

Mineralogical Constraints on Diagenesis of the Sheepbed Mudstone, Gale Crater, Mars, as Determined by the CheMin XRD Instrument and Examples of the Use of NASA Spinoff Technology in the Oil and Gas Industry*

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Abstract

Sediments of the Yellowknife Bay Formation (Gale crater, Mars) include the Sheepbed Member, a mudstone cut by light-toned veins. Two drill samples, John Klein and Cumberland, were collected and analyzed by the CheMin XRD/XRF instrument during Curiosity's Yellowknife Bay campaign. The CheMin XRD analysis shows that the mudstone contains basaltic minerals (Fe-forsterite, augite, pigeonite, plagioclase), as well as Fe-oxide/hydroxides, Fe-sulfides, ~20% trioctahedral phyllosilicates and ~20-30% amorphous materials. The light-toned veins that intersect the drill hole contain Ca-sulfates; anhydrite and bassanite are detected by XRD, but gypsum is also indicated from Mastcam spectral mapping. These sulfates appear to be almost entirely restricted to late-diagenetic veins. The presence of phyllosilicates indicates that the activity of water was high during their formation and/or transport and deposition (should they have been detrital). Lack of chlorite places limits on the maximum temperature of alteration (likely <80°C). The presence of Ca-sulfates rather than Mg- or Fe-sulfates suggests that the pore water pH was near-neutral and of relatively low ionic strength. The presence of a surplus of magnetite (~7-9%) and the near absence of olivine (~0-3%), when compared to previous CheMin soil measurements and Mars normative basalts, suggests that saponitization of olivine (a process analogous to serpentinization) could have occurred. All of these early diagenetic features appear to have been preserved in this more than 3 billion-year-old rock with minimal alteration since their formation, as indicated by the ease of drilling (weak lithification, lack of cementing phases), the presence of amorphous material, and the late-stage fracturing with emplacement of calcium sulfate veins. The CheMin XRD/XRF now operating robotically on Mars is the product of a 22-year NASA technology development effort. CheMin is 30×30×30 cm, weighs 10 kg, has only one moving part (the wheel which holds the transmission-geometry sample cells) and operates on 50 watts. Commercial spinoff instruments have been developed using CheMin technology that are now widely used in the oil and gas industries. One example is the Terra XRD/XRF, a battery-powered, field portable unit that can assist in real-time mudlogging to provide full mineralogical information useful in the geosteering of horizontal wells. Terra is currently being deployed at the well site by some of the major service companies.

Reference Cited

Vaniman, D.T., D.L. Bish, D.W. Ming, T.F. Bristow, et al., 2014, Mineralogy of a mudstone at Yellowknife Bay, Gale Crater, Mars: Science, v. 343/6169 (January 24).



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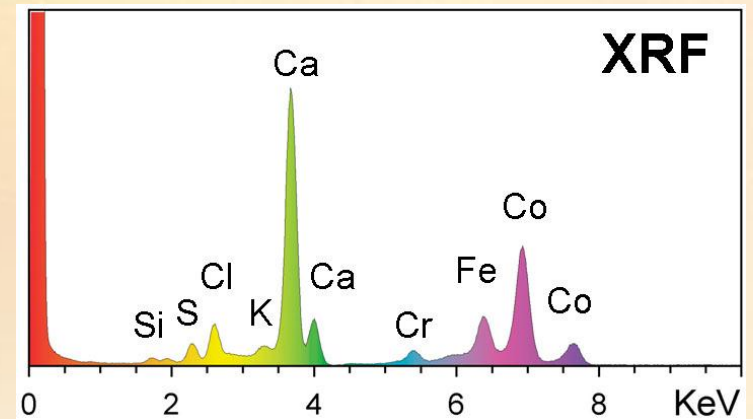
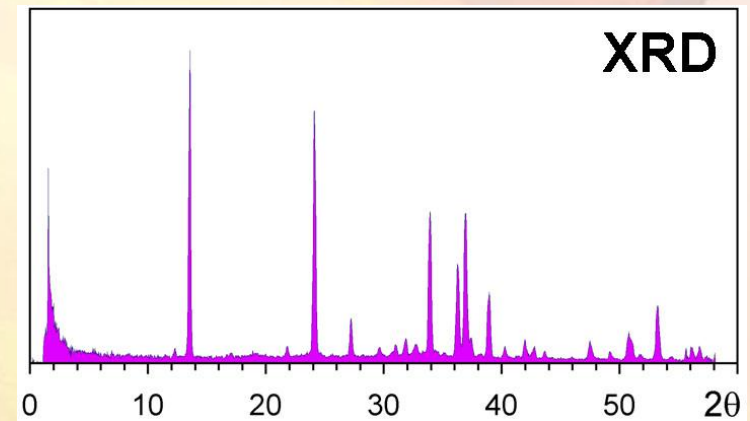
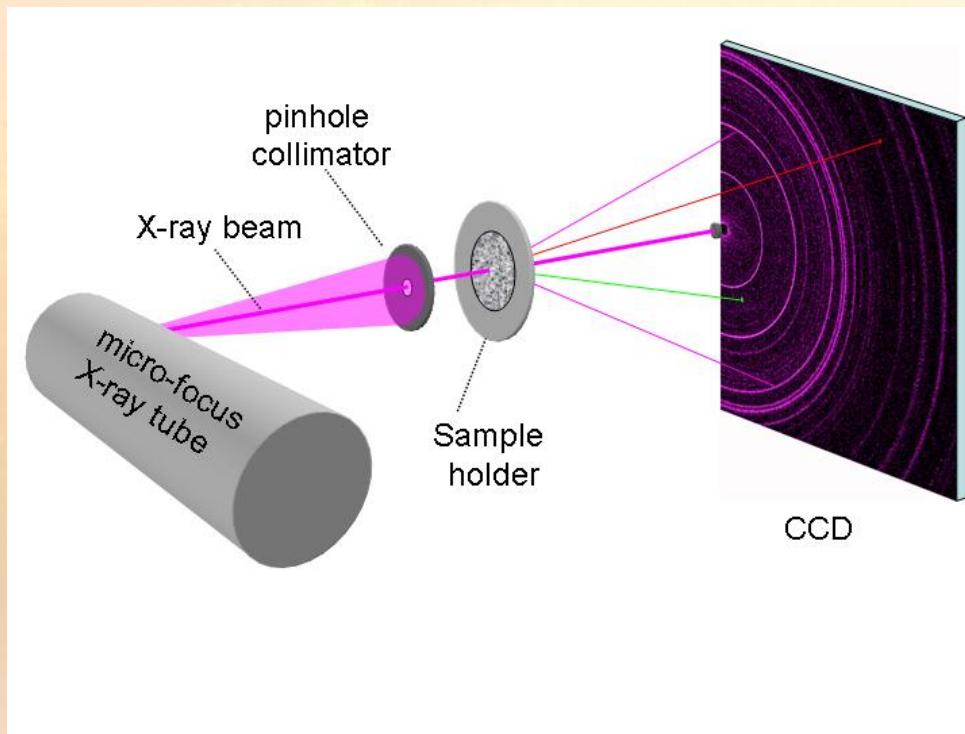


