Workshop on Martian Phyllosilicates: Recorders of Aqueous Processes?

Interpreting Martian phyllosilicates: Transferability of an inferential framework from terrestrial experience to Mars

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Purpose

- Regardless of where we get our data – orbital spectroscopy & imagery, lander/rover data & imagery, Mars meteorites or (eventually) returned samples – the data are interpreted using geochemical concepts.
- This contribution reviews what can be inferred about mineral-environment interactions from the study of the clay-mineral products of mineral-water interactions, emphasizing low-temperature surface phenomena (weathering).

Process-product

- Nature (& experiments, & forward models):
- Process (conditions) → Product/Response
    - Primary minerals + Water + Dissolved reactants ➔ Residual primary minerals + Product minerals + Dissolved products
- Historical Geoscience: Work back from observed products to infer processes
- Process ← Scientific Inference ← Observed Product
- Our question: How to infer past processes & former conditions (e.g., properties of solutions that are no longer present) from observations of remaining solids, esp. products?

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- Then we apply this understanding to water-absent systems.

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Outline

- *Interpretive approaches*
- *Formation of phyllosilicates as weathering products & implications for relationship between clay minerals and environmental conditions*
- *What can clay minerals tell us about alteration conditions on Mars?*

Outline

- *Interpretive approaches*
- Thermodynamic approaches
- Geochemical-kinetics approaches
- *Formation of phyllosilicates as weathering products & implications for relationship between clay minerals and environmental conditions*
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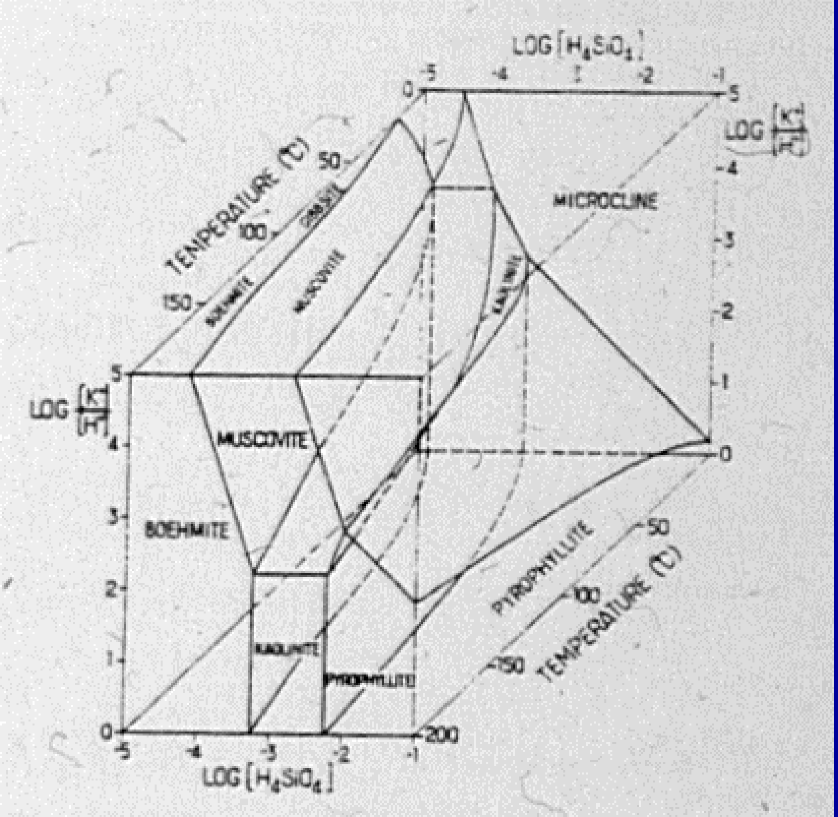
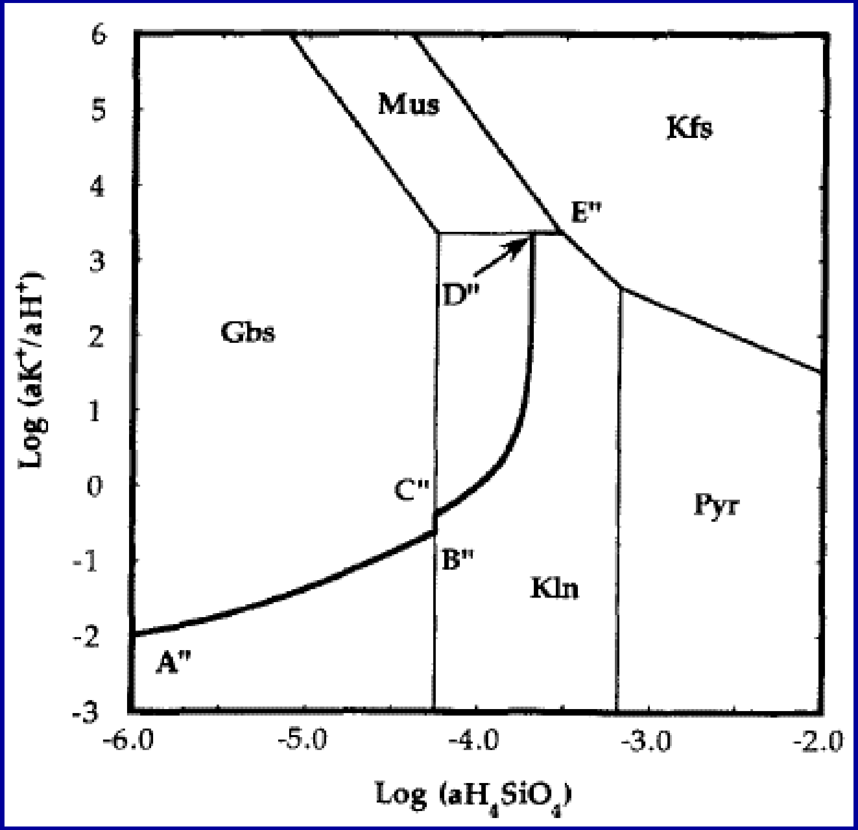
Thermodynamic approach



- Many published papers and talks use equilibrium thermodynamic stability diagrams.
- Applications to Mars incl. Gooding (1978) & others.
- On Earth, kinetics dominate below ~60 °C, equilibrium obtains above ~100 °C. (Lasaga, 1984, JGR).
- Partial equilibrium – disequilibrium - kinetics for "low-T" systems.

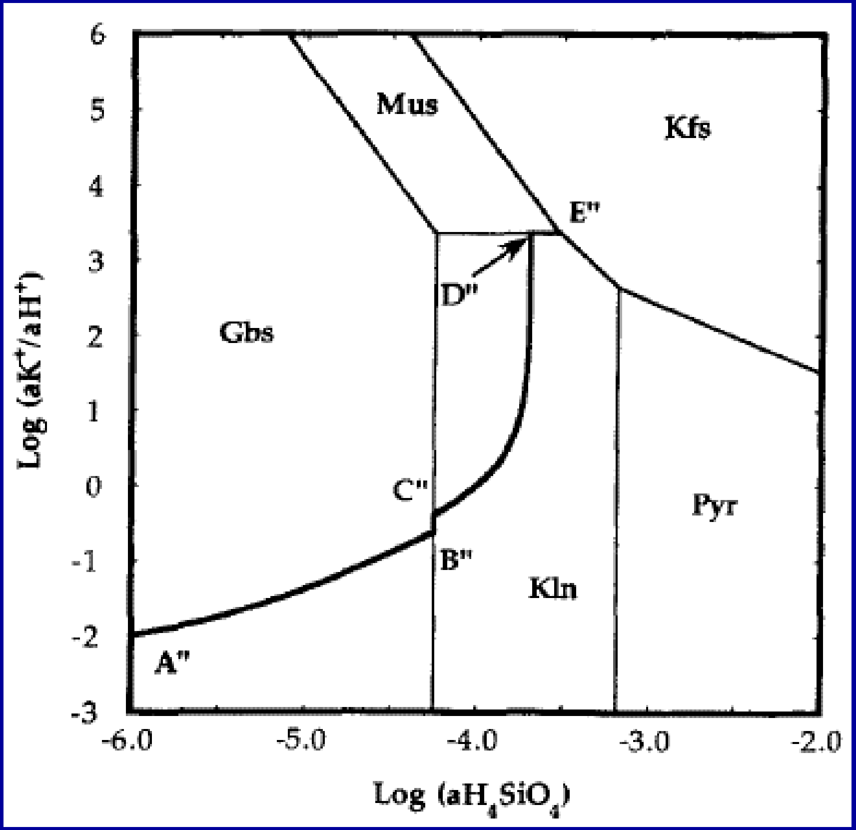
Partial equilibrium & kinetics: Closed system



