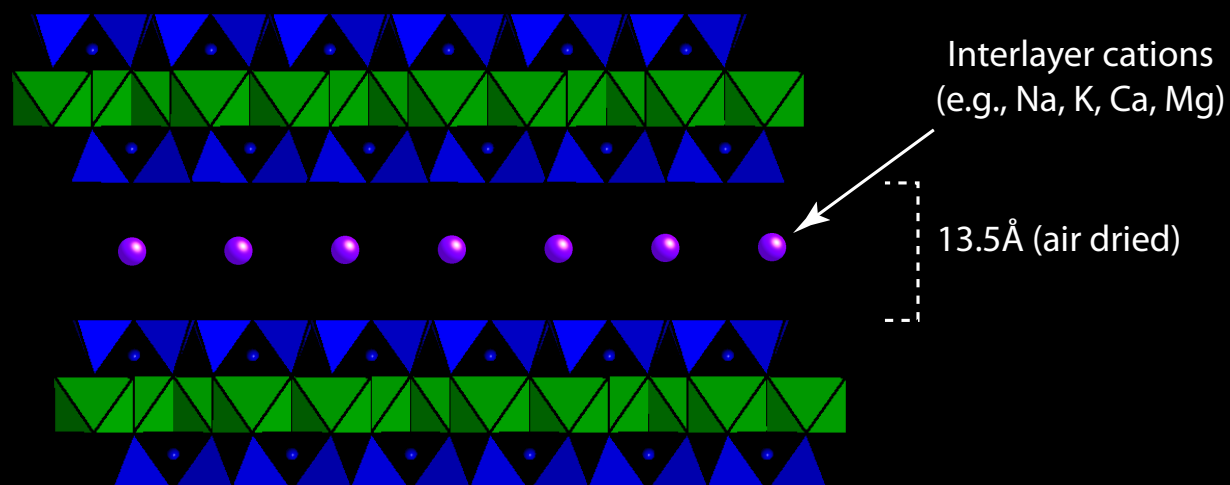
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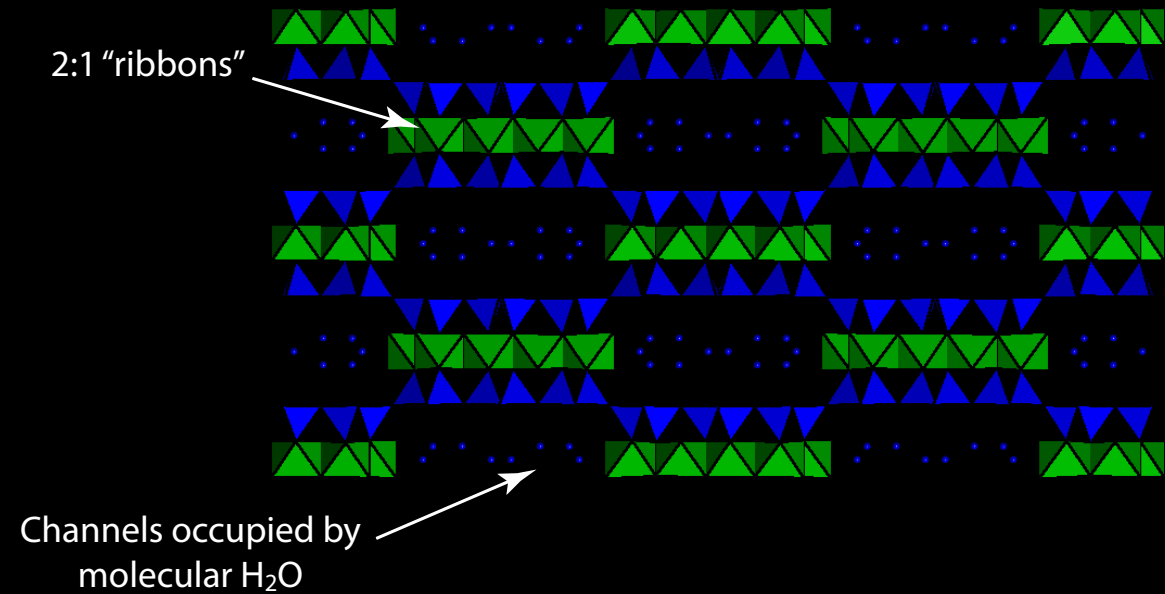
Kerolite



Stevensite (Mg-smectite)