CheMin: A miniature XRD for Solar System Exploration and terrestrial field work

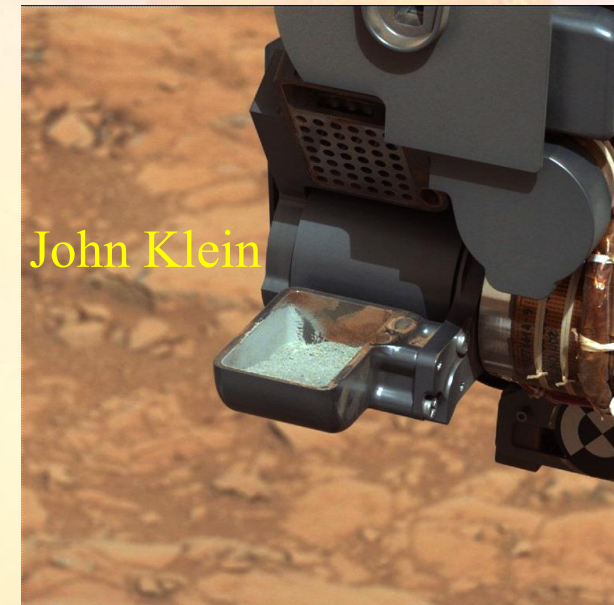
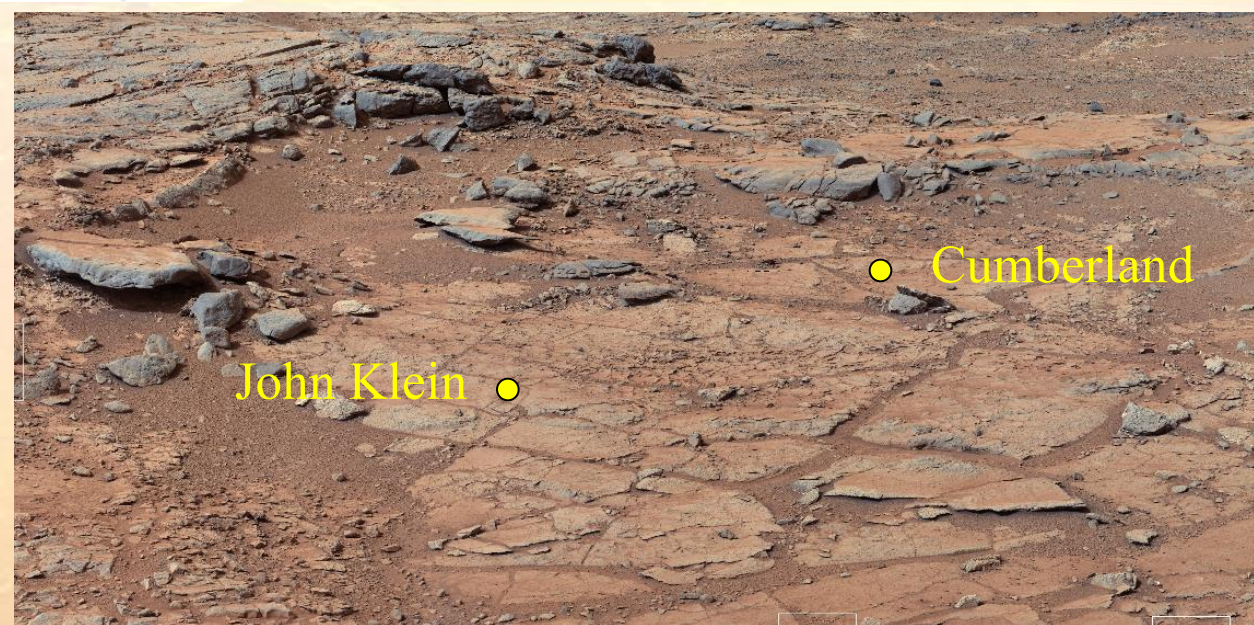


The CheMin XRD/XRF experiment

A single detector measures energy, position and intensity of the X-rays emanating from the sample



XRD analysis of mudstone at Yellowknife Bay



Sheepbed Member: A mudstone cut by light-toned veins.

John Klein & Cumberland were analyzed by *Curiosity's* entire instrument complement. However, only mineralogy will be presented here.



What is Habitability?

Wikipedia definition (from the Astrobiology roadmap):

- Extended regions of liquid water
- Conditions favorable for the assembly of complex organic molecules
- Energy sources to sustain metabolism

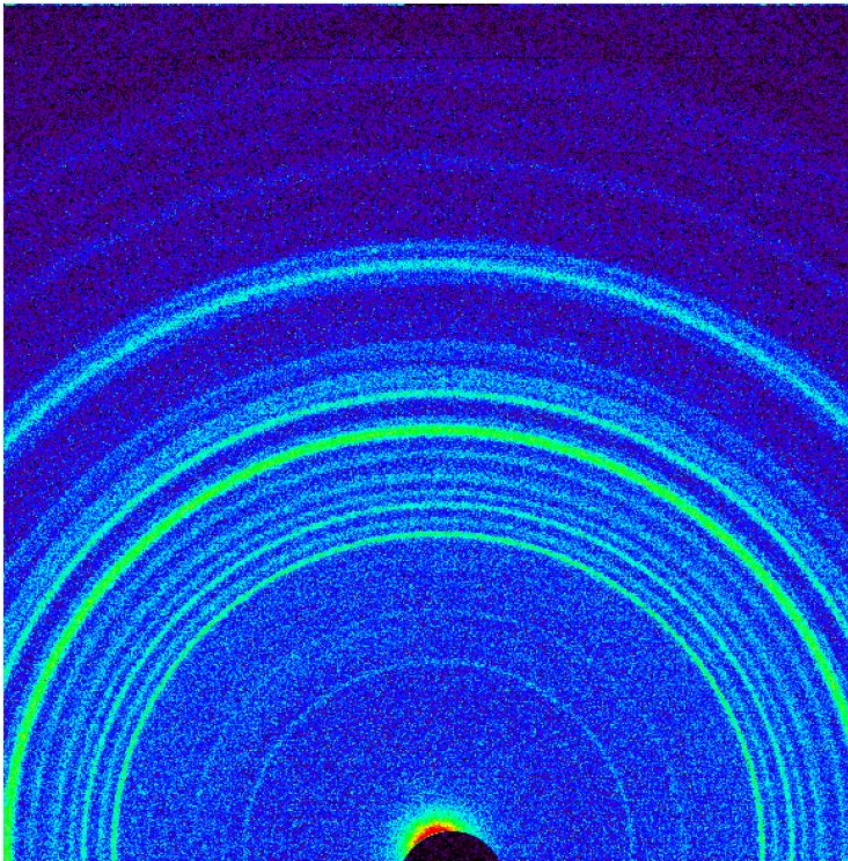
Elements and conditions needed to sustain life as we currently understand them:

- Water
- Potential source of energy
- Chemical building blocks (C, S, O, H, P + certain metals)
- Viable temperature, pH, eH, water activity
- Longevity of conditions

