Cyprus Natural Analogue Project: what are the benefits to NDA-RWMD?

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GEOSCIENCES multidisciplinary consultancy BEDROCK

British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

NDA
Nuclear Decommissioning Authority

Acknowledgements

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GEOINVEST

SUERC
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Project objectives

