Reaction of bentonite in low-alkali cement leachates: An overview of the Cyprus Natural Analogue Project

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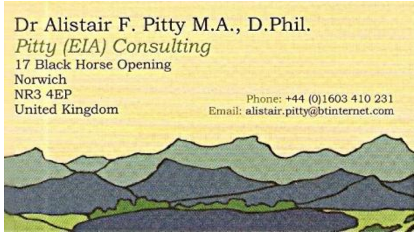

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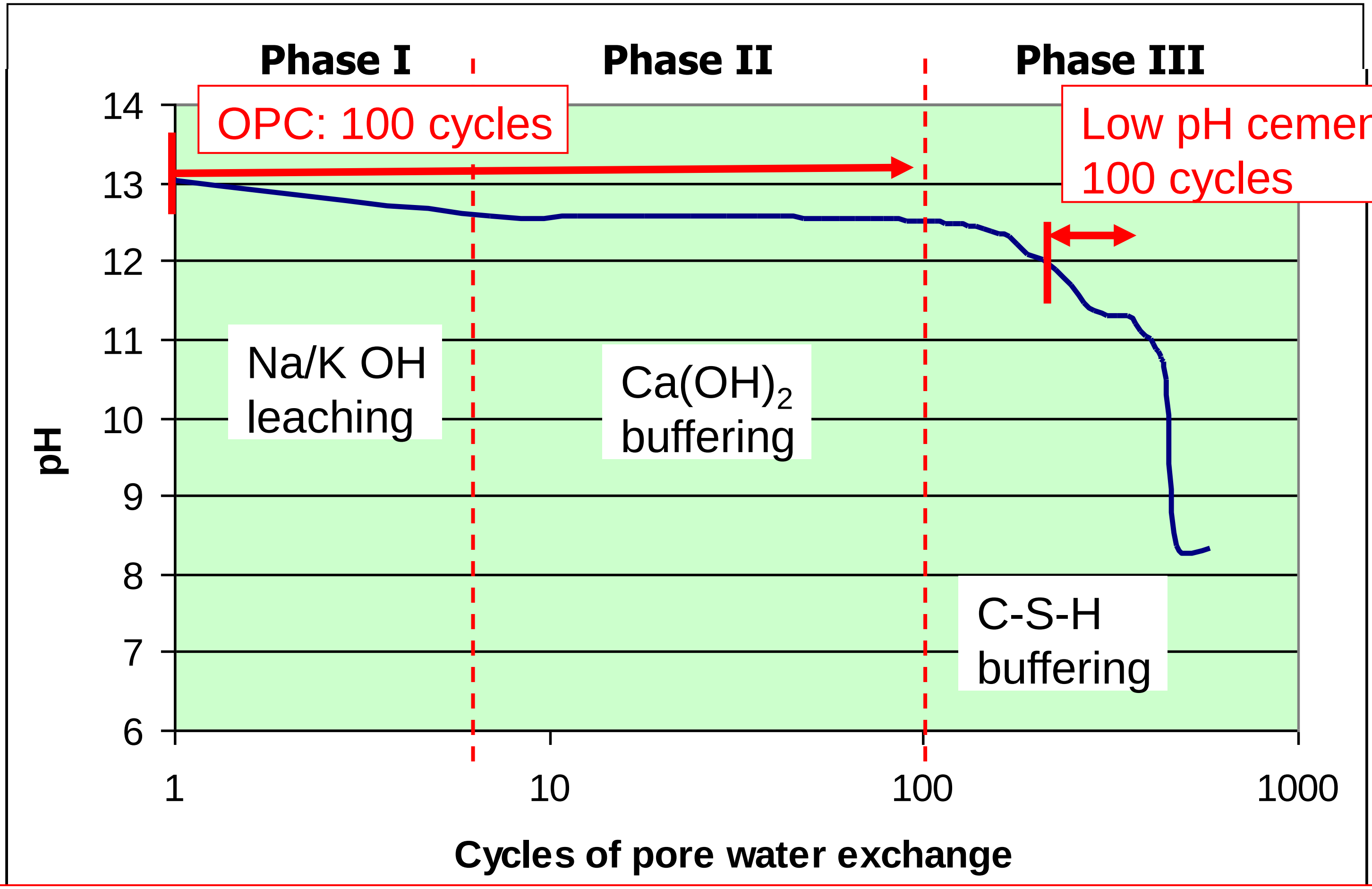
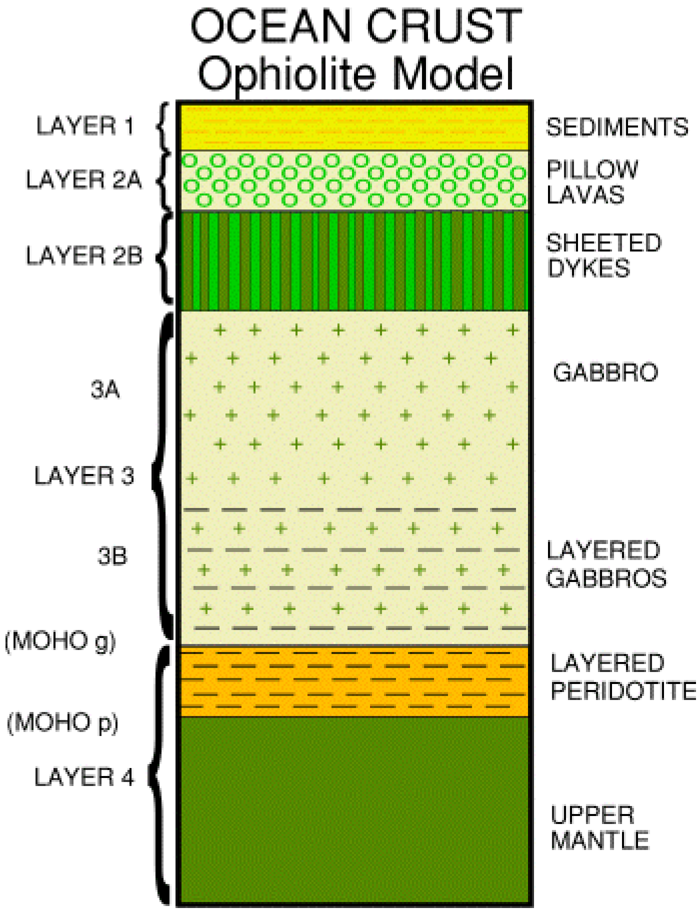
  - **Petrography and microanalysis:** *Jeremy Rushton*
  - **Chemical analysis:** *Helen Taylor, Charles Gowing, PANalytical (Nottingham) Ltd.*

Why low-alkali cements?



NB from cement mixing tank model; logarithmic scale!
- in low K rocks, duration of a “cycle” may be in the order of ka
- evolution may be accelerated by carbonation (long open periods or organic wastes)

Background – model ophiolite



Main reaction pathways to serpentine involve olivine ($(Fe,Mg)_2SiO_4$)* interaction with CO_2 → serpentine ($Mg_3Si_2O_5(OH)_4$)

Additional products can include:

- magnetite (Fe_3O_4)
- magnesite ($MgCO_3$)
- brucite ($Mg(OH)_2$)
- methane (CH_4)
- hydrogen (H_2)

* in all cases, pyroxene group minerals can replace olivine as precursor phase

Natural alkaline groundwaters (pH 9-12) are associated with low-temperature sepentinisation reactions

Distribution of ophiolites

- There are a number of locations worldwide where such an analogue might be found – e.g. the Philippines, Oman, UAE., PNG, Bosnia, California, Japan, China, Korea, Portugal, Switzerland, United Kingdom and Cyprus
- Many of these sites have been studied in depth – but not as NAs (other than Oman - trace element speciation, microbiology, BPM etc)
- Philippines was the first attempt to study a NA of bentonite/low alkali leachate interactions – now we have Cyprus too….

Methane, hydrogen and .....cigarettes

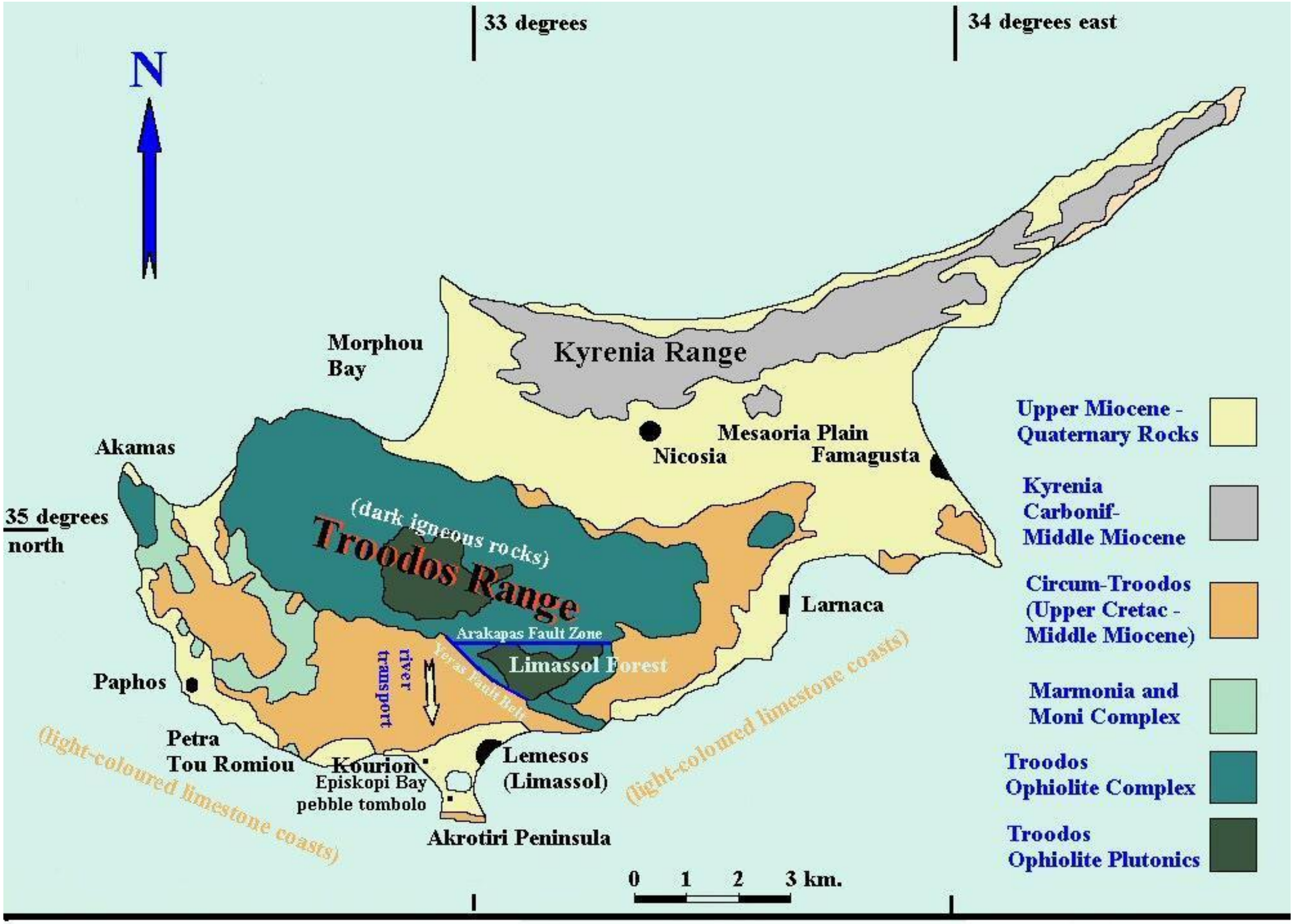
Hyperalkaline groundwater compositions

Location	pH	Na	K	Ca	Mg	Cl	SO_4	SiO_2
Cyprus 3a	11.5	385	15.1	1.0	0.3	420.0	251.0	24.0
Cyprus 3b	11.2	163.0	1.2	93.0	0.5	190.0	207.0	3.4
Greece	11.3	24.0	1.0	34.0	0.3	15.0	3.0	2.0
Bosnia	11.7	35.0	1.5	29.0	7.0	20.0	2.0	0.9
Oman	11.5	132	4.8	34.0	1.3	127.5	22.5	3.0
New Caledonia	10.8	15.0	3.0	14.0	2.3	22.0	0.8	0.4
Western USA	11.5	19.0	1.0	40.0	0.3	63.0	0.4	0.4
Philippines	11.1	28.0	0.5	18.6	0.2	17.4	5.1	nd
Cement leachate								
ALL-MR f63	11.0	42	7.3	20	<0.5	52	12	49.2
OL-SR f63	10.0	4400	150	4300	0.56	13000	247	32.1