Comparison of Aeolian Bedform mineralogy with John Klein

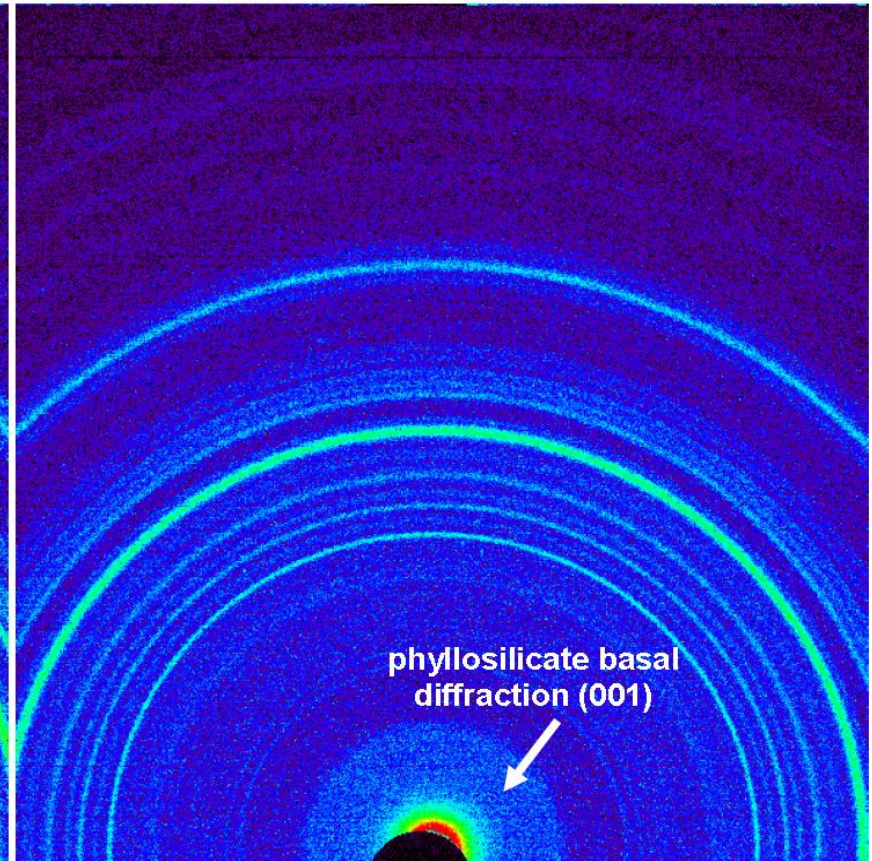
CheMin 2D X-ray Diffraction Images

Eolian Bedform
Rocknest_Scoop_5 (sum of 63 minor frames)



Major Crystalline Phases: Plagioclase, forsterite, augite, pigeonite, and magnetite with minor phases including anhydrite.

Drill Fines from Mudstone
John_Klein (sum of 46 minor frames)



Major Crystalline Phases: Plagioclase, forsterite, augite, pigeonite, magnetite and smectite with minor phases including anhydrite and bassanite



Comparison of Rocknest, Sheepbed Mineralogies



| Mineral | Rocknest | John Klein | Cumberland |
|----------------------|-------------|------------|------------|
| Plagioclase | 40.8 | 44.8 | 41 |
| Fe-forsterite | 22.4 | 5.7 | 1.9 |
| Augite | 14.6 | 7.6 | 9 |
| Pigeonite | 13.8 | 11.3 | 16 |
| Orthopyroxene | | 6.1 | 9 |
| Magnetite | 2.1 | 7.6 | 9 |
| Anhydrite | 1.5 | 5.3 | |
| Bassanite | | 2.1 | 1.2 |
| Quartz | 1.4 | 0.9* | 0.2* |
| Sanidine | 1.3* | 2.4 | 3.5 |
| Hematite | 1.1* | 1.2* | 1.3 |
| Ilmenite | 0.9* | | 1.2* |
| Akaganeite | | 2.3 | 3 |
| Halite | | 0.3* | 0.3* |
| Pyrite | | 0.6* | |
| Pyrrhotite | | 2.0 | 1.9 |

Comparison of Sheepbed to Rocknest:

- ✓ Decrease in olivine
- ✓ Increase in magnetite
- ✓ Presence of Ca-sulfate hydrate (bassanite)
- ✓ Presence of clay minerals (smectite)

| | Rocknest | John Klein | Cumberland |
|----------------------|------------|------------|------------|
| Amorphous* | 27% | 28% | 31% |
| Clay minerals | - | 22% | 18% |

*Amorphous component includes allophane-like constituents

Data are from Vaniman et al., 2014 (Science)



Clay Mineral Analysis with CheMin

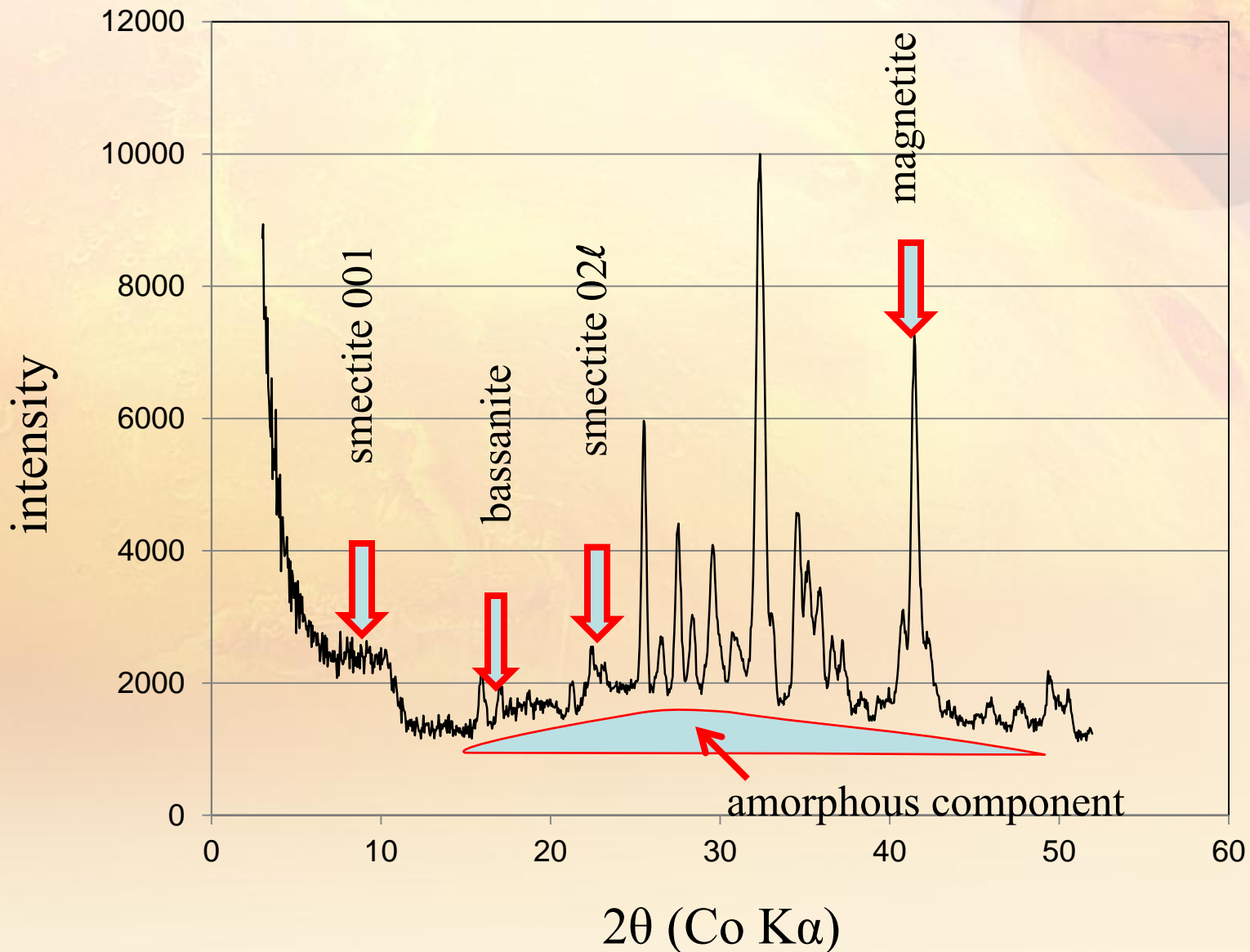


- 1) Common processing methods in terrestrial labs not possible
 - Purification by sonic disaggregation and sedimentation
 - Preparation of oriented mounts, glycolation
 - Heat treatment

- 2) Upper limit of $\sim 50^\circ$ $2\theta^*$ does not permit detection of 06 ℓ band. In earlier considerations we assumed that this would preclude our ability to distinguish dioctahedral from trioctahedral phyllosilicates. However, 02 ℓ works for this.

