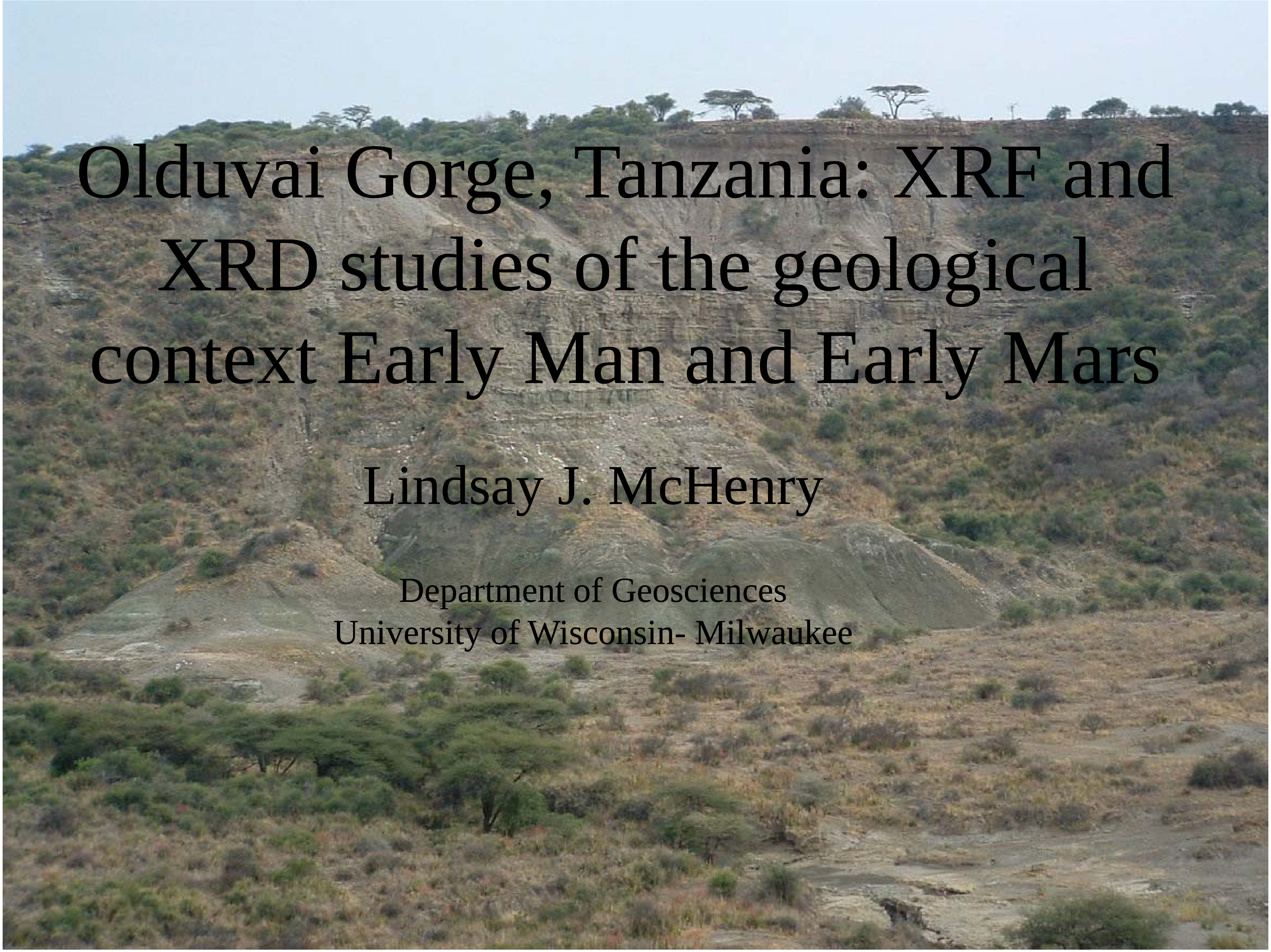

Olduvai Gorge, Tanzania: XRF and XRD studies of the geological context Early Man and Early Mars

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Permits: Tanzania Department of Antiquities, The Ngorongoro Conservation Area Authority, COSTECH

Outline

Part 1: Tephrostratigraphy and Geoarchaeology

Using the unique chemical composition of volcanic ash layers to improve the stratigraphic and age control of Olduvai Gorge archaeological sites.

Part 2: Geochemistry

The weathering of volcanic ash at Olduvai Gorge: can we still use altered ash in tephrostratigraphy?

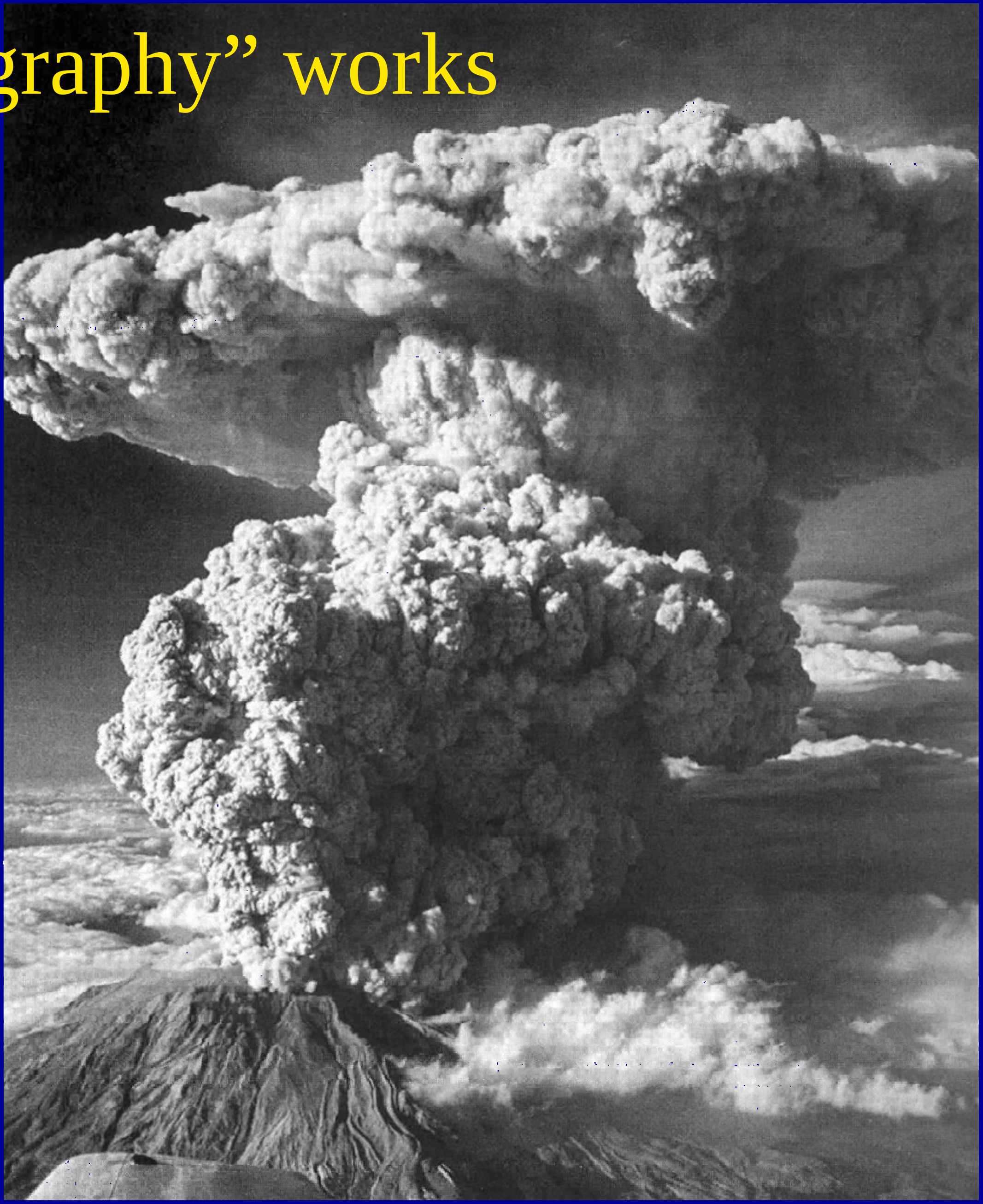
Part 3: Mars

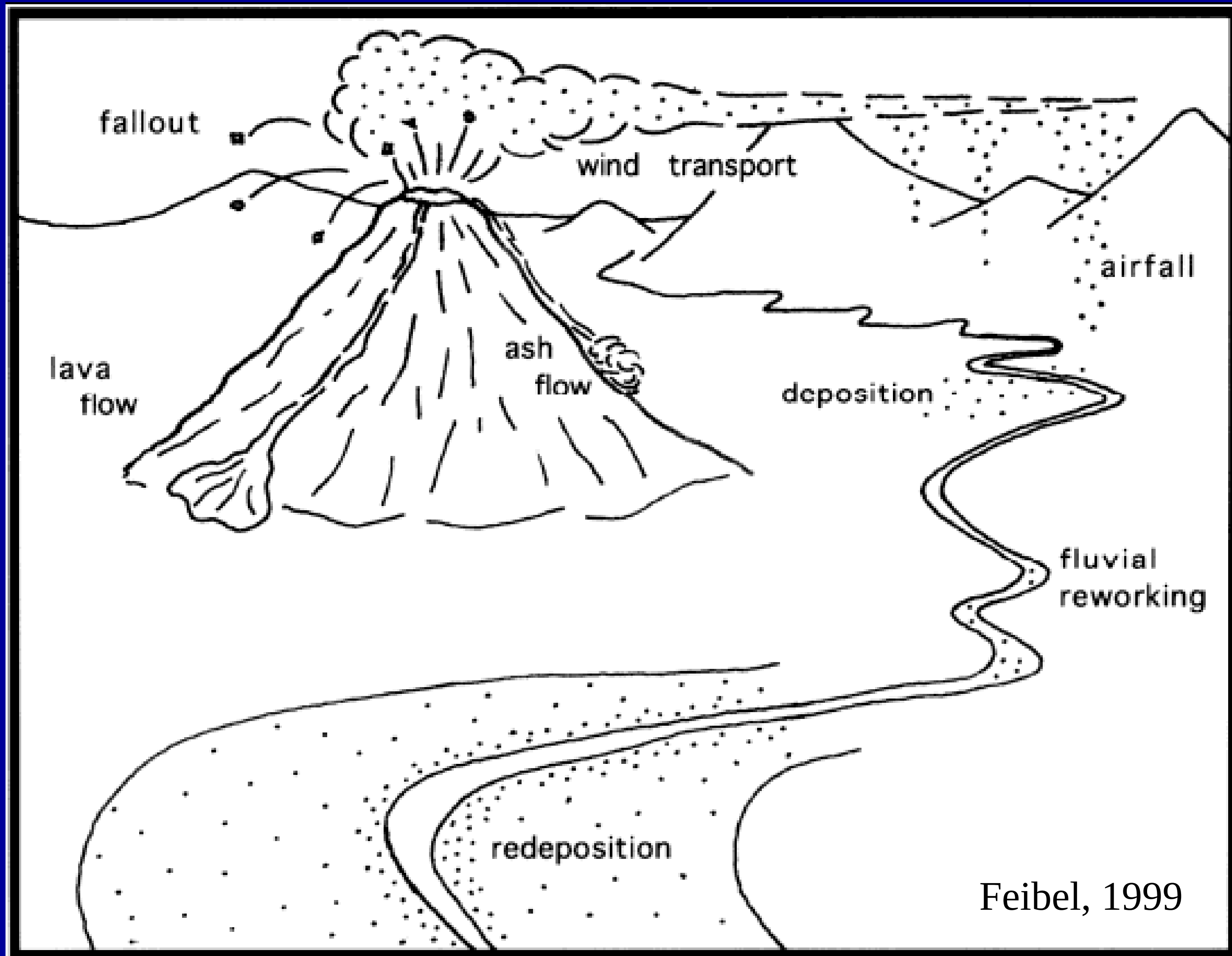
The weathering of volcanic ash at Olduvai Gorge: analogue for Mars?

How “tephrostratigraphy” works

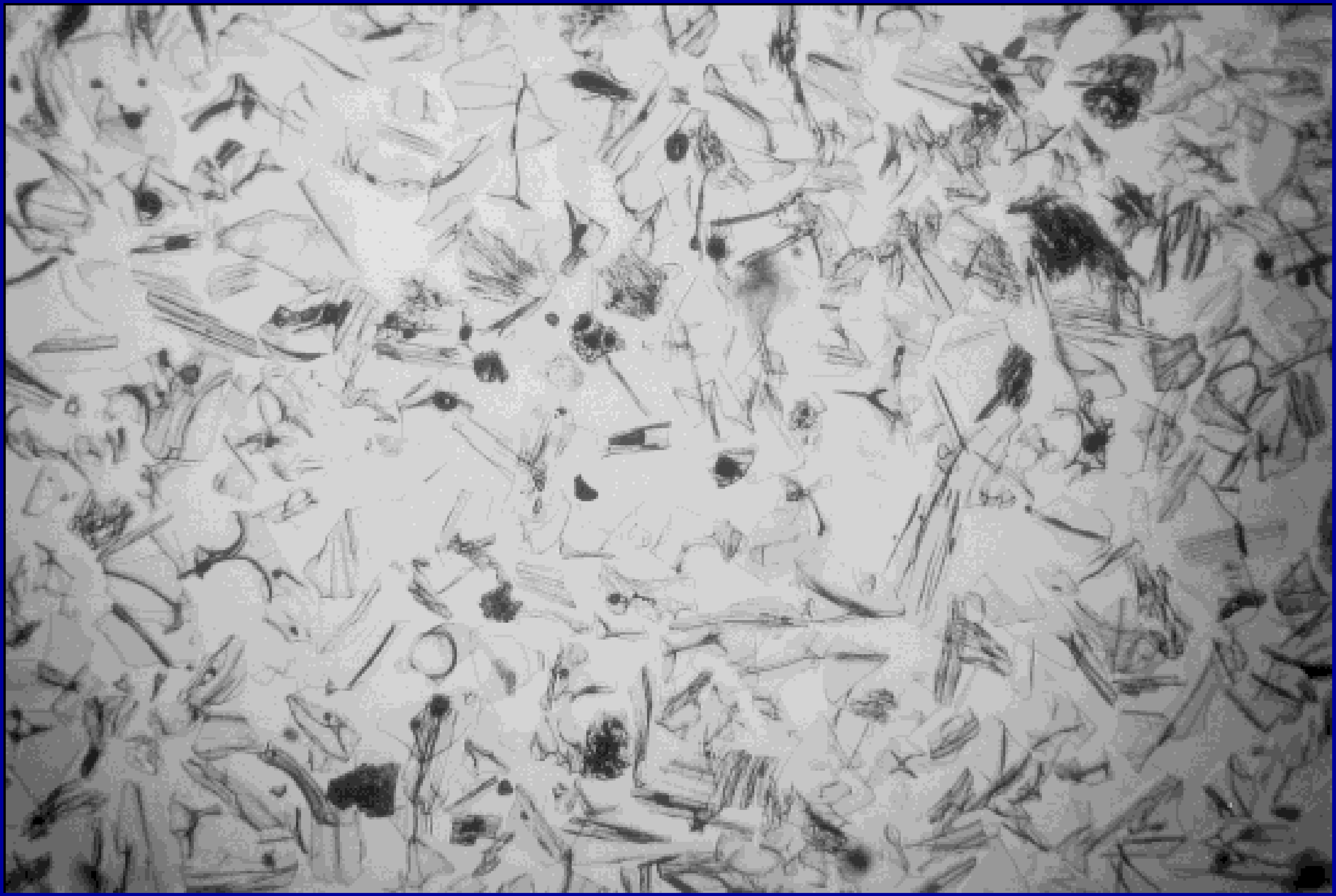
Major explosive eruptions blanket the landscape with volcanic ash.