- Partial equilibrium
- Reaction progress
- Reaction path
- Primary-mineral dissolution kinetics
- Secondary-mineral precipitation & dissolution kinetics

Steinmann & al. (1994) Clays & Clay Minerals, v. 42 p. 197

Partial equilibrium & kinetics: Closed system



- Starting w/dilute mildly acidic water
- Solution evolves from lower left to upper right
- Sequence of secondary minerals forms as solution evolves toward equilibrium w.r.t. primary mineral

Steinmann & al. (1994) Clays & Clay Minerals, v. 42 p. 197

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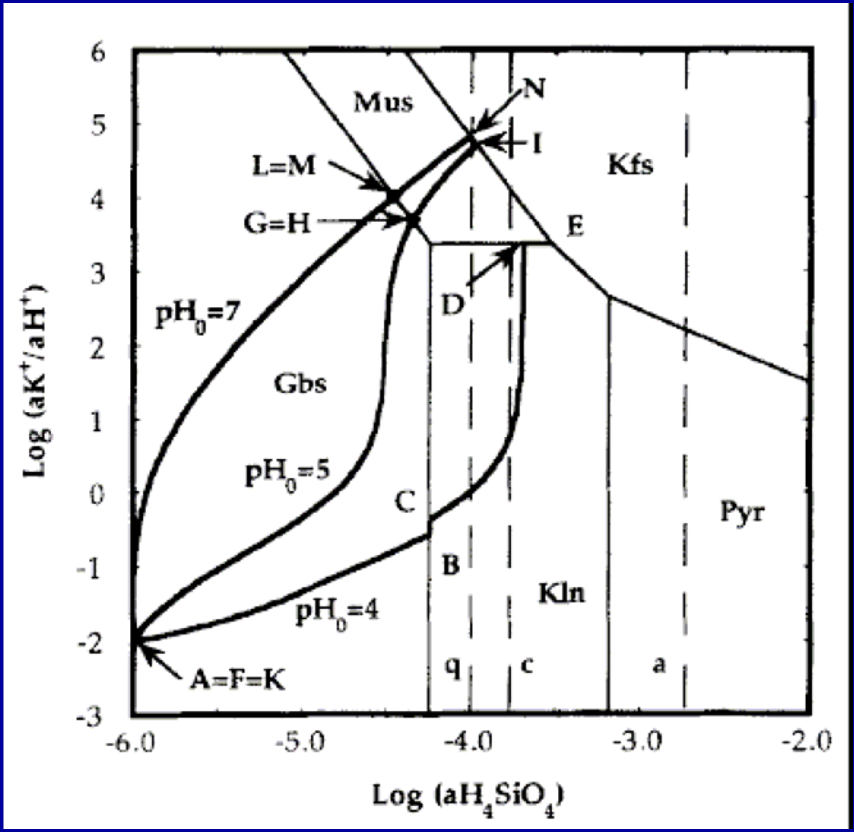
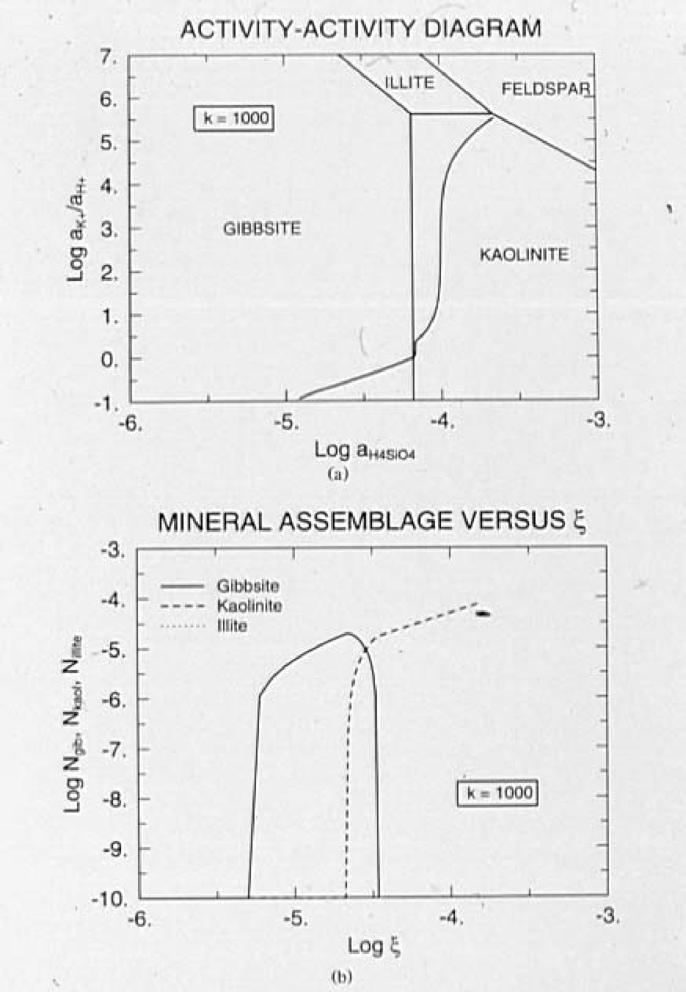
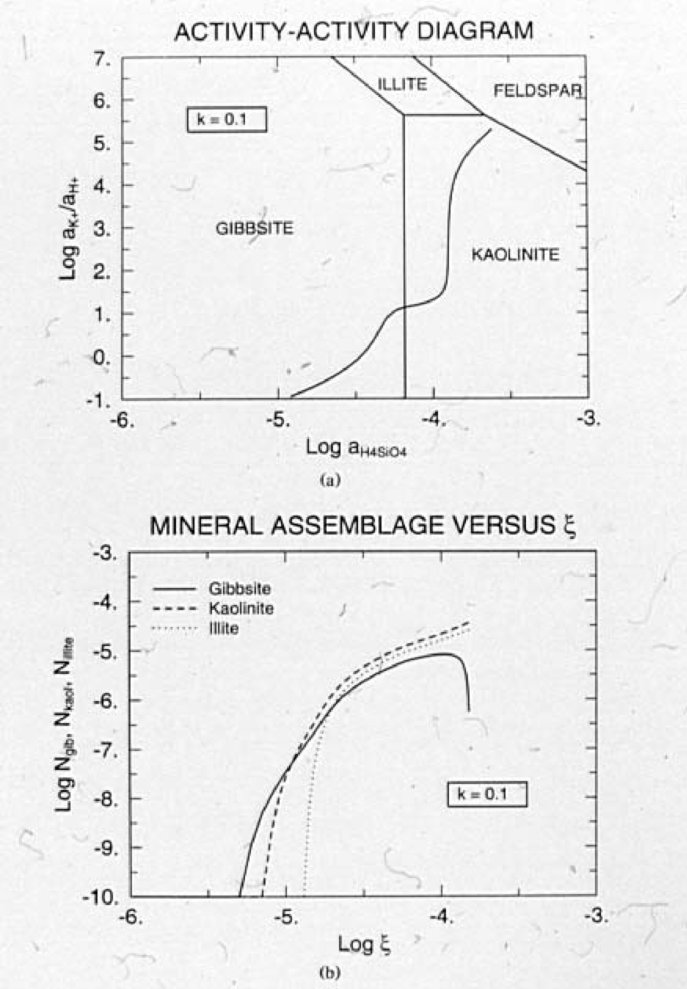