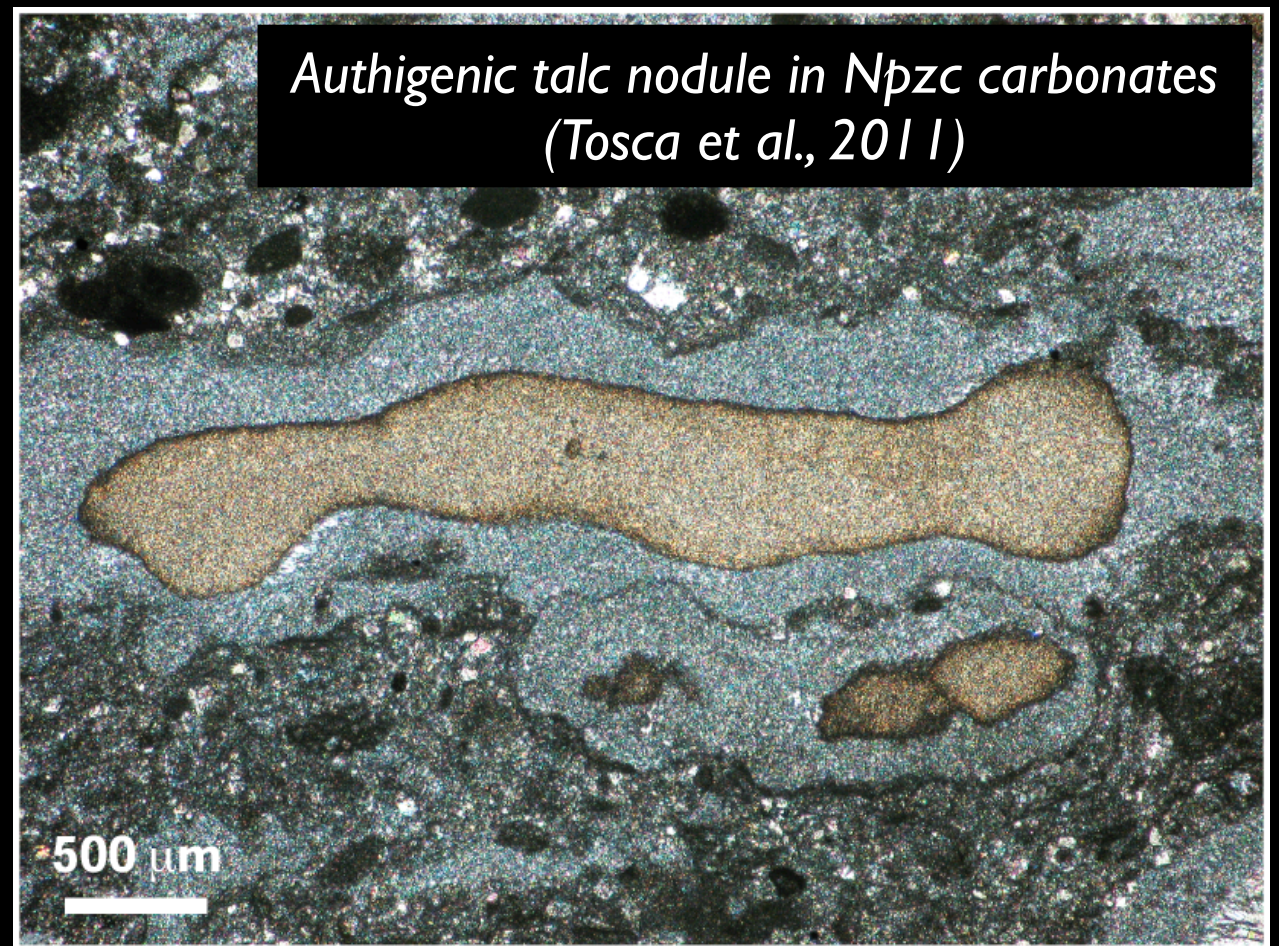
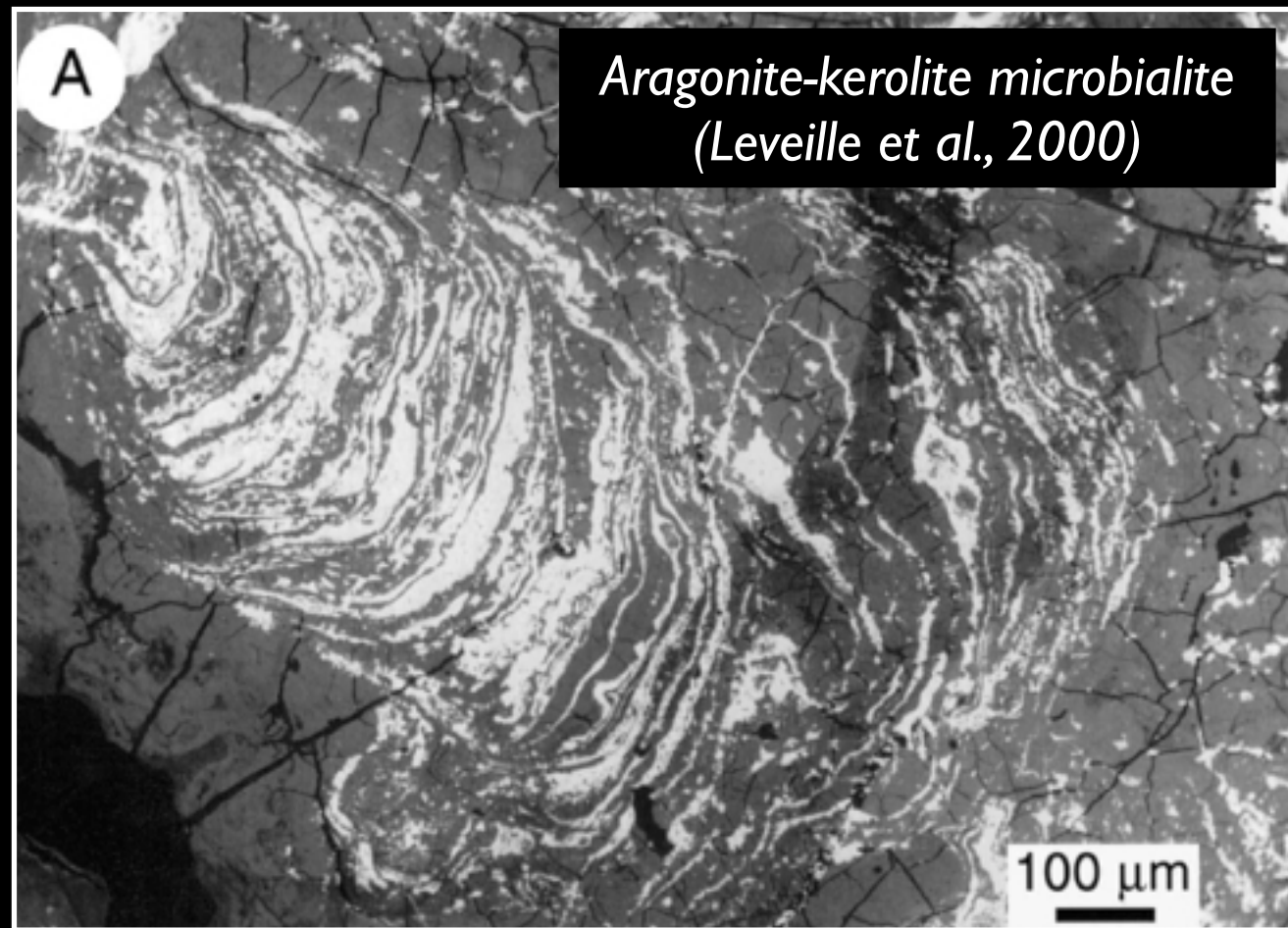


Sepiolite



- *Nominally Al-free*
- *Structures closely related*
- *Each phase has slightly different chemical stability*