Most volcanoes produce ash that is uniquely identifiable based on its chemical composition

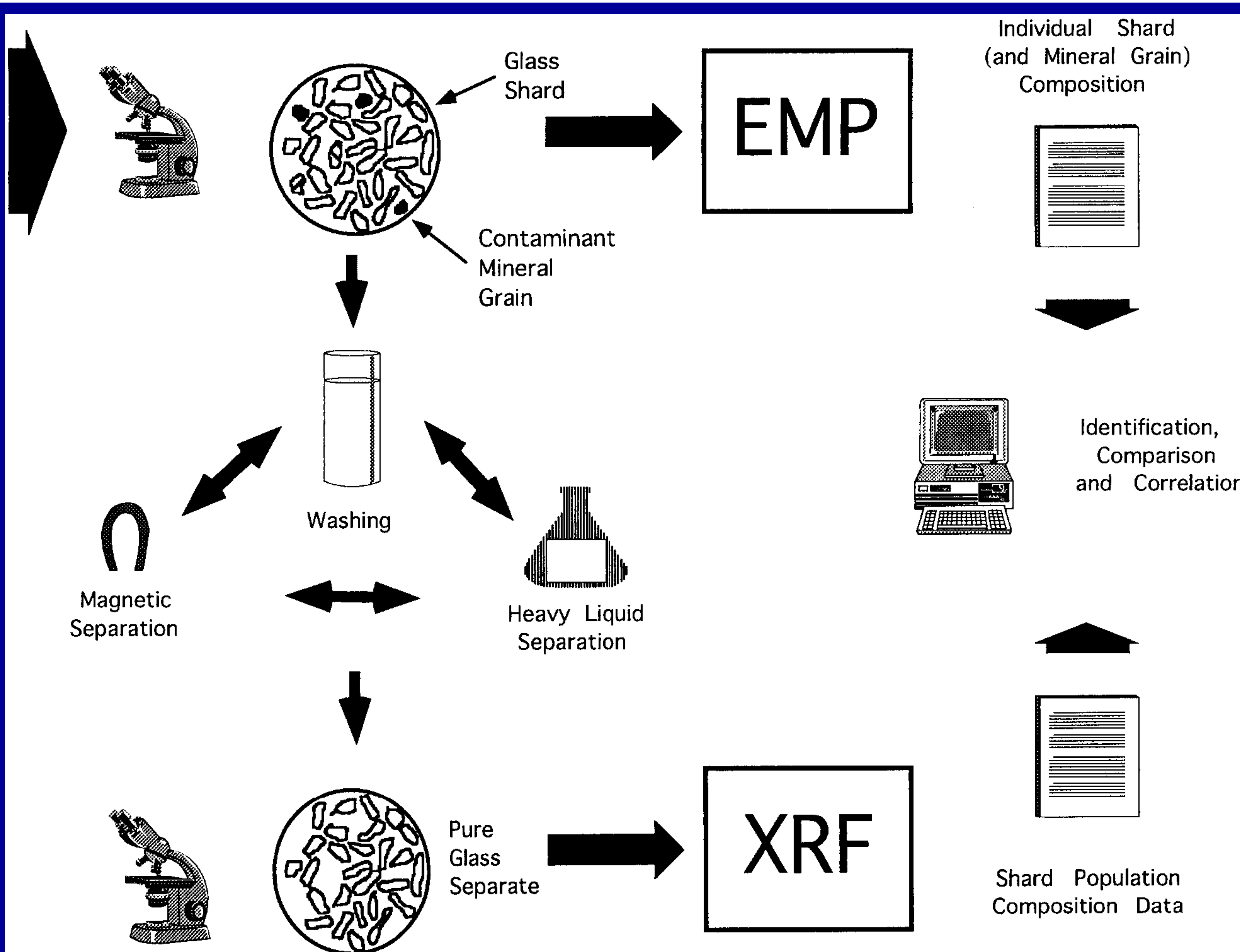



fallout
wind transport
airfall
lava flow
ash flow
dcposition
fluvial reworking
redeposition

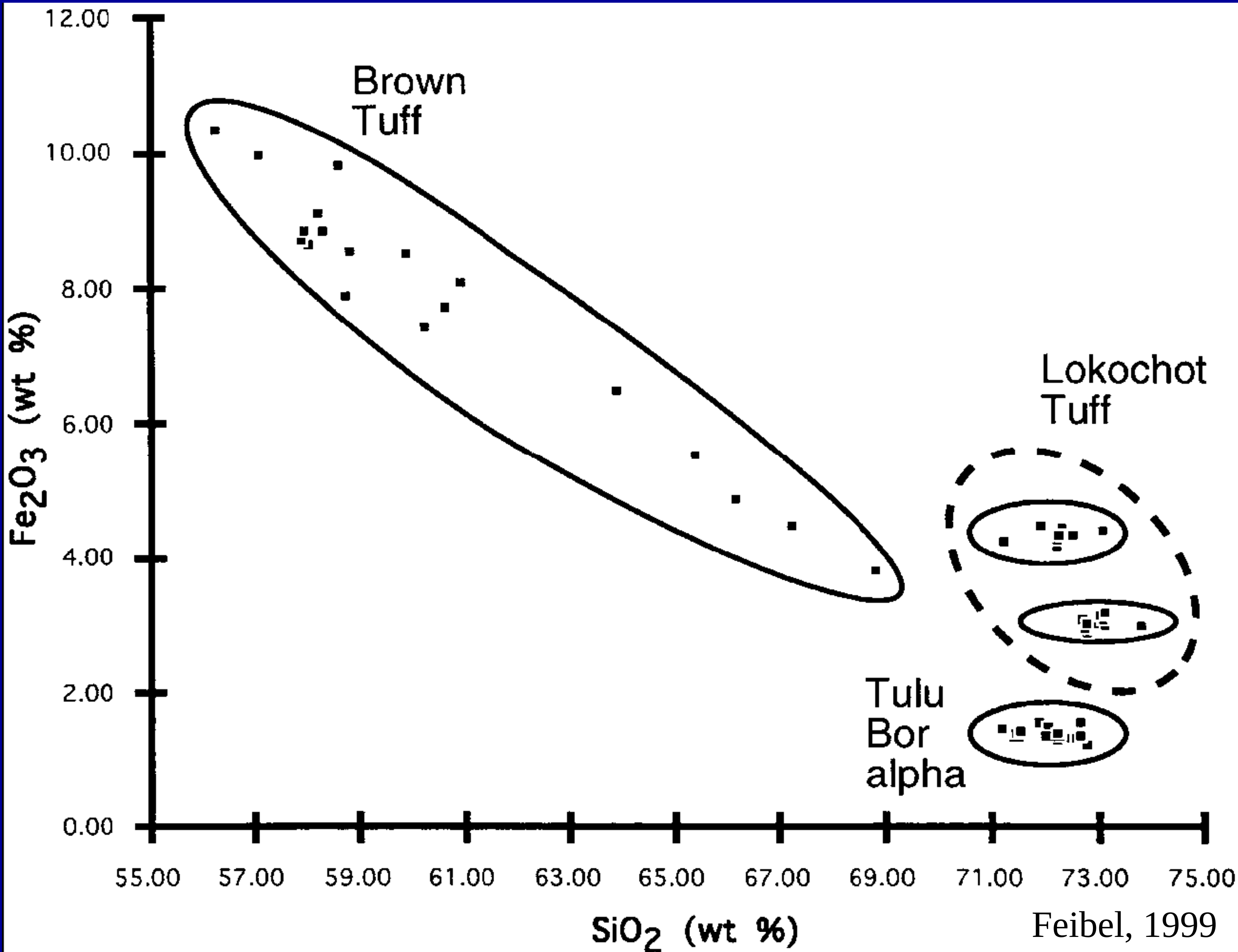
Feibel, 1999



Volcanic ash = shards of glass + tiny mineral grains

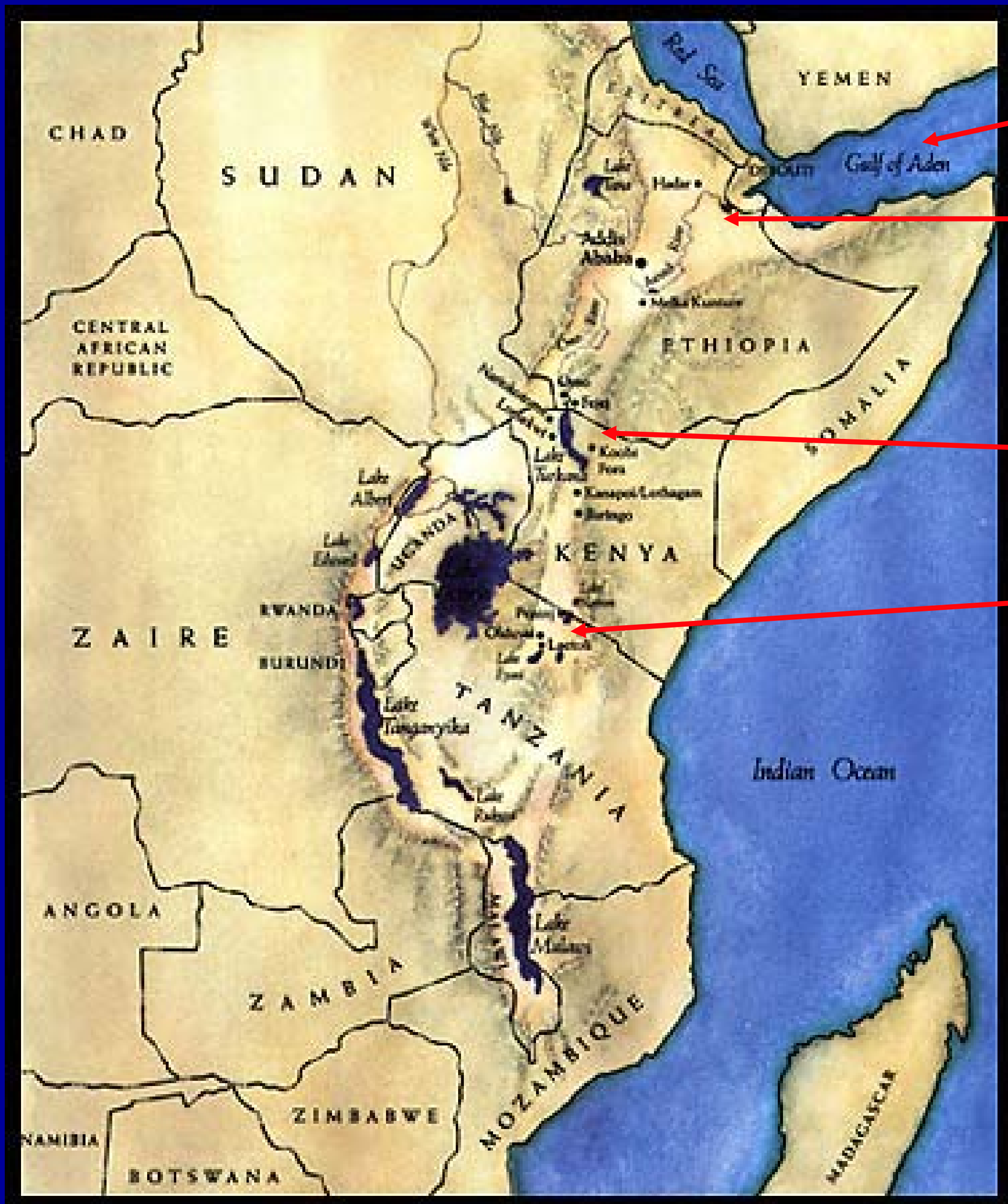


Sample prep for compositional analysis of ash. (Feibel, 1999)



Feibel, 1999

Some ashes (e.g. Tulu Bor) are well suited to a "bulk" compositional technique like XRF, others are not