- Specific reaction path, and specific sequences of products formed, depend on initial value of pH and initial activities of other dissolved species
- Example: vary pH_o
- Minerals formed early are the same (gibbsite) but
- Minerals formed later differ with differences in initial pH

Steinmann & al. (1994) Clays & Clay Minerals, v. 42 p. 197

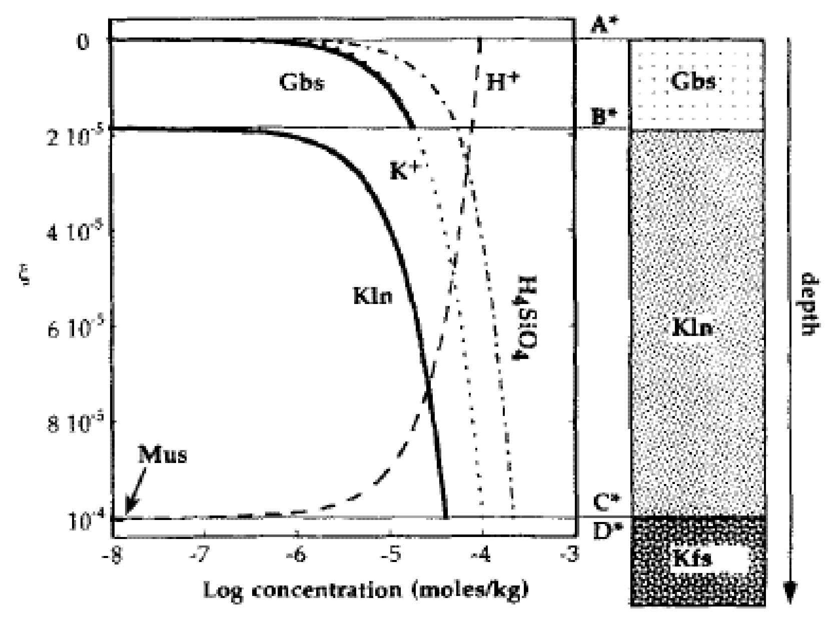
Specific reaction path, and specific sequences of products formed, also depend on product dissolution and precipitation kinetics





Lasaga (1998) Kinetic Theory in the Earth Sciences, ch. 1

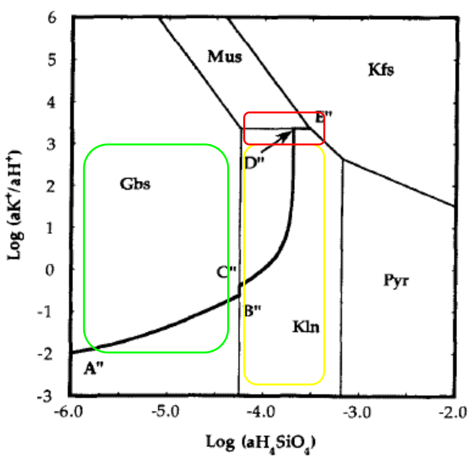
Partial equilibrium & kinetics: Open system

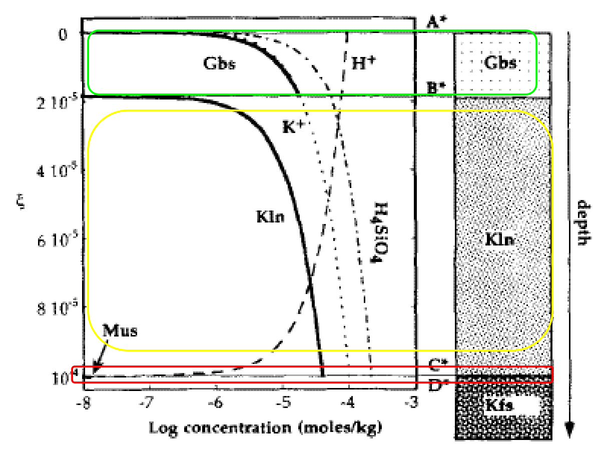


- If water is moving (e.g., through regolith or weathering rind) while reacting (kinetically) with K-feldspar,
- sequence of secondary minerals forms in space (“weathering profile”) rather than time.

Steinmann & al. (1994) Clays & Clay Minerals, v. 42 p. 197

Partial equilibrium, kinetics, solution composition, and product minerals





- In either closed (left) or open, flow-through (right) systems,
- and however much (partial) equilibrium is modified by kinetics:
- Si-poor clays (e.g., 1:1) are favored by acidic, dilute solutions (low dissolved rock-forming elements, low pH)
- Dilute acidic solutions = little rxn w/PRFM = slow primary-mineral rxn kinetics or short mineral-solution contact times (high flow rates)
- Si-rich phyllosilicates (e.g., 2:1) are favored by evolved solutions (high dissolved rock-forming elements, high pH)
- Evolved solutions = extensive rxn w/PRFM = fast primary-mineral rxn kinetics or long mineral-solution contact times (low flow rates)

Steinmann & al. (1994) Clays & Clay Minerals, v. 42 p. 197

Partial equilibrium and kinetics: Summary

- Clays formed by weathering vary with the interplay between
- (1) the dissolution kinetics of primary minerals that release silica and cations to solutions (and consume acid) and
- (2) the leaching intensity of the weathering environment
- Info on entire mineral assemblage, including both (kinetically inhibited) primary minerals and (partial equilibrium) secondary minerals, is required to draw inferences about solution composition and leaching intensity

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- Transformation
- Neoformation
- *What can clay minerals tell us about alteration conditions on Mars?*

Transformation of pyroxene to smectite

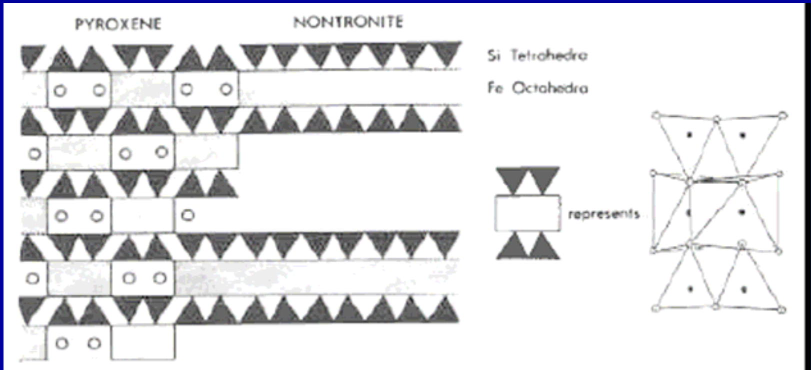
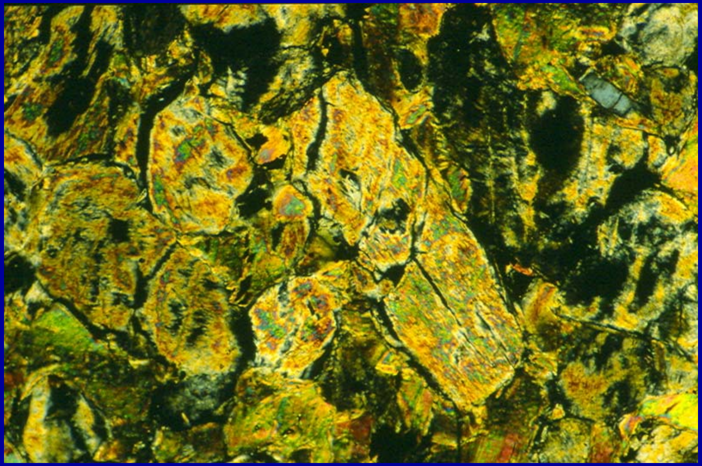


FIG. 5. Diagram of the relation between pyroxene and nontronite, viewed along the chain axis (pyroxene *z*).