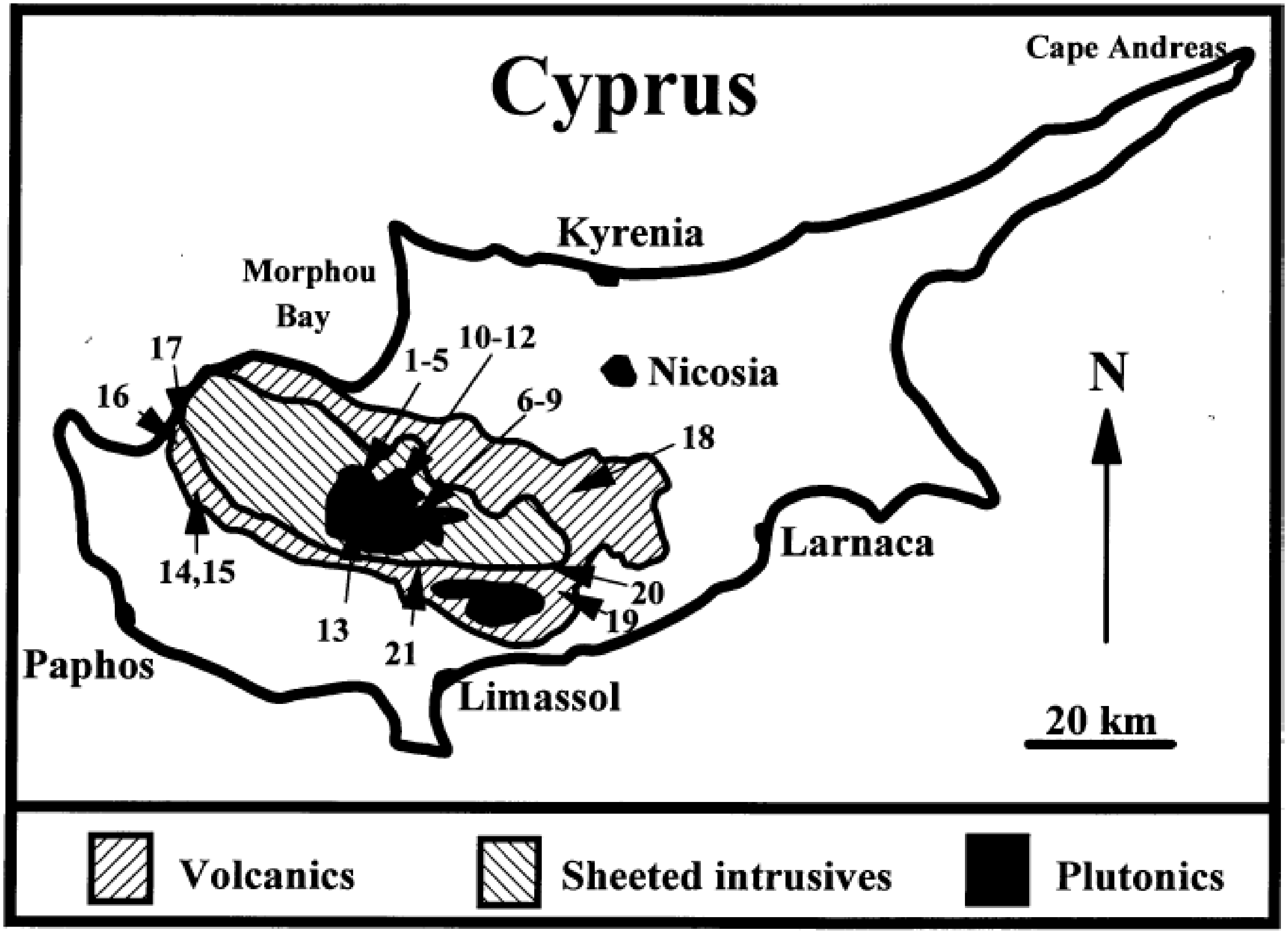
Preliminary outcomes

- ***Phase I: 30 sites surveyed (drove 2000 km in 10 days…..lots of tracks)***
- ***Phase II: focussed on 10 sites, sampled groundwaters, sediments at active systems and fossil systems – serpentinite…..***
- ***Phase IIa: recce of a further 7 sites, contracted drilling and construction companies***
- ***Phase III: planned to sample 1 active and 2 fossil sites…..***

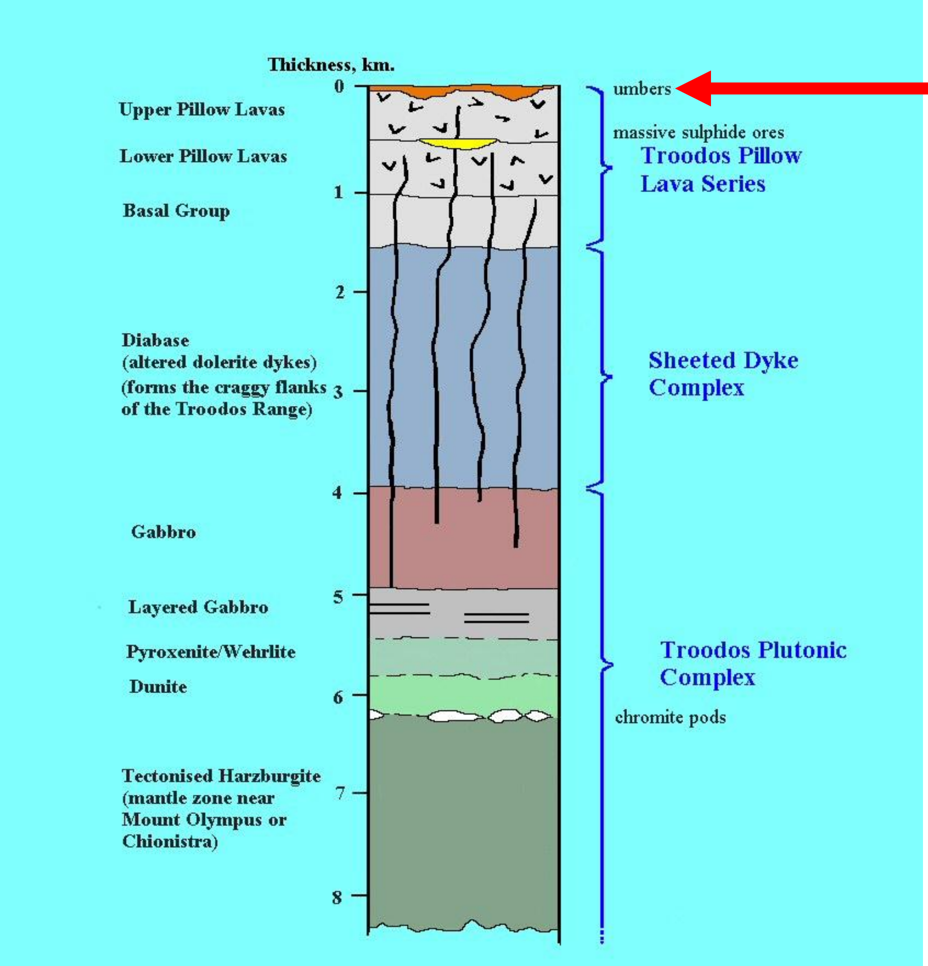
Overview of the geology of Cyprus



Hyperalkaline groundwater sources



Geology – Troodos Ophiolite sequence



The ophiolite succession in the Troodos Mountains of Cyprus, shown schematically.
Redrawn with modifications after Greensmith (1994). Ian West & Joanna West (c) 2007.

<u>Peripedhi Formation:</u>

Ophiolitic sediments: deep ocean floor - umbers, manganoan shales, finely-banded radiolarian shales and and mudstones,and **<u>bentonites</u>**

Sequence represents uplifted and eroded “window” of ancient **ocean crust and mantle** rocks

Schematic lithographic section of the Troodos ophiolite

[From West, 2007]

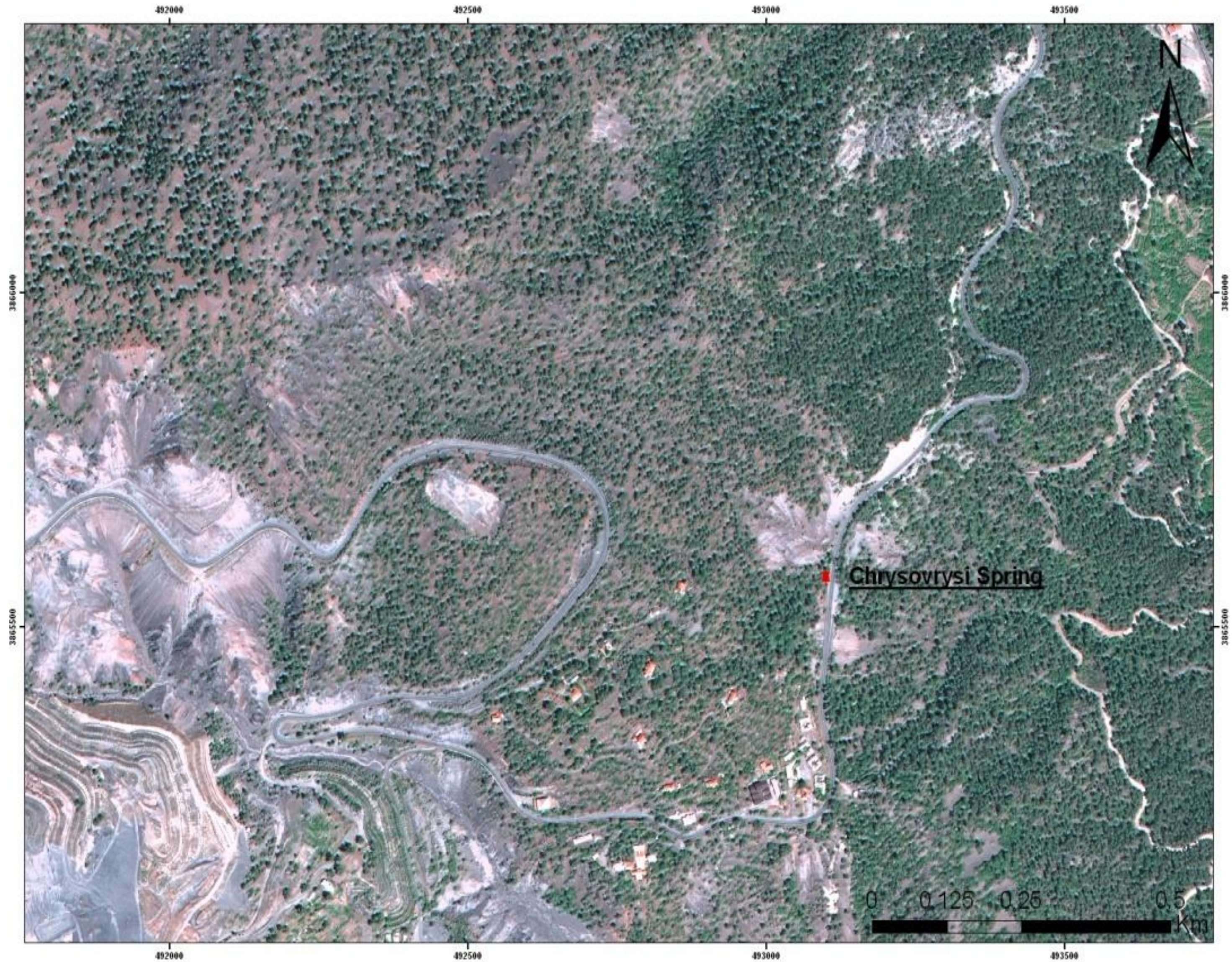
Allas Springs–groundwater from the ophiolite

Allas Springs – A1-2

Allas Springs – white tufa produced when hyperalkaline groundwaters take up CO_2

Valley E

Chrisovrysi Springs



Chrisovrysi Springs

Trimiklini

D (waterfall site)

Parsata (Almond Orchard site) – hyperalkaline groundwaters at depth below the bentonite

High T serpentinisation

When considering the origin of the hyperalkaline groundwaters at most ophiolites, two processes generally need to be considered:

- **medium temperature alteration**
- **low temperature precipitation**

- **The former often shows itself in the form of pervasive serpentinisation of the entire mantle sequence and is presumed to be pre- or syn-tectonic. This hydrothermal alteration may be characterised by the reaction:**
- $6Mg_2SiO_4 + Mg_3Si_4O_{10}(OH)_2 + 9H_2O \rightarrow 5Mg_3Si_2O_5(OH)_4$

forsterite talc serpentine

Low T serpentinisation

In this case, $Mg(HCO_3)_2$-type meteoric groundwaters react with the ultramafic rocks of the ophiolite in an essentially open system and produce $Ca(OH)_2$-type (spring) waters. Of course, without petrological details and kinetic information, the total reaction equation is indeterminate

olivine dissolution

$$3H_2O + 2\ Mg_2SiO_4 \rightarrow 5Mg_3Si_2O_5(OH)_4 + Mg^{2+} + 2OH^-$$

forsterite serpentine

$$2H_2O + Fe_2SiO_4 \rightarrow 2Fe(OH)_2 + SiO_2$$

fayalite

Low T serpentinisation

pyroxene dissolution

$$2H_2O + 3MgSiO_3 \rightarrow Mg_3Si_2O_5(OH)_4 + SiO_2$$

$$H_2O + FeSiO_3 \rightarrow Fe(OH)_2 + SiO_2$$

$$H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2OH^- + SiO_2$$

precipitation

$$3(Mg^{2+} + 2OH^-) + 2SiO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + H_2O$$

(involves a balance between Mg and the input groundwater with SiO_2 – so serpentine precipitation is buffered by differential olivine-pyroxene dissolution)

Low T serpentinisation

hydroxide is produced, but the (Mg^{2+} + $2OH^-$) of olivine dissolution is consumed in the precipitation reaction, leaving only Ca and Fe sources, with Ca likely to dominate based on the source mineralogy

any HCO_3^- in the input groundwater is generally consumed (below), giving rise to aragonitic to dolomitic secondary carbonates and output groundwaters dominated by Ca-OH-Na-Cl compositions

$$Mg^{2+} + HCO_3^- + OH^- \rightarrow MgCO_3 + H_2O$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O$$

CNAP hydrochemistry

Sample	Field pH	Lab pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}
P1-2010a	nd	11.1	48.3	0.11	96.5	1.34	5.40	nd	80.9	149	<0.200
P1-2010b	nd	11.1	50.1	0.11	97.2	1.39	7.20	nd	85.6	159	<0.200
P1-2010c	nd	11.1	48.8	0.10	95.0	1.35	9.00	nd	85.1	158	<0.200
P1	11.42	10.3	36.5	0.021	116	<0.5	27.6	<10	80.9	149	<0.03
A4-1	n.d.	9.77	3.20	58.7	747	31.4	127	152	1093	87.2	0.343
A4-2	n.d.	9.90	3.43	58.4	893	40.5	161	121	1342	106	1.82
A4-3	n.d.	9.71	3.37	58.8	921	40.7	140	154	1321	106	2.40
A5	9.8	9.22	1.34	64.2	224	9.76	n/a	307	346	27.7	1.98
A3	9.84	9.29	1.32	63.9	238	10.2	50.5	203	369	30.5	2.22
A2	9.69	9.04	1.61	65.5	172	7.33	38.5	232	254	22.8	1.66
A1-1	11.9	11.3	37.2	0.101	1435	63.1	n/a	272	2177	101	<1.5
A1-3	10.01	9.31	12.2	0.554	1337	60.1	54.1	96.4	1926	114	10.3
A1-2	9.26	8.82	4.87	48.3	502	23.7	25.8	288	699	50.7	3.90
A1-4	9.78	9.27	11.2	5.73	1214	54.0	61.2	124	1748	78.5	8.33
A6	9.67	9.60	2.22	50.7	921	42.9	102	150	1383	97.0	7.31
E1-1	9.5	9.48	1.07	56.4	75.3	2.62	52.2	190	92.7	7.128	1.03
C2	9.58	8.90	1.69	67.9	4.79	<0.5	23.7	255	8.361	3.207	0.580
C1	9.41	8.85	1.80	68.3	4.68	<0.5	n/a	309	8.486	3.272	0.640
C3	9.69	9.11	1.67	92.7	5.14	0.926	44.5	311	18.2	2.484	1.86

Parsata

- **Other than Li and B, trace elements all very low**

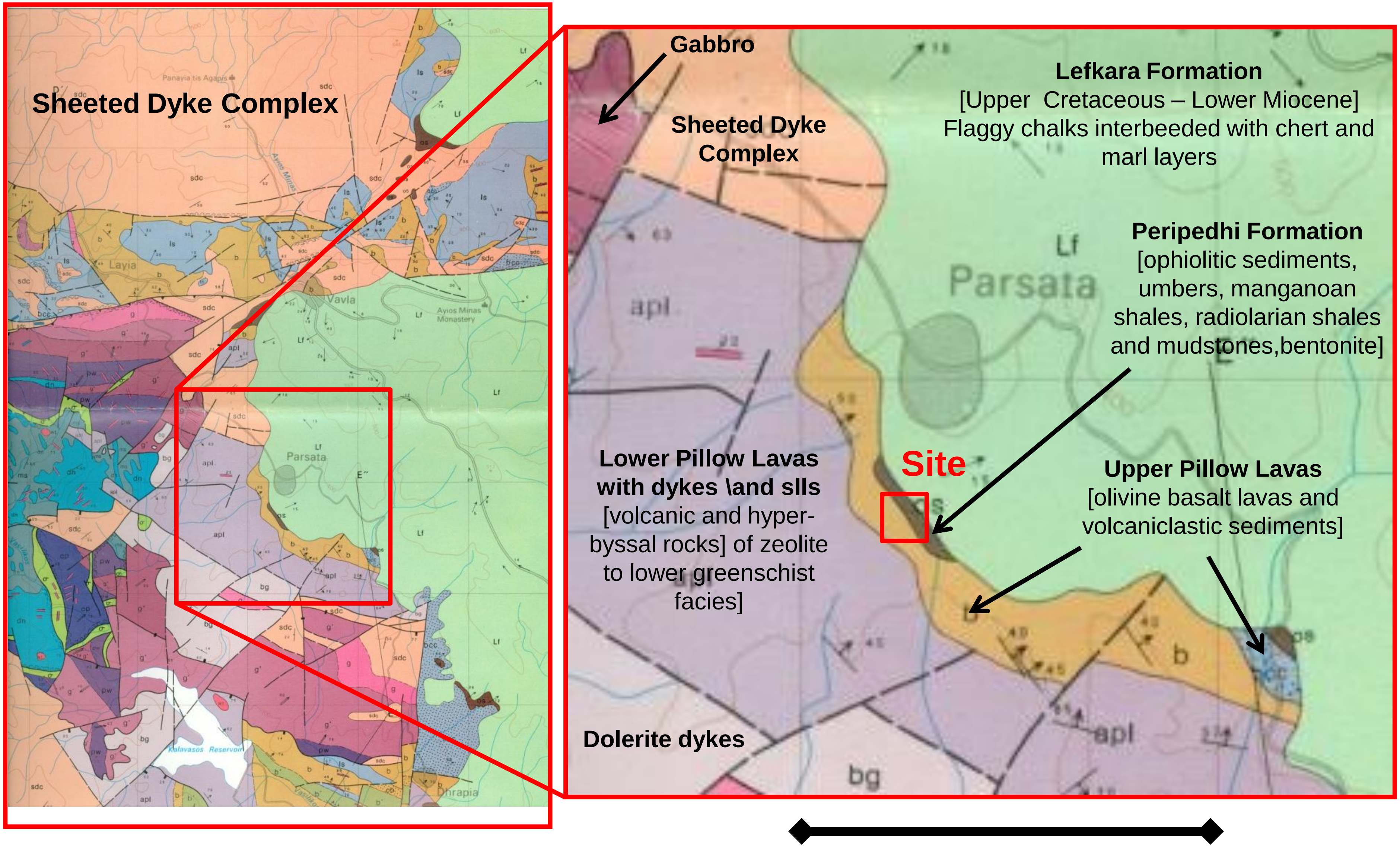
- **Li/Cl and B/Cl ratios provide a useful guide to the fluid/rock mass ratios**

- **all samples lie very close to $3x10^{-3}$ (cf. seawater with ~$8.4x10^{-6}$)**

- **most samples have a B/Cl ratio of between and 4.2 - $4.4x10^{-3}$, (cf. seawater $3.3x10^{-3}$)**

- **P1 has B/Cl ratio of 9.7 $x10^{-3}$, indicating B enrichment (NB could we measure it in the clays?)**

Geology of the Parsata site

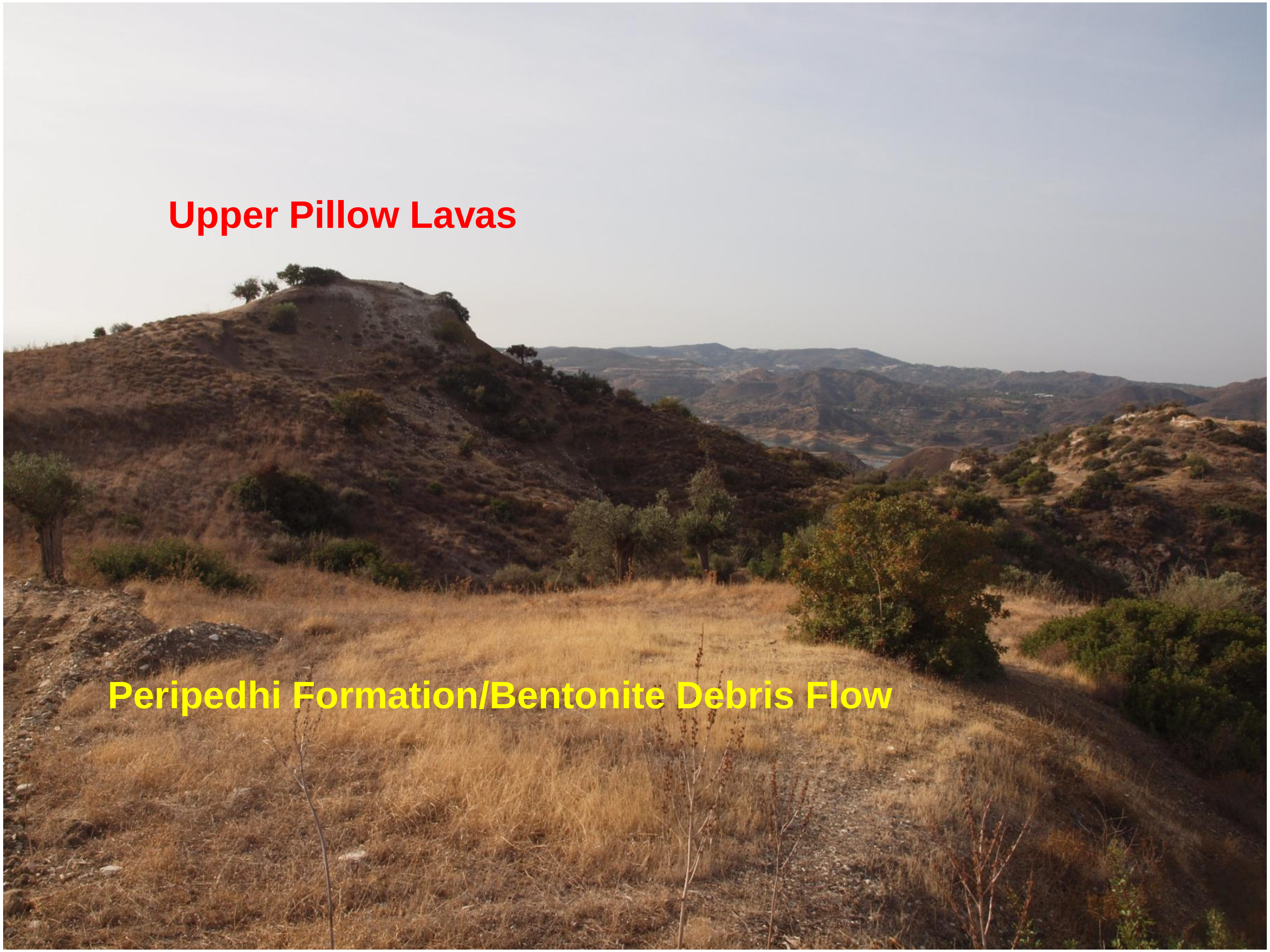


[Modified after Gass et al., 1994]