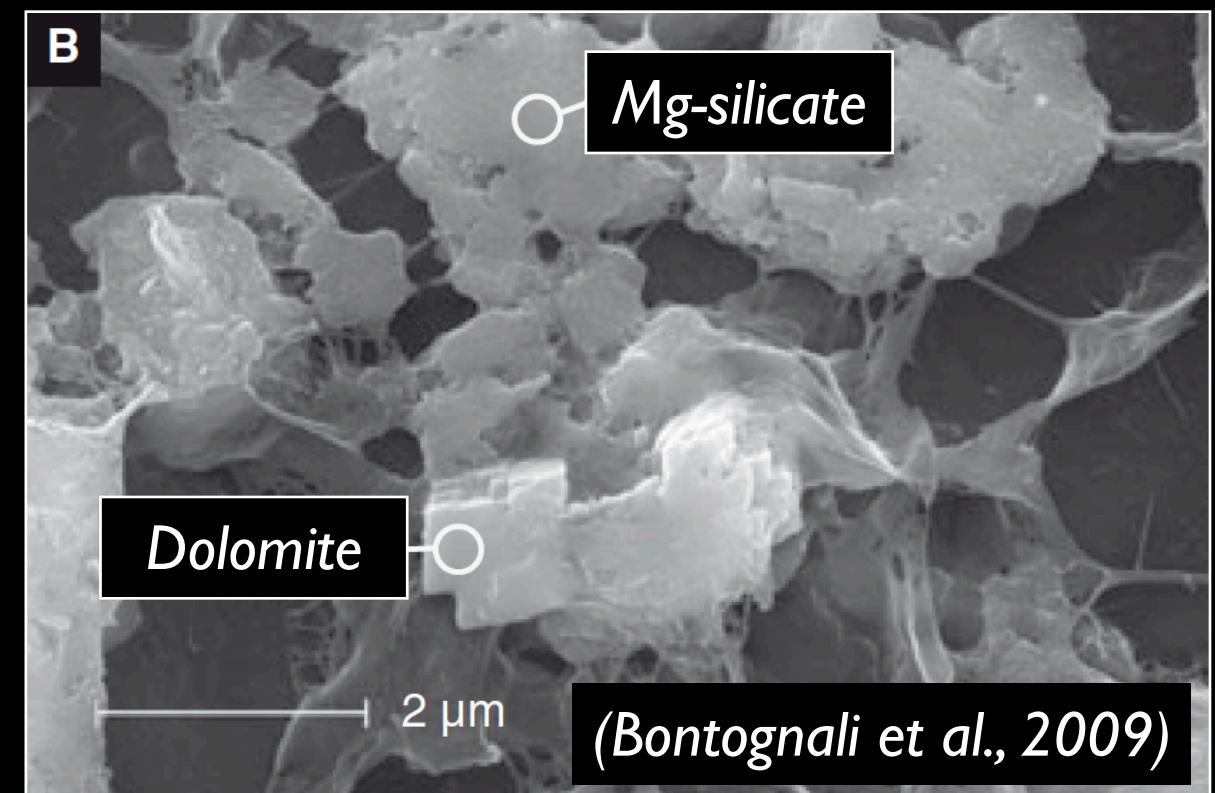
Unusual clays, unusual behaviour



- Unlike other clays, Mg-silicates are *geochemically labile*
- Mg-silicates exhibit *congruent dissolution*:
 - Composed of easily hydrolysable Mg-O bonds
 - No structural Al^{3+} (only Mg and Si)
- Unlike most common (Al-bearing) clays, Mg-silicate dissolution *does not* result in formation of secondary aluminosilicates

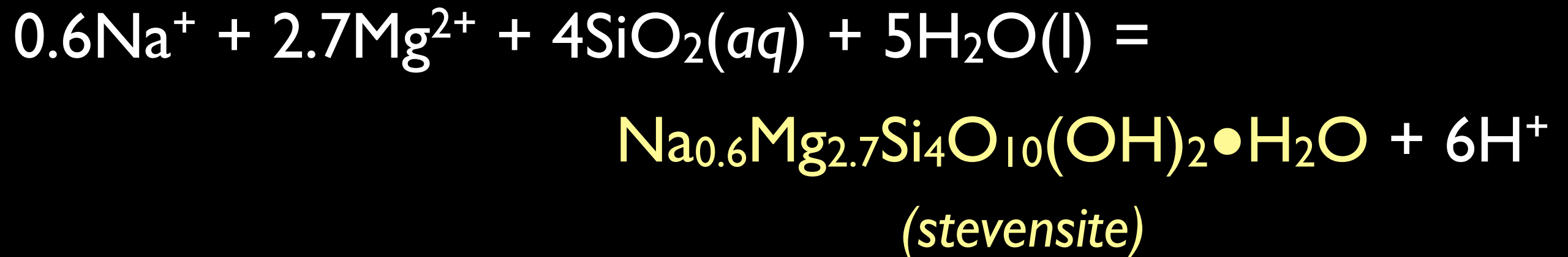
Mg-Si clay formation: Chemical controls

- **Homogeneous nucleation**
(directly from solution)
 - Requires *rapid supersaturation* (e.g., fluid mixing, evaporation, CO₂ degassing)
- **Heterogeneous nucleation**
(on pre-existing surface)
 - Most commonly detrital clays, silica & biological surfaces (EPS)
 - Requires lower supersaturation
 - Localised & dependent on extent of nucleating surface



Mg-Si clay formation: Chemical controls

Consider the precipitation of stevensite from water:

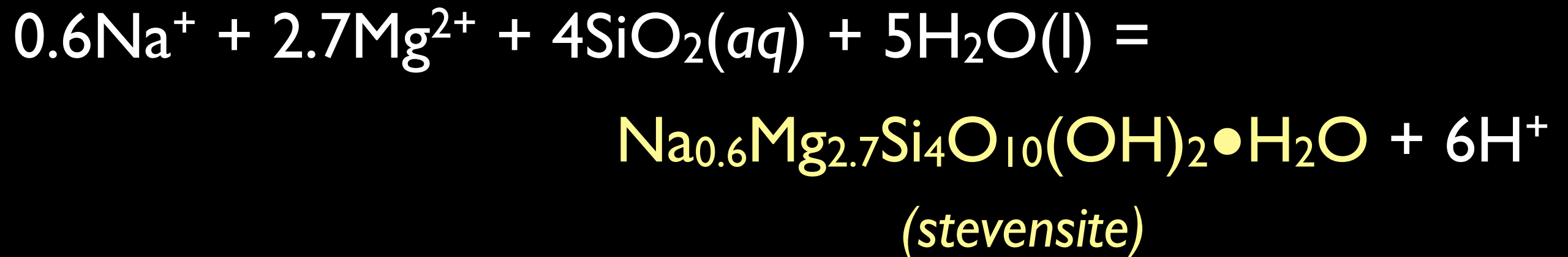


Main controls:

- Mg^{2+} concentration (or activity)
- $\text{SiO}_2(\text{aq})$ concentration (or activity)
- pH
- $\text{H}_2\text{O}(\text{l})$ activity (related to salinity or ionic strength)

Mg-Si clay formation: Chemical controls

Consider the precipitation of stevensite from water:

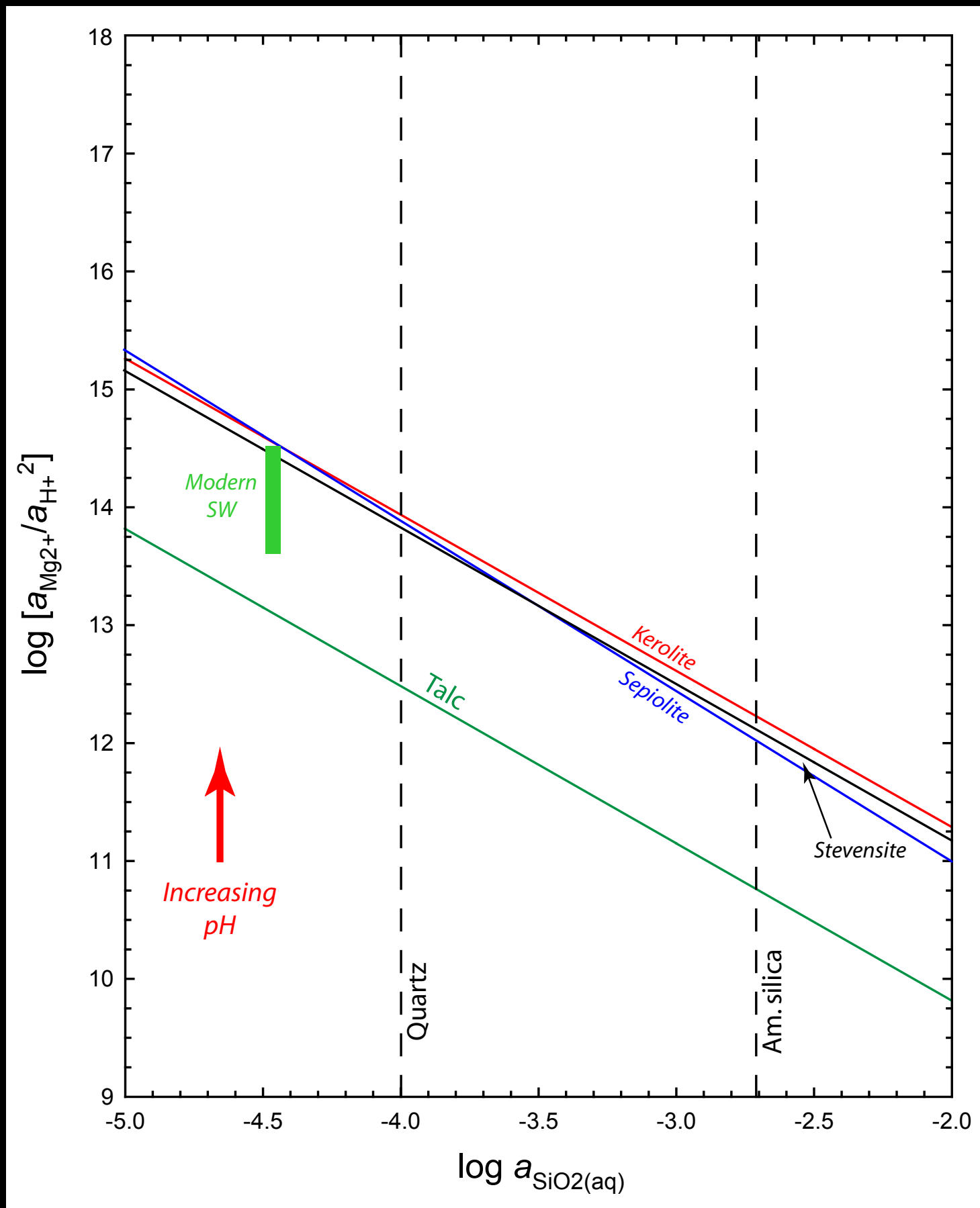


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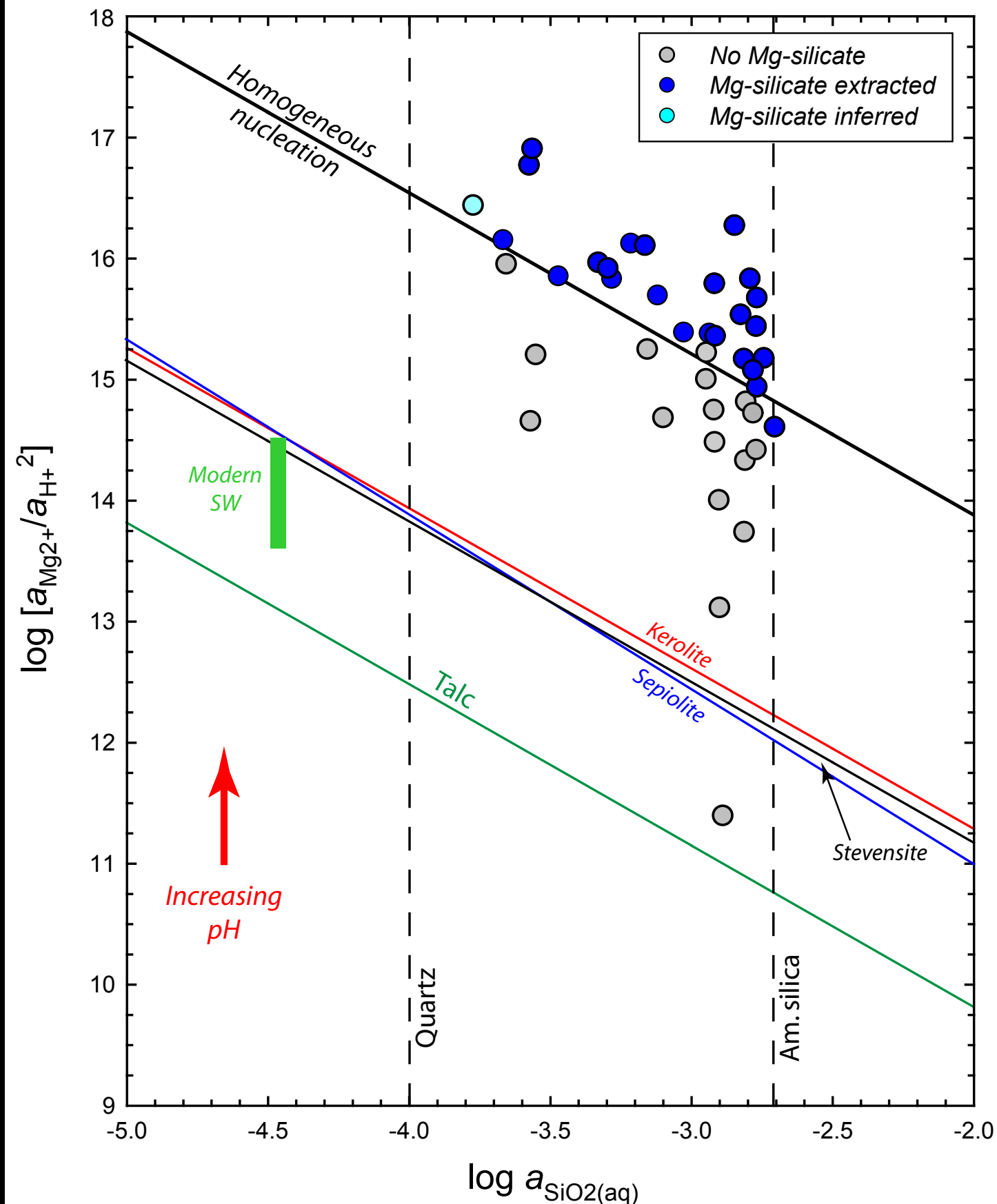
At what point will this really occur?