- Transformation:
- T-O-T (chain) → 2:1 (T-O-T sheet) → 1:1 → &c.
- Products inherit portions of reactant-mineral structure

Left: Eggleton (1975), American Mineralogist, v. 60, p. 1063-1068.
Right: Koua Bocca Complex px, XPL (cf Delvigne, 1998, image #293); frame is 1.5 mm wide.

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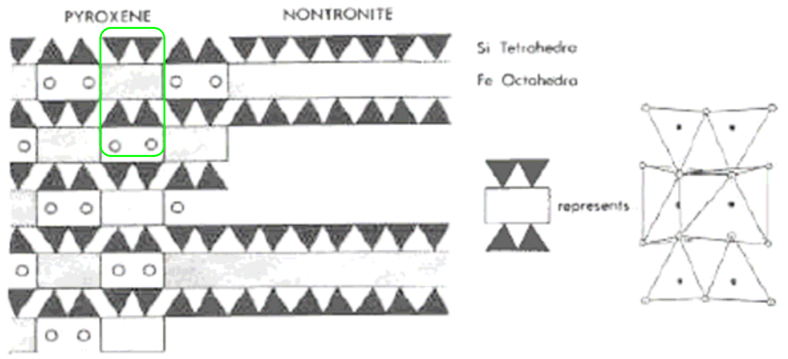

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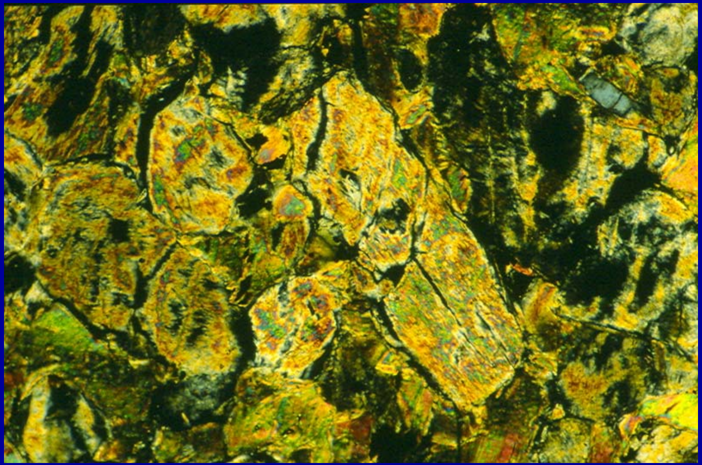

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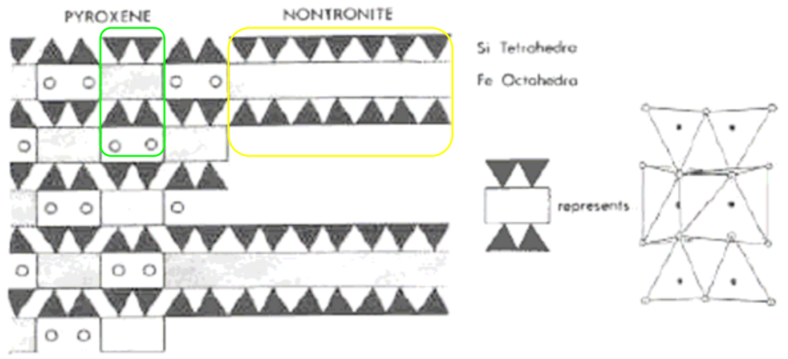

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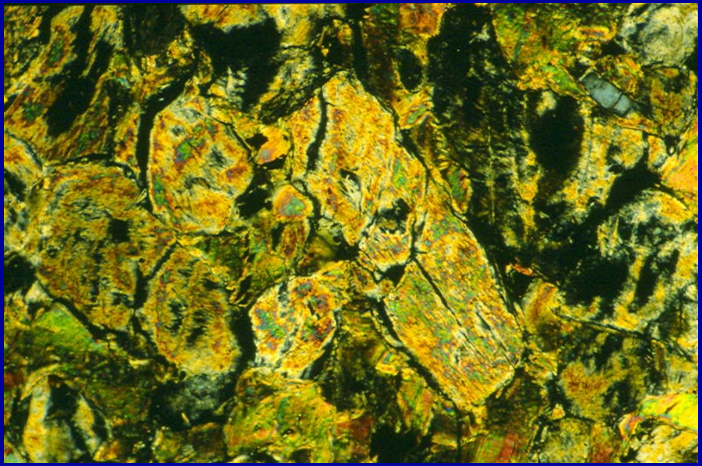

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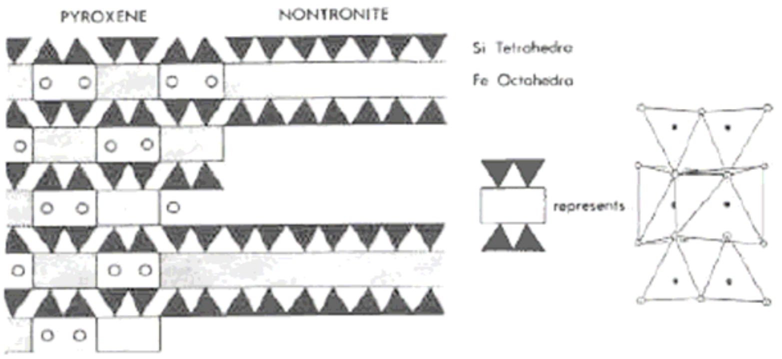
What can be inferred about clay-solution relations depends on the mechanism of product formation



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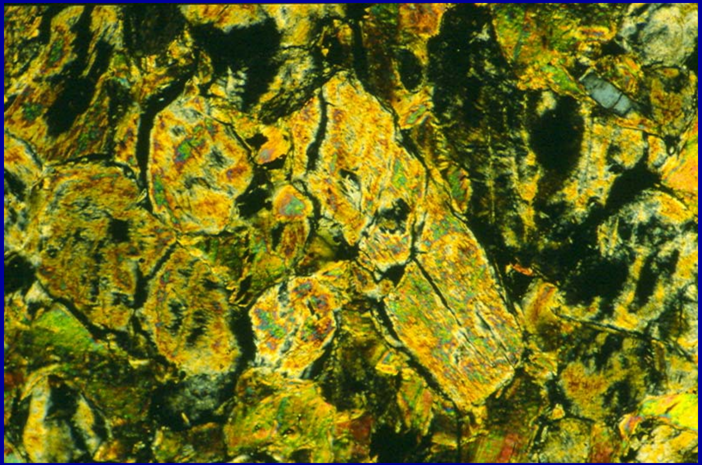

- *Transformation*:
- T-O-T → 2:1 → 1:1 → “0:1”
- Decreased influence of reactant-mineral structure w/increased extent of weathering
- Reactant unstable w.r.t. product, but little other solution info can be retrieved.