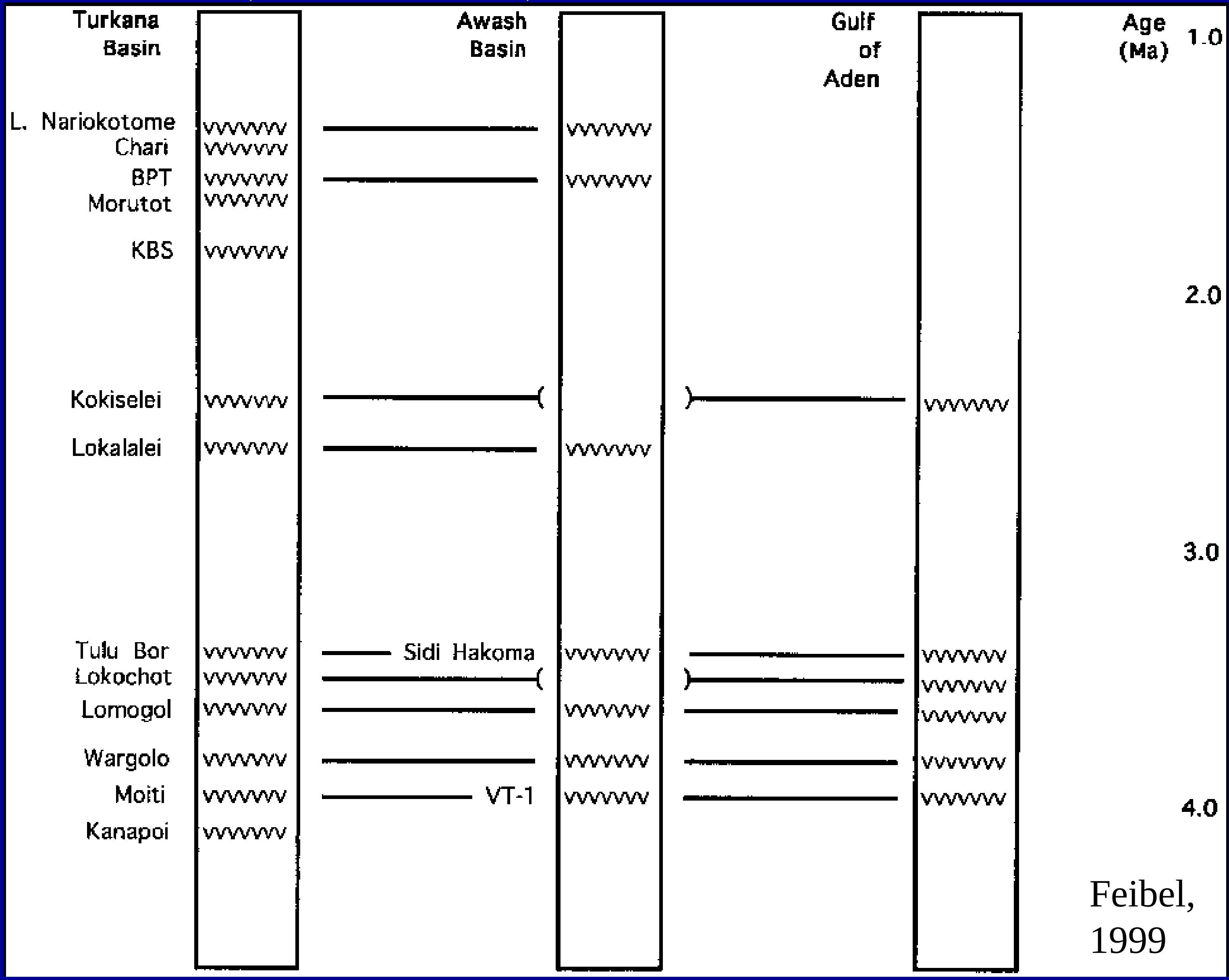
Gulf of Aden

Awash

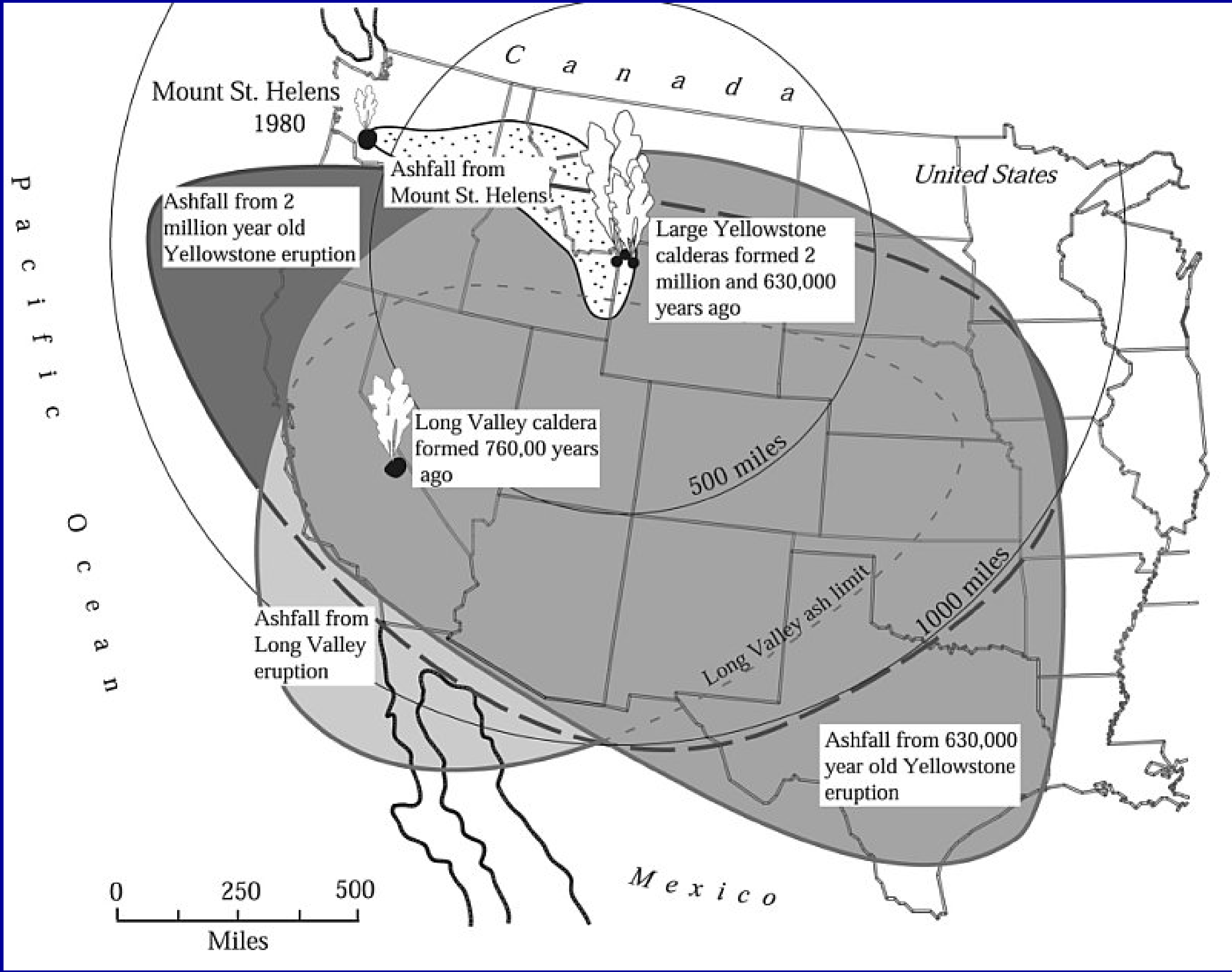
Turkana

Olduvai Gorge

Regional tephra correlations: Turkana (Kenya) to Awash (Ethiopia) and offshore (Gulf of Aden)

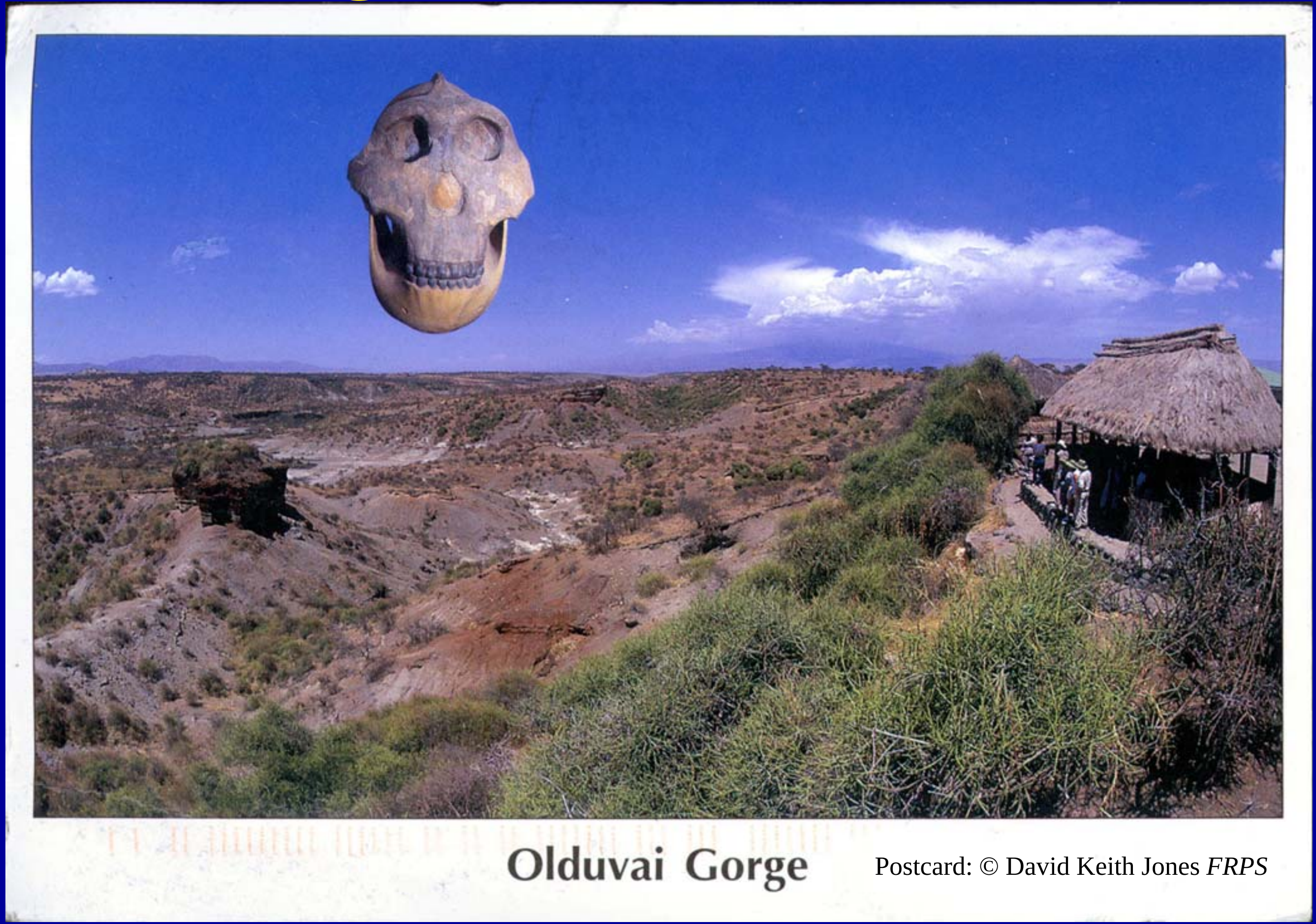


Feibel, 1999



Ash layers from Yellowstone and Long Valley calderas

Olduvai Gorge, Tanzania: Pleistocene



Postcard: © David Keith Jones *FRPS*

Many hominid fossils: *Homo habilis, Homo erectus, Australopithecus boisei, Homo sapiens*.

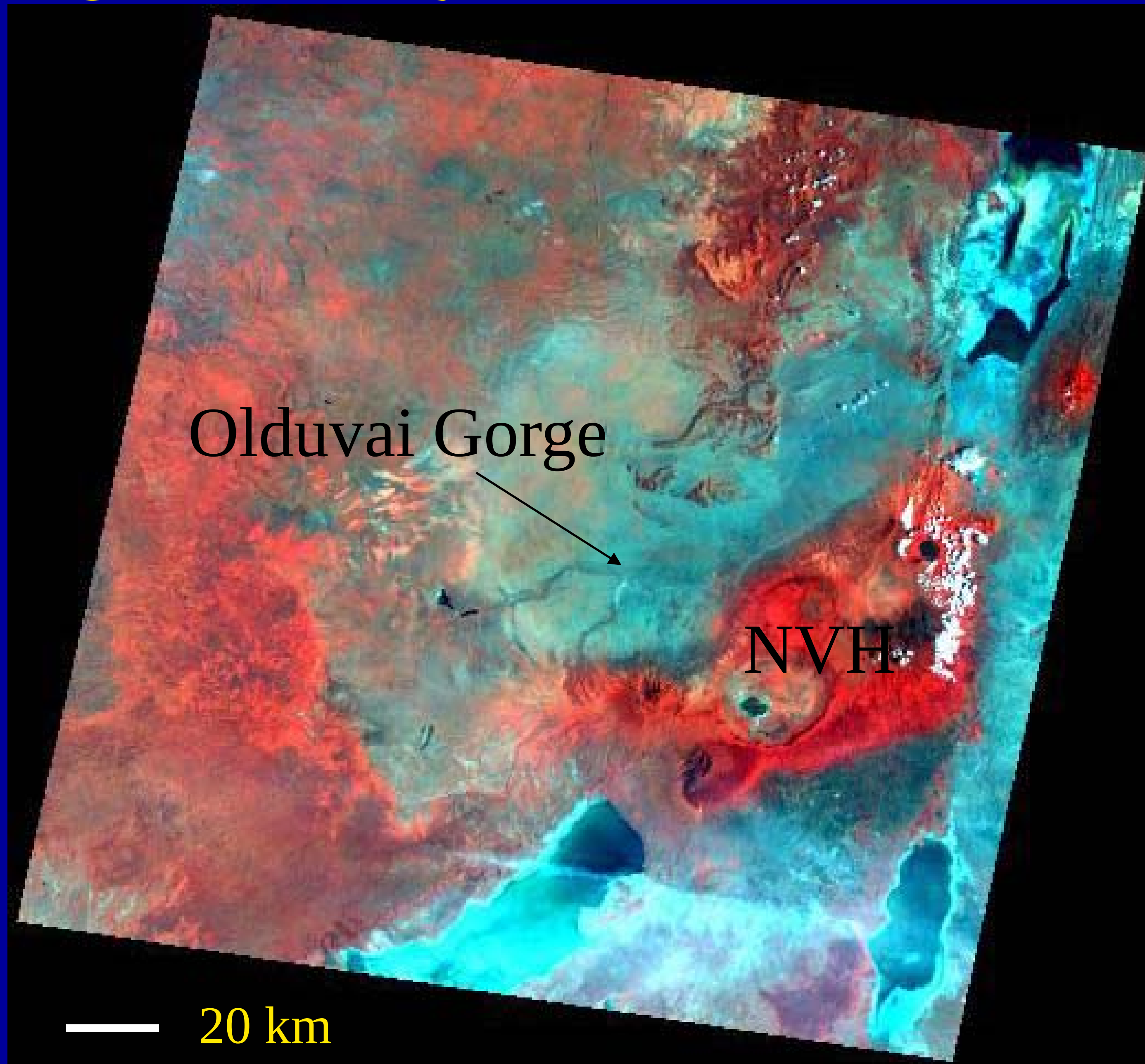
Stone artifacts: Oldowan, Developed Oldowan, Acheulean, etc.