Parsata village

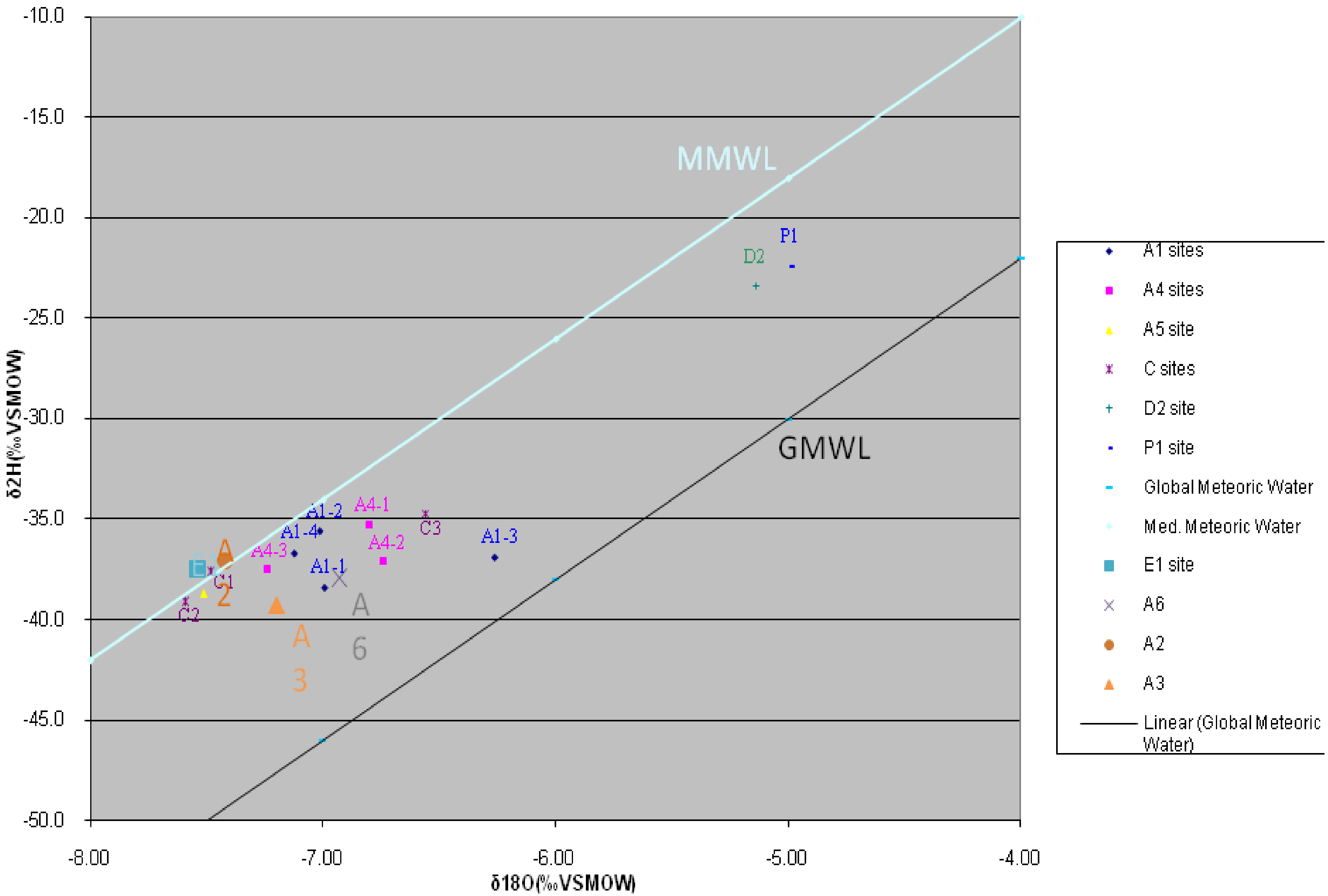
Parsata study site

Parsata study site

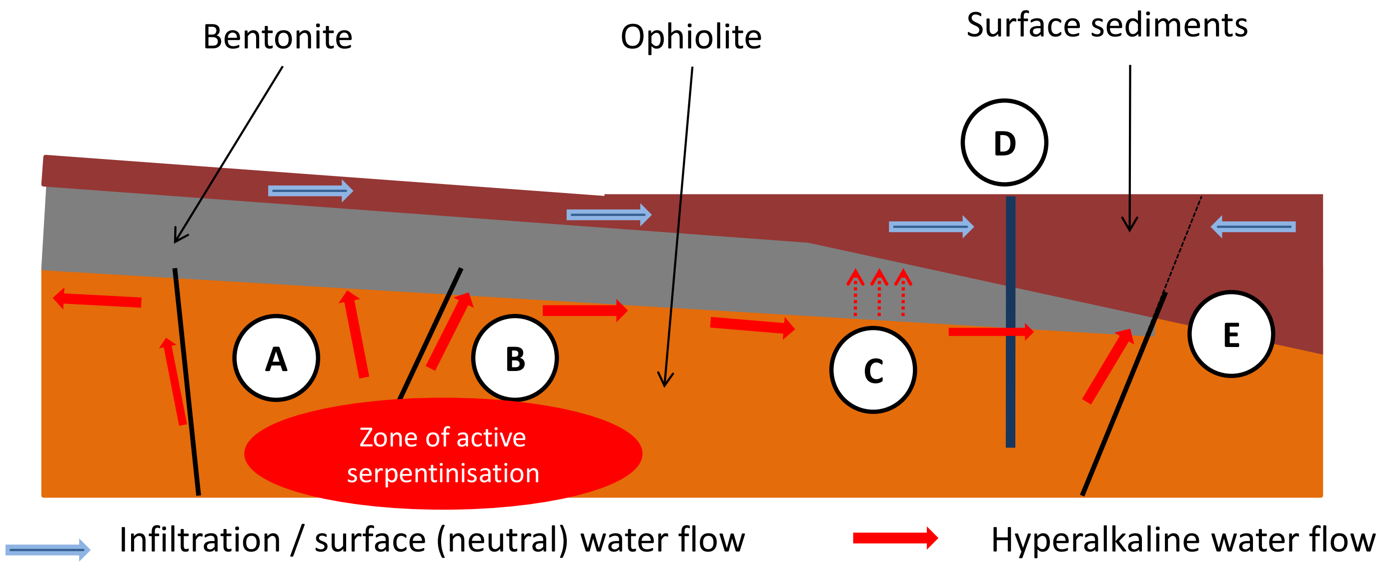


Sampling isn't rocket science

Stable isotopes



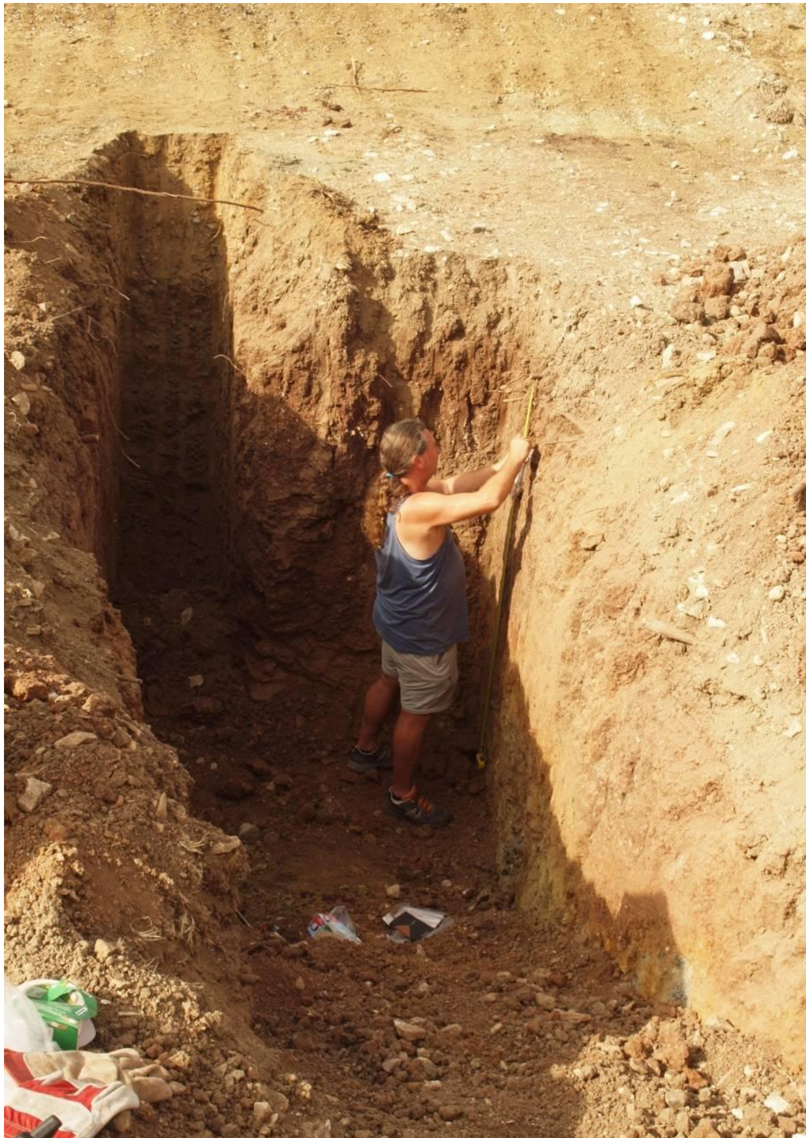
conceptual model

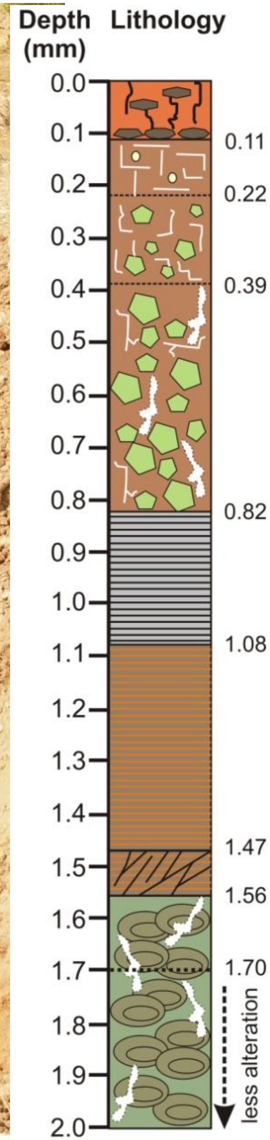


A – Active serpentisation producing hyperalkaline groundwater and H_2/CH_4 gas
B – High pH water under bentonite, neutral water above it
C – Potential interaction of high pH waters with base of bentonite (diffusion into it?)
D – Borehole through bentonite and into pillow lavas
E – Dispersed release of high pH waters into deep sediments?

Parsata study site

Parsata trench – lithological sequence





Description

Soil: Dk.red-brown to choc.-brown, highly fissured with blocks <5-50 mm. Stoney,with limestone and basalt clasts up to 40 mm. Upward increase in stones.

Dark brown,compact, highly fissured clay. Fine (0-1 mm) orthogonal fissure network filled by powdery white $CaCO_3$. Scattered 1 mm calcrete nodules.

Bentonite regolith or debris-flow deposit:
Highly weathered mudstone. Dark brown massive, compact clay with barely-discernable residual angular fragments of hard, dark olive-green clay up to 4 mm. Rare fine fissues up to 1 mm wide, filled by white powdery $CaCO_3$.

Partially weathered bentonite regolith or debris-flow deposit:
Partially weathered mudstone comprising residual angular fragments of hard, olive-green clay (up to 4 mm) within a matrix of red-brown clay. Primary sedimentary lamination lost. Fissured, with discontinuous fissures coated with thin (<1 mm), white, powdery $CaCO_3$, and diffuse patches of white, powdery, $CaCO_3$.

Grades upward over 0.1 m into highly weathered mudstone.

Manganese oxide impregnated bentonite:
Compact, hard, finely-laminated bentonite with buff-brown clay with very thin (<1 mm) partings of black to metallic-grey manganese oxide, and small (1-2 mm) “nodules” and “dendrites” of manganese oxide along bedding partings.
No goethitic iron oxide mineralisation visible.

Iron oxide impregnated bentonite:
Compact, hard, finely-laminated bentonite with buff to chocolate-brown clay with very thin red-brown ferruginous clay partings. Discrete goethite coatings along some laminae partings.