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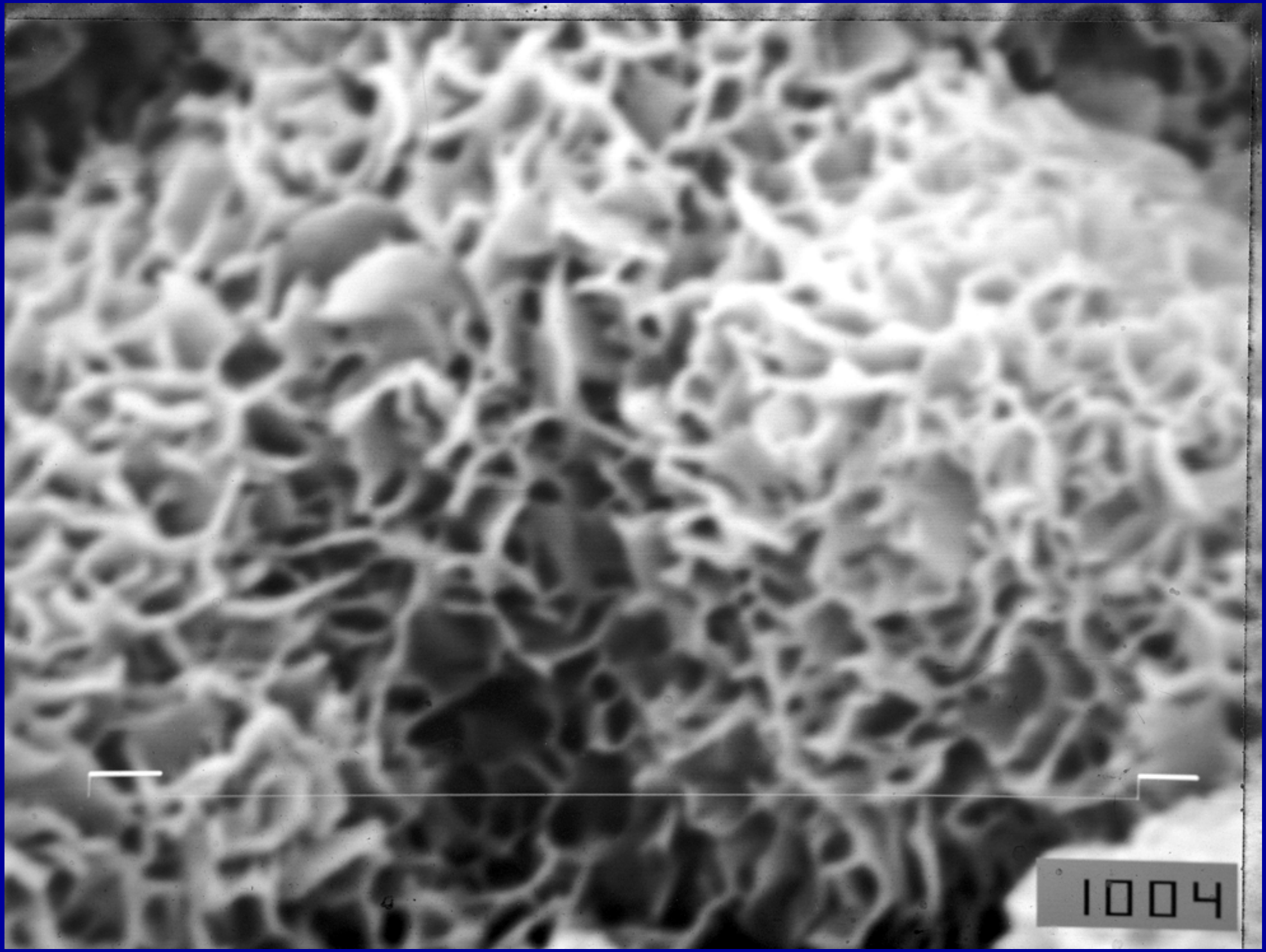
Neoformation of smectite from pyroxene: Precipitation of smectite from solution



Classic “cornflake” growth texture of smectite on pyroxene, Koua Bocca ultramafic complex, Ivory Coast, J. Delvigne sample, M. Velbel unpublished. Scale marks (square-waveforms) are 10 µm apart. Velbel (1989) Clays and Clay Minerals, v. 37, p. 515-524 for dissolution-reprecipitation mechanism.

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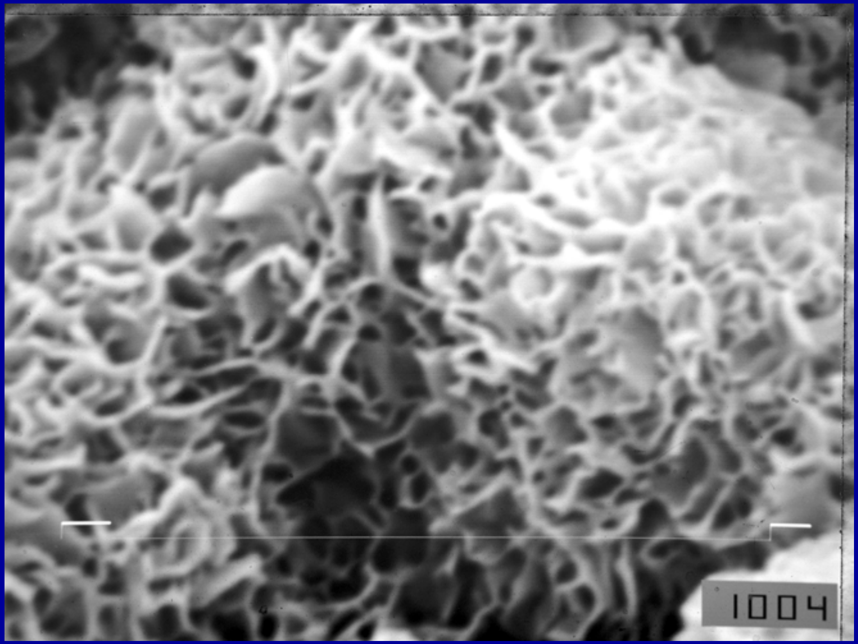

- *Neoformation*:
- Intensity of weathering (leaching intensity, e.g., rainfall, effective precipitation).
- Less intense leaching results in cation- and silica-rich solutions, from which precipitate cation- and silica-rich clays (e.g., smectites).
- More intense leaching results in cation- and silica-deficient solutions, from which precipitate cation- and silica-deficient clays such as kaolinite (and also hydroxides/oxyhydroxides).

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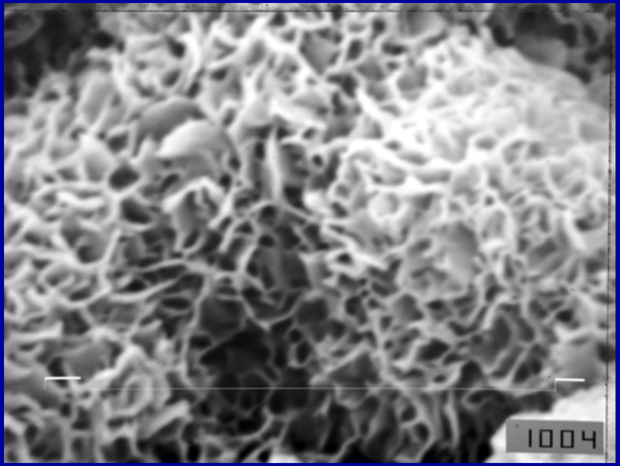

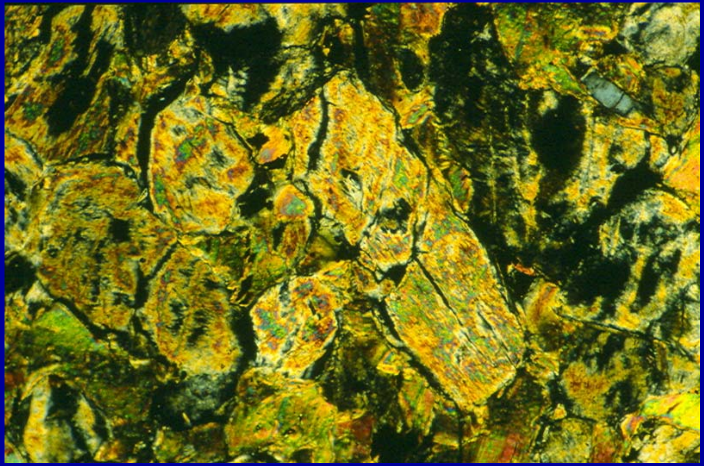

- *Because of reaction mechanisms & kinetics, less than thermodynamics would suggest.*
- Neoformed clays *are* environmental indicators (of solution composition & conditions).
- Transformed clays *are not* (or, much less so).
- To interpret the geochemical/environmental significance of smectite, we must know by which mechanism it formed.