Extensive faunal remains

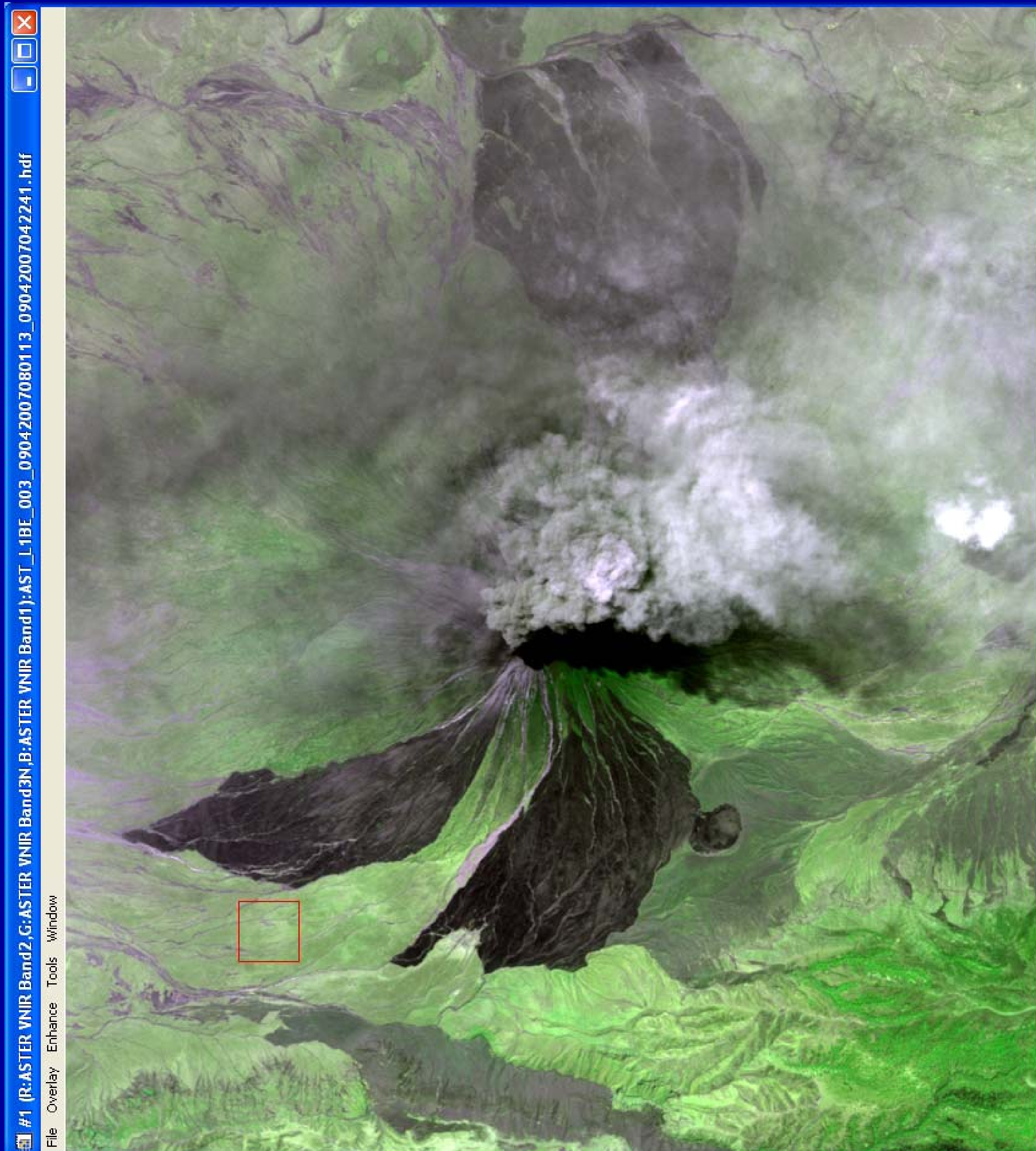
Olduvai Gorge and nearby volcanic sources

Ngorongoro
Volcanic
Highlands
(NVH)

Active 4.32 Ma
to today




Collecting samples: summit of Oldoinyo Lengai volcano, Tanzania, July 23, 2007



Oldoinyo Lengai, Sept. 4, 2007 (satellite image)

(glad I wasn't there at the time)

Olduvai: Near source volcanoes, with a good ash record.

To conduct landscape archaeological research, you need to be able to identify the same "time slice" across the landscape

At Olduvai this is accomplished using volcanic ash layers, or "Tuffs"

Tuff IF

Ng'eju Tuff

Tuff IE

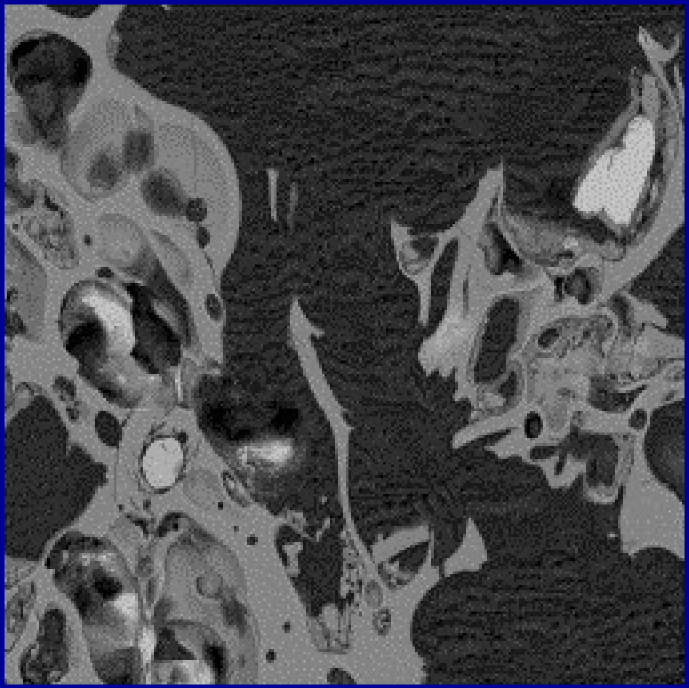
Tuff ID

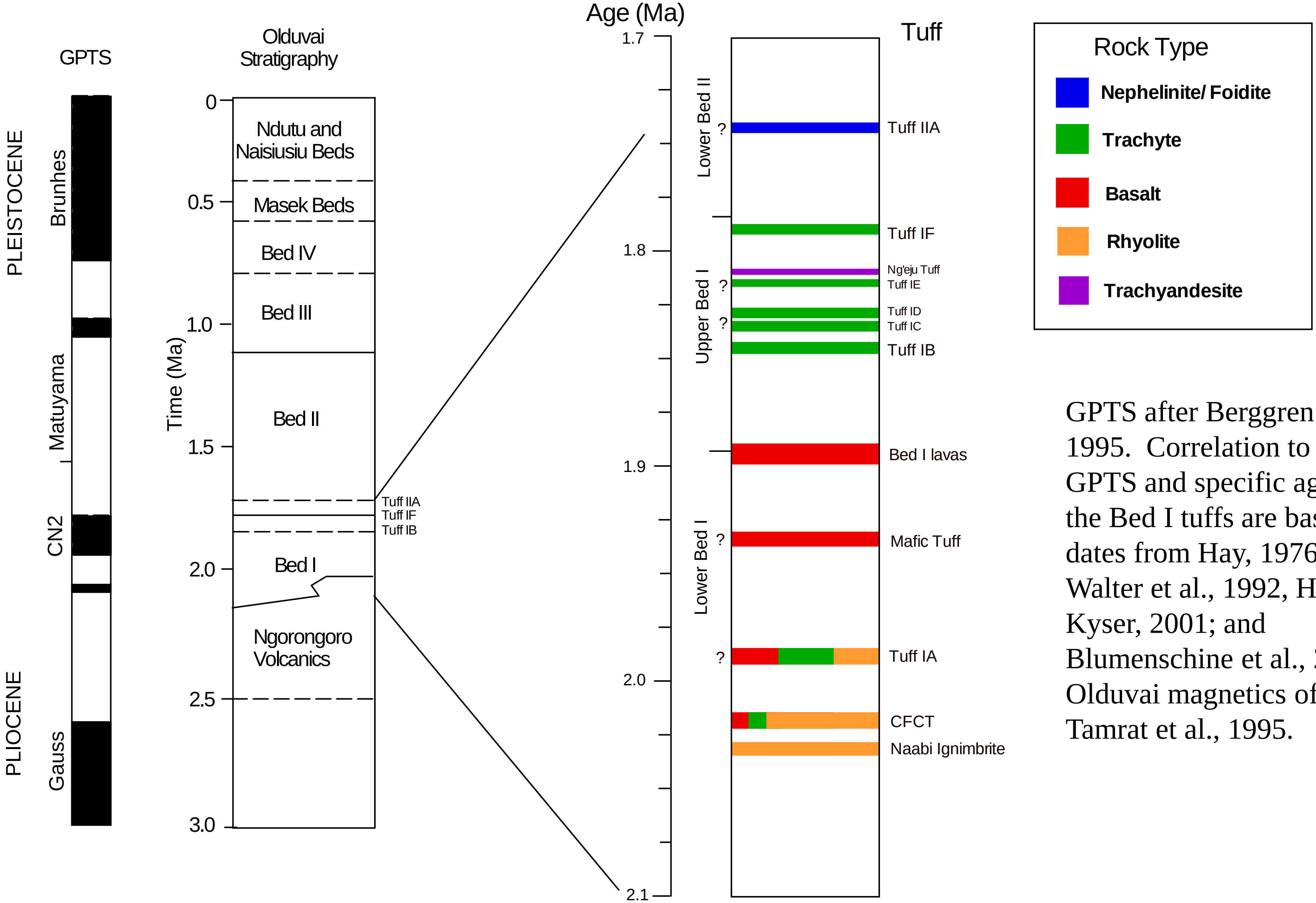
Upper Bed I tuffs at the "Zinjanthropus" site

Principal Method:

Elemental analysis of volcanic minerals and volcanic glass, where available.

Most tephrostratigraphy research uses glass alone. This is impossible at Olduvai, where glass is rarely preserved.

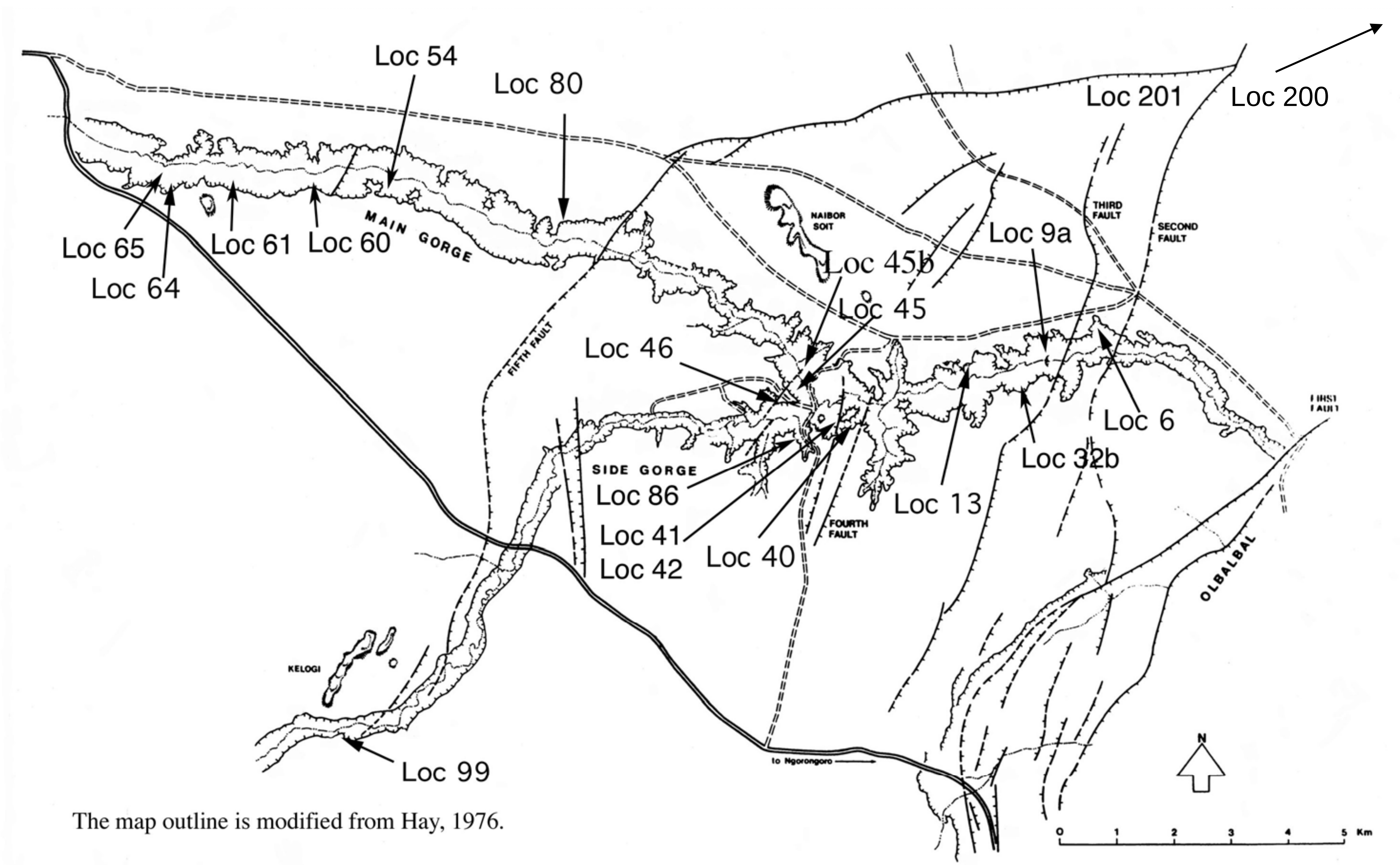




GPTS after Berggren et al., 1995. Correlation to the GPTS and specific ages for the Bed I tuffs are based on dates from Hay, 1976, Walter et al., 1992, Hay and Kyser, 2001; and Blumenschine et al., 2003. Olduvai magnetics of Tamrat et al., 1995.

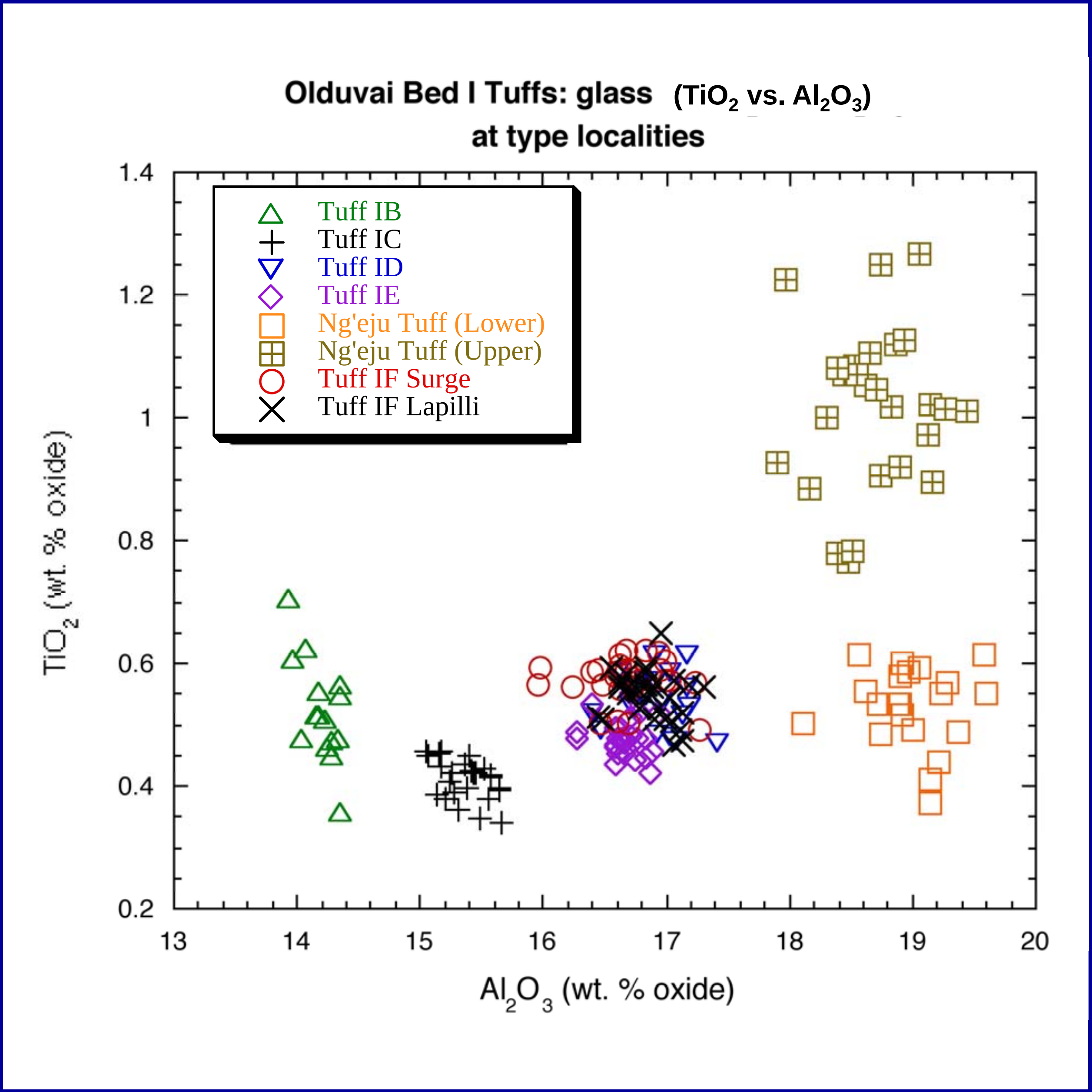
Bed I tuffs in context.