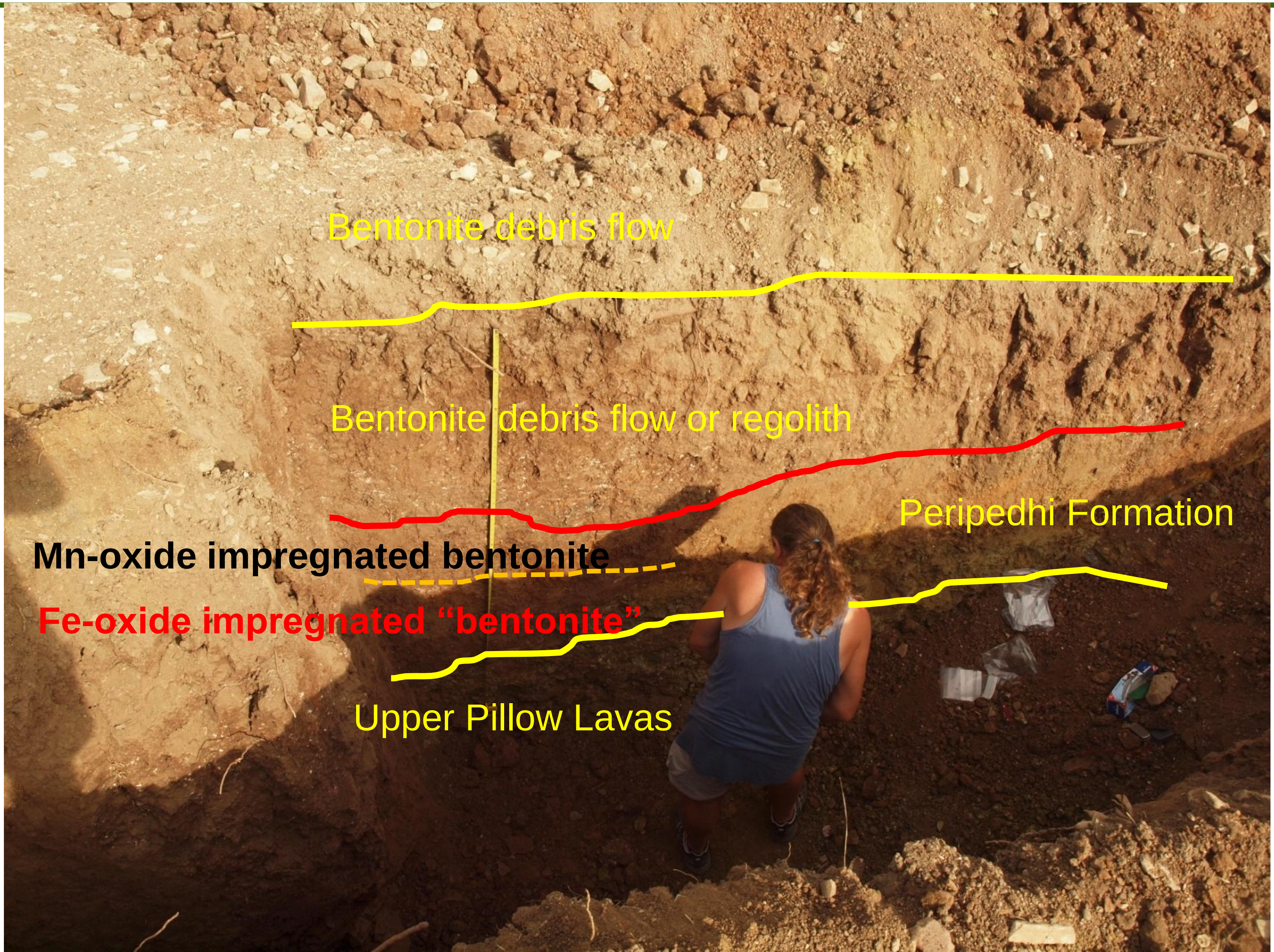
No manganese oxide mineralisation visible.

Compact, fractured, finely-laminated bentonite. Dark chocolate-brown. Horizontal and inclined 30°, slickensided surfaces with traces of white secondary minerals.

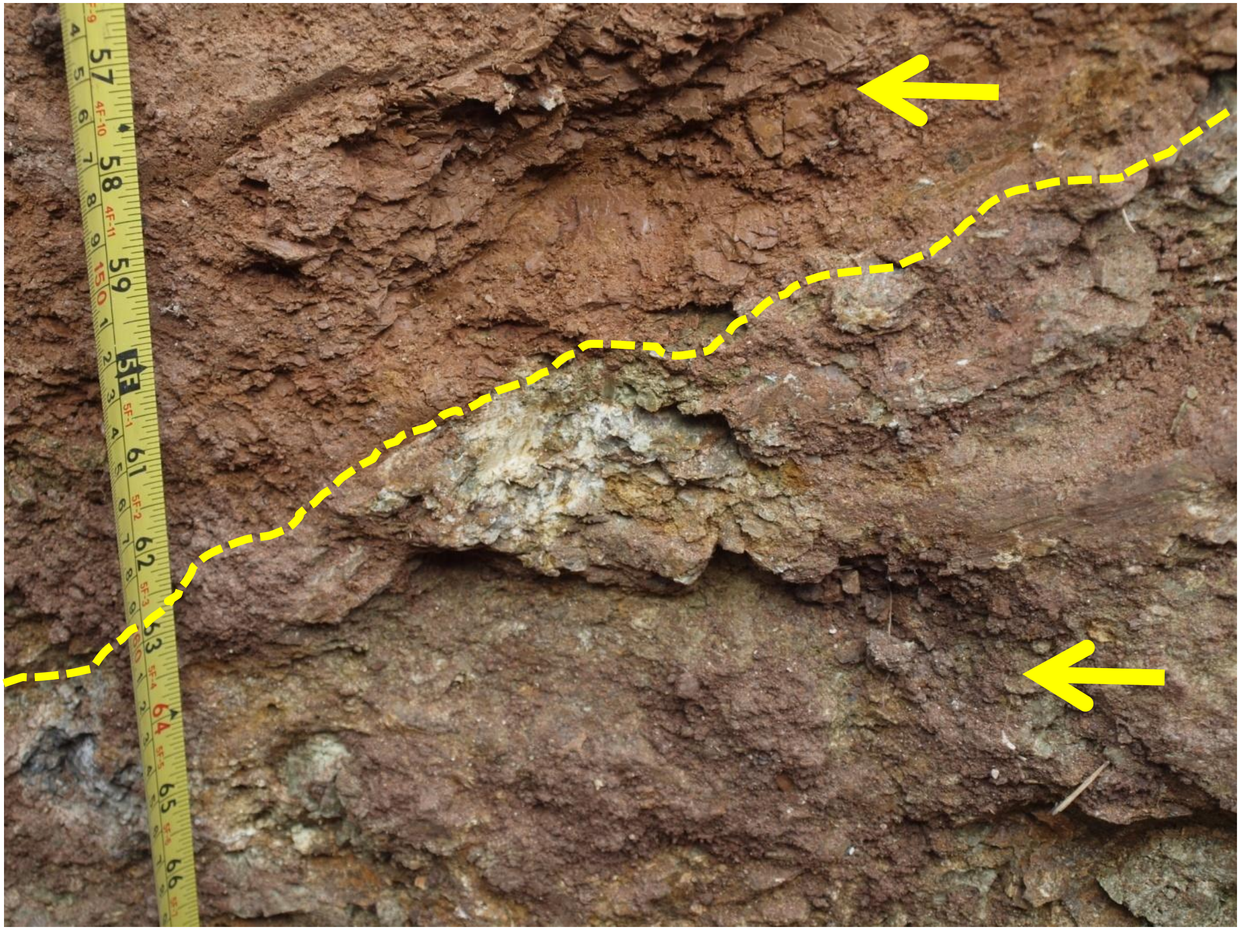
Pillow Lava Series:

Basaltic pillow lava. Highly altered with argillised spheroidal (onion-skin) alteration rinds around black unaltered basalt “corestones” up to 10 mm diameter. Altered white plagioclase phenocrysts still visible. Green, “soapy” altered clay matrix between basalt pillows. White powdery secondary mineralisation forms coatings around basalt pillows and fills irregular subvertical fissures. Green, soapy or waxy altered basalt above 1.70 m, becoming less altered below 1.70 m.