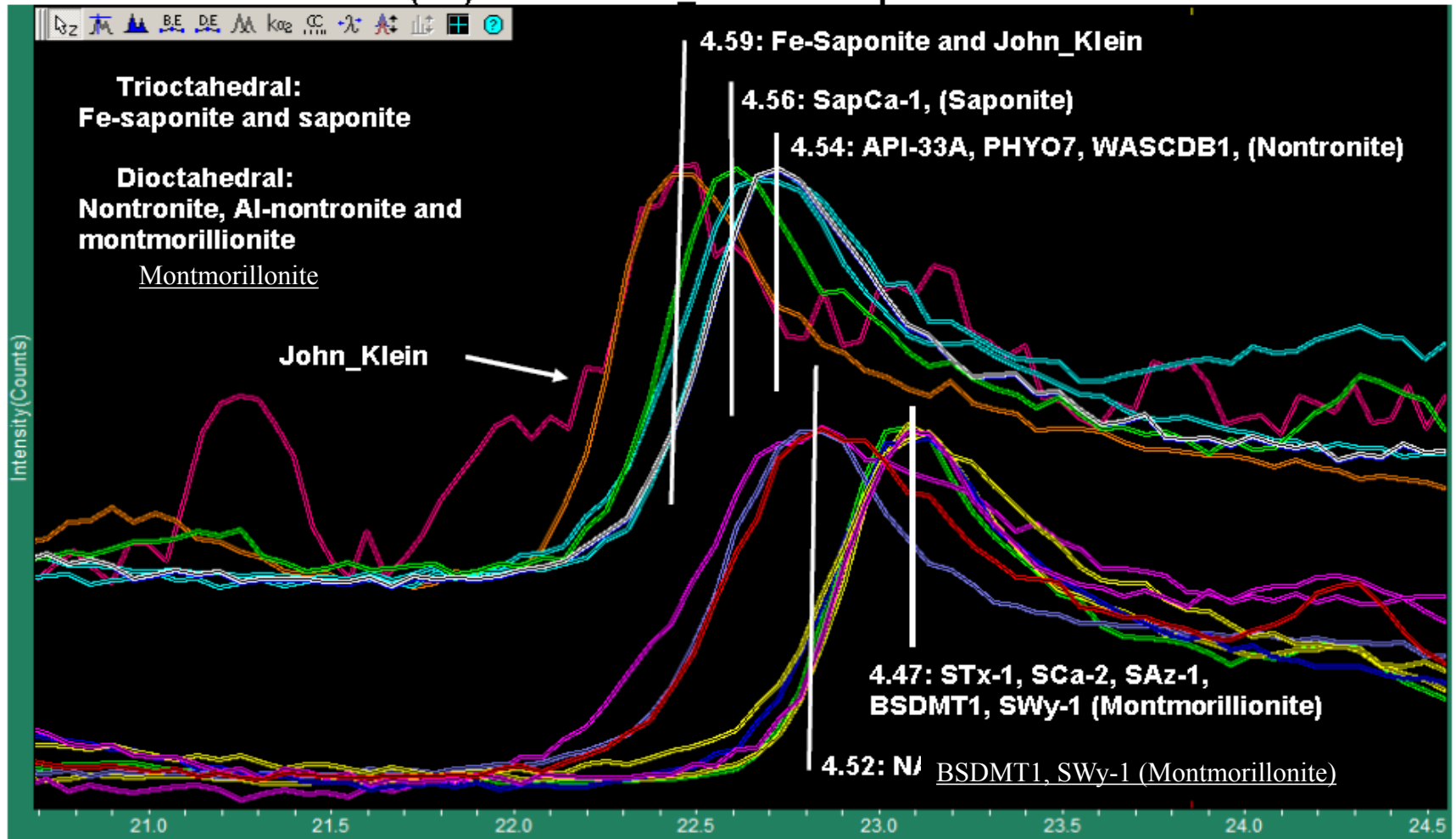
* All 2θ values mentioned or plotted in this presentation are for Co $K\alpha$.

CheMin 1D XRD Pattern of John Klein



The Position of the 02ℓ peak is indicative of dioct./trioct. clay type

Position of (02ℓ) line for John_Klein and representative smectites



02ℓ diffraction band for a range of trioctahedral (e.g., saponite) to dioctahedral (e.g., montmorillonite) clay minerals (data from Morris, Rampe)



Di octahedral vs. Trioctahedral: bears on composition and origins



| | tetrahedral | octahedral | classification |
|-----------------|----------------------------------|---|--------------------|
| Saponite | Si_3Al | $\text{Mg}_2\text{Fe}^{2+}$ | trioctahedral |
| Hectorite | Si_4 | $\text{Mg}_{2.7}\text{Li}_{0.3}$ | trioctahedral |
| “Griffithite”* | $\text{Si}_{2.3}\text{Al}_{0.7}$ | $\text{Mg}_{1.9}\text{Fe}^{2+}_{0.1}\text{Fe}^{3+}_{0.8}$ | ~80% trioctahedral |
| Nontronite | Si_3Al | Fe^{3+}_2 | dioctahedral |
| Beidellite | $\text{Si}_{3.5}\text{Al}_{0.5}$ | Al_2 | dioctahedral |
| Montmorillonite | Si_4 | Al_2 | dioctahedral |

*ferrian saponite

Conclusion: The clay minerals in John Klein and Cumberland are ferrian-saponites. A terrestrial analog with similar characteristics is Griffithite.

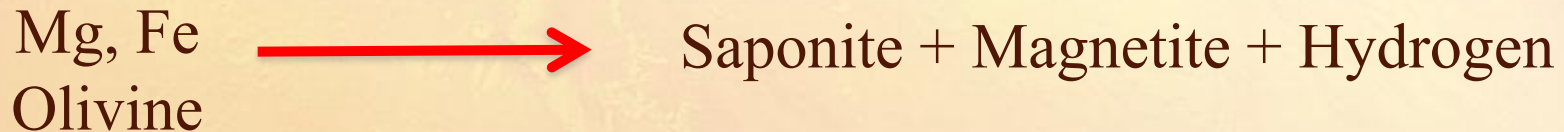


Magnetite Formation at Yellow Knife Bay

- Magnetite enrichment
- Saponite formation
- Low olivine content

} Key mineral observations
in Sheepbed

Suggests the reaction:



General serpentinization reaction:





Why saponite rather than serpentine?

- Olivine, serpentine, and saponite have metal/Si ratios of 2.0, 1.5, and 0.75, respectively.
- Need to leach metals or have reactive Si (and Al) available.
- Amorphous material potential source at YKB?





Saponitization?