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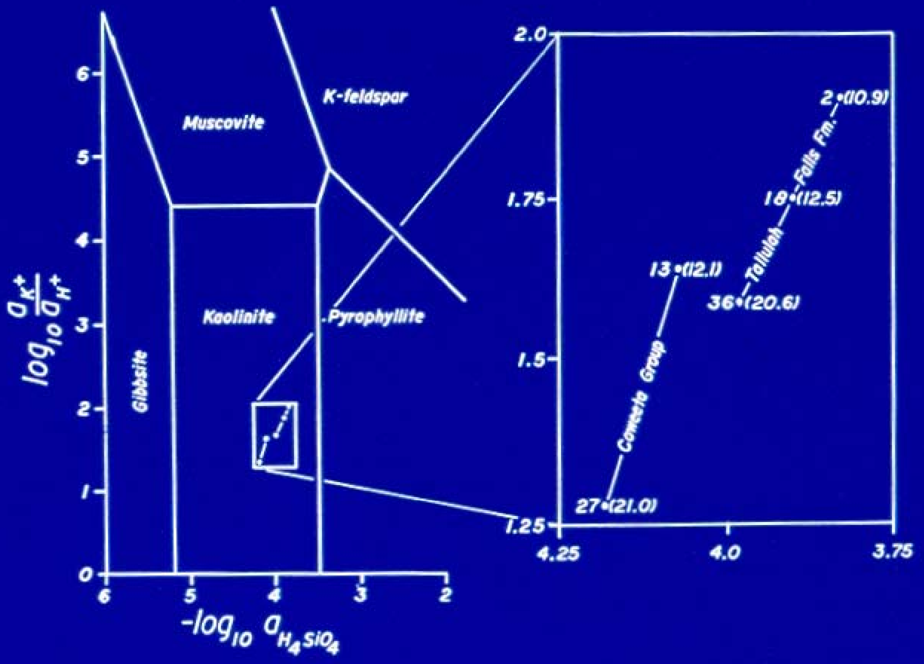
Below: Koua Bocca Complex px, XPL (cf Delvigne, 1998, Canadian Mineralogist, Special Publication 3, 495 pp., image #293); frame is 1.5 mm wide.

Reality check: How well does all this clay-solution partial equilibrium theory work on Earth?



- Sometimes, fairly well.
- SBR/CHL watershed solutes accurately reflect the last clays formed by neoformation (kaolin-group minerals) that the water contacted.
- However, clays formed by transformation (e.g., vermiculite from mica) in the same weathering profiles do not appear to be in thermodynamic partial equilibrium with the fluid.

Velbel (1985) in Drever, J.I. (editor), The Chemistry of Weathering, NATO-ARW.

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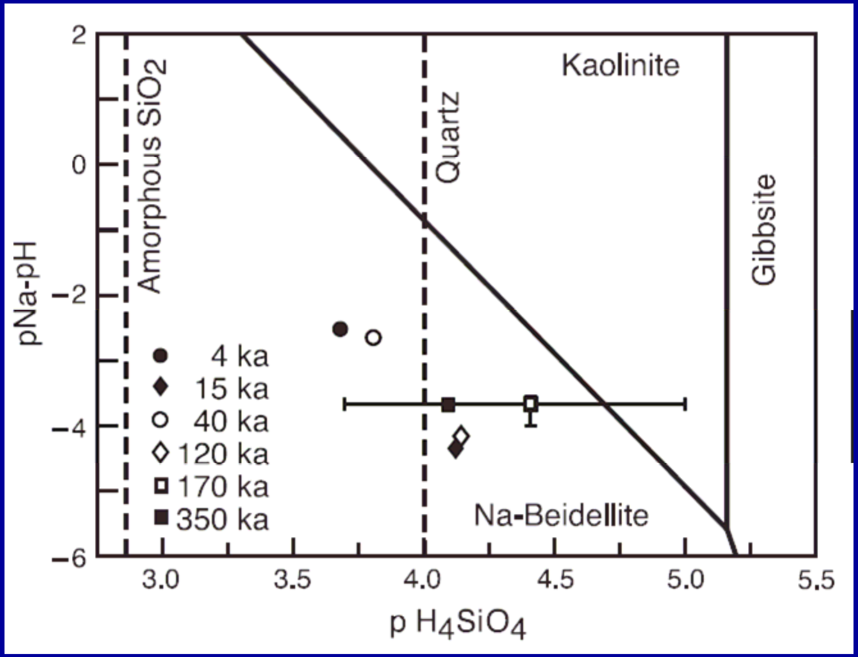
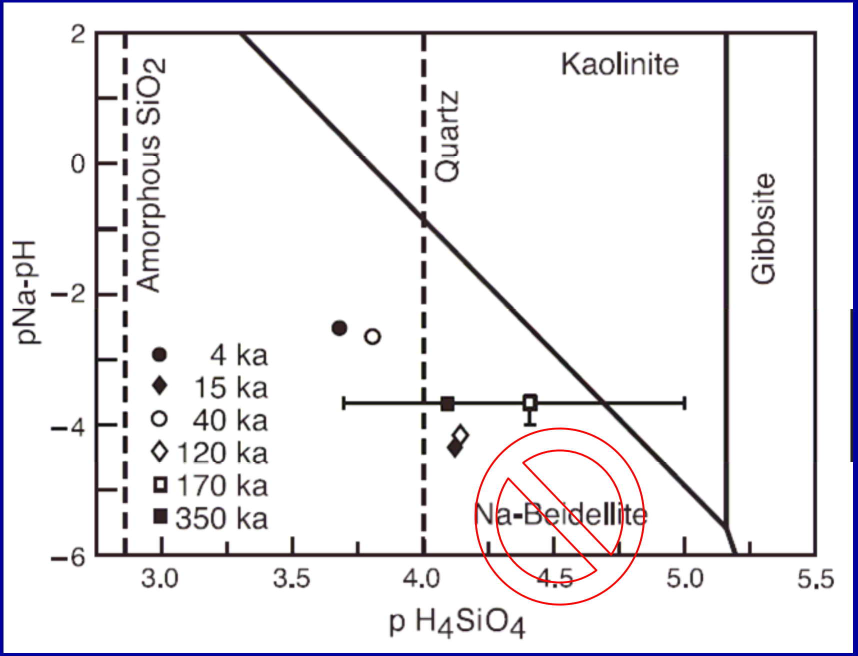


- Elsewhere: Not well.
- Conventional wisdom attributes smectite to weathering in poorly leached (w/slow flushing) or arid) environments.
- However, in such environments on Hawai'ian basalt, halloysite actually forms, despite forming from soil solutions that "should" be in partial equilibrium with smectite.

Ziegler & al. (2003), Chem. Geol., v. 202, p. 461-478.

Clay-solution disequilibrium



- In episodically/cyclically wet-dry environments, smectite apparently cannot form w/o a 2:1 phyllosilicate precursor (e.g., aeolian mica) for transformation to (2:1) smectite.
- The kinetics appear to be such that neoforming 1:1 clays and dolomite is much easier than neoforming the (thermodynamically favored) smectite.
- Oliver Chadwick’s group

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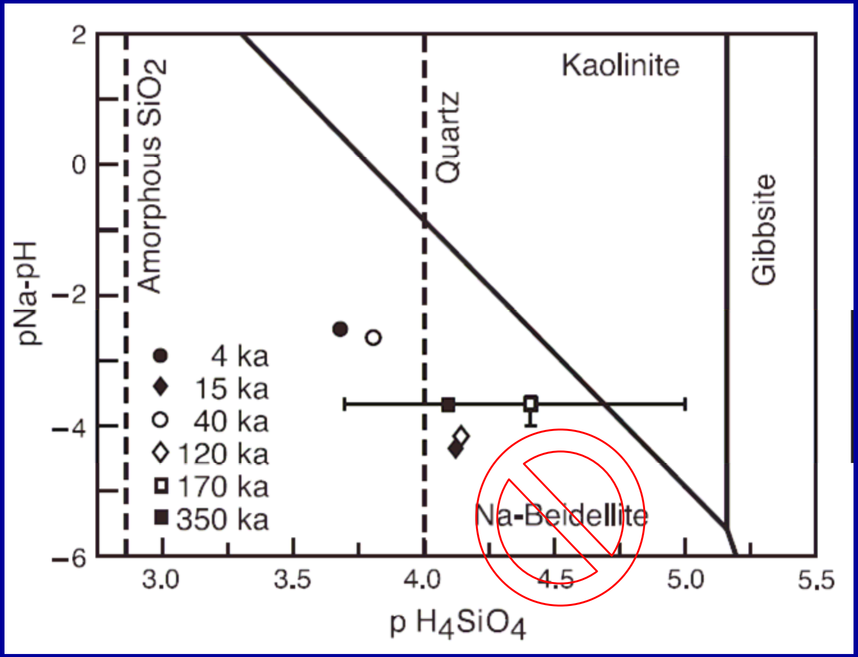

- Our question: How to infer past processes & former conditions (e.g., properties of solutions that are no longer present) from observations of remaining solids, esp. products,
- when even terrestrial clay-solution systems don’t follow the rules?