Sample Sites

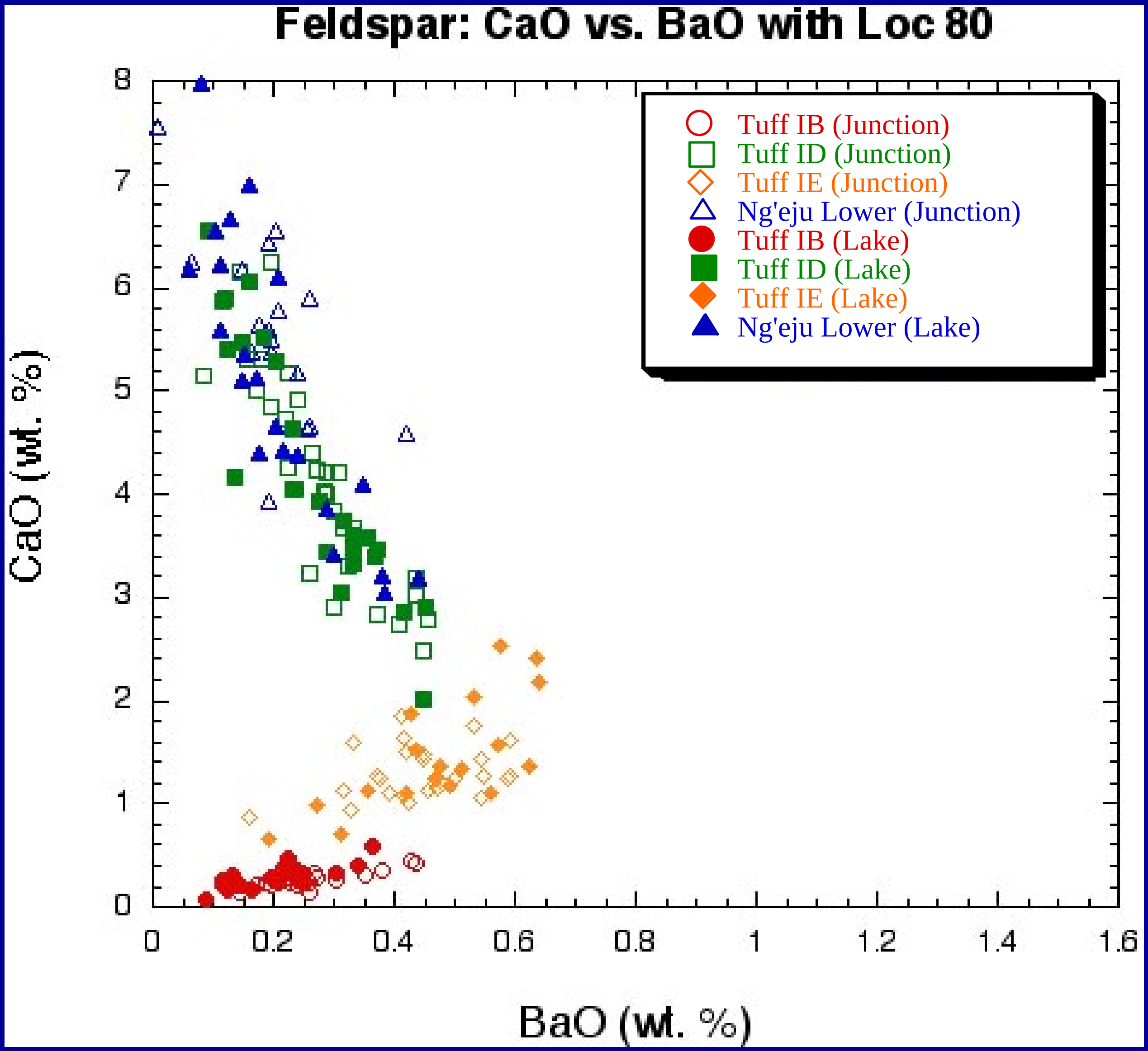


The map outline is modified from Hay, 1976.

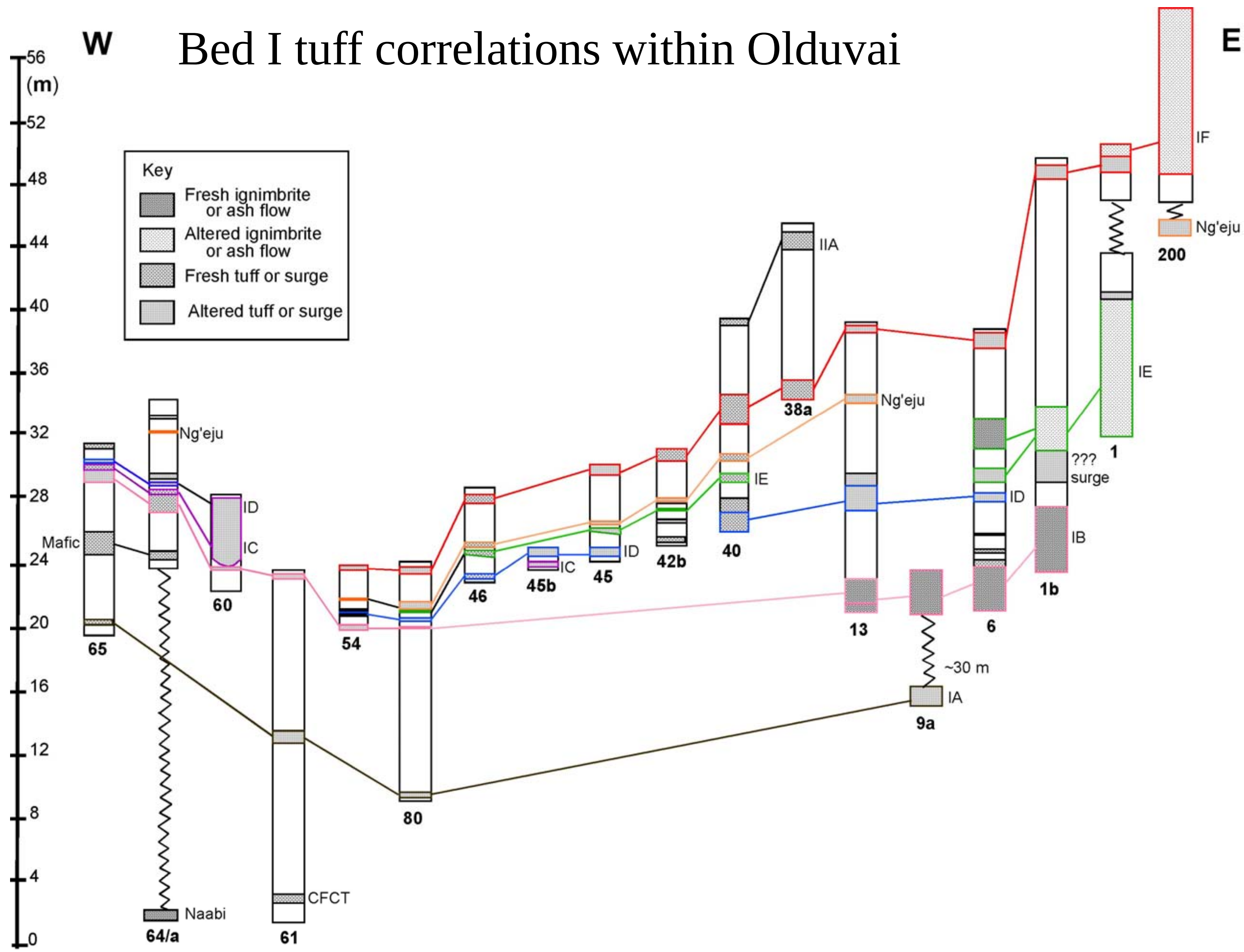
Fresh glass: Great where you've got it!



Feldspar: Great everywhere!



Bed I tuff correlations within Olduvai



Stratigraphic placement of Olduvai hominid 65

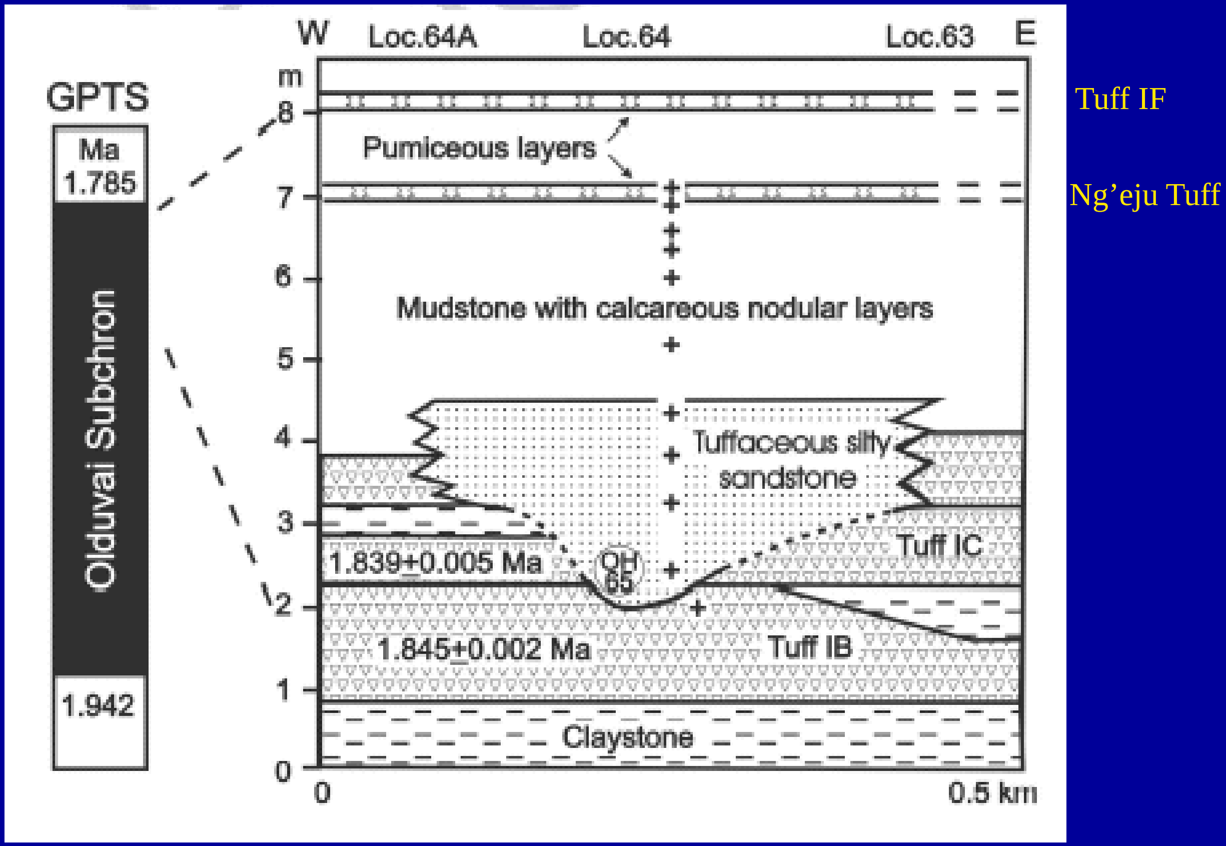


Figure 2 from Blumenschine et al., 2003

Part 2: Geochemistry

A serious limitation of the method used for tephrostratigraphy at Olduvai is that volcanic minerals don’t vary much in composition.

Analyzing fresh glass would be ideal, but it is no longer preserved at Olduvai.

Would it be possible to use the “bulk” composition of the altered volcanic ash for fingerprinting?