Parsata trench – lithological sequence



Parsata trench – pillow-lava bentonite contact



Fe-rich bentonite

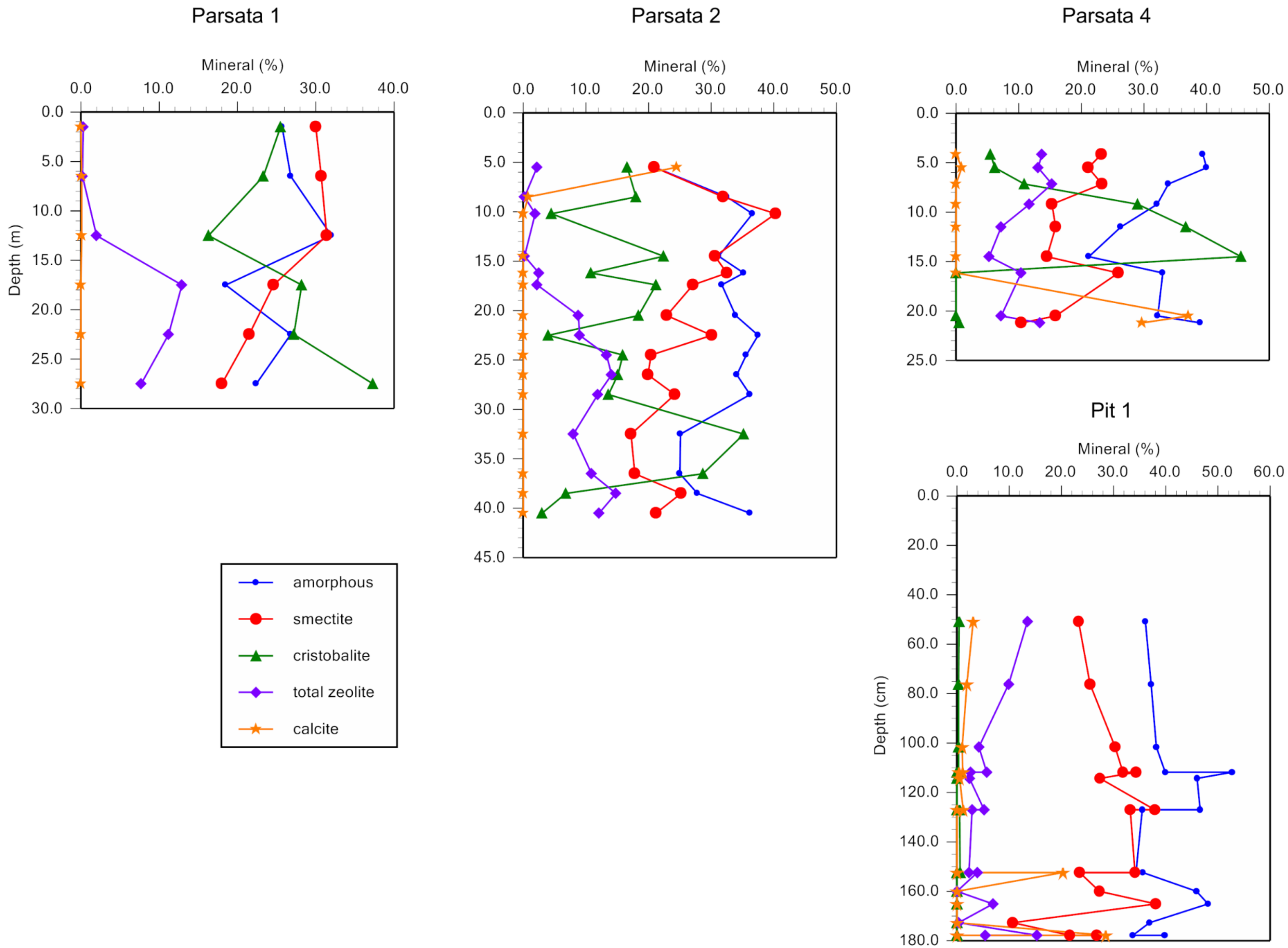
Altered pillow lava

Alteration in Pillow Lavas and contact

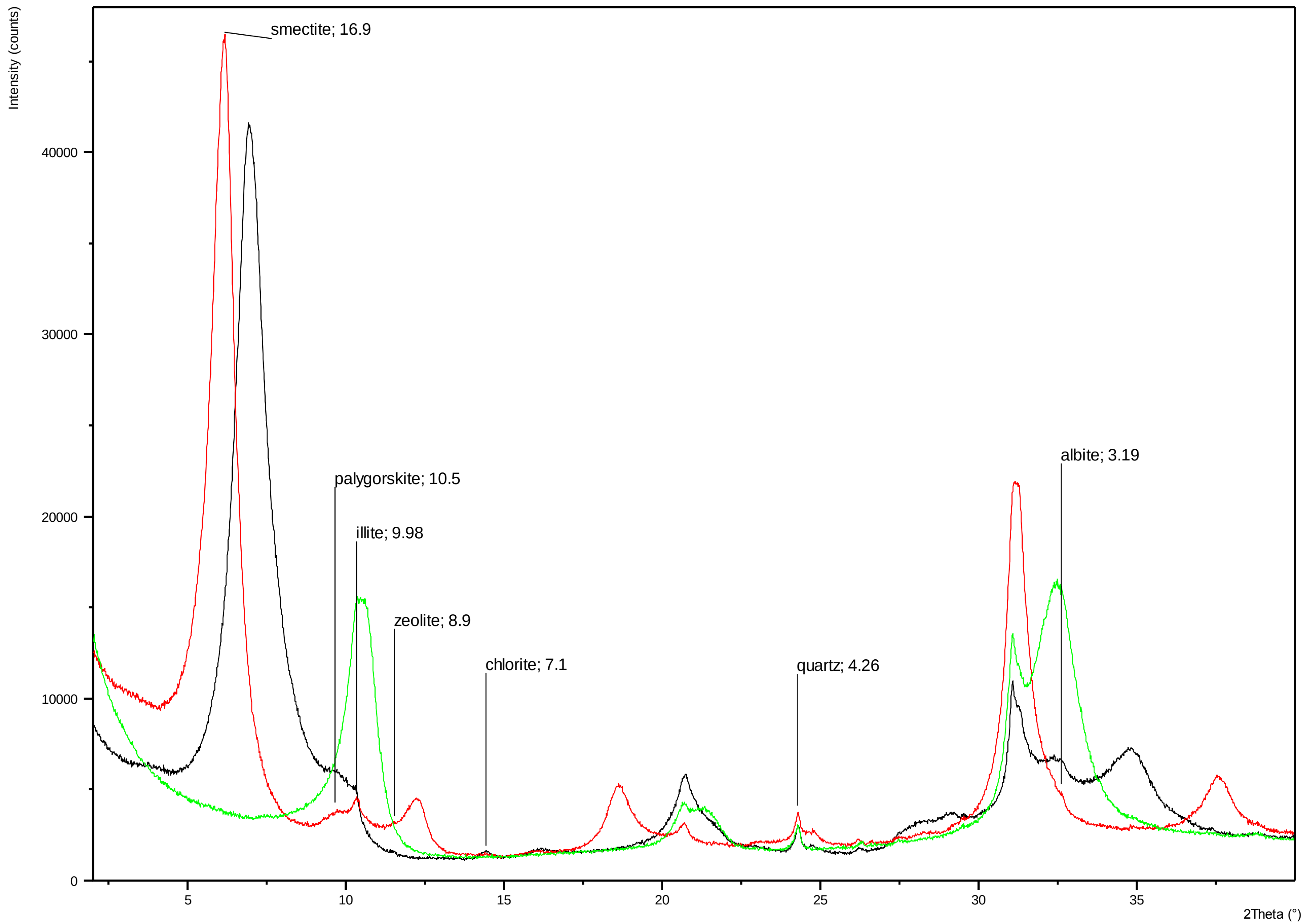
Mineralogy and chemistry – samples 1

Borehole	Depth (m)		Location Description	BGS Lab No.	XRD analysis		XRFS analysis	
	Top	Bottom			Bulk	Clay	Majors	Traces
Parsata 1	1	2	Green-brown clay (brown on fresh surfaces). Fe- and Mn-oxides on (fracture) faces. Also white precipitates on oxides.	MPLP862	yes	yes	yes	yes
Parsata 1	6	7	Green-brown clay (brown on fresh surfaces). Fe- and Mn-oxides on (fracture) faces. Also white precipitates on oxides.	MPLP863	yes	yes	yes	yes
Parsata 1	12	13	Highly friable green-brown clay.	MPLP864	yes	yes	yes	yes
Parsata 1	17	18	Green clay (brown on fresh surface). Very friable	MPLP865	yes	yes	yes	yes
Parsata 1	22	23	Brown clay	MPLP866	yes	yes	yes	yes
Parsata 1	27	28	Green and brown clay, some fragments soft.	MPLP867	yes	yes	yes	yes
Parsata 2	5	6	As above, but white material dispersed throughout the clay	MPLP869	yes	yes	yes	yes
Parsata 2	8	9	Green-brown clay with Mn-oxide stains on (fracture) faces and white fracture infill.	MPLP870	yes	yes	yes	yes
Parsata 2	10	10.4	Stiff green clay with rare filled voids of white material which were present on recovery of the core.	MPLP871	yes	yes	yes	yes
Parsata 2	14	15	Grey-green clay	MPLP873	yes	yes	yes	yes
Parsata 2	16.2			MPLP874	yes	yes	yes	yes
Parsata 2	17.2	17.6	Stiff grey-green clay. Fe staining on probable fracture face.	MPLP875	yes	yes	yes	yes
Parsata 2	20	21	Grey-green clay	MPLP877	yes	yes	yes	yes
Parsata 2	22	23	Brown clay with admixed harder whitish material (showing texture/orientation?)	MPLP878	yes	yes	yes	yes
Parsata 2	24	25	As above, but white material now very rare	MPLP879	yes	yes	yes	yes
Parsata 2	26	27	Brown clay	MPLP880	yes	yes	yes	yes
Parsata 2	28	29	Pale grey clay with white fracture filling (regular boundary between white material and clay)	MPLP881	yes	yes	yes	yes
Parsata 2	32	33	Red-brown clay with significant admix of white material - too disaggregated to tell if fracture fill or not. White material harder than clay	MPLP883	yes	yes	yes	yes
Parsata 2	36	37	Red-brown clay with paler clay fragments admixed	MPLP885	yes	yes	yes	yes
Parsata 2	38	39	Much darker brown, white fracture fill material visible.	MPLP886	yes	yes	yes	yes
Parsata 2	40	41		MPLP887	yes	yes	yes	yes
Parsata 4	4.0	4.3	Cored section. Massive, uniform, brown clay, partly baked by heat of drill?	MPLP888	yes	yes	yes	yes
Parsata 4	5.0	6.0	Massive, uniform, brown clay. Some faces (fractures?) show thin black coating - Mn oxides?	MPLP889	yes	yes	yes	yes
Parsata 4	7.0	7.3	Cored section. Massive, uniform, brown clay, partly baked by heat of drill? White secondary precipitates (not post drilling) both disseminated and on (fracture?) faces.	MPLP890	yes	yes	yes	yes
Parsata 4	9.0	9.4	Cored section. Pale grey clay with white filling in microfractures.	MPLP891	yes	yes	yes	yes

Depth variation in major minerals

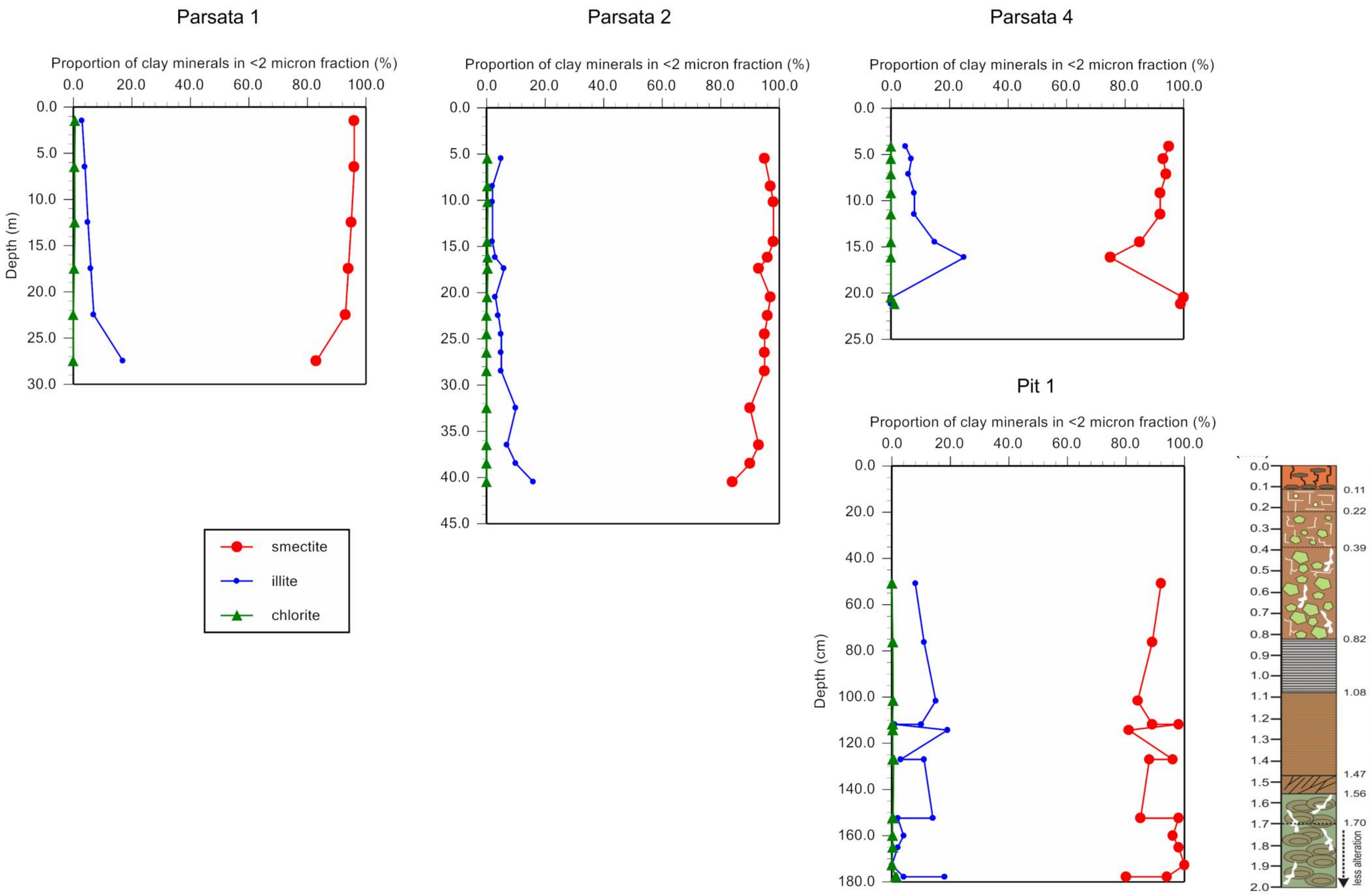


XRD results – Clay mineralogy



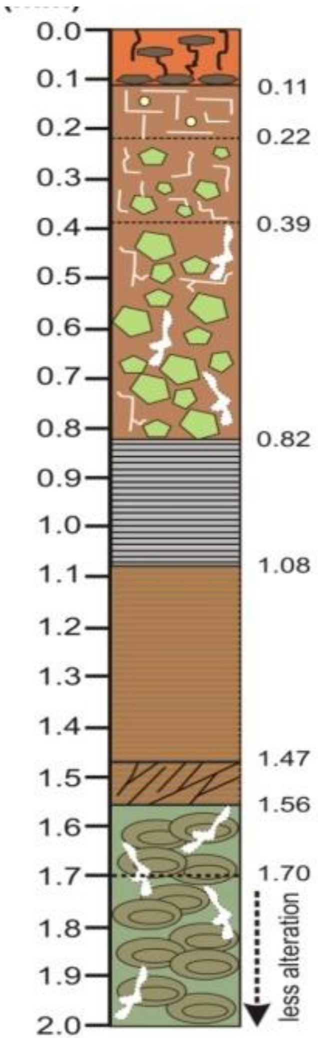
Example <2 µm XRD traces to illustrate the typical clay mineral assemblage, black trace (air dry), red trace (glycol-solvated), green trace (heated 550˚C/2 hours), Trench, sample 6, depth 111.8 cm.

