# WHAT CAN CLAY MINERALOGY TELL US ABOUT ALTERATION ENVIRONMENTS ON MARS?

#### **David Bish and David Vaniman**



#### **Products of Mineralogical Studies**

- Mars' surface mineralogy can provide:
  - clues to its hydrologic, atmospheric, and geochemical histories
  - constraints on past alteration processes, both surface and subsurface
- Distribution of clay minerals over time and with depth  $\Rightarrow$  time-resolved information on alteration
- *Presumably*, organics/biology did not participate in the low-T formation of clay minerals.

### What can clay minerals tell us?

- That liquid water was present!
- That alteration took place at (relatively) low temperatures (e.g., weathering)
- Water compositions
  - open vs. closed hydrologic systems
- Whether any post-formation alteration took place
  - diagenesis, metamorphism

Cheto bentonite, Arizona



Mineralogy vs. intensity of weathering (modified from Velde, 1985).

## Importance of Silica Activity

- Silica activity often controls the formation of both clay minerals and zeolites
  - zeolites and smectites are stable at elevated silica activities
  - depend on open- vs. closed-system hydrology
- Numerous recent suggestions of amorphoussilica deposits on Mars
  - hydrothermal alteration or from acidic vapors with small amounts of liquid water.
- Stability diagrams can shed light on alteration conditions.



Stability diagram for minerals in the  $AI_2O_3$ -SiO<sub>2</sub>-H<sub>2</sub>O system. "p" in axis labels refers to -log[] (Kittrick, 1969).

#### Alteration of Volcanic Glass to Clinoptilolite



St. Cloud Mining, Buckhorn, NM

### Smectites vs. Zeolites

- Smectites or zeolites can form from volcanic ash, depending on conditions
  - basaltic ash does not *always* alter to phyllosilicates
  - smectite—near- or below-neutral pH conditions
  - zeolites—alkaline conditions
  - smectites and zeolites *together* would indicate a more persistent and evolved hydrogeologic system

- Kaolinite stable at low pH, low Na, and high silica
- Smectite stable at high silica, medium pH, and medium to high Na
- Note the analcime stability field at high pH's and high Na



Stability relations of phases in the Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at  $25^{\circ}$ C and 1 atm.

From Garrels and Christ (1965)

### Smectites vs. Kaolin Minerals

 Kaolin minerals form on Earth most commonly in tropical climates, usually under more-acidic conditions and with high water:rock ratios (i.e., well drained).



- But, they can form hydrothermally, accompanied by amorphous silica and  $TiO_2$  minerals such as anatase.
- On Mars, a Ti-Si association has been considered to support acid-vapor alteration (Yen et al., 2007)—not a unique solution.

 Kaolinite stable at low pH, low K, and a(SiO<sub>2</sub>) > qtz

 Mica stable at low a(SiO<sub>2</sub>), med pH, and med-high K



Stability phases in the K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at 25°C/1 atm. Solid circles represent of waters from arkosic sediments. From Garrels and Christ (1965)

#### Halloysite vs. Kaolinite

Detection of 10Å hydrated halloysite, a more hydrated kaolin mineral, on Mars would imply that the mineral had never experienced dehydration after formation.

Halloysite implies very different formation processes than kaolinite.



## Nontronite on Mars

 Nontronite has long been speculated to occur on Mars and has been identified spectrally.

 Generally considered that nontronite forms at *low temperatures* under *reducing* conditions (where Fe is soluble).



+ : nontronite formation; --- : no formation Stability fields from Garrels & Christ (1965) (Harder, 1976).



Correlation of T-dependent mineral assemblages in shales and volcanic rocks (Hoffman and Hower, 1979)



The occurrence of "higher-grade" clay minerals such as illite and illite/smectite would suggest the occurrence of diagenetic and low-grade metamorphic reactions.



Relationship between T and extent of smectite-to-illite reaction

# Time-temperature limits on clay minerals (modified from Velde, 1992).



This figure implies that mixed-layer illite/smectites are not stable over long times even at low temperatures.

### Long-Term Clay Mineral Stability on Mars

- Poorly ordered clay minerals (e.g., smectites and illite/smectites) do not occur in old rocks on Earth
  - often assumed that they gradually transform to more stable phases such as illite, micas, and chlorites.
- Discovery of smectites in Noachian terrains has important implications for the long-term stability of clay minerals and suggests an alternative hypothesis
  - tectonic activity on Earth eventually results in the progressive alteration of low-temperature minerals to higher-temperature assemblages.
- Smectites on Mars in rocks >3 Gya would rewrite our understanding of clay mineral stability
  - in the absence of (plate) tectonic activity, "metastable" clay minerals may be "stable" for times on the order of the age of the planet.

#### Summary

The occurrence of clay minerals ⇒ aqueous alteration has occurred.

Specific clay minerals can put limits on the conditions of mineral formation, e.g.,

-kaolin  $\Rightarrow$  high water:rock, low pH

-zeolites ⇒ low water:rock, closed system, high pH

-smectites  $\Rightarrow$  open system, med pH, I/S  $\Rightarrow$ 

 ID of "old" smectites on Mars can rewrite our understanding of clay stability.

 Clay mineralogy can clarify alteration mechanisms the entire mineral assemblage can greatly constrain processes responsible for today's martian mineralogy.