Part 2: Geochemistry

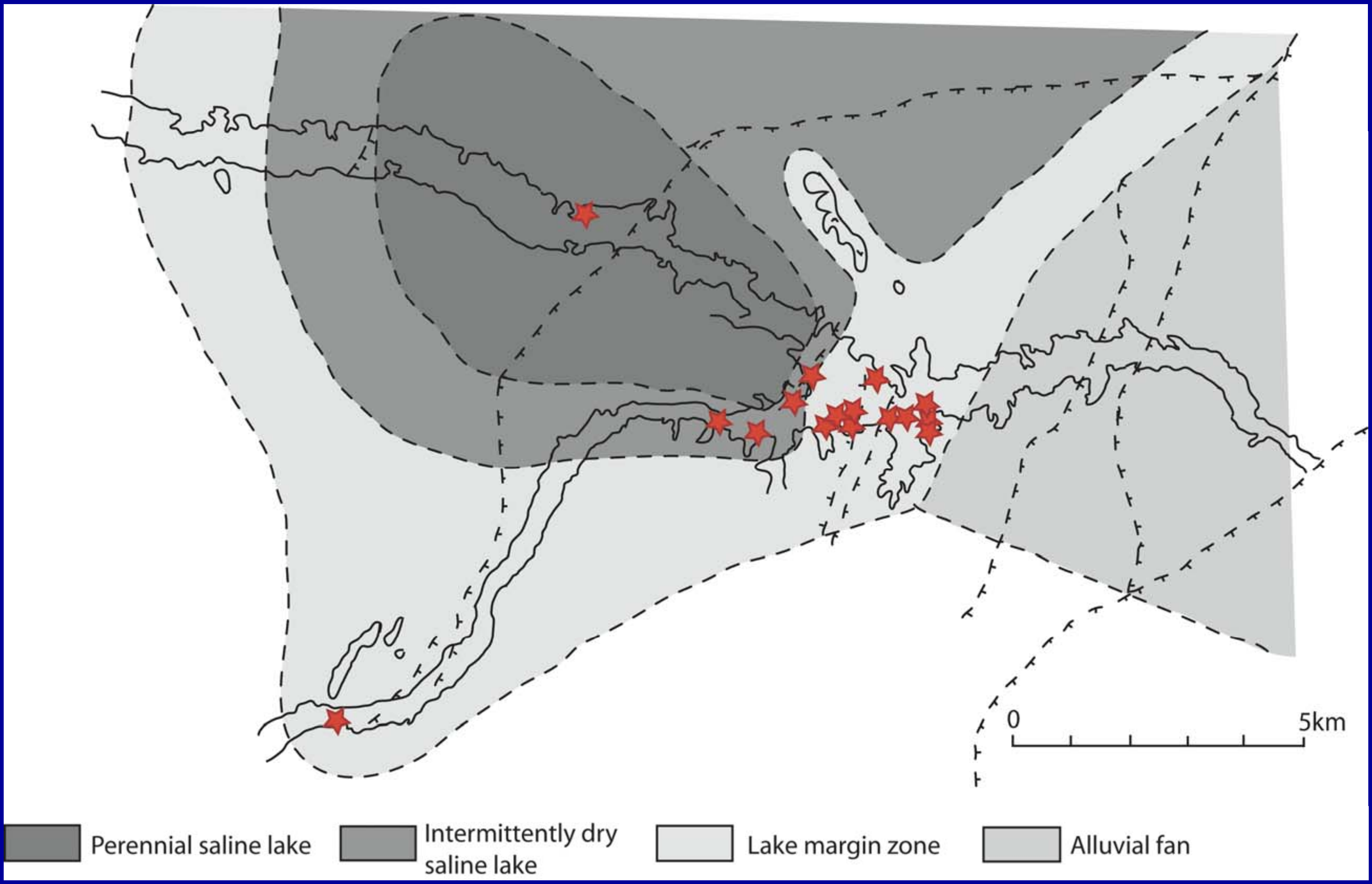
Some elements (e.g. Al, Ti, Zr, Nb, Th,Ta) are considered “immobile” during weathering.

However, most studies have involved materials altered under neutral or slightly acidic conditions.

Are the same elements immobile during zeolitic alteration under saline-alkaline conditions, such as at Olduvai?

The target: a single layer of Tuff IF
1. A major Olduvai Gorge marker tuff, at about 1.79 Ma.
2. Preserved and easily identified over a broad area.

Sample sites, in relation to the "paleo-lake" environments of Upper Bed I.



Paleoenvironments after Hay, 1976

Methods

Lapilli hand-picked and cleaned

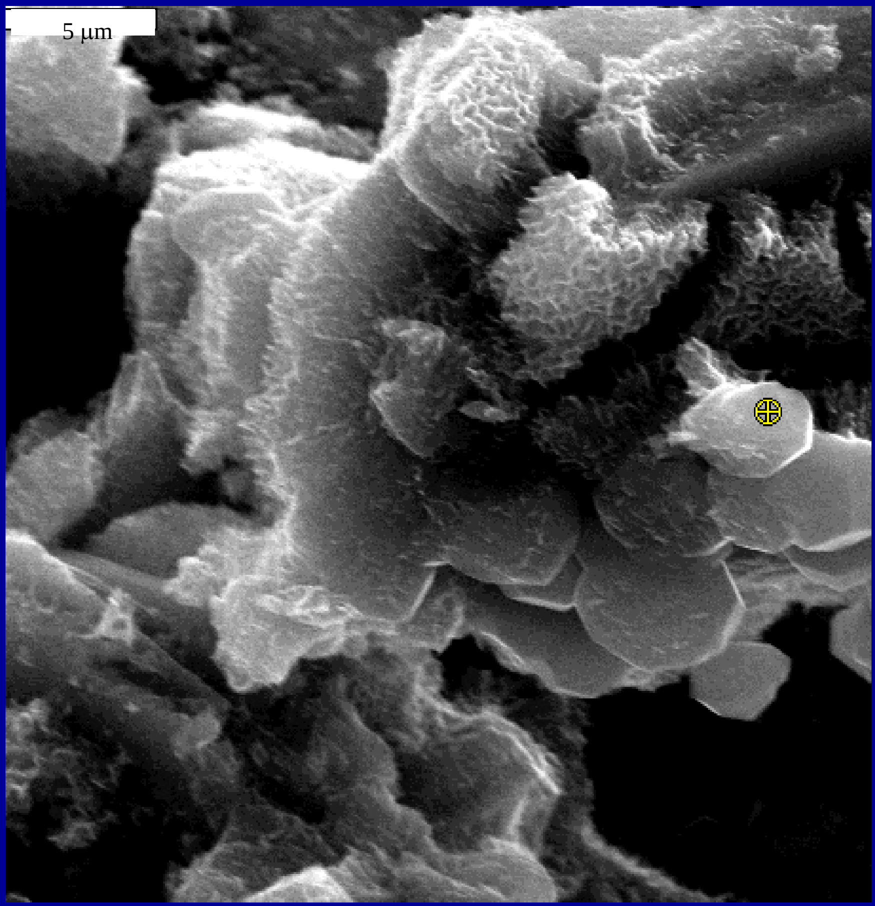
XRF of powdered lapilli separates for major and minor elements.

ICP-MS of powdered lapilli separates for trace elements

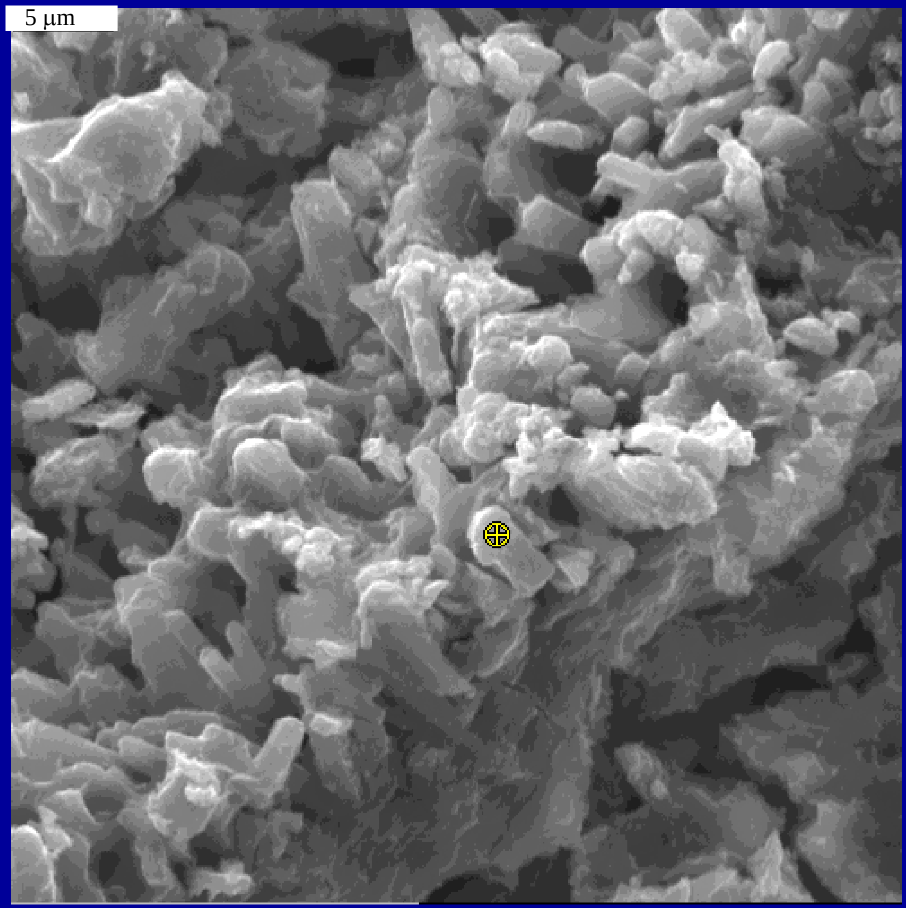
XRD of powdered lapilli separates for phase identification

SEM of intact lapilli for textural imaging.

Volcanic glass is replaced by zeolites in the lake center, and by clay minerals in the lake margin.

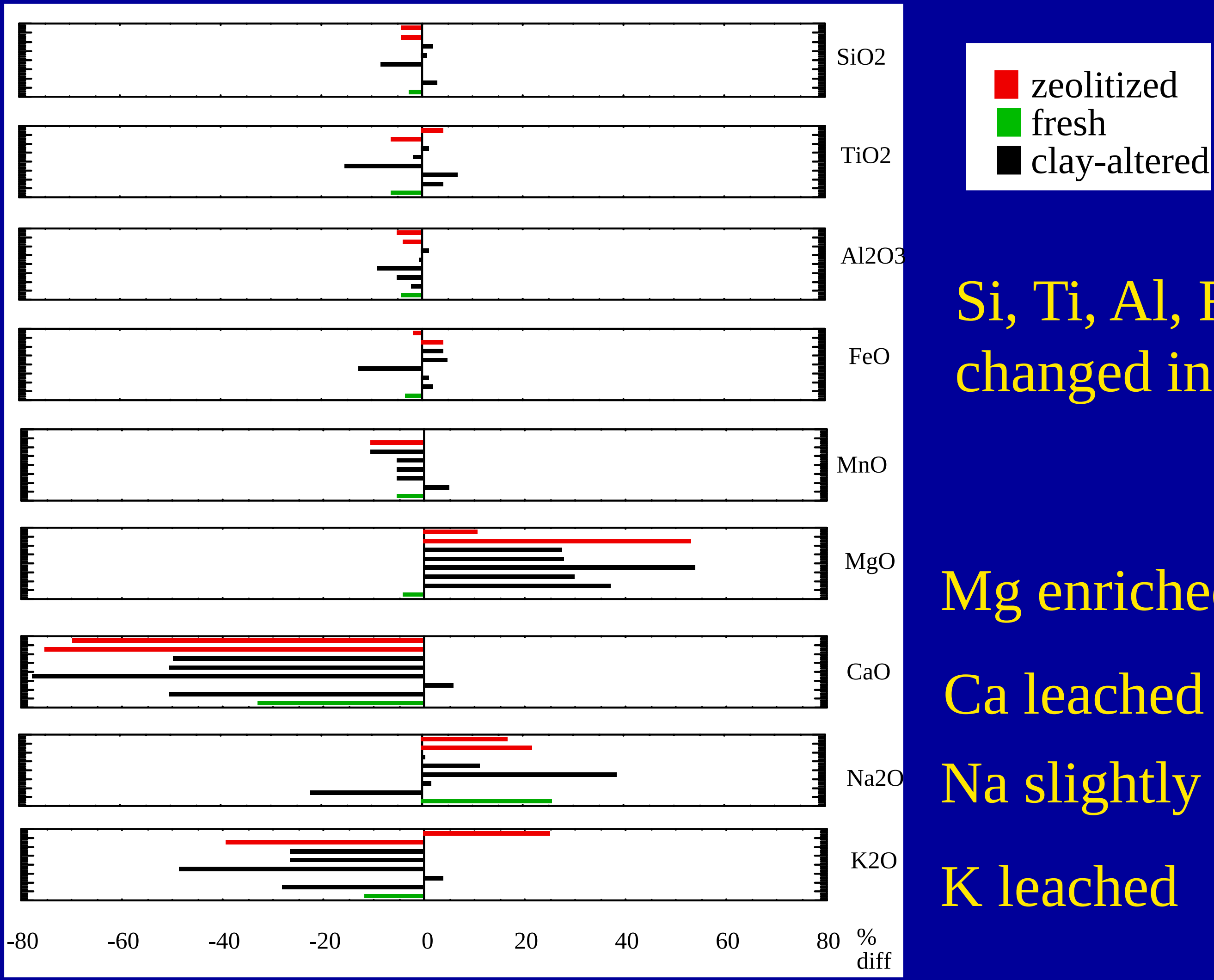


Clay and minor analcime, lake margin.



Phillipsite laths, intermittently dry saline lake.

Major element mobility during alteration of Tuff IF lapilli: zeolitic vs. clay alteration



Si, Ti, Al, Fe, Mn little changed in either.

Mg enriched in both

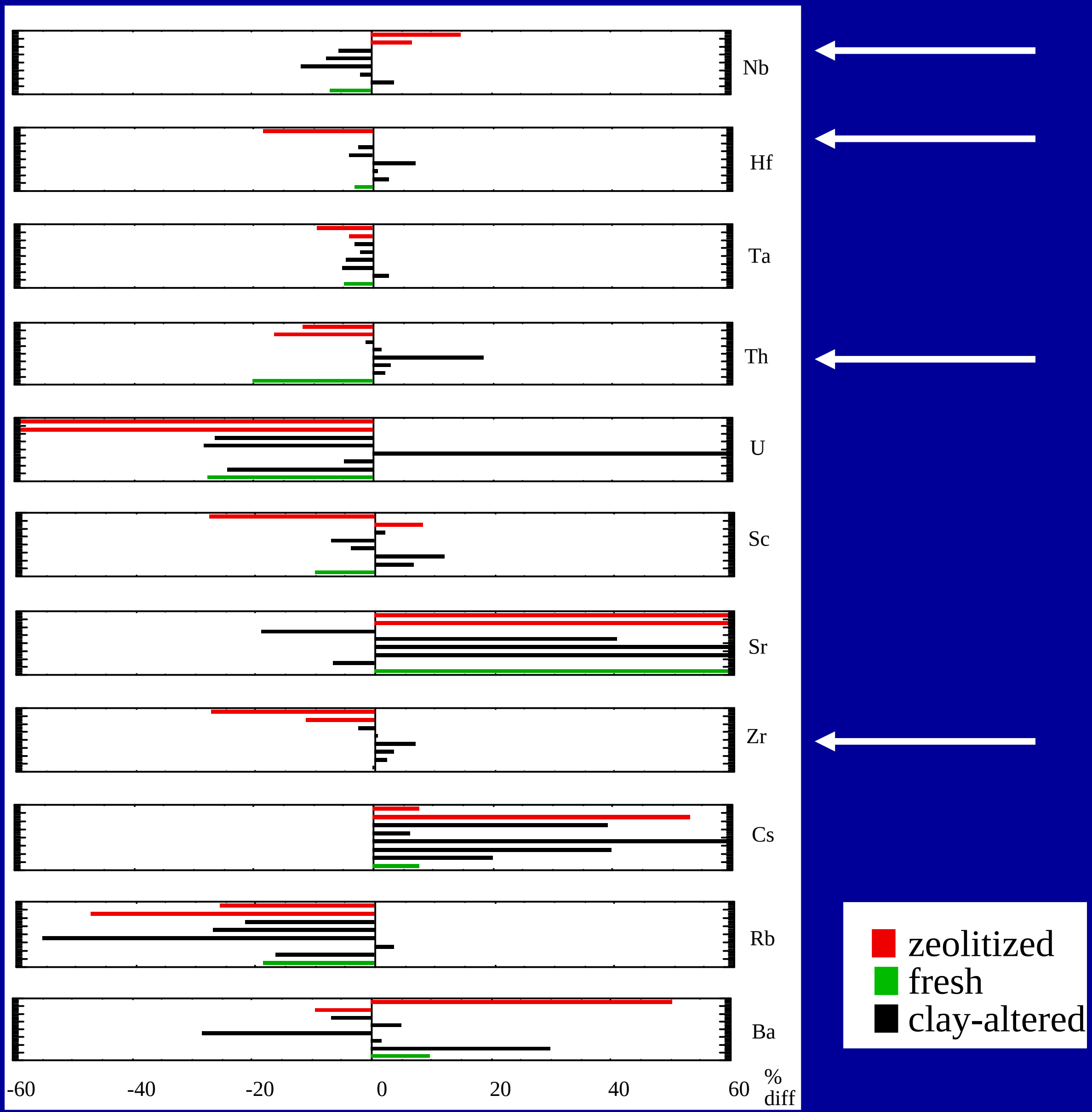
Ca leached in both

Na slightly enriched

K leached

% difference compared to “fresh” sample from Locality 40 (MCK)