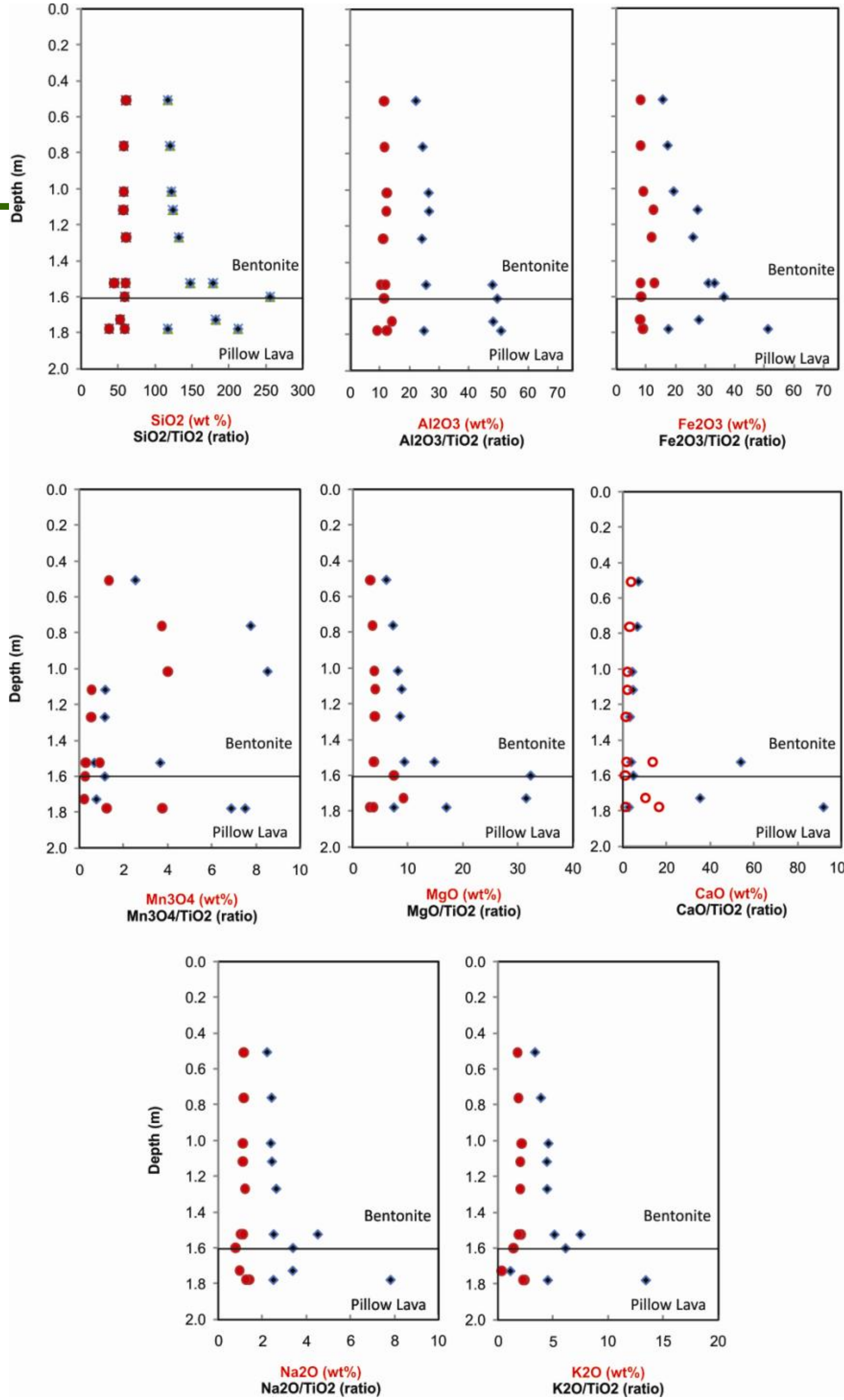
Depth variation in clay mineralogy



Major elements

Trench





Whole rock chemistry - summary

- Little systematic variation with depth – variations could reflect detrital variations
- TiO_2-normalised variations indicate relative increases in Si, Fe, Mn, Mg, Ca, K and Na with depth.
- Marked increase in Mn and Fe corresponding to Fe- and Mn oxide impregnation of bentonite – marked at base of trench
- Increased Mg at base of bentonite (trench) – corresponds to abundance of secondary palogorskite (XRD, petrography)
- Increase Ca at base of bentonite (trench) corresponds to late calcite fracture mineralisation at contact / close to contact and within the Upper Pillow Lava
- High concentration of Cr, Mn, Fe, Ni, Co, Pb, Zn indicates a closer correlation with Peripedhi Formation rather than the major bentonite-bearing Kanaviou Formation *(fits with earlier geological mapping of Parsata)*

Petrography – Bentonite analogue - 1

➢Primary constituents:

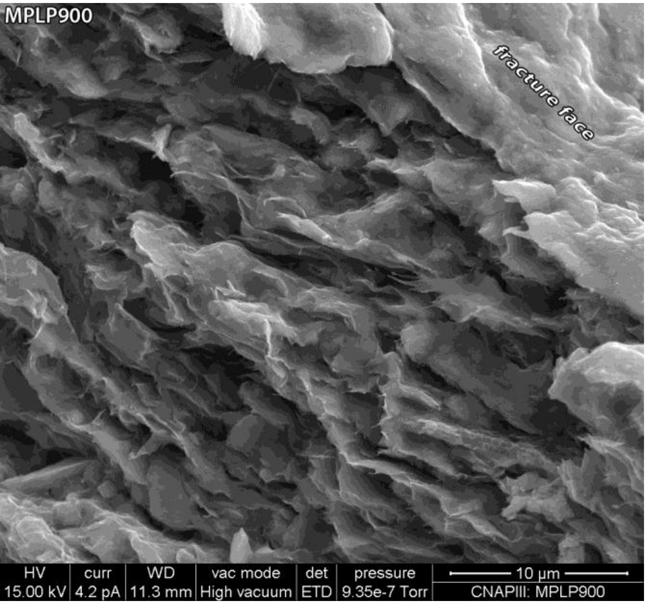
- Major detrital smectite, biogenic silica (radiolaria diatoms), altered volcaniclastic grains
- Minor-subordinate illite/mica, plagioclase, apatite, zeolite, quartz, chlorite
- Plant debris
- Rare limestone grains
- Rare garnet

➢Authigenic constituents:

- Major smectite associated with matrix clays and alteration of volcanic clasts
- Crystobalite
- Zeolites, analcite
- Feldspars
- Calcite
- Mn and Fe-oxides
- **Palygorskite – replacing smectite***
- Calcium Sulphate

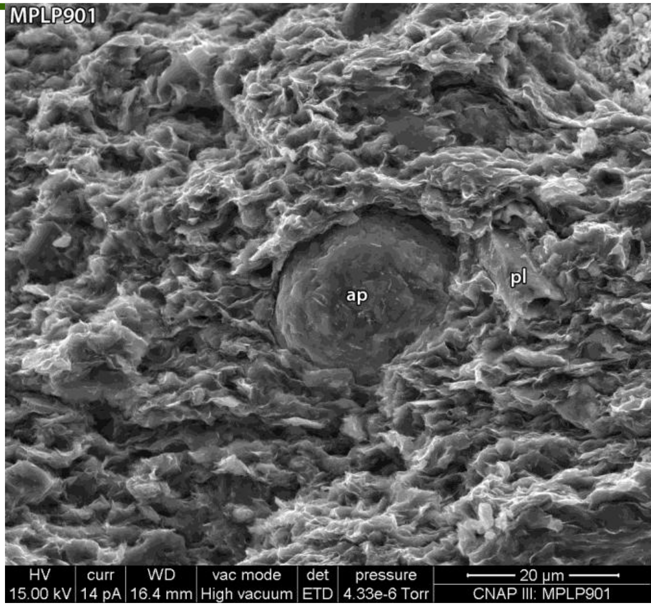
*Palygorskite and sepiolite (Mg-rich clay minerals were recently identified as “long-term”reaction products in >15 years experiments at the BGS reacting high-pH fluids with BVG rocks

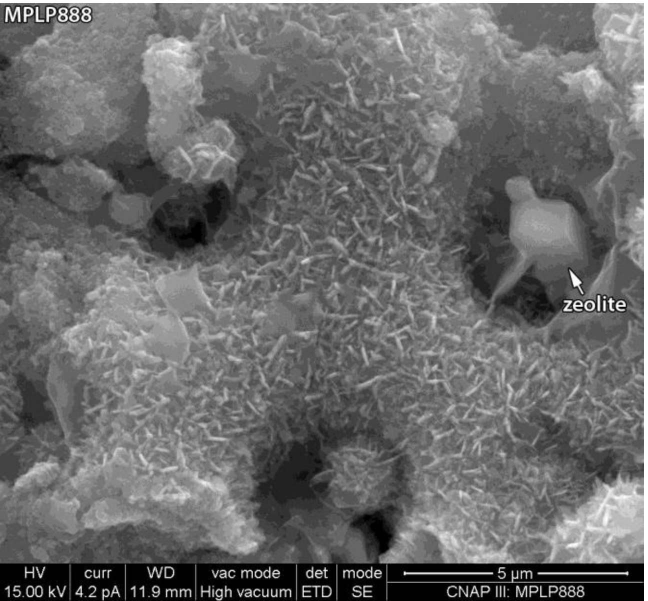
Petrography – Bentonite analogue -2



LEFT: Close-packed smectite

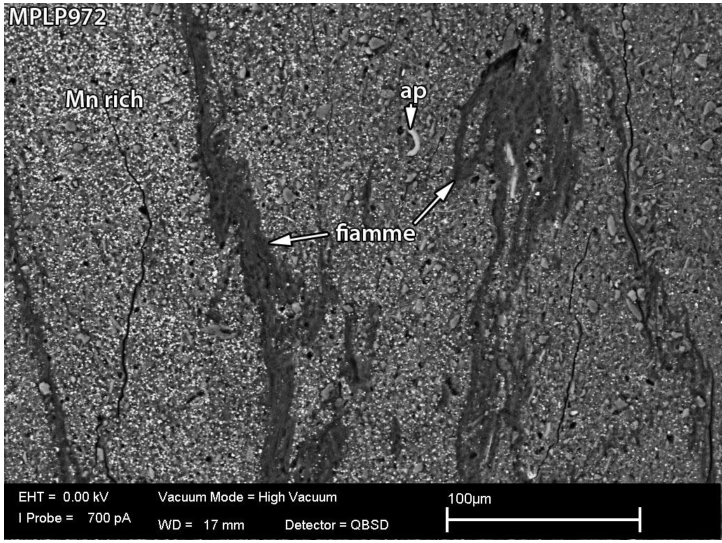
RIGHT: Detrital plagioclase in smectite matrix



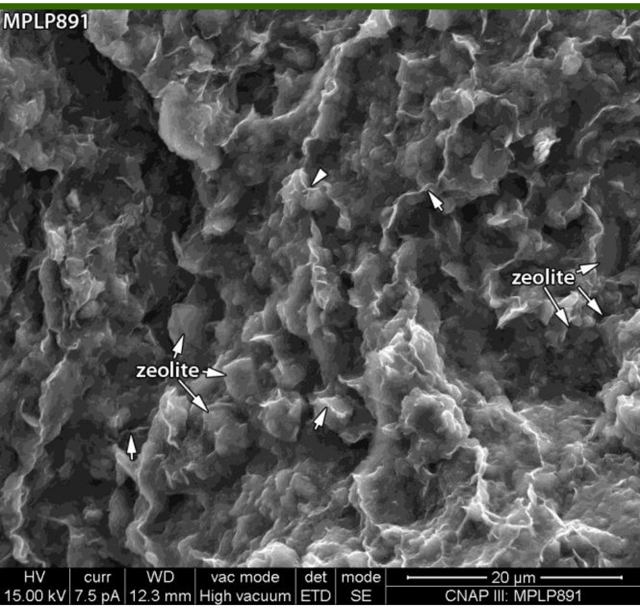


LEFT: Amorphous biogenic silica particle (radiolarian) being replaced by authigenic crystobalite and zeolite

RIGHT BSEM image of altered (smectite-replaced) fiammé (former glass shards) in smectite matrix