- Fine-grained mixtures of olivine and amorphous material reacted with pore fluids.
- Outcomes:
 - 1) Consumption of olivine, production of saponite, magnetite
 - 2) Production of H₂ gas.
 - Related to voids in mini-bowls?
 - Potential energy source for life?



Not so Fast!



- Preliminary modeling results indicate difficult to form significant magnetite from olivine at $<80^{\circ}$ C.
- Experimental data and observation of natural serpentinizing systems at low temperatures indicate very small yields of hydrogen – not necessarily linked to magnetite formation.
- Unclear if H_2 produced in terrestrial low T systems is adequate to support life. Hard to argue this energy source for YKB.
- Nevertheless, there is strong evidence for authigenic production of magnetite.



Habitability based on Mineralogy:

The presence of phyllosilicates indicates that the activity of water was high during their formation.

The smectites are authigenic because:

- Clays delivered from elsewhere would be much more diverse
- Mineralogy and mass balance support formation in situ.

The absence of Fe-sulfates such as Jarosite and the presence of Ca-sulfates, trioctahedral smectites argue for circum-neutral pH,

Evidence of apparent low salinity in the primary and early diagenetic environments

Magnetite excess: Either authigenic formation or a sedimentary concentration mechanism. The context argues for authigenesis.



Other Mineralogical clues



Loss of Fe-forsterite and presence of saponite + excess magnetite:
Saponitization reaction?

Lack of chlorite places limits on the maximum temperature of alteration (likely <80 C).

The presence of Fe and S in both reduced and oxidized states represents chemical disequilibria that could have been utilized by chemolithoautotrophic biota, if present.

Sheepbed Mudstone mineralogy favors both formation and preservation of the markers for habitability:

- Formed in an aqueous depositional environment
- Late diagenesis limited to fractures isolated from sediment matrix
- Little or no evidence of late-stage hydrous alteration.



Conclusions

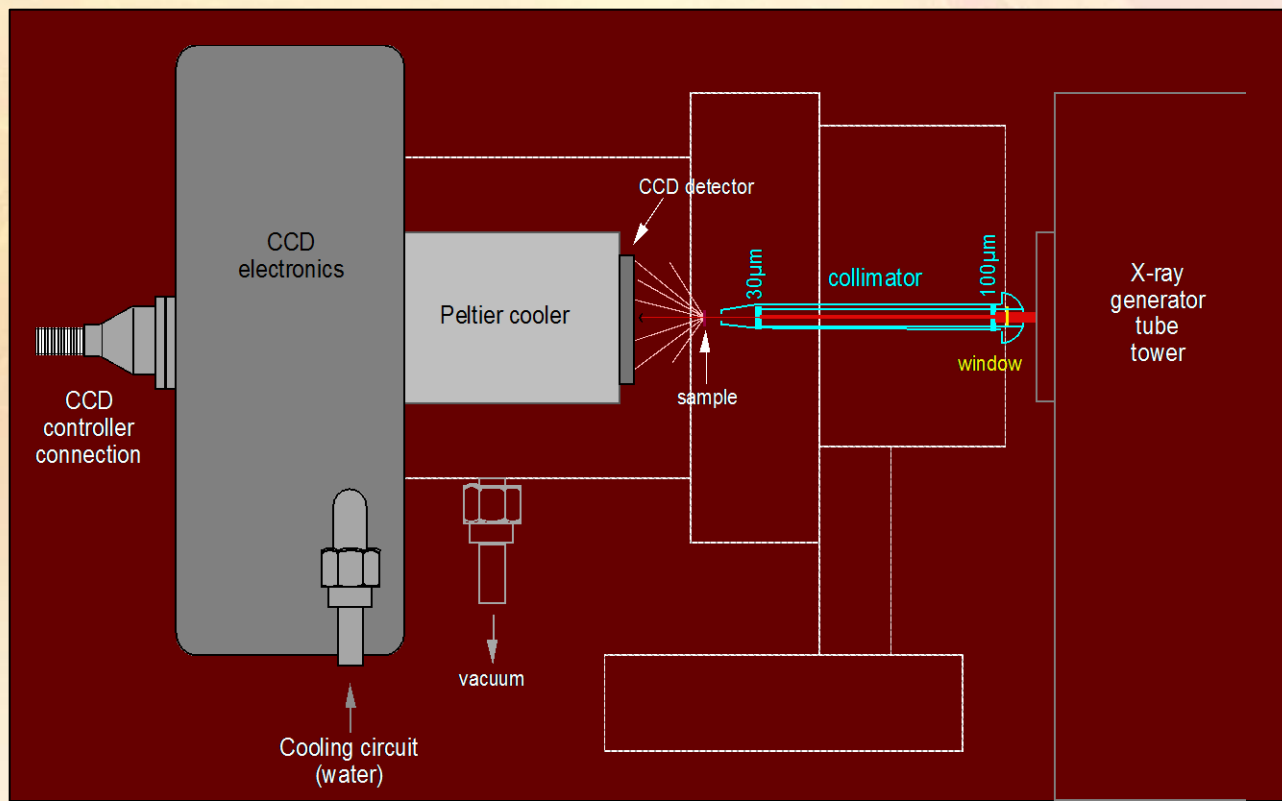
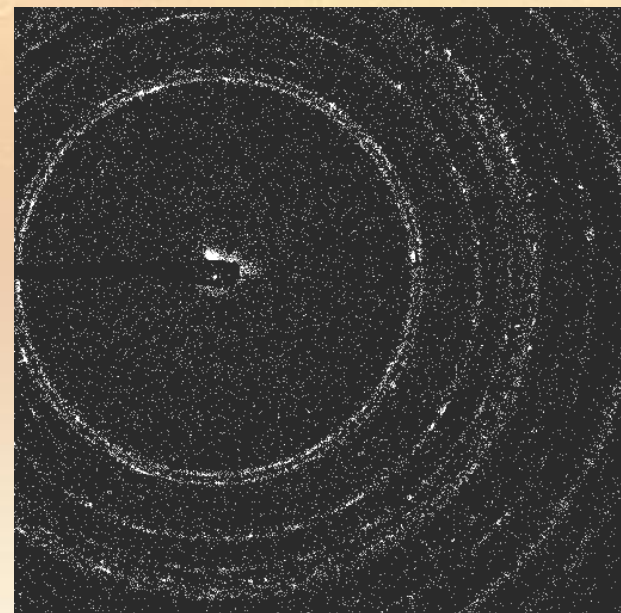
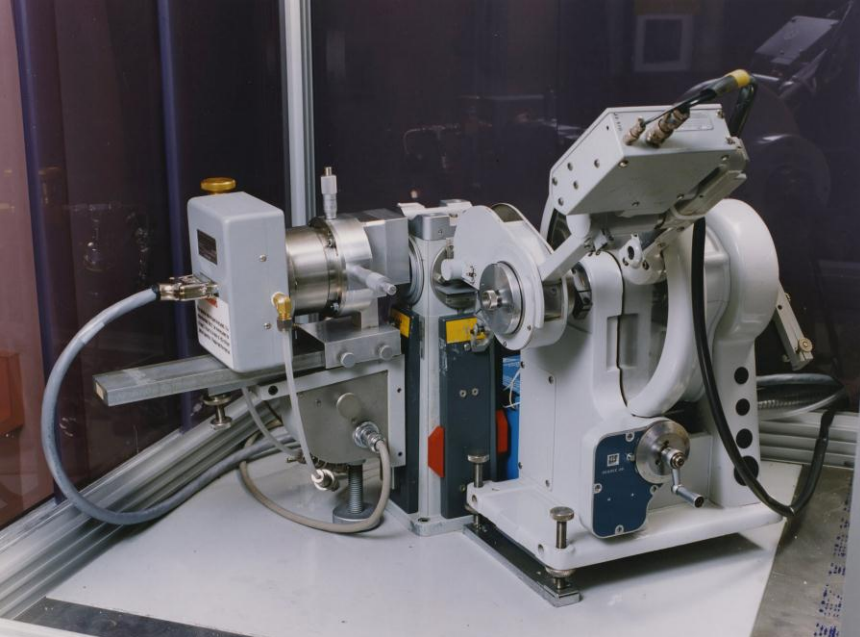


Sheepbed mudstone meets all the requirements of a habitable environment: Aqueous deposition at clement conditions of P, T, pH, Eh and ionic strength, plus the availability of sources of chemical energy.