Mg-Si clay formation: Chemical controls



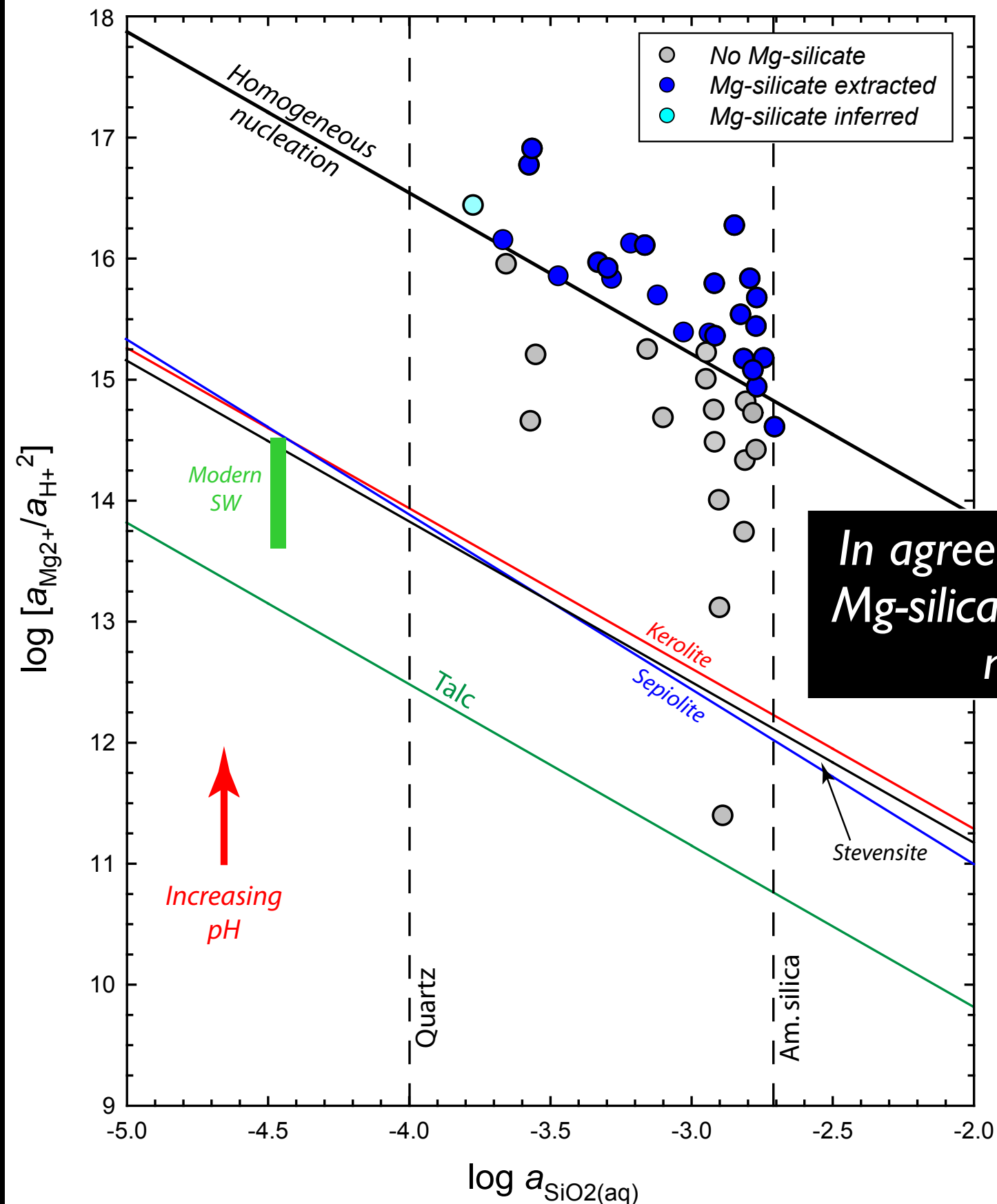
Mg-Si clay formation: Chemical controls

(data from Tosca
et al., 2011; Tosca
& Masterson,
2014)



