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# The effect of prograde metamorphism on the chlorine isotope compositions of sedimentary rocks

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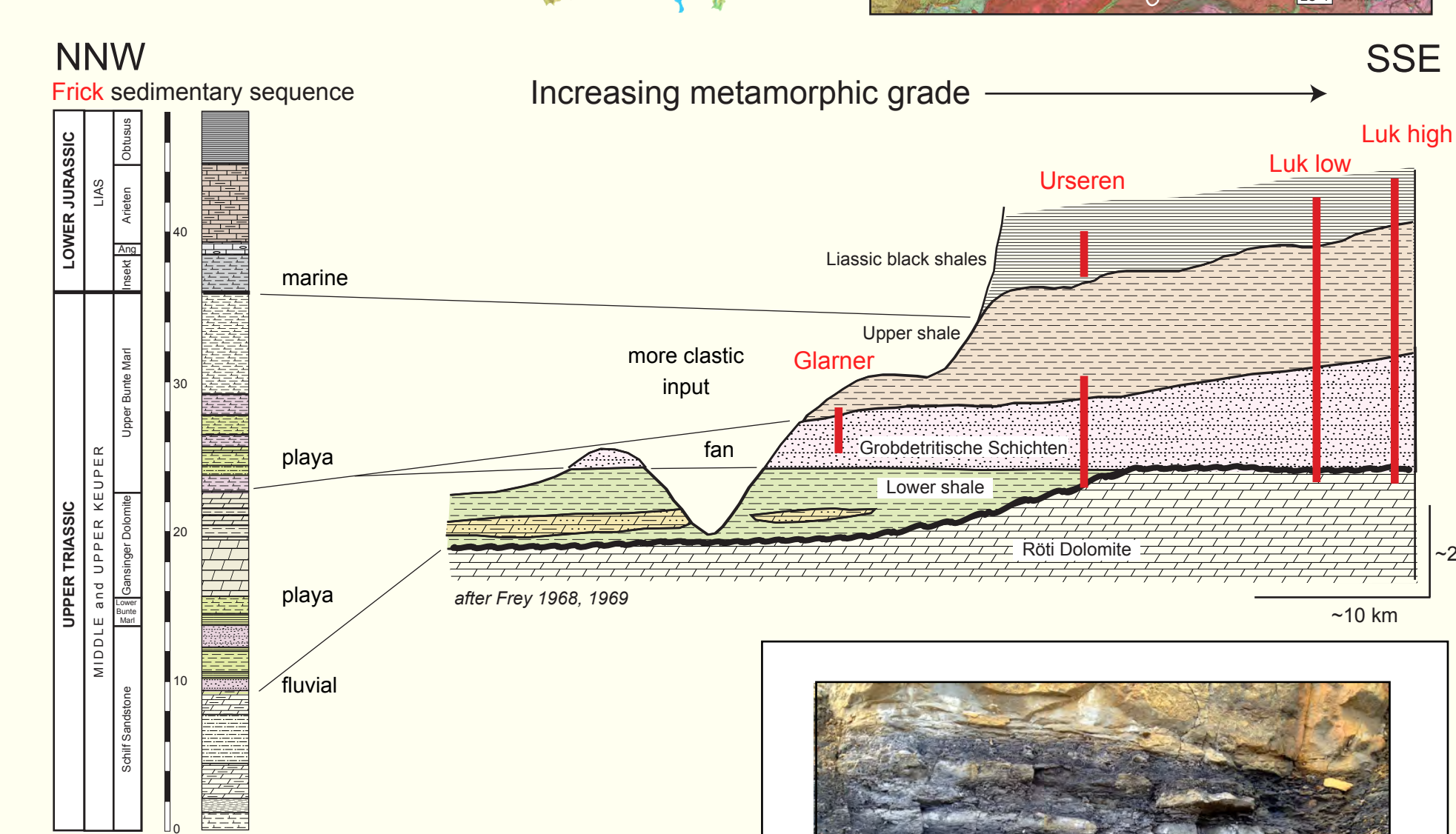
- \* How does prograde metamorphism affect Cl isotope compositions of rocks?
  - \* Can individual protolith reservoirs be identified from metamorphic samples?
  - \* Does subduction zone metamorphism affect isotopic compositions?
  - \* How do metamorphic fluid compositions relate to host solids?
- We need baseline studies of sed sequences to answer these questions

## Geologic Setting: Switzerland

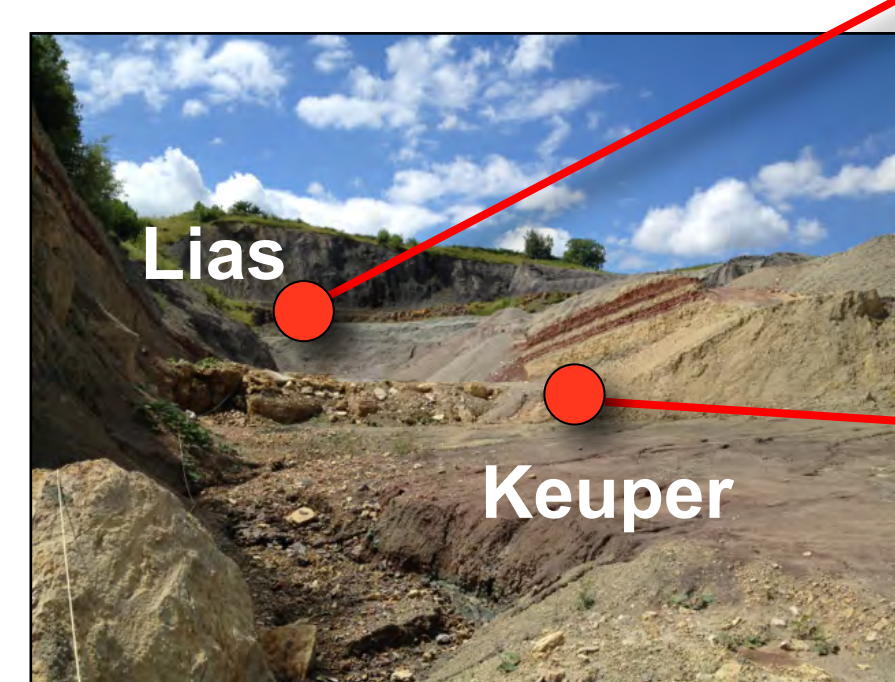
Upper Triassic Keuper series: fluvial and deltaic sediments overlain by playa deposits that interfinger with fan deposits to SE.