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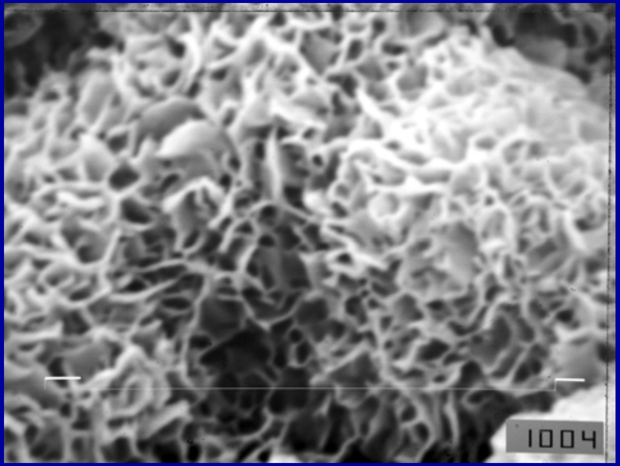

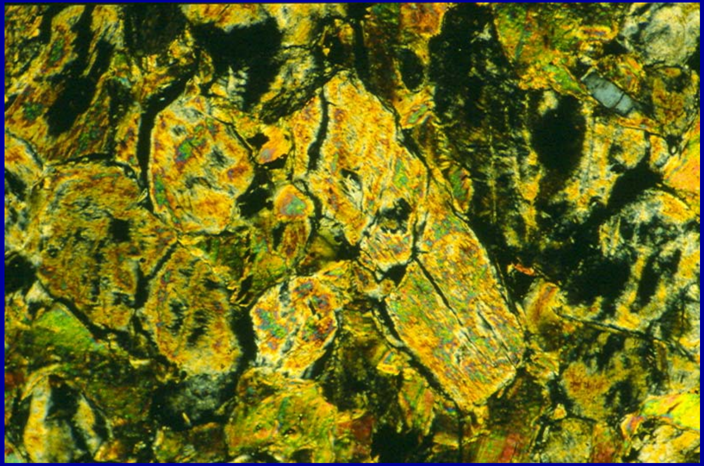

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Below: Koua Bocca Complex px, XPL (cf Delvigne, 1998, Canadian Mineralogist, Special Publication 3, 495 pp., image #293); frame is 1.5 mm wide.

What can clay minerals tell us about alteration conditions on Mars?

- Because of reaction mechanisms & kinetics, less than thermodynamics would suggest.
- Smectites
- Kaolinite and other kaolin-group minerals

If smectite is observed, were aqueous conditions in the smectite stability field?

- Smectites may not indicate low leaching, but may instead indicate early stages of transformation;
- only smectite formed by neoformation would unequivocally indicate solute-rich solutions and low leaching.

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If kaolinite is observed, were aqueous conditions in the kaolinite stability field?

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- but may instead indicate aridity and secondary-mineral formation (neoformation) kinetics prohibitively complex for smectite neoformation (cf Chadwick, Hawai’i).

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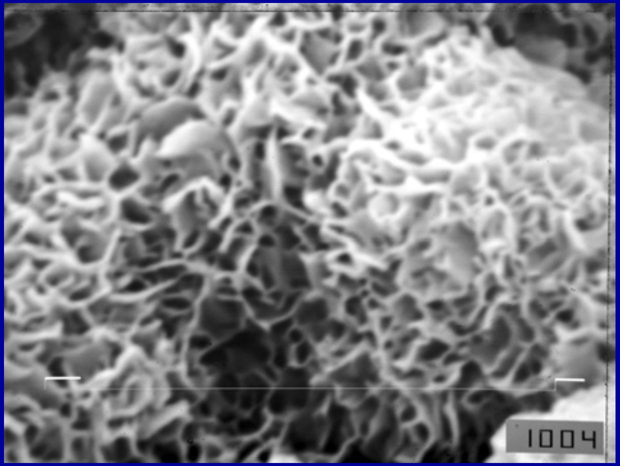
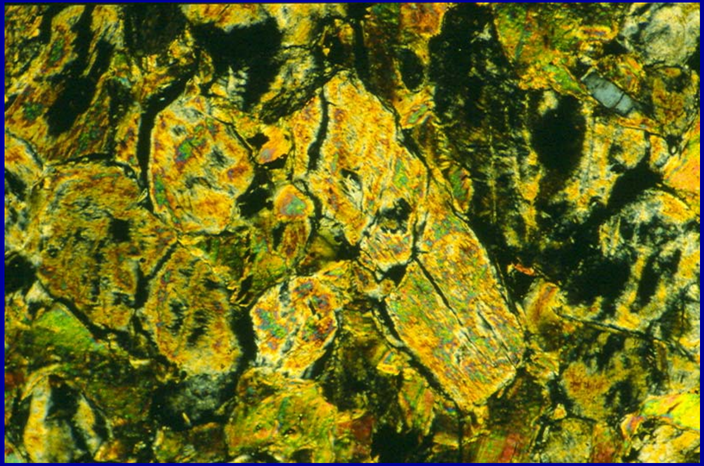
Summary: The stories clays tell





- Clay-mineral/environment relations can be non-unique.
- There are different mechanisms of phyllosilicate formation from parent materials during mineral-solution reactions.
- The different mechanisms create different relationships between mineral and solution properties.
- Reconstruction of solution attributes from mineralogy must account for the influence of clay-forming mechanism.

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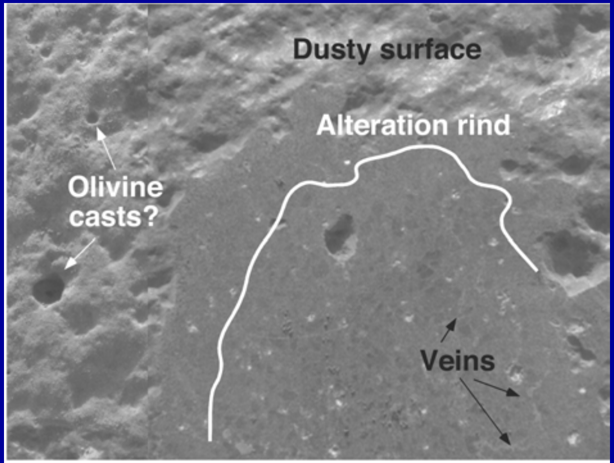
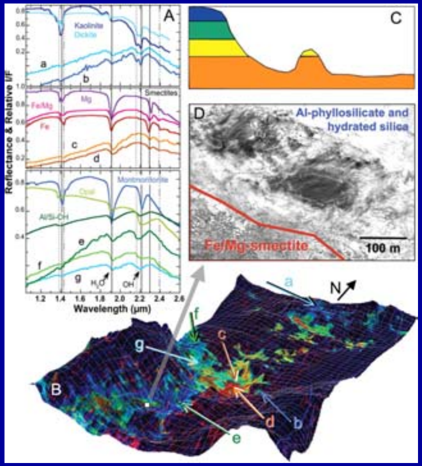
Info from solid-phase samples