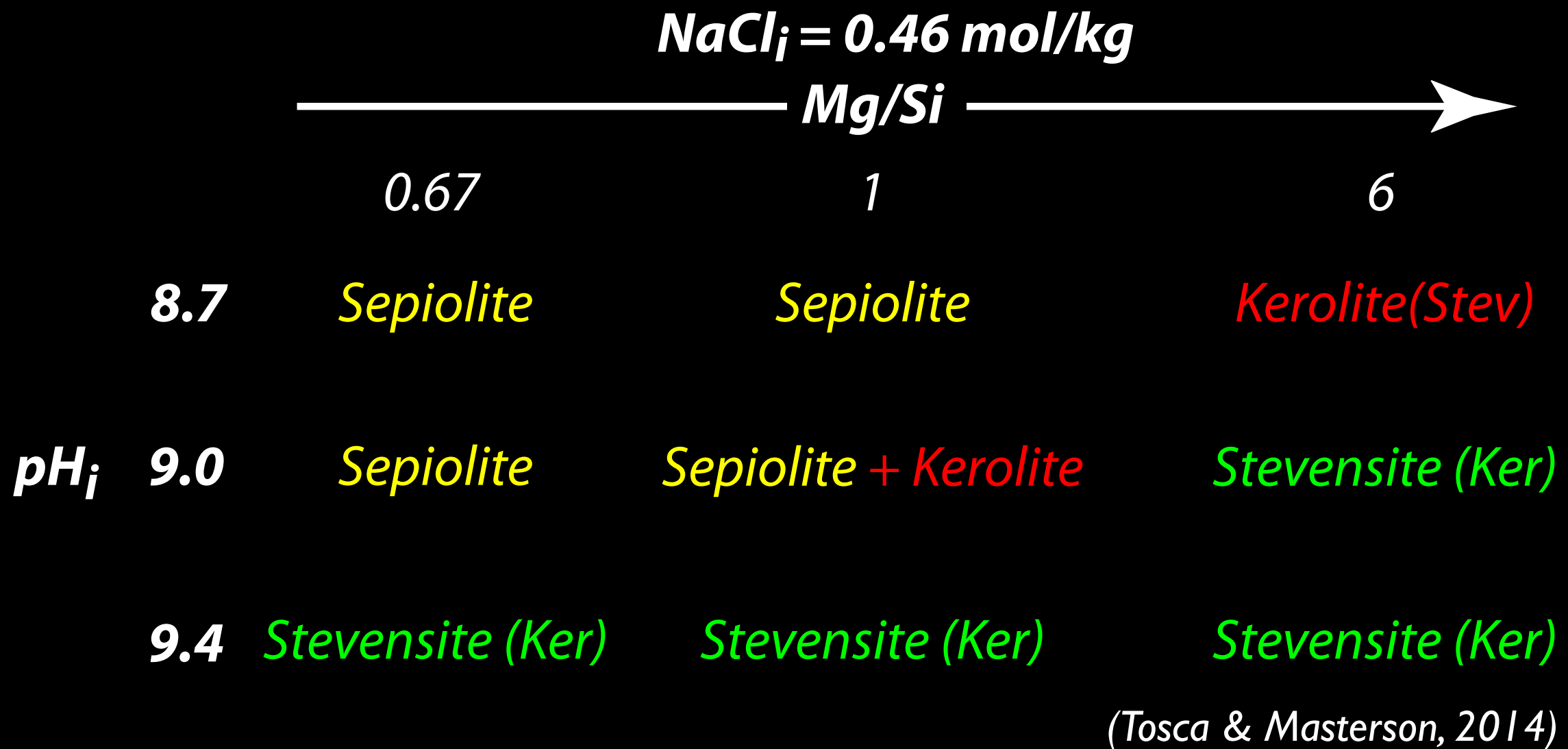
Mg-Si clay formation: Chemical controls

(data from Tosca
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In agreement with studies of
Mg-silicate precipitation from
modern lakes

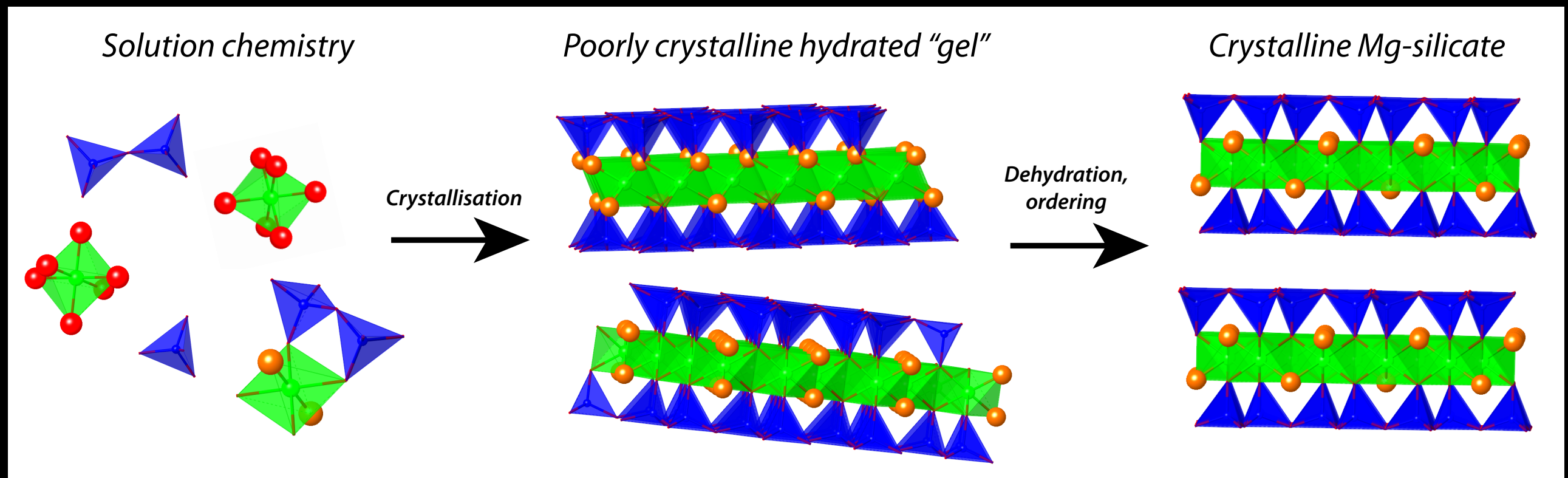
Mg-Si clay formation: Chemical controls



- Identity of Mg-silicate phase (e.g., kerolite, stevensite, etc.) controlled by:
 - Mg/Si ratio
 - Salinity
 - pH
 - Presence of Al (detrital substrate)