CheMin Proof-of-concept prototype 1994

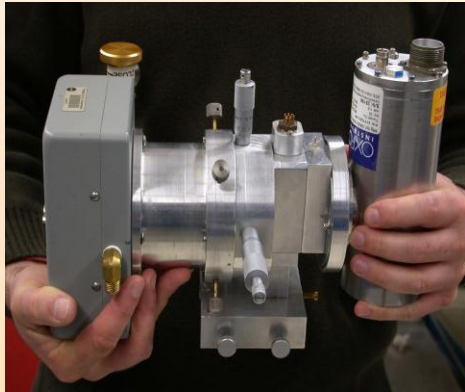




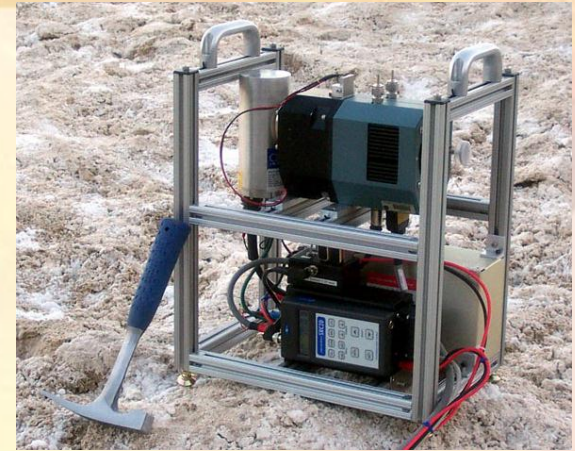
CheMin prototypes, 2000-2008

CHEMIN III Lab instrument (2003)

CHEMIN II (Oct. 2001)



CheMin III field instrument, (2004)
Badwater basin, Death Valley



CHEMIN IV Field instrument (2006)
Spitzbergen, Norway (78° N)

CHEMIN V Field instrument (2007)
Taylor Glacier, Antarctica





Support for NASA-funded field research and Education Outreach



ASTEP (AMASE, 2009)
Svalbard, Norway



Phoenix field test (2006)
Antarctica



Canadian fieldwork, 2008
High arctic



NAI Education Outreach,
Calif. Academy of Sciences



NAI Education Outreach,
Red Bluff High School
Red Bluff, CA



Commercial Applications

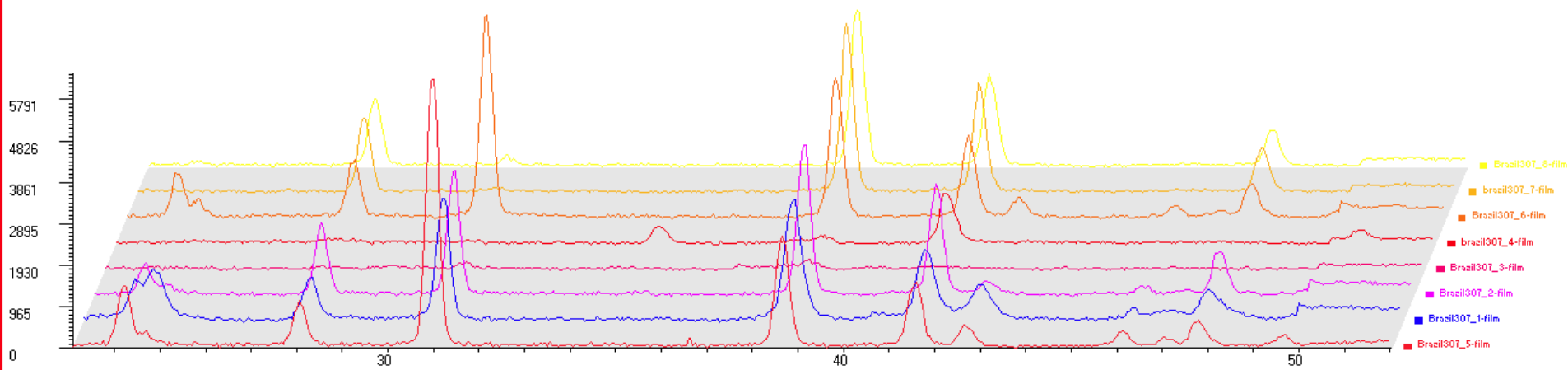
2008; Commercial Instrument “Terra” Introduced by InXitu, Inc.
2009: Won gold medal as “best new instrument” at PITTCON
2014: Several hundred instruments sold.



Mining Industry
Cement Industry
Petroleum Industry
Food Industry
Homeland Security
Department of Defense
Food and Drug Administration
Pharmaceuticals Industry
Art & Antiquities Preservation

Analyzing ore for potash content, 7 Km
deep in a Potash mine, New Mexico

Ore samples from a Brazilian Iron Mine

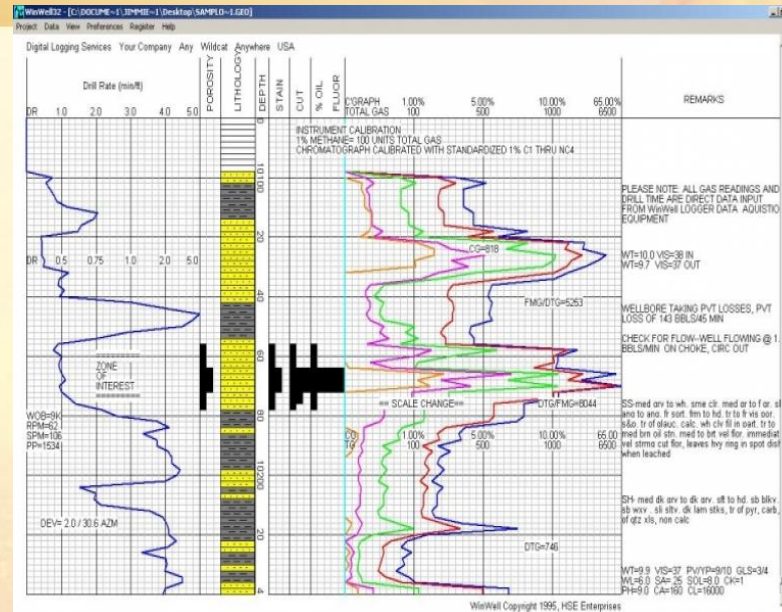


Sample Analysis

| Mineral | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 |
|-----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Quartz | 52.7 | 57.6 | 19.1 | n/a | 73.3 | 70.8 | n/a | 8.4 |
| Hematite | 26.3 | 40.4 | 10.7 | 16.5 | 26.7 | 27.2 | 100 | 91.6 |
| Goethite | 18.9 | 2.1 | 4.3 | 1.5 | n/a | 2 | n/a | n/a |
| Magnetite | n/a | n/a | n/a | 70.7 | n/a | n/a | n/a | n/a |
| other | 2.1 | n/a | 66 | 11.4 | n/a | n/a | n/a | n/a |