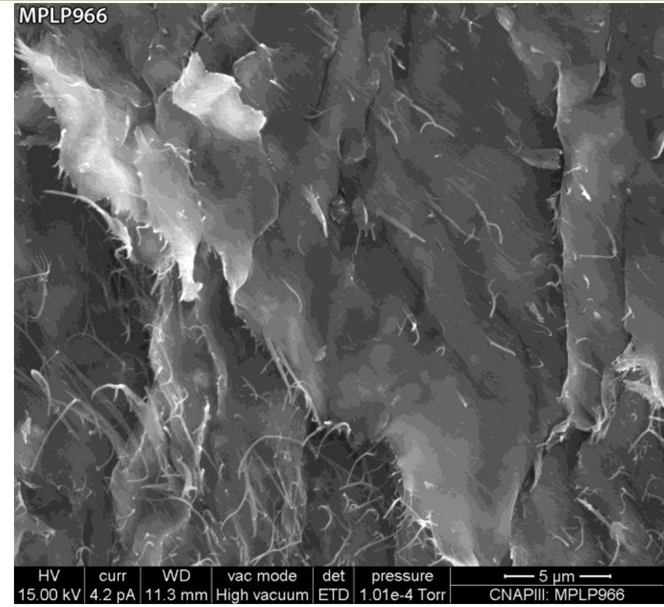


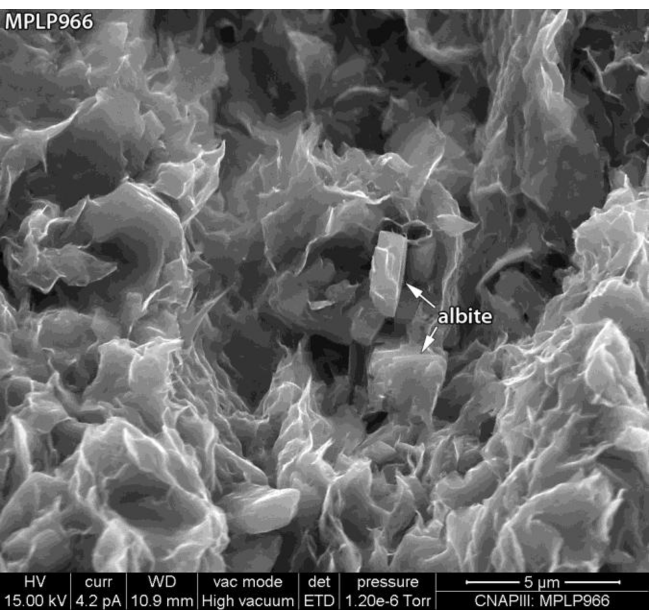
Petrography – Bentonite analogue -4



LEFT: Subhedral athigenic zeolites coated with fine secondary smectite

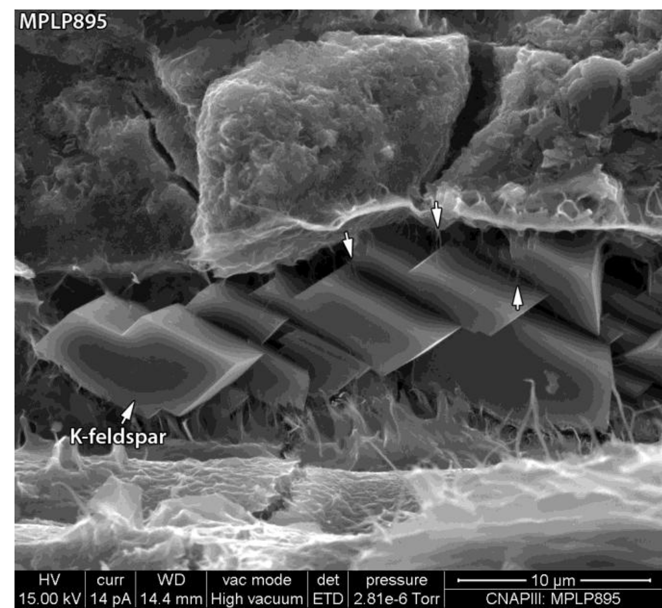
RIGHT: Sheets of smectite with fibrous palygorskite growing from smectite edges and surfaces





LEFT: Wispy smectite flakes with secondary fibrous projections of palygorskite

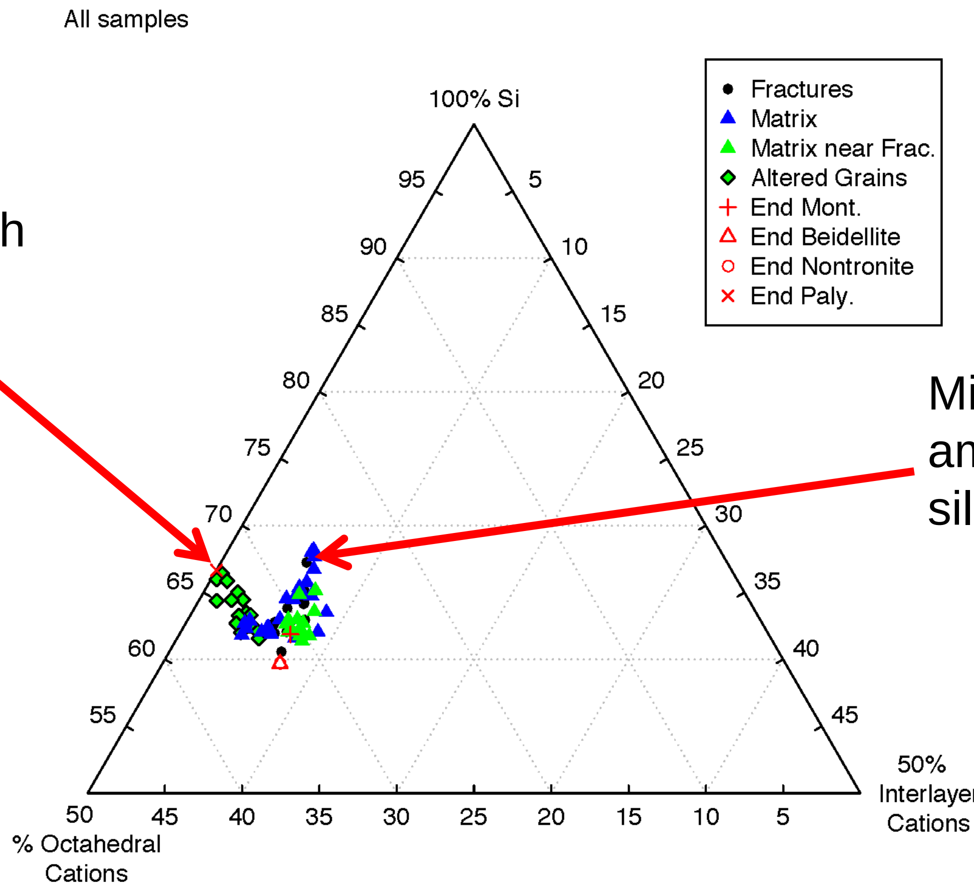
RIGHT Fibrous palygorskite nucleating from and partialy replacing smectite. Blocky secondary zeolite in dissolution cavity



Clay mineral compositions - 1

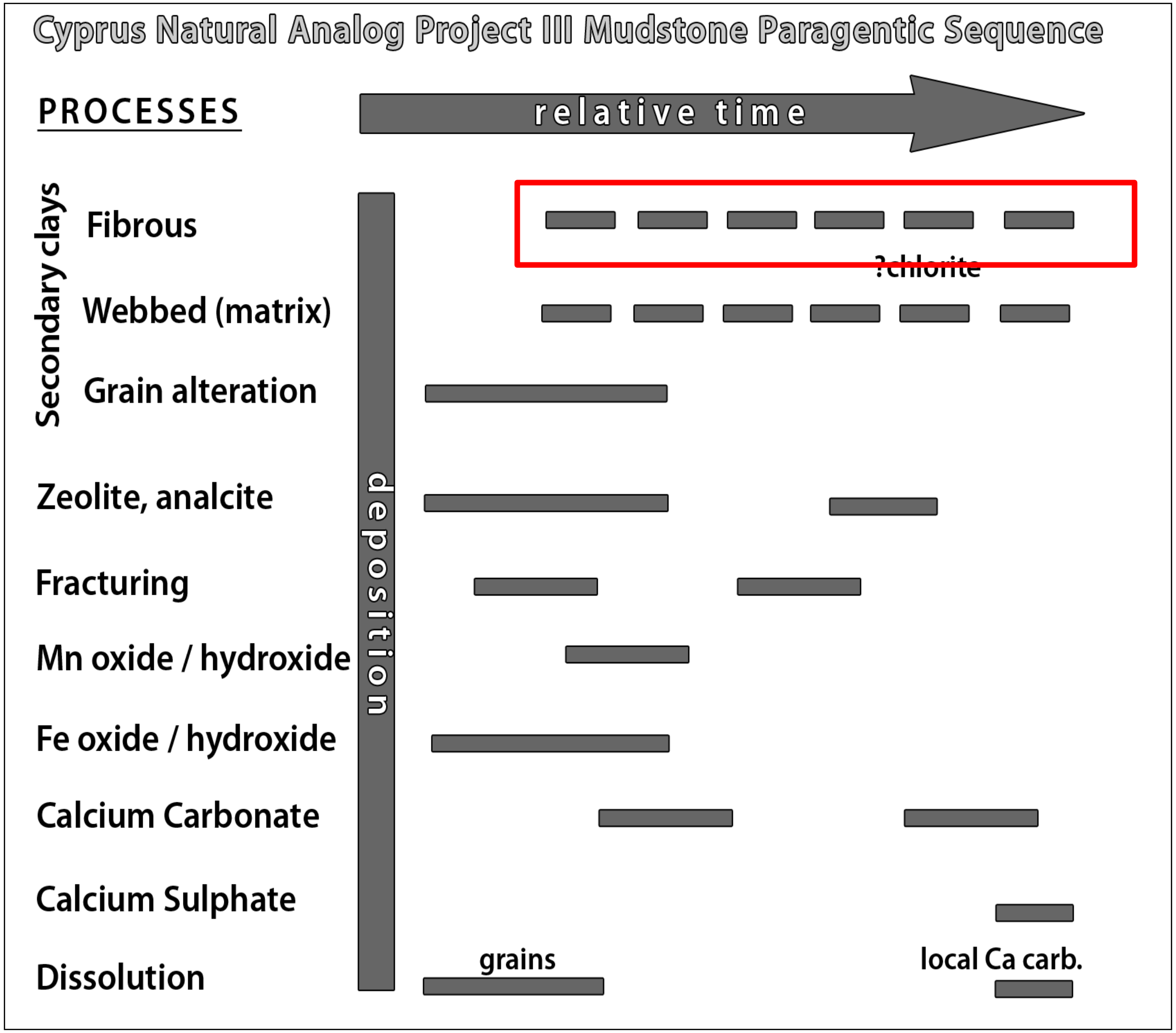
Triangular compositional plot of EDXA-EPMA data for *Si-octahedral cations-interlayer cations* for all clay in the bentonite

Mixed analyses with palygorskite



Mixed analyses with amorphous/biogenic silica

Paragenesis



Palygorskite

Bentonite in Cyprus

	MX-80 %	Kunigel VI %	Parsata %
Montmorillonite	65-75	46-49	17-40 (+ 18-53% amorphous)
Quartz	10-14	0.5-0.7	Trace
Amorphous silica	-	37-38	10-20
Feldspar	5-9	2.7-5.5	trace
Mica and chlorite	2-4	-	trace
Carbonate	3-5	4.1-5.4	trace
Analcite Zeolites	- -	3.0-3.5 -	trace 2-15
Heavy minerals	1-3	0.5-0.7	trace

Conclusions

- **The results suggest that there has been some reaction (smectite-to-palygorskite transformation) in the bentonite, probably due to alkaline groundwater**

- **However, it is not yet possible to rule out a hydrothermal alteration (U/Th/Ra will help as other hydrothermal events were early)**

- **reaction from infiltrating surface waters seems unlikely as the bentonite appears to be very tight (could be tested)**

Conclusions

- **Reaction of bentonite is restricted to close to the PLV and very close to fractures**
- **This is probably not due to a limited supply of OH^-,**
- **Probably more likely due to very tight bentonite**
- **It is possible that the smectite-to-palygorskite transformation is a fast reaction (**cf. BIGRAD batch experiments
- **Palygorskite is a common authigenic clay mineral in "alkaline lake" environments, evaporative soil environments (where alkaline pH implicated), serpentinisation alteration in modern oceanic floor)**

Recommendations 1

- Some simple permeability measurements could be carried out on bentonite carefully sampled in soil-sampling boxes in a new trench immediately adjacent to the Parsata trench
- Samples could be collected at several distances vertically from the PLV to assess the actual in-situ permeability and if this varies much throughout the bentonite
- This would allow a better comparison between the data collected at Parsata and the environment in a repository bentonite buffer or barrier

Recommendations 2

- Open vs closed laboratory bentonite/hyperalkaline fluid experiments using material from Parsata for comparison with the results from sites such as Searles Lake
- This will help to put the more numerous work from open systems into perspective for the repository safety assessment as the repository will be more akin to a closed syste
- Establish links between calcite precipitated from alkaline groundwater (Allas Springs) and secondary precipitate in Parsata (?stable isotopes to differentiate processes)


Thank you for your attention