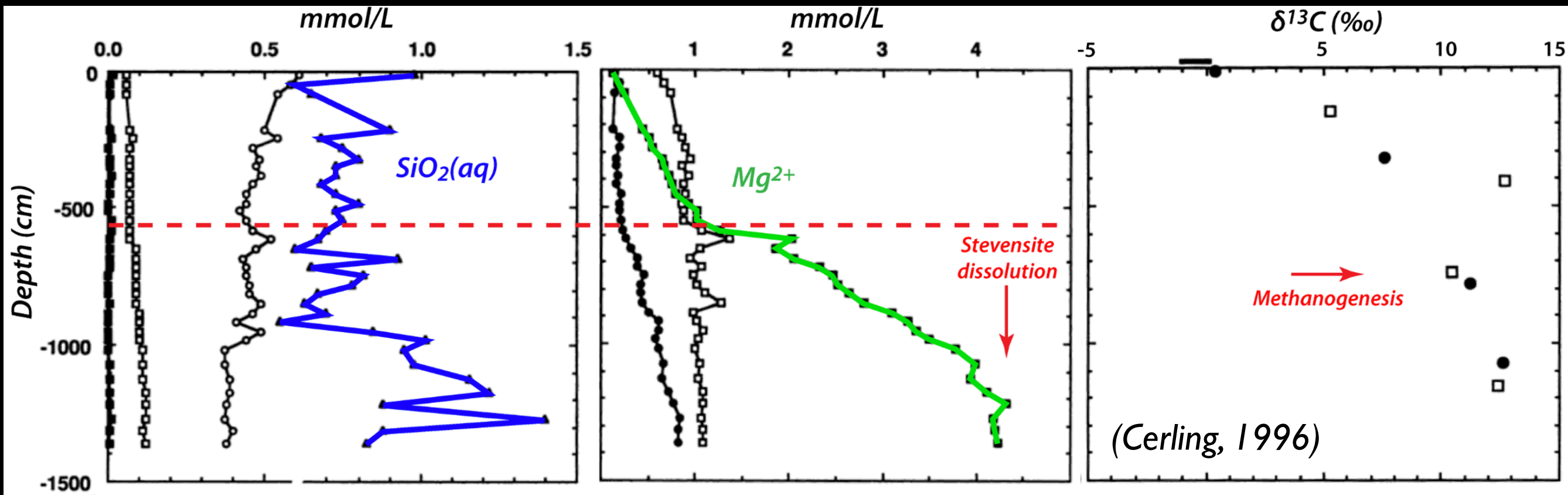
How do Mg-silicates form?

- Rapid nucleation & slow crystal growth produces abundant nano-particles
- Nanoparticles extensively hydrated (~20 wt. % H₂O) & coalesce to form a *Mg-silicate gel* (hydrated nanoparticle aggregate)
- Gel dehydration drives transition to crystalline Mg-silicate
- Mg-silicate gels would:
 - Act as major sink for Mg²⁺
 - Favour spherulitic calcite through high supersaturation & diffusion-limited growth



Early diagenetic reactions

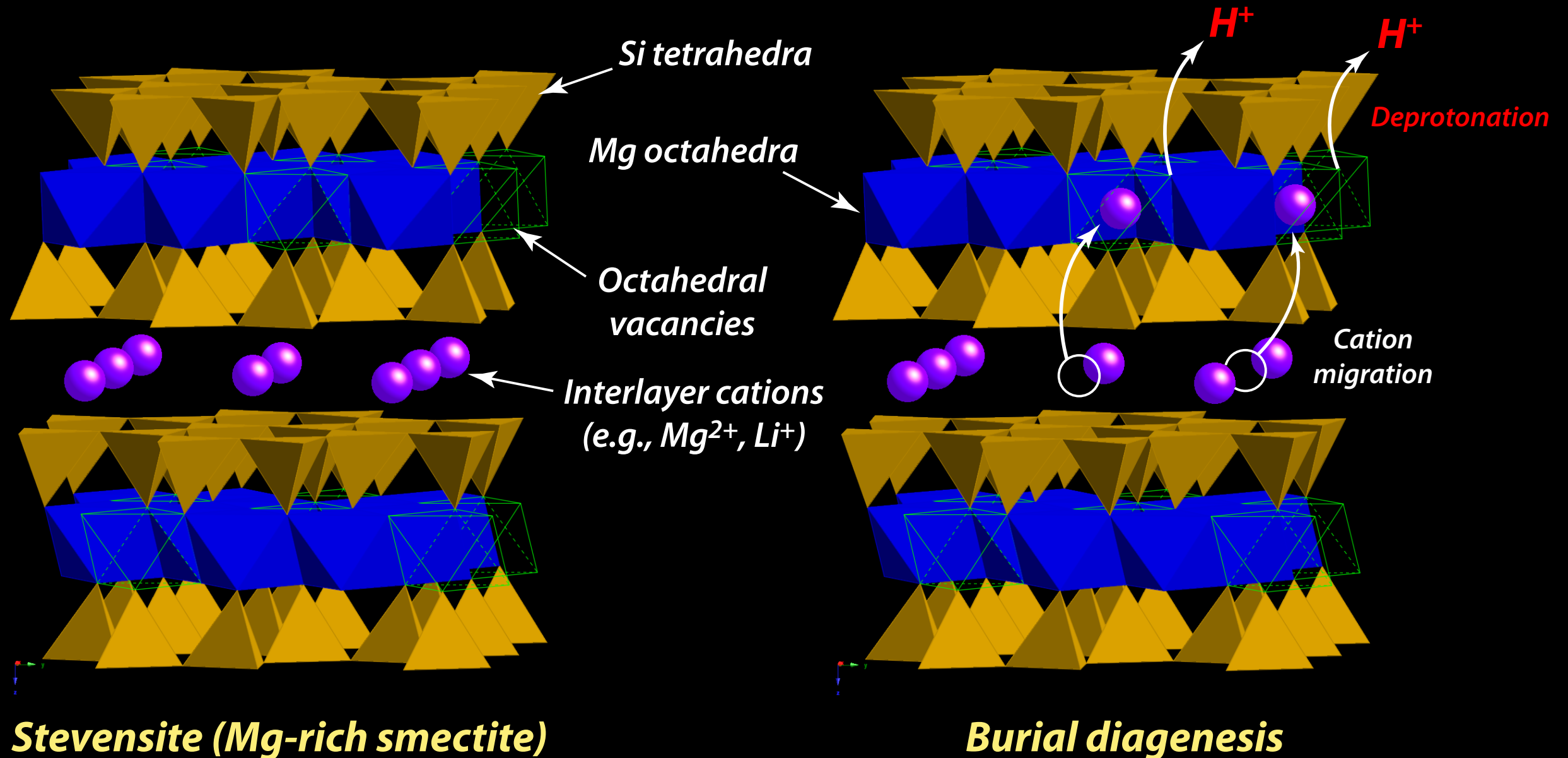
- Mg-silicates show high sensitivity to P_{CO_2} & rapid dissolution kinetics (mainly from extremely high surface area)
- Example: Cerling (1996) observed stevensite dissolution in Lake Turkana sediment cores driven by *methanogenesis*, imparting heavy $\delta^{13}\text{C}$ signature to HCO_3^- :