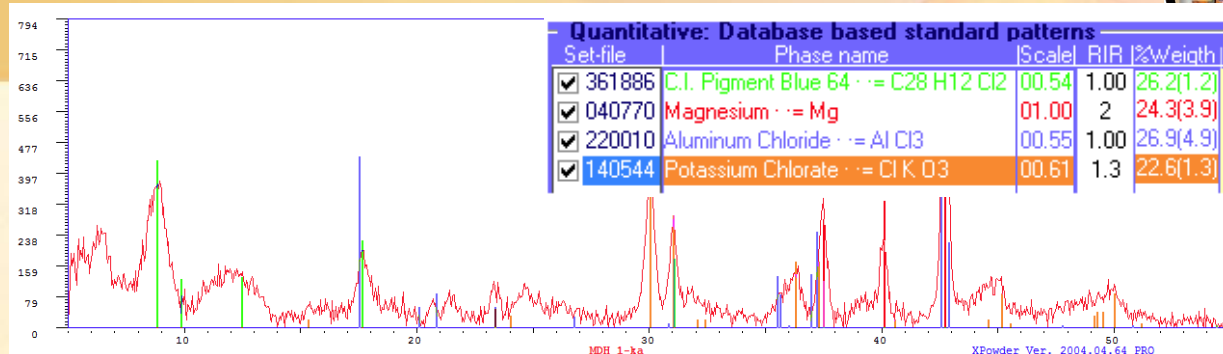
Mud logging – shale analysis



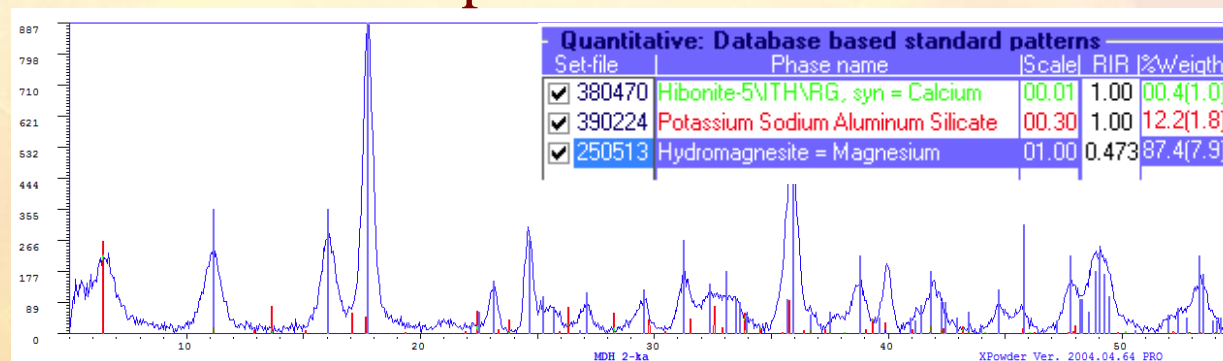
Quantitative Analysis Summary comparison: inXitu Terra vs. present laboratory based XRD analysis

| Sample | Chlorite % | Illite % | Calcite % | Quartz % | Albite % | Apatite % |
|------------------|------------|----------|-----------|----------|----------|-----------|
| 11670 – inXitu | 12.7 | 31.2 | 12.3 | 24.5 | 4.4 | 4.1 |
| 11670 - Given | 14.0 | 34.0 | 12.0 | 21.0 | 5.0 | 3.0 |
| 11677 – inXitu | 13.9 | 36.7 | 5.1 | 20.7 | 5.2 | 1.4 |
| 11677 - Given | 16.0 | 38.0 | 5.0 | 19.0 | 5.0 | 2.0 |
| 11908.9 - inXitu | 15.0 | 39.3 | 7.1 | 21.6 | 4.5 | 1.4 |
| 11908.9 - Given | 16.0 | 38.0 | 6.0 | 20.0 | 4.0 | 2.0 |
| 11953 - inXitu | 12.0 | 23.7 | 16.8 | 26.5 | 7.9 | 2.1 |
| 11953 – Given | 11.0 | 27.0 | 16.0 | 25.0 | 7.0 | 3.0 |