Lower Jurassic marine black shales and dolomitic limestones. Highly fossiliferous in lower section.

Sequences can be traced from unmetamorphosed sedimentary rocks up to amphibolite facies conditions.



## Frick Quarry: unmetamorphosed



## Metamorphic Equivalents

slates & phyllites,  $T_{max} \leq 350^\circ\text{C}$



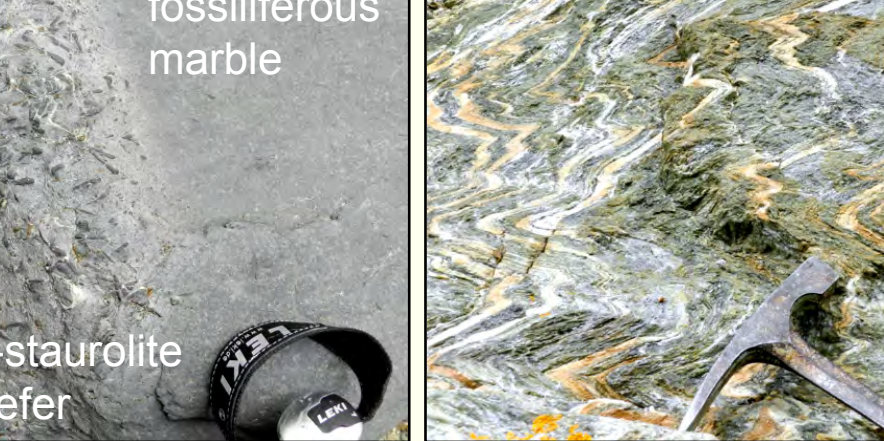
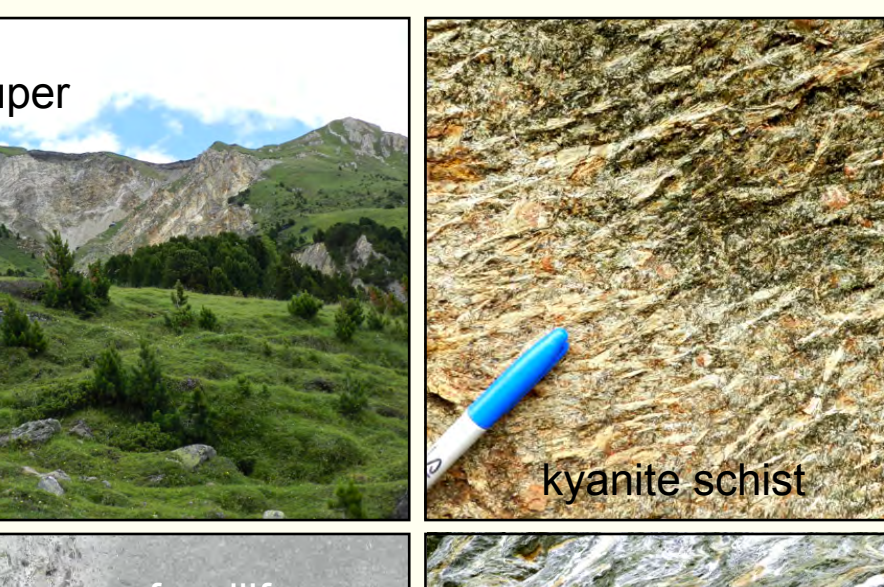
lower greenschist facies,  $T_{max} \sim 425^\circ\text{C}$