Late diagenetic reactions

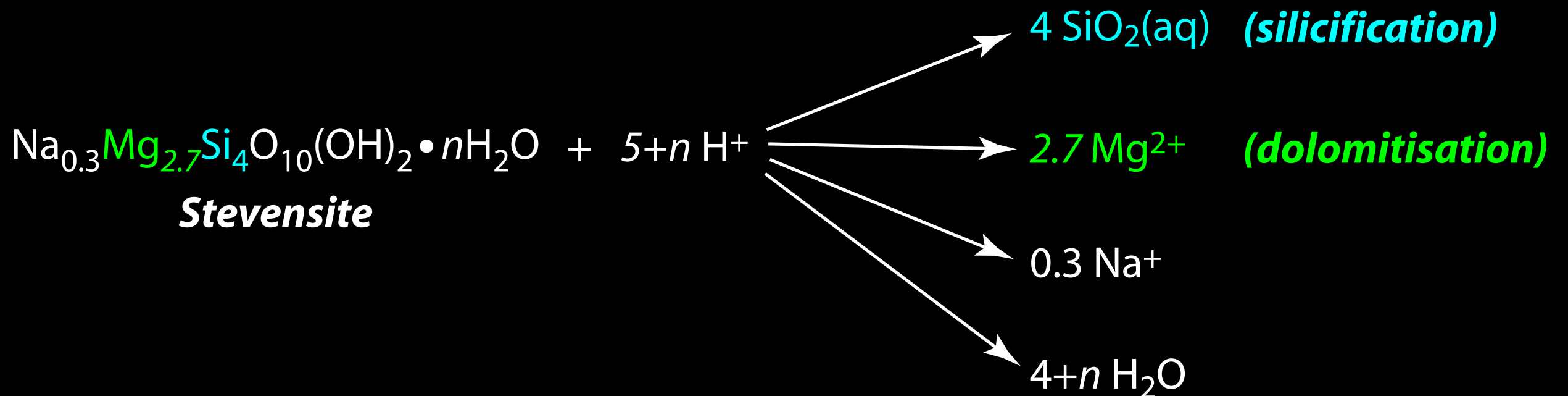
Stevensite cation migration & gel dehydration

- Stevensite (an abundant Mg-Si-clay) contains structural “vacancies”
- Burial diagenesis fills vacancies, producing H^+ and H_2O
- Mg-silicate gel loses up to 20% H_2O at $T < 150^\circ C$



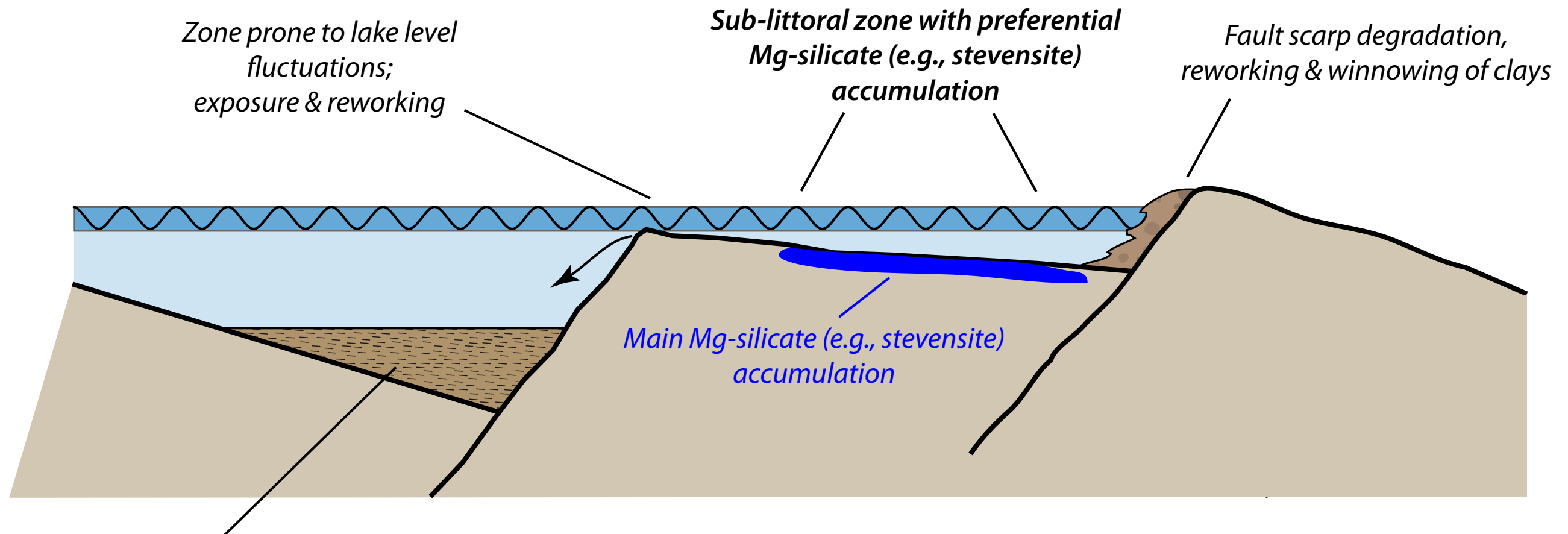
Mg-silicate diagenesis: Summary

- Mg-silicates are easily destabilised early in diagenesis by pH and/or P_{CO_2} fluctuations
- Hydrated Mg-silicate gel is a significant source of diagenetic H_2O and may have been inherently acidic
- A lack of Al^{3+} leaves dolomite & silica as main secondary products



Controls on Mg-Si clay distribution & accumulation

Idealized rift setting



Organic-rich profundal sediments

- Methanogenesis & high P_{CO_2}
- Shallow Mg-silicate dissolution (minor CC dissol.)
- Minor Mg-silicate accumulation
- Secondary porosity in laminites
- Elevated $\delta^{13}C$?

Chemical: Requires $pH > 9.5$; intervals of lower pH (e.g., pluvial events) prevent Mg-silicate formation

Physical: Gels accumulate in lower energy settings, winnowed from areas affected by wave action or subaerial exposure

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