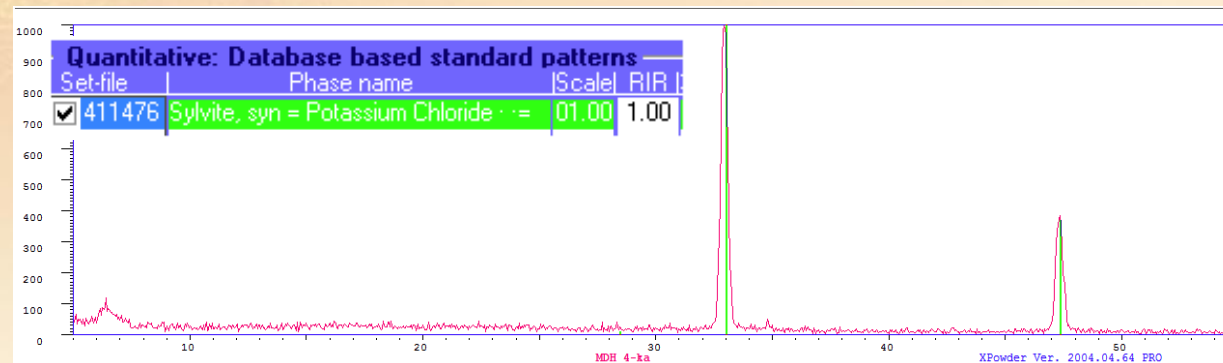
Hazardous materials analysis



Explosive

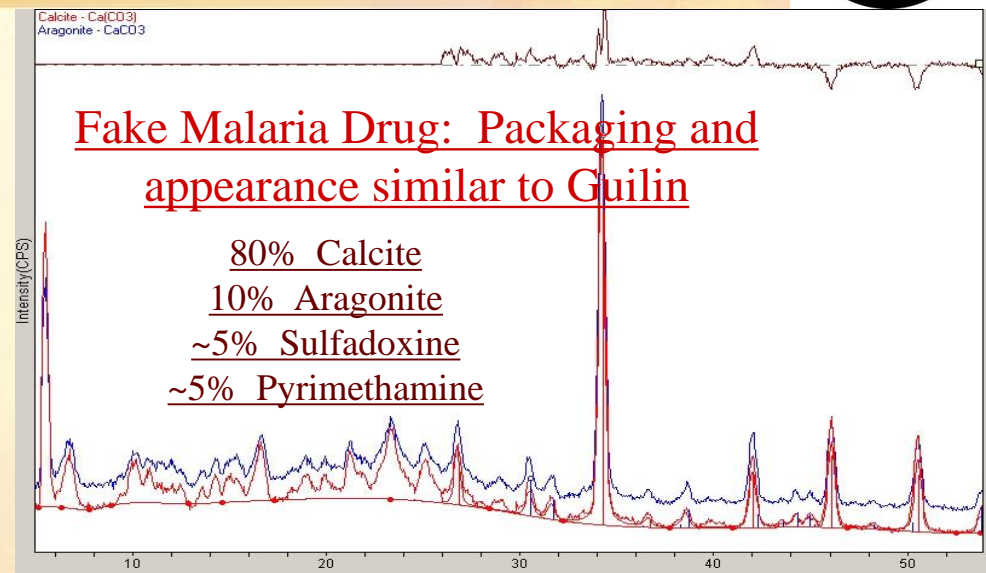
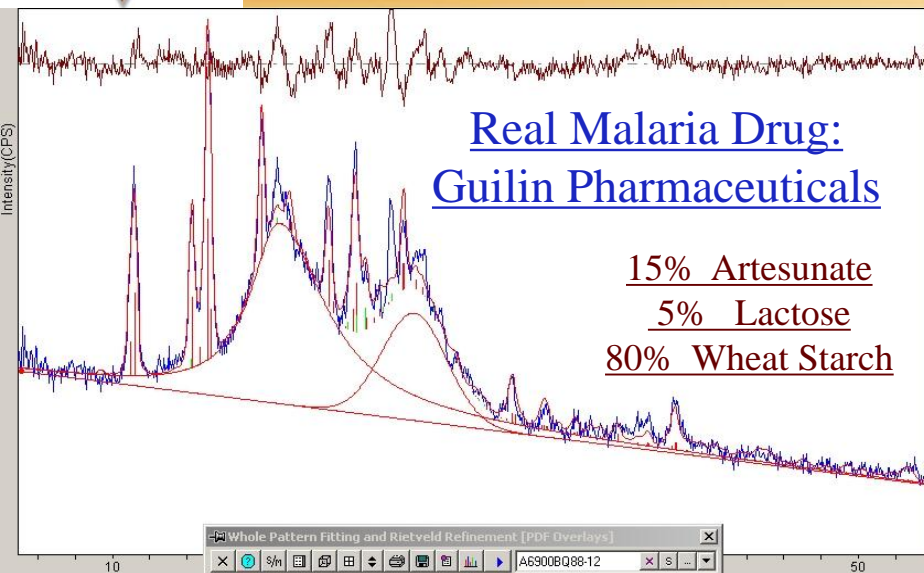


Fire retardant



Potassium salt (potash)

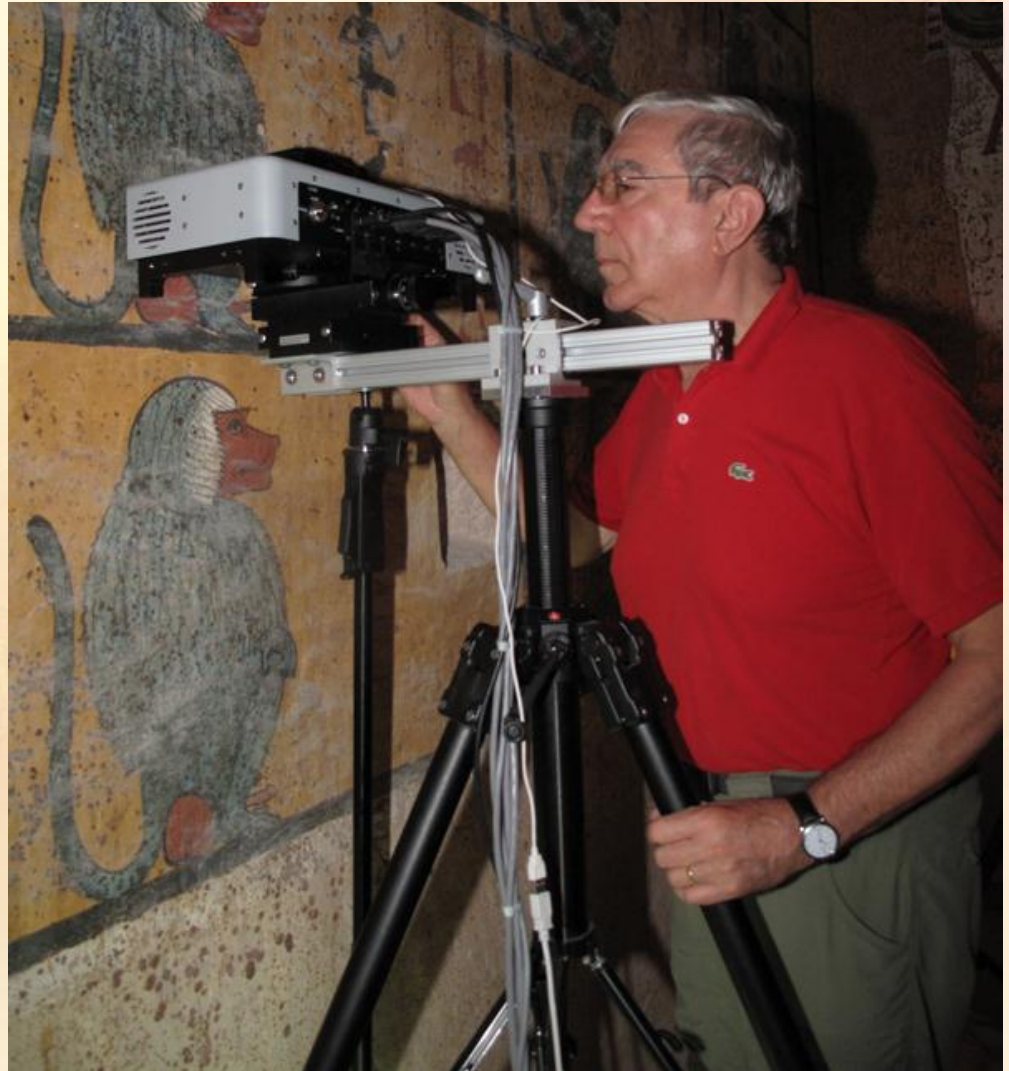
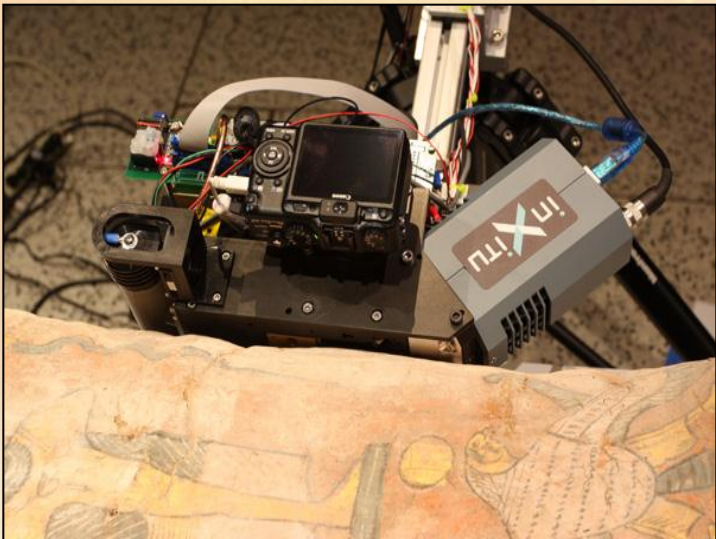
Counterfeit Pharmaceuticals



> 50% of all pharmaceuticals in SE Asia and Africa are counterfeit, causing tens of thousands of deaths and creating resistance to the medicines.

Terra is being evaluated for counterfeit detection in collaboration with Drs. Robert Downs of Univ. Arizona and Dr. Terry Blaschke of the Gates Foundation.

Duetto: used by the Getty Museum for artworks and antiquities preservation



Giacomo Chiari, Chief Curator of the Getty Museum in King Tut's tomb