Trace element mobility during alteration of Tuff IF lapilli



Nb enriched in zeolitic, depleted in most clay-altered samples

Hf, Th, and Zr depleted in zeolitic, conserved (or enriched) in clay-altered samples

% difference compared to “fresh” sample from Locality 40 (MCK)

Conclusions

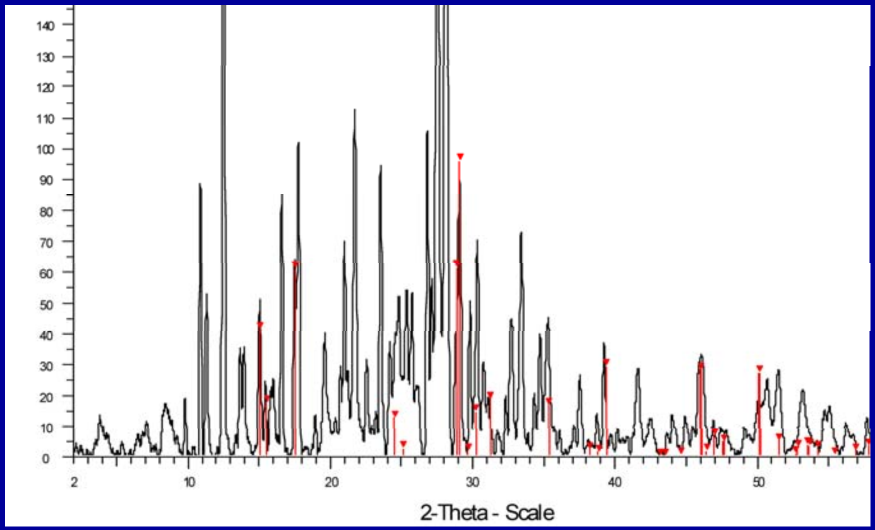
Unfortunately, the generally "immobile" elements Ti and Zr appear to be mobile under the saline-alkaline conditions at Olduvai.

Of the elements analyzed, only Al and Ta appear to remain immobile (within 10%) across all alteration environments studied.

Bulk composition of altered ash is thus NOT a viable method for tephrostratigraphy in this environment.

An interesting, and unexpected, discovery made during this study:

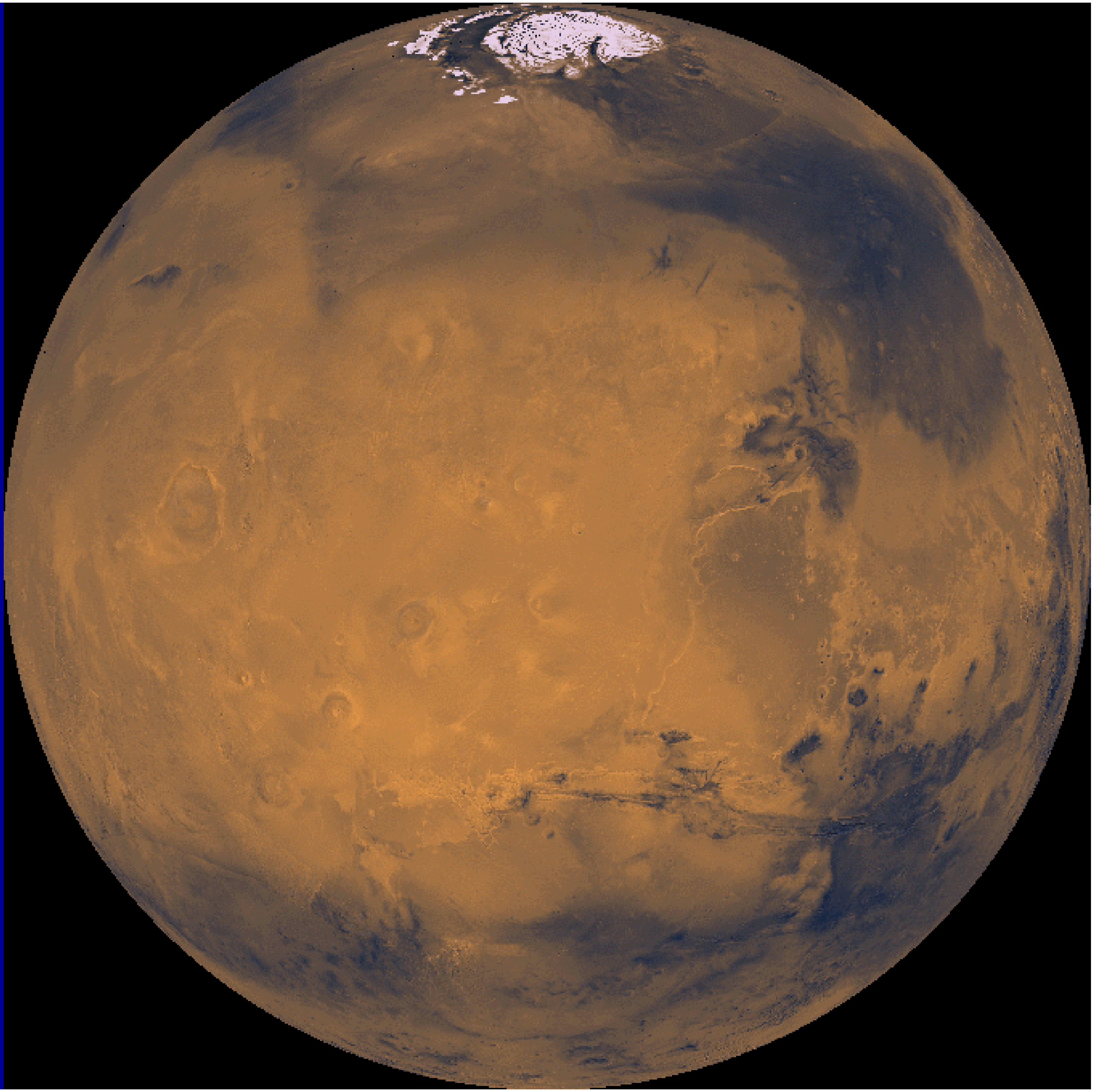
Jarosite and phillipsite in the saline-alkaline lake sample (Loc 80)



XRD (K-jarosite peaks in red)

and this leads us to…

Part 3: Mars



Initial observations:

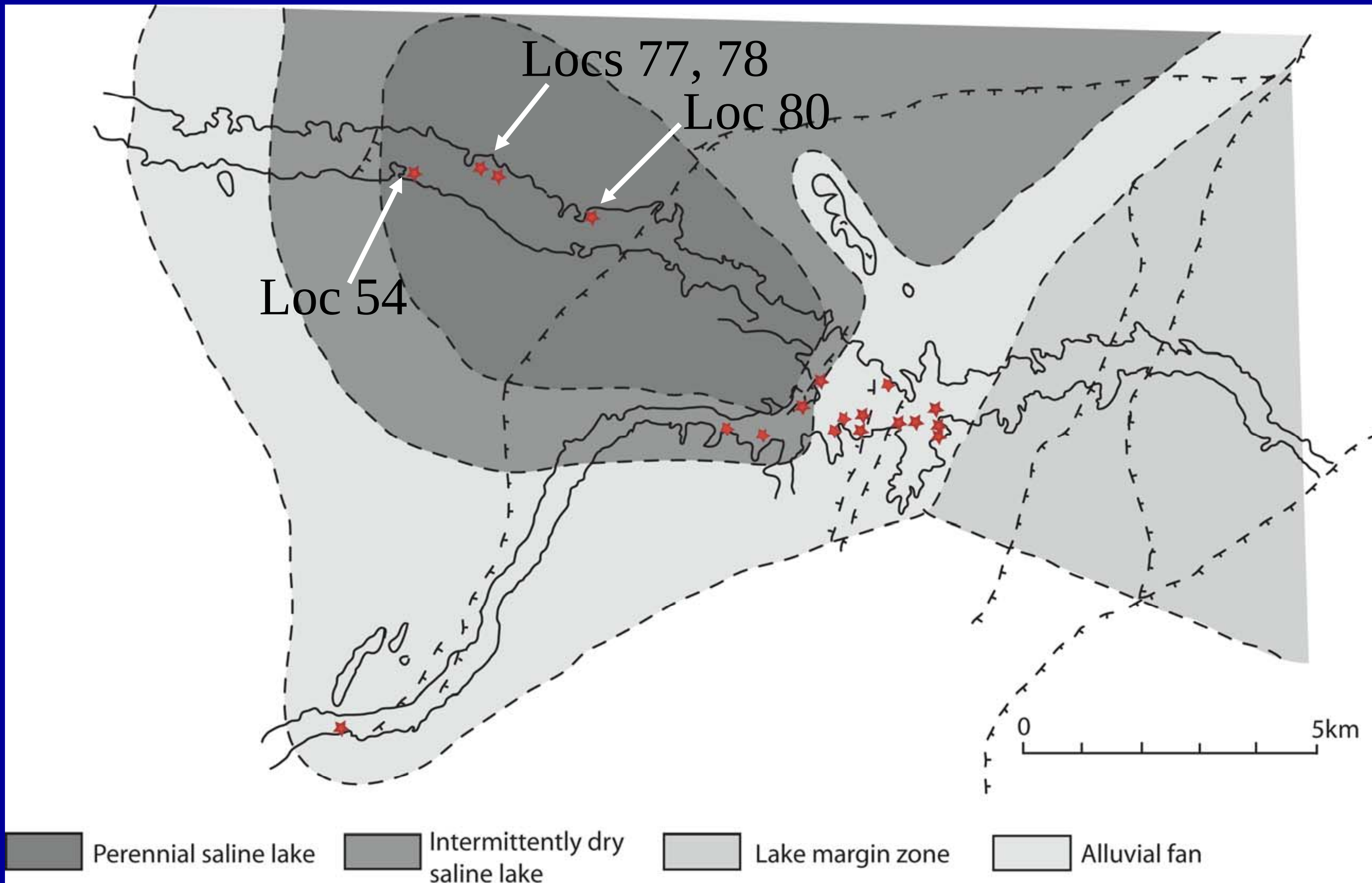
Some altered ashes from the paleo-lake contain jarosite in a deposit otherwise dominated by phillipsite.

Conventionally, jarosite indicates acidic conditions ($pH < 5$). Its presence on Mars is a leading line of evidence in support of a wet, acidic past.

Conversely, phillipsite is a zeolite characteristic of K-rich, saline-alkaline conditions ($pH > 8$, usually >9).

Question:

How could these two phases coexist?



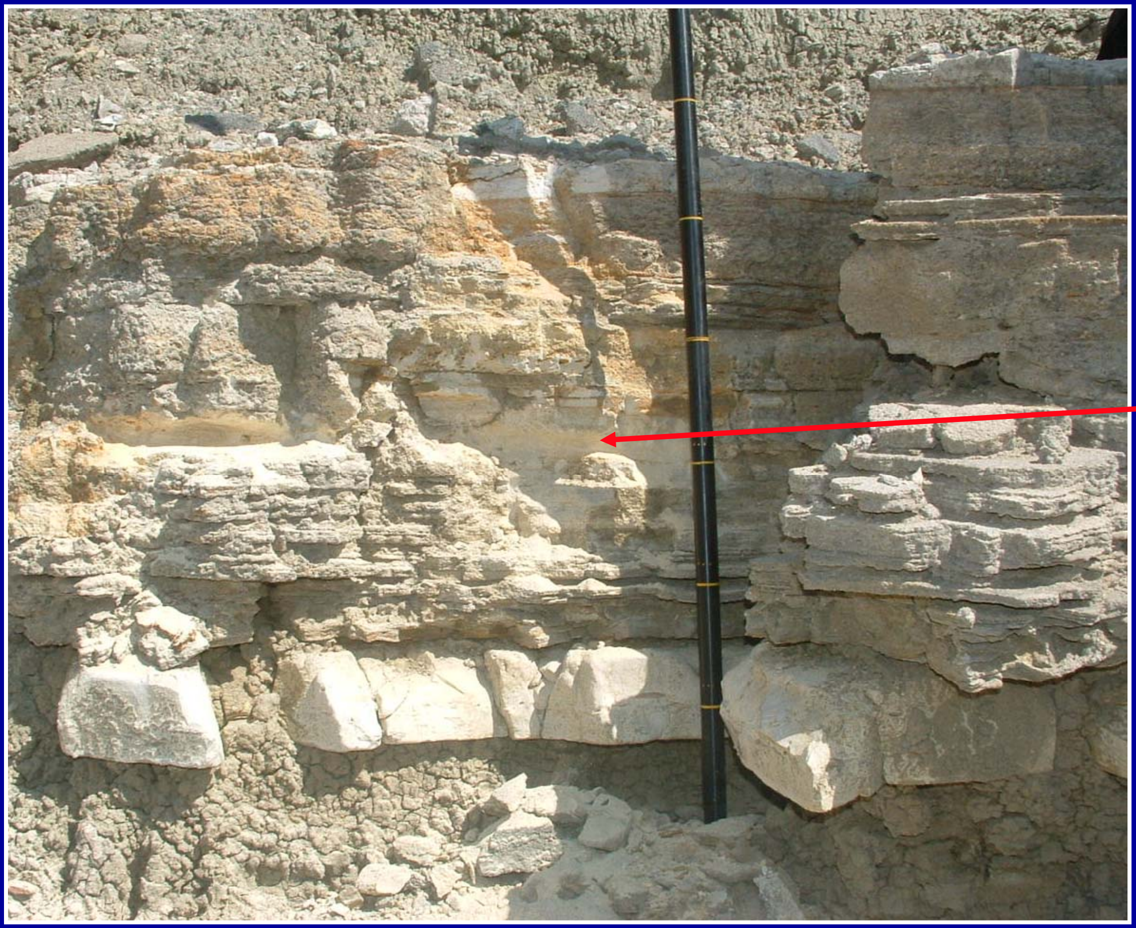
Map of sampled localities and Olduvai paleoenvironments at time of Tuff IF deposition.