Glärner

Urseren

middle amphibolite facies,  $\sim 550^\circ\text{C}$



lower amphibolite facies,  $\sim 500^\circ\text{C}$

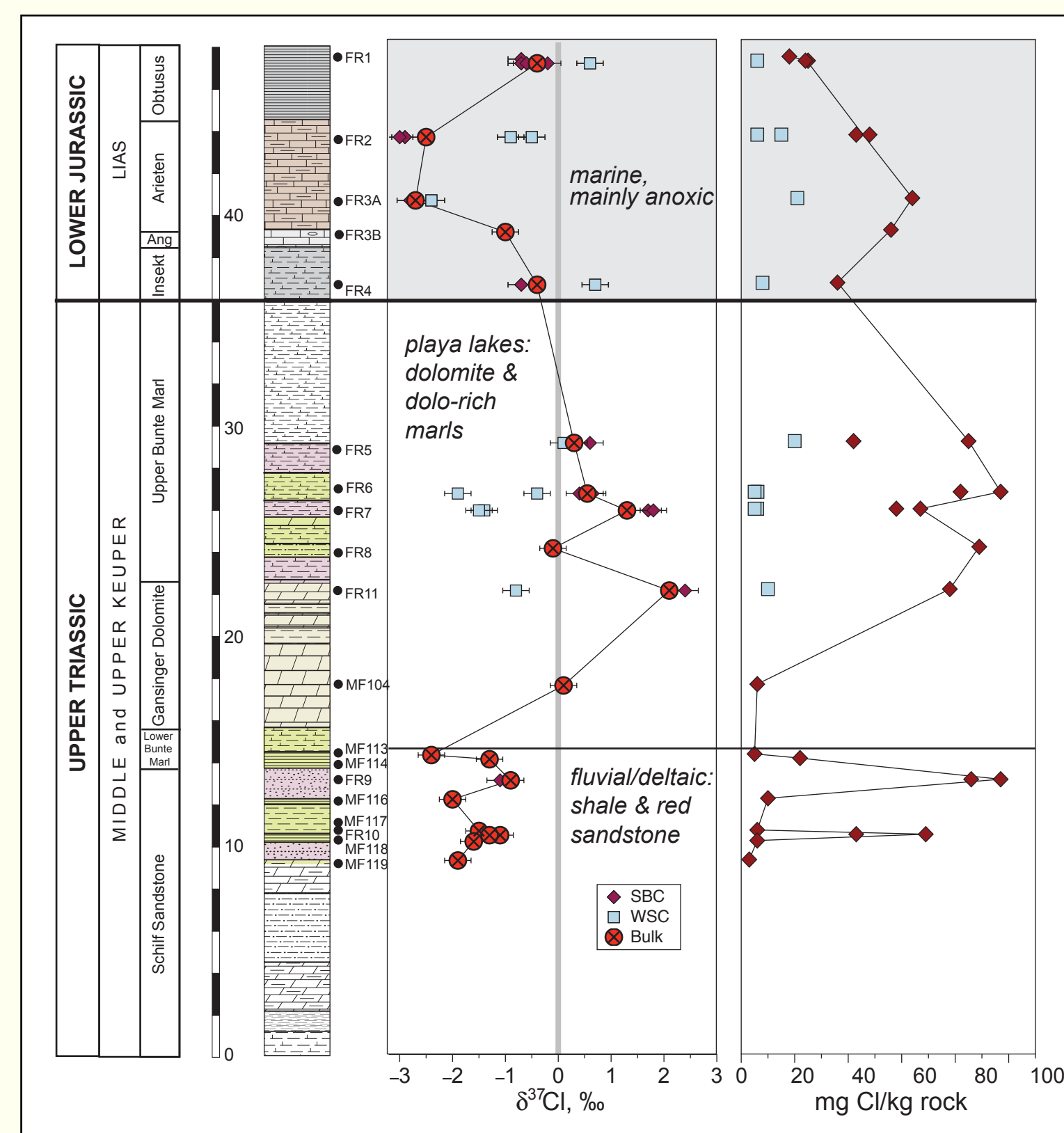


Lukmanier: low-grade

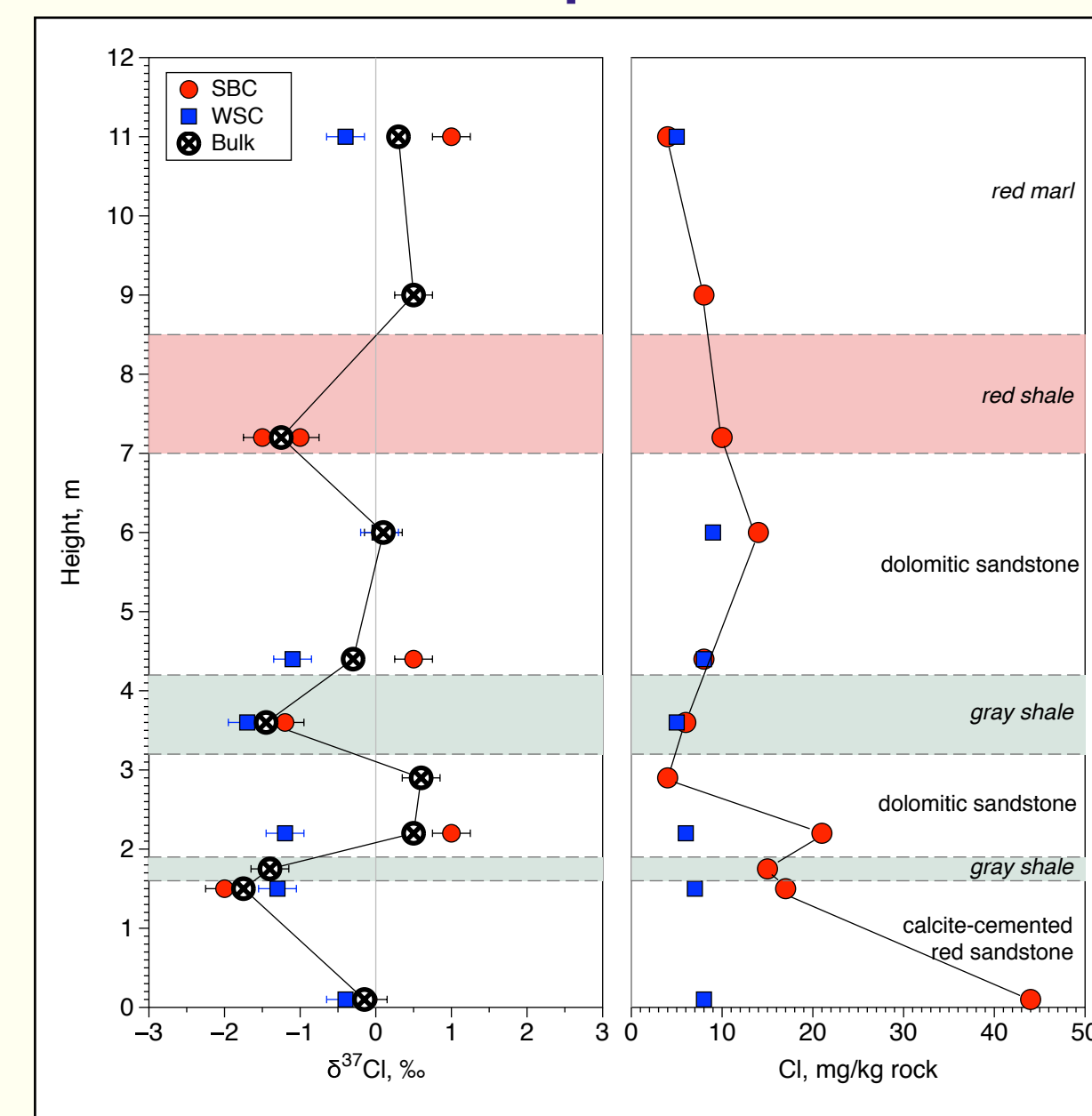
Lukmanier: high-grade

## The Data

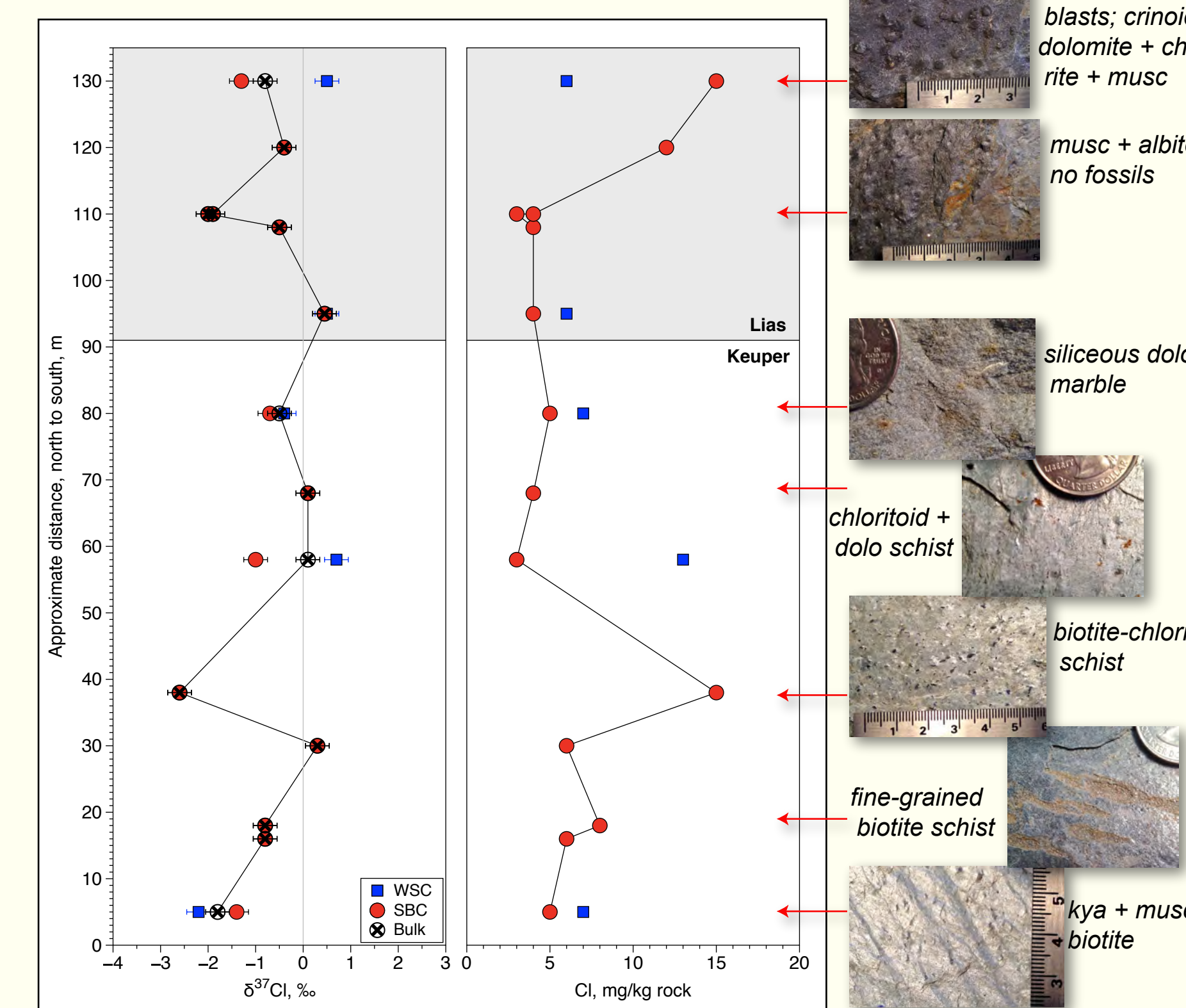
## Frick Quarry: unmetamorphosed



## Representative Chlorine Isotope Profiles

Glärner Alps:  $\leq 350^\circ\text{C}$ 

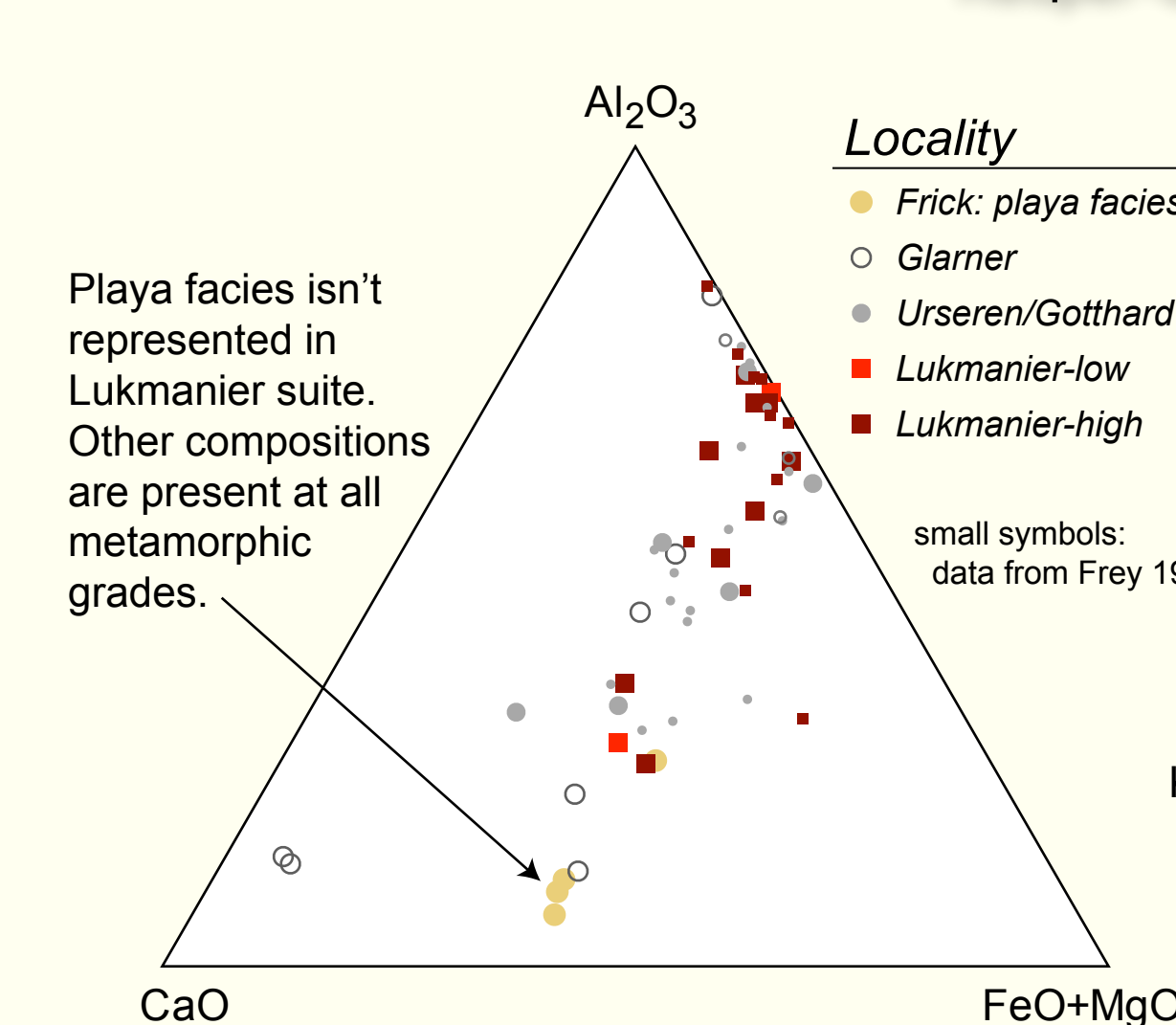
Shale layers are systematically depleted in  $^{37}\text{Cl}$  relative to dolomitic sandstones and marls. This is the same relationship that is seen at Frick, although the Glärner rocks record higher clastic input at the basin margin.

Lukmanier Pass:  $\sim 500^\circ\text{C}$ 

Broadly similar to Frick & Glärner profiles: Dolomite-bearing rocks are enriched in  $^{37}\text{Cl}$  relative to shale protoliths.

## Bulk Chemical, Stratigraphic, and Isotopic Correlations

## Keuper-Quartenschiefer



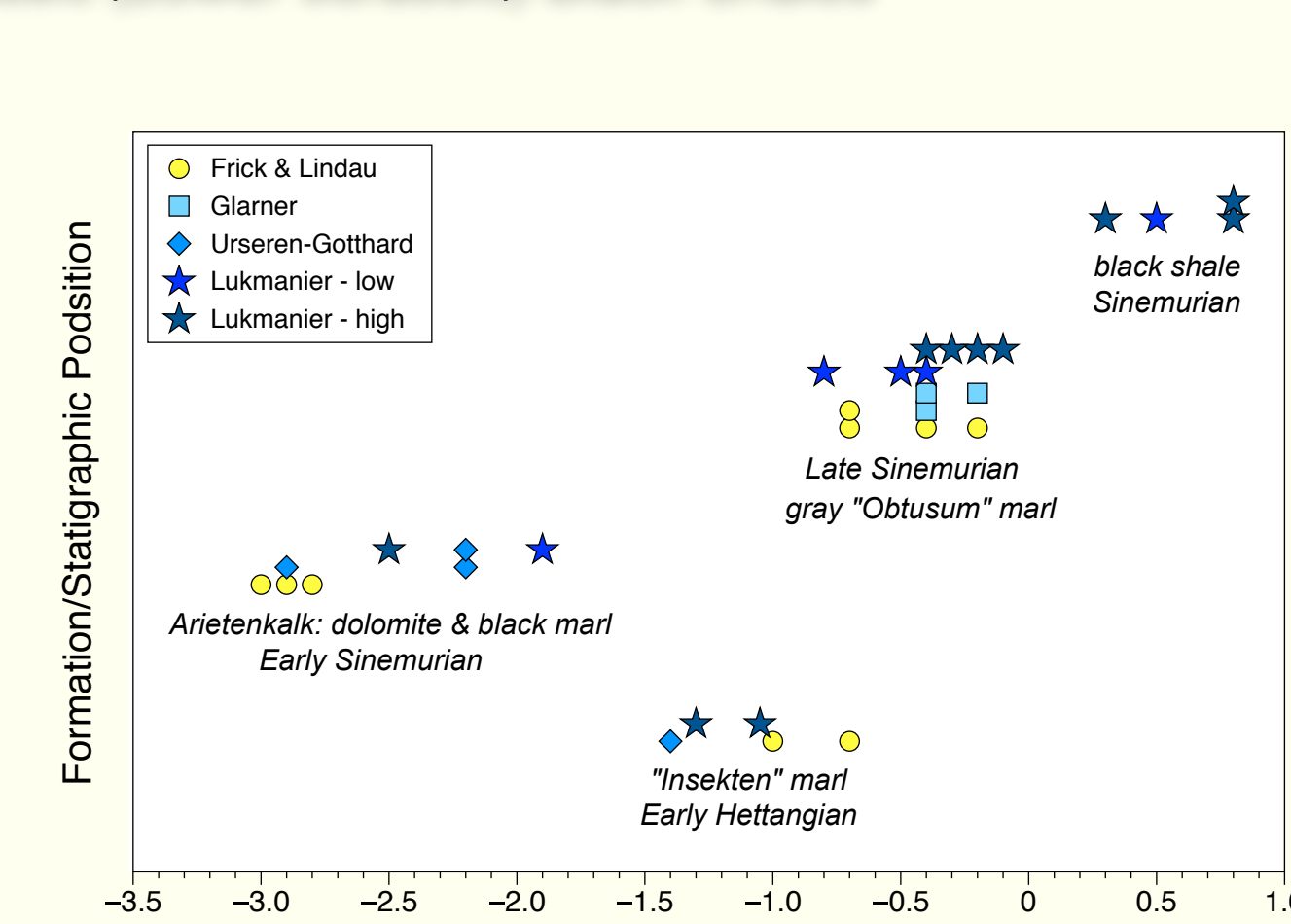
## Compositional groups

$\delta^{37}\text{Cl}$  ranges:

- $\geq +1.0\%$
- $+0.5$  to  $+0.6\%$
- $-0.1$  to  $+0.3\%$
- $-0.8$  to  $-0.4\%$
- $-1.4$  to  $-1.0\%$
- $-2.0$  to  $-1.9\%$
- $\leq -2.5\%$

— All carbonate rocks are (+)  
— All shales are (-)  
— Marls are isotopically variable

## Lias (Lower Jurassic) Black Shales



Specific horizons within the Lias section retain their Cl isotopic composition across all metamorphic grades.

## How Can Cl Isotopic Heterogeneities be Produced in Protoliths and in Metamorphic Samples?

A)  $\delta^{37}\text{Cl}$  variability is a primary depositional characteristic

- \* Detrital micas and clays:  $\delta^{37}\text{Cl} = ??$
- \* Evaporation in playa lake:  $\delta^{37}\text{Cl}_{\text{salt}} = 0$  to  $+1\%$
- \* Marine aerosols:  $\delta^{37}\text{Cl} = -0.6$  to  $+2.4\%$
- \*  $\text{Cl}_{\text{org}}$  from soils, algae, leaf litter, etc.:  $\delta^{37}\text{Cl} \ll 0\%$
- \* Biodegradation of  $\text{Cl}_{\text{org}}$ :  $\delta^{37}\text{Cl} > 0\%$  in remaining residue

C)  $\delta^{37}\text{Cl}$  values are modified during metamorphism

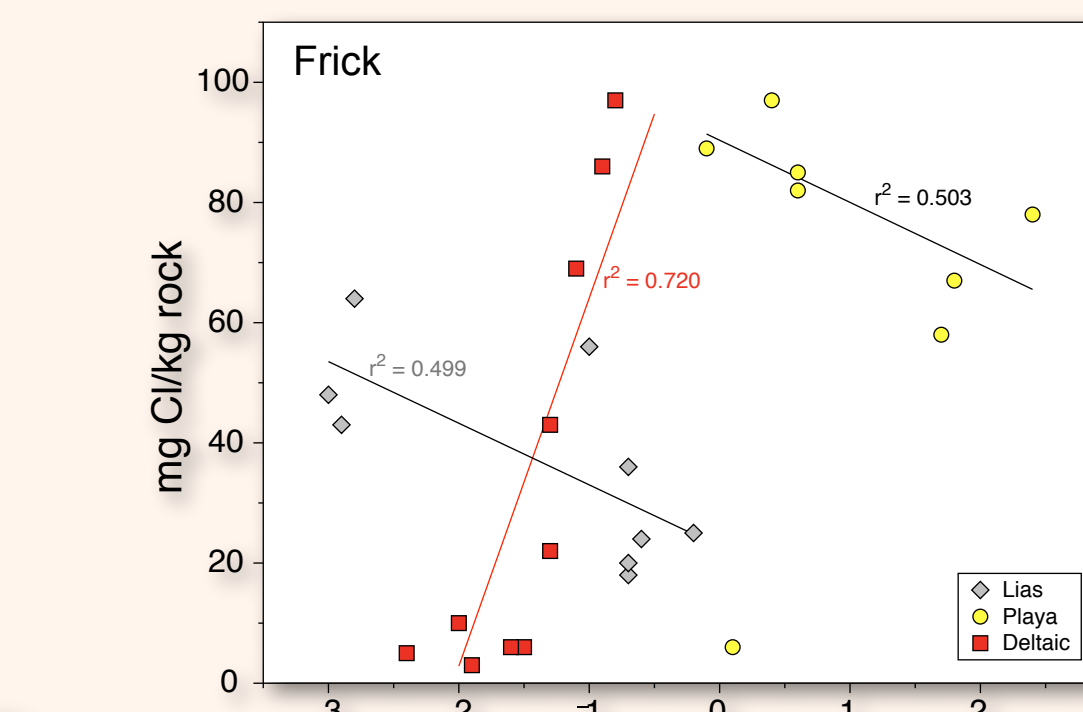
- \* Fractionation with  $\delta^{37}\text{Cl}_{\text{fluid}} < \delta^{37}\text{Cl}_{\text{rock}}$  (predicted by theory)
- \* Fractionation with  $\delta^{37}\text{Cl}_{\text{fluid}} > \delta^{37}\text{Cl}_{\text{rock}}$  (organohalogen involvement?)
- \* No fractionation during metamorphic devolatilization
- \* Interaction with externally derived fluids, e.g. from devolatilization of underlying nappes

Dehydration should have greater influence on Cl isotopic compositions than decarbonation reactions. How do mixed-volatile reactions affect chlorine fluid-rock fractionation?

B)  $\delta^{37}\text{Cl}$  variability reflects post-depositional processes

- \* Diffusion: positive correlation between  $[\text{Cl}]$  and  $\delta^{37}\text{Cl}$
- \* Ion Filtration: negative correlation between  $[\text{Cl}]$  and  $\delta^{37}\text{Cl}$ , small effect
- \* Mixing of different waters, e.g., meteoric, seawater, playa brines

All of these processes have been described in studies of sedimentary pore fluids. However, no studies of the correlative silicate-bound  $\delta^{37}\text{Cl}$  values have been carried out to date.

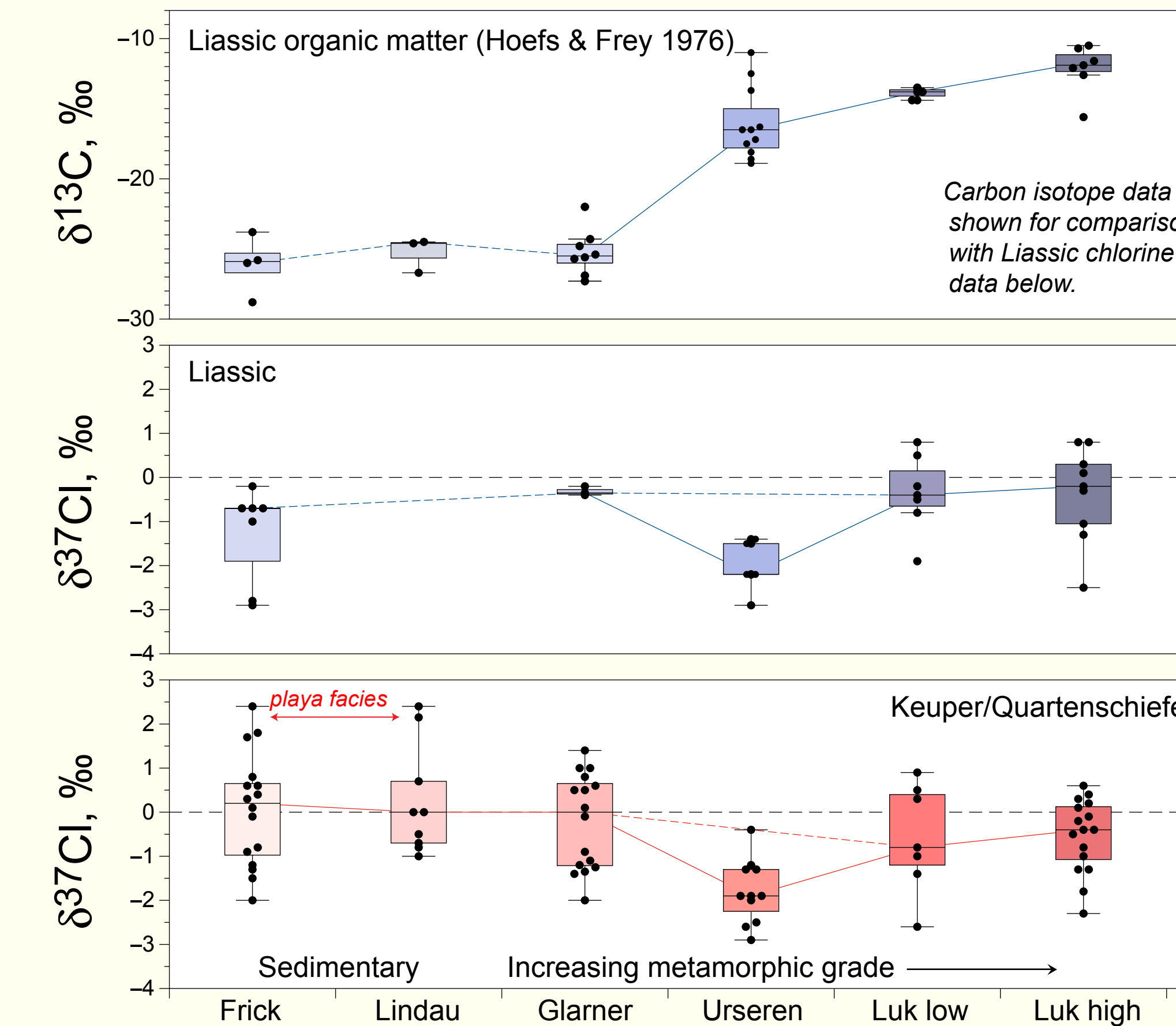


Data from Frick are consistent with equilibration between silicates and diffusion-modified pore fluids in the fluvial-deltaic facies, but only if diagenetic reactions mapped the fluid compositions directly onto the silicates: unlikely.

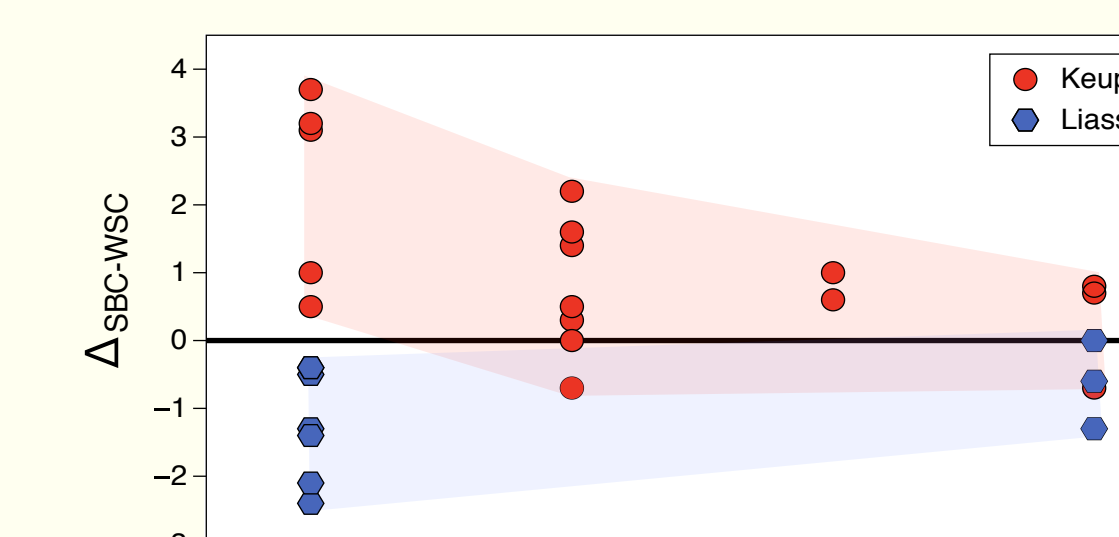
## Summary:

There are many ways to produce isotopically heterogeneous rocks prior to the onset of metamorphism. Metamorphic processes need to be evaluated in the context of heterogeneous starting materials.

## Overview of Isotopic Data

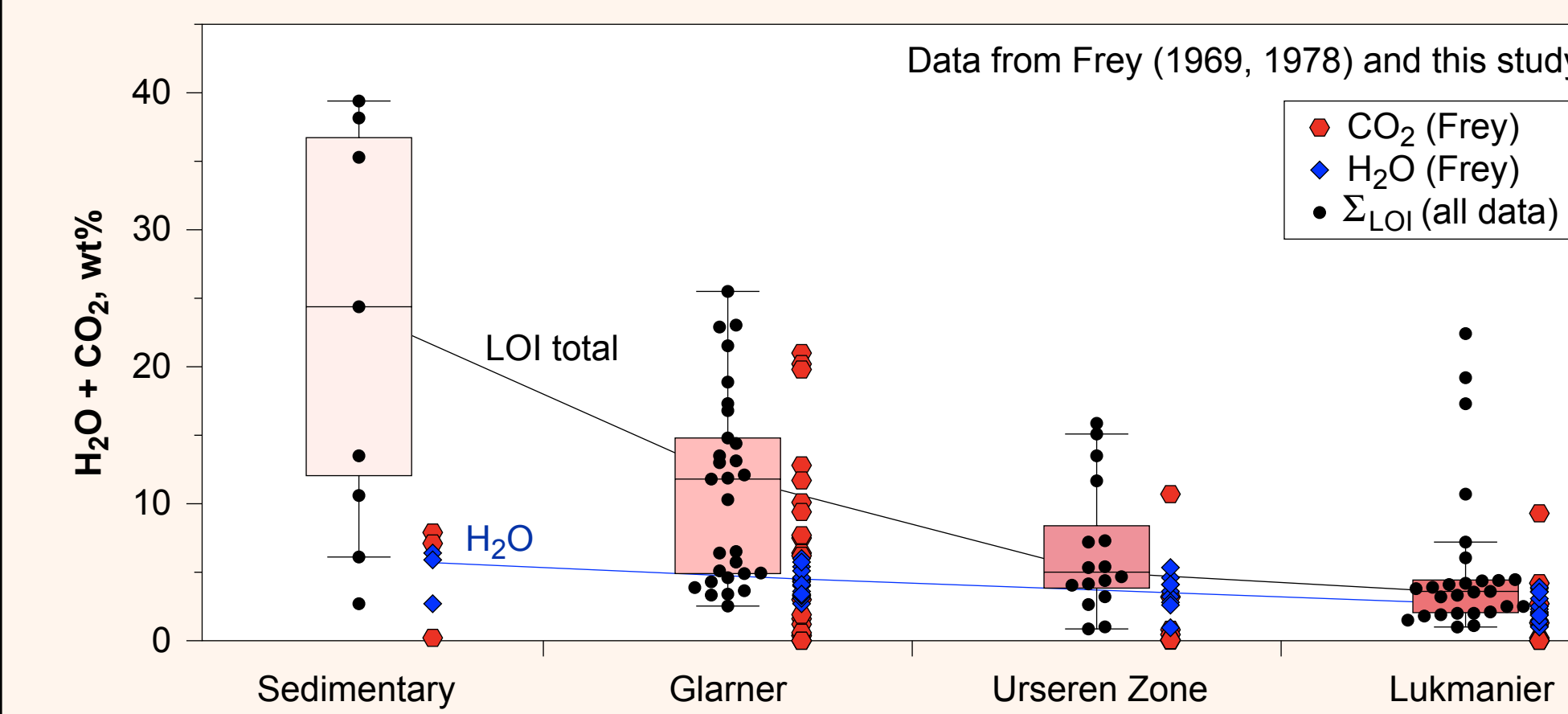


- \* No systematic change in  $\delta^{37}\text{Cl}$  with increasing metamorphic grade
- \* Small apparent shift to lower  $\delta^{37}\text{Cl}$  in Keuper results from absence of playa facies at Lukmanier.
- \* Urseren Zone values are anomalous:
  - Tectonic duplication biased samples towards small part of the sedimentary section
  - Rocks were modified by fluid flow through Urseren shear zone.



- \* Water-soluble Cl fraction is isotopically lighter than silicate-bound fraction in the Keuper.
- \* Water-soluble Cl fraction is isotopically heavier than silicate-bound fraction in the Lias. This is opposite to theoretical predictions.
- \* Fractionation between SBC and WSC fractions decreases with increasing metamorphic grade – suggests equilibration during metamorphism, little subsequent fluid infiltration (but based on small data set).

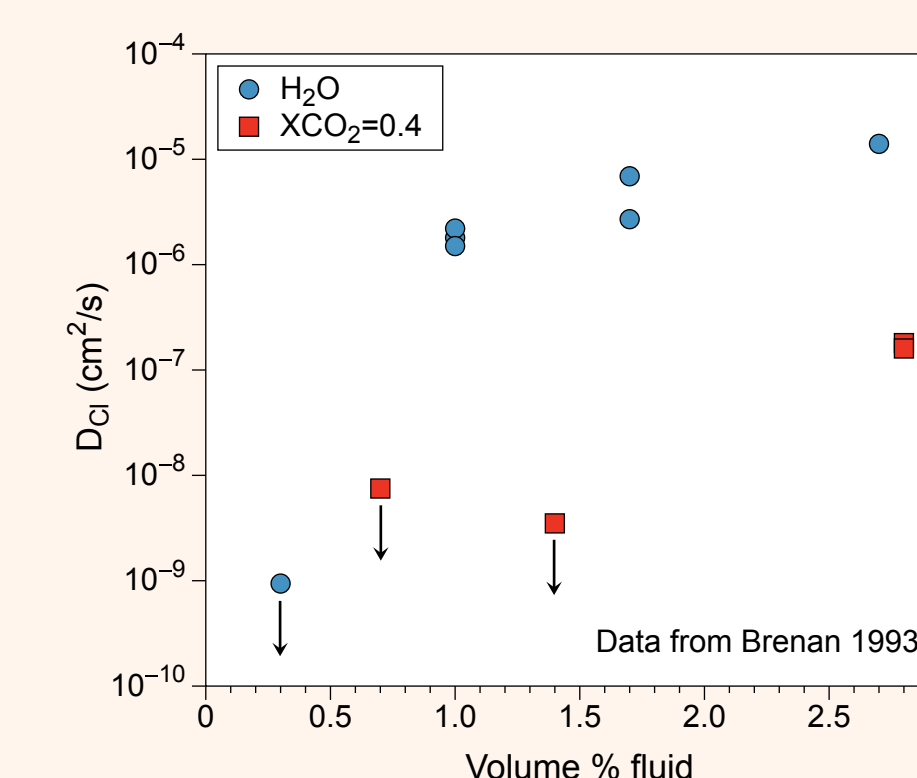
## Preservation of Cl Isotope Heterogeneities During Metamorphism: The Role of CO₂



- \*  $\text{Cl}^-$  occupies  $(\text{OH})^-$  sites in minerals, should be released during dehydration.
- \* Rocks released mixed  $\text{H}_2\text{O}-\text{CO}_2 \pm \text{CH}_4$  fluid(s) during low-grade metamorphism.
- \* Salts are less soluble in  $\text{H}_2\text{O}-\text{CO}_2$  fluids than in pure  $\text{H}_2\text{O}$  (and induce immisc).
- \* Diffusion coefficients for Cl are lower in  $\text{H}_2\text{O}-\text{CO}_2$  than in pure  $\text{H}_2\text{O}$  fluid (below).
- \* Dihedral angles are higher in  $\text{H}_2\text{O}-\text{CO}_2$  fluids than in  $\text{H}_2\text{O}$ , so fluid less likely to leave reaction site.

These factors will inhibit partitioning of Cl into the fluid and transport during the initial stages of metamorphism.

At higher temperatures, smaller  $\Delta_{\text{solid-fluid}}$  values will prevent significant shifts in isotopic composition during further devolatilization.



Addition of  $\text{CO}_2$  to aqueous fluid reduces bulk Cl diffusion coefficient by several orders of magnitude. Decrease in amount of fluid also significantly reduces D value.

## Conclusions

- \* Sediment Cl isotope compositions are heterogeneous and do not change during prograde metamorphism:
  - Simplistic Cl isotope reservoir models for sedimentary rocks need to be abandoned
- \* Cl is not lost during metamorphism when decarbonation occurs with dehydration:
  - Cl is less hydrophilic in mixed  $\text{H}_2\text{O}-\text{CO}_2$  fluid
- \* Cl likely to be retained in hydrous silicates to greater depths than previously thought in subduction settings
  - Mixed  $\text{H}_2\text{O}-\text{CO}_2$  fluid dominates metaseds
- \* Melting - not devolatilization - may be the main slab-to-arc Cl transfer mechanism

## Some Relevant References

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