- In the systems of interest here, solutions no longer exist, and we seek to infer their properties from the minerals that persist.
- Mineral assemblages
- Mineral associations (pseudomorphic, contact)
- Reactant corrosion-replacement textures
- Secondary-mineral distributions, textures
- Parent-product compositional relations

Inferring clay-forming mechanism

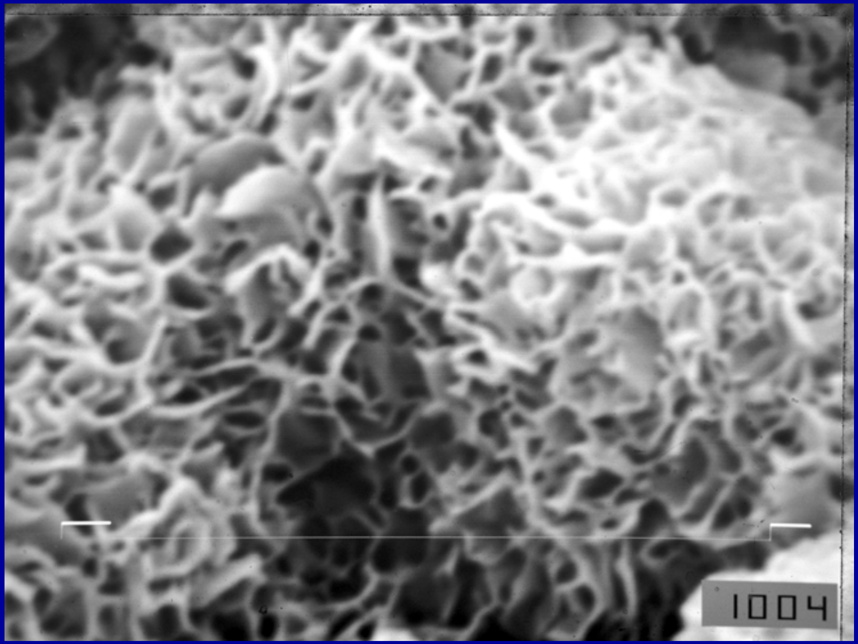


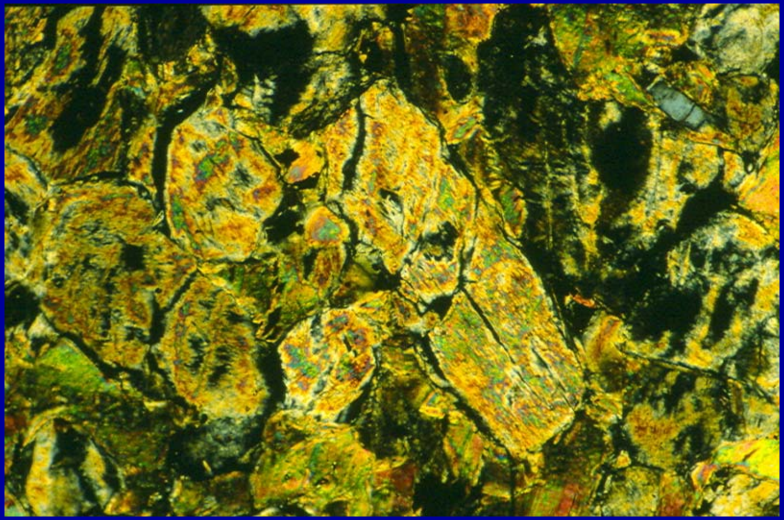


- Returned samples
- Surface observations
- Orbital observations

Above: Euhedral olivine at Gusev Crater (MER-A MI; “Composite MI image (no. 2M131690279EFF1155P2939M2M1) of an oblique RAT grind into Humphrey, illustrating its natural surface containing hexagonal casts …. The view is ~3 cm wide.” From McSween et al. (2004), Science v. 305, p. 842-845.) Below: J. L. Bishop et al., Science 321, 830 -833 (2008)

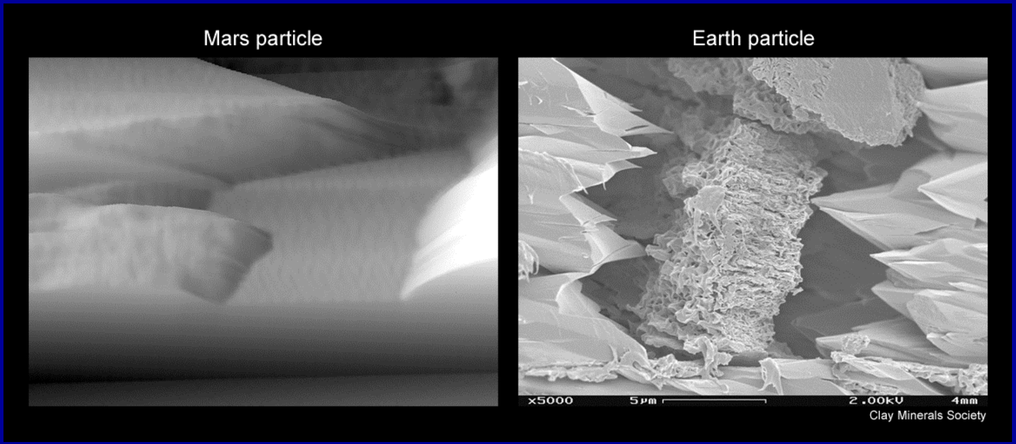
Most information about solution composition comes from neoformed clays

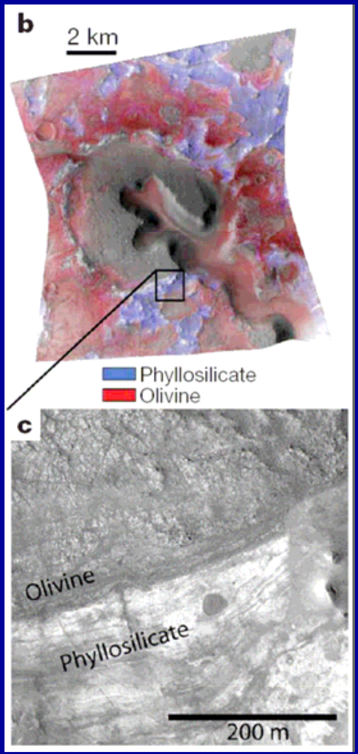




Left: Classic “cornflake” growth texture of smectite on pyroxene, Koua Bocca ultramafic complex, Ivory Coast, J. Delvigne sample, M. Velbel unpublished. Scale marks (square-waveforms) are 10 µm apart. Velbel (1989) Clays and Clay Minerals, v. 37, p. 515-524 for dissolution-reprecipitation mechanism. Right: Koua Bocca Complex px, XPL (cf Delvigne, 1998, Canadian Mineralogist, Special Publication 3, 495 pp., image #293); frame is 1.5 mm wide.

What can clay minerals tell us about alteration conditions on Mars?





- The most complete interpretation of ancient aqueous geochemistry is possible if we know the *presence and identity of (kinetically inhibited) primary minerals associated with (parent minerals of?) phyllosilicates* and *(ideally) crystallographic and textural relations between primary minerals and phyllosilicates, to ascertain whether the latter formed by transformation or neoformation from the former*.
- Fortunately, information about parent minerals *associated with* clays, and the nature of the association, is attainable from orbital & surface observations.

Left frame, left image: MPL MECA AFM image of denticle, MPL landing site. Left frame, right image: FEG-SEM SE image of corroded (denticulated) pyroxene w/associated smectite (air dried), weathered Koua Bocca ultramafic complex, Ivory Coast (Velbel & Barker, 2008, Clays and Clay Minerals, v. 56, p. 111-126, Fig. 9). NASA press release 29 Sep 08; NASA Planetary Photojournal, image PIA11206. Right frame: Mustard & al. (2008) Nature, v. 454, p. 305-308.