Figure after Hay, 1976

Methods:

- XRD of all samples: phase identification.
- XRF of samples with and without jarosite. Compositional difference?
- SEM and EPMA of a few confirmed jarosite occurrences
    - Crystal shape, association, qualitative composition
- NIR spectroscopy of a few jarosite-bearing samples.
- Mössbauer analysis of a few jarosite-bearing samples, using MER-like Mössbauer Spectrometer at Mainz.

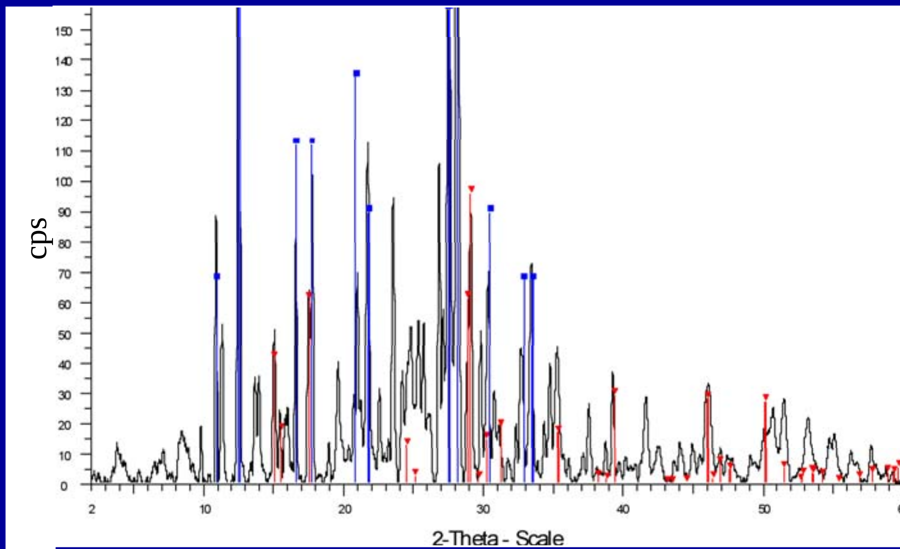
Occurrence of Jarosite: 10 / 58 samples, from four sites, contained measurable jarosite. All were dominated by phillipsite.



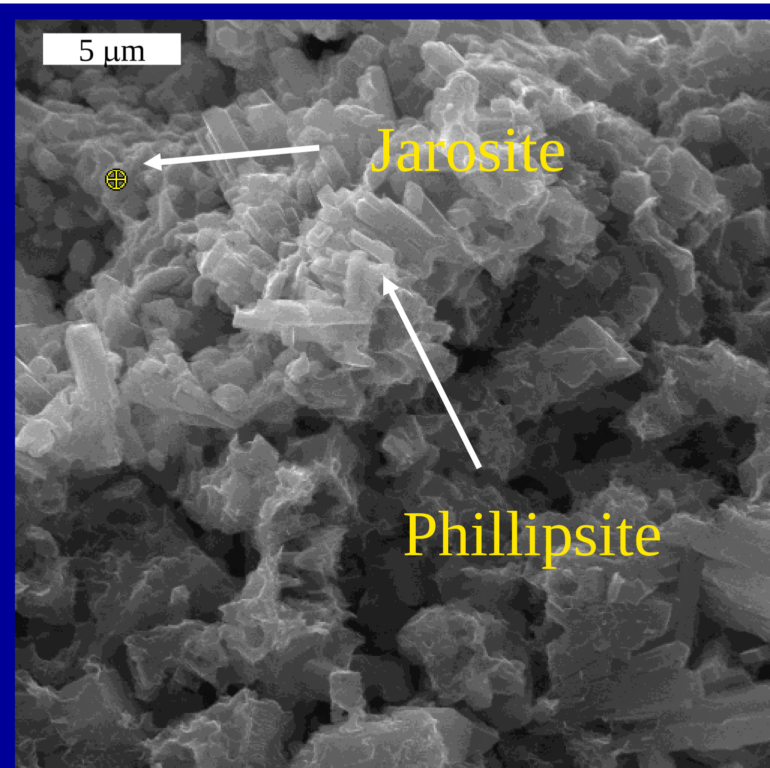
Example: Loc 80

6% jarosite
41% phillipsite
20% authigenic K-spar
4% analcime
contains smectite

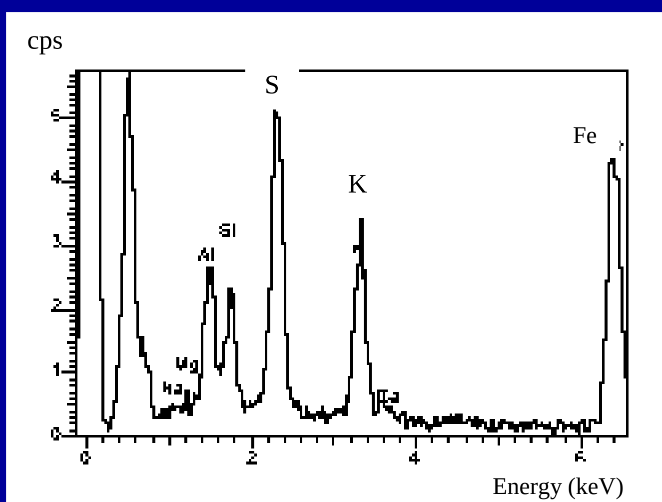
Jarosite and phillipsite in saline-alkaline lake altered phonolitic Tuff IF, Loc 80



XRD (K-jarosite peaks in red, phillipsite in blue)

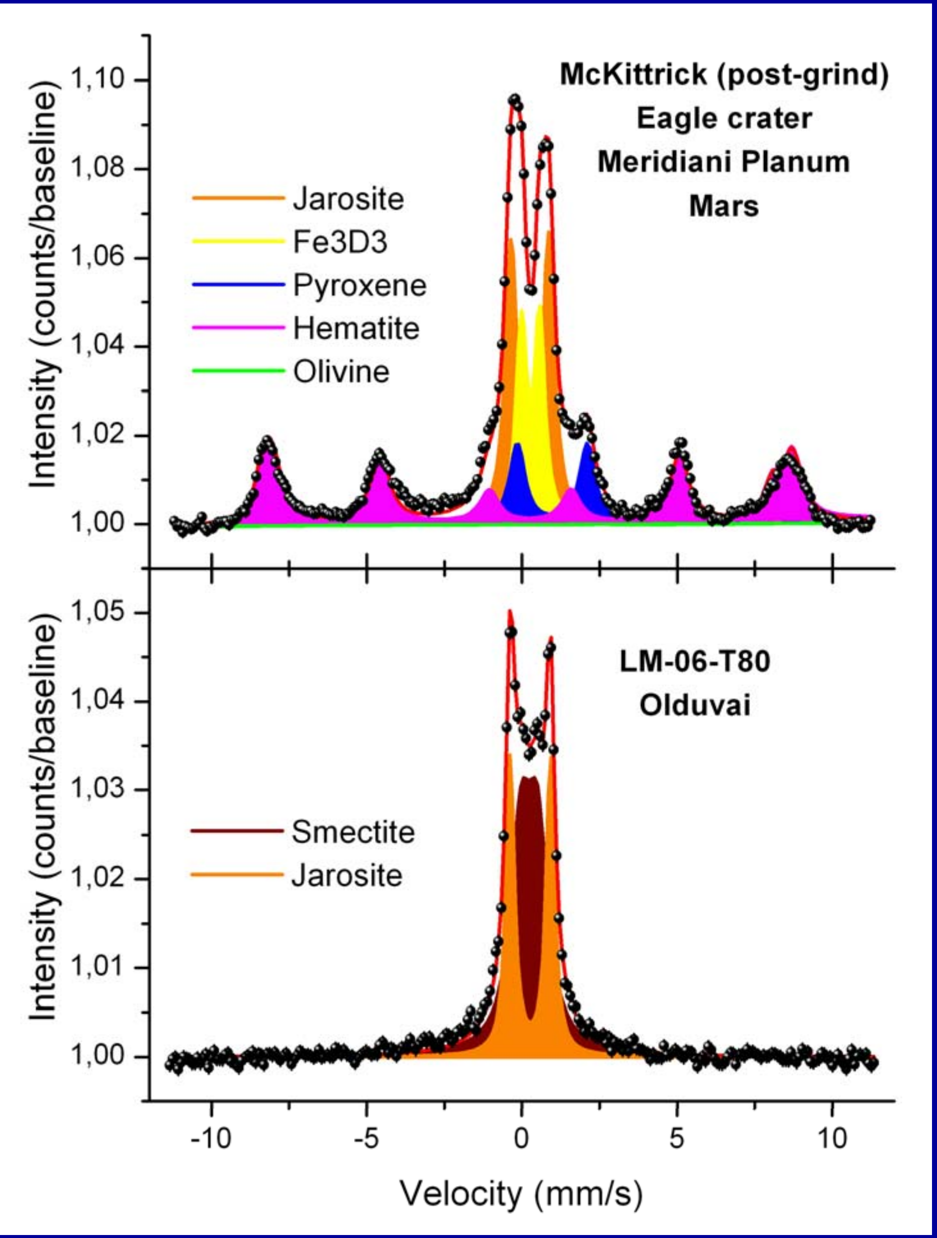


SEM SE image



EDS spectra (S, K, and Fe labeled)

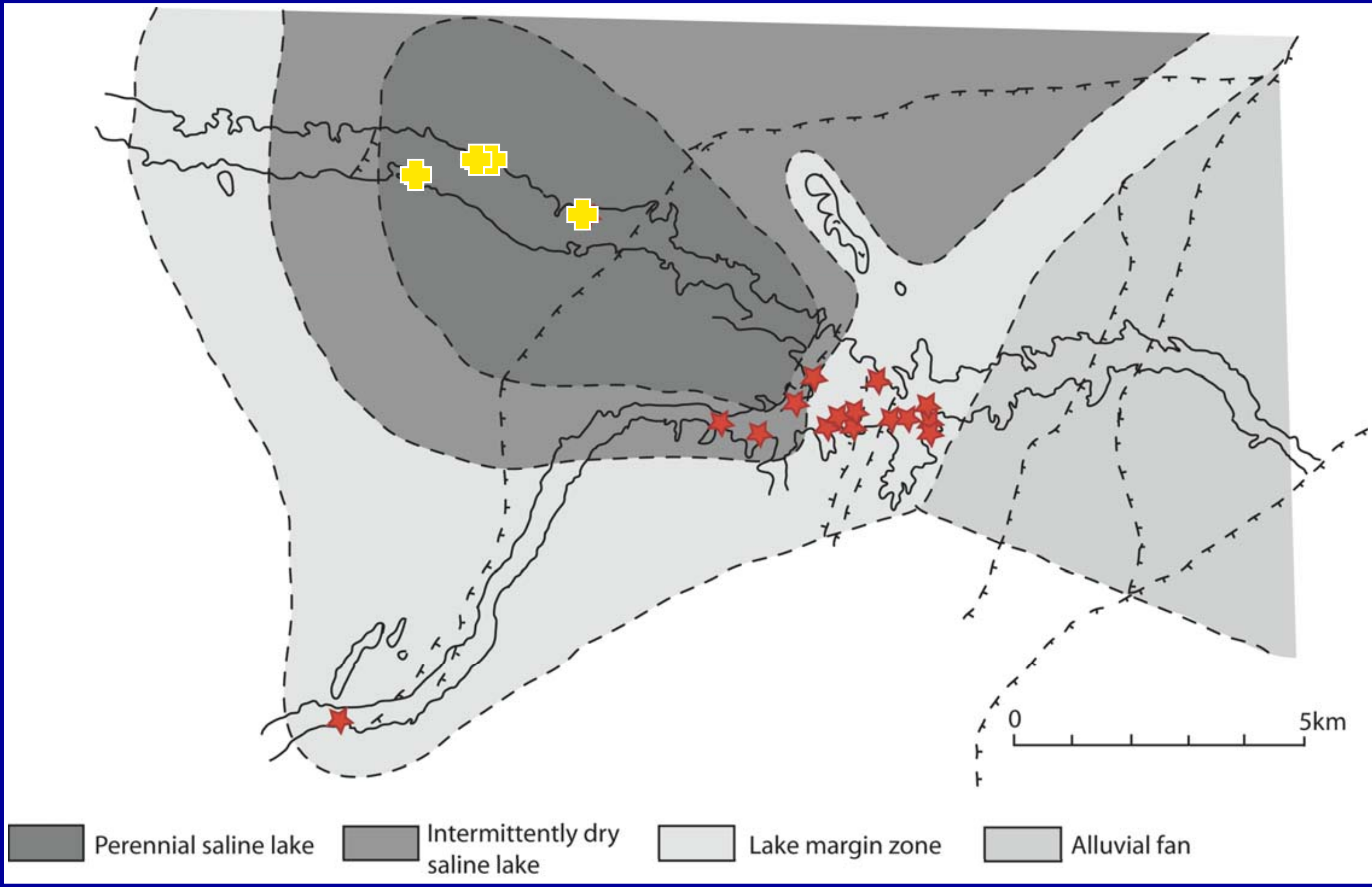
Olduvai vs. Martian jarosite: M□össbauer results



Meridiani Planum jarosite and hematite

Olduvai jarosite and smectite

Klingelhöfer et al. (2004), Science 306, 1740-1745; Morris et al. (2006), JGR 111, E12S15



- sites where jarosite has been identified by XRD
- ★ sites where Tuff IF has been XRDed, no jarosite

Jarosite is limited to the most altered samples, formed under the most saline-alkaline conditions.

Is the modern groundwater saline-alkaline, or acidic?

Evidence for modern saline-alkaline groundwater:

- Na-bicarbonate spring precipitates (dominantly trona)
- High pH (9.29-9.54)

Hypothesis: The jarosite is younger than the zeolites, formed by recent pyrite oxidation.

Phillipsite and pyrite formed initially in high-pH, reducing lakewater.

More recently, pyrite was oxidized. This process can lead to locally acidic conditions:

$FeS_2 + 15/4\ O_2 + 7/2\ H_2O = Fe(OH)_3 + 2H_2SO_4$

XRF data confirms: higher Fe, S in jarosite-bearing samples

Conclusion

The presence of jarosite alone does not require widespread acidic conditions. Jarosite can exist, at least locally, under dominantly saline-alkaline and other non-acidic conditions.

On Mars, additional lines of evidence are needed to be certain that jarosite-bearing sediments and rocks were formed under exclusively acidic conditions.

Dedicated to the memory of Dr. Richard Hay, 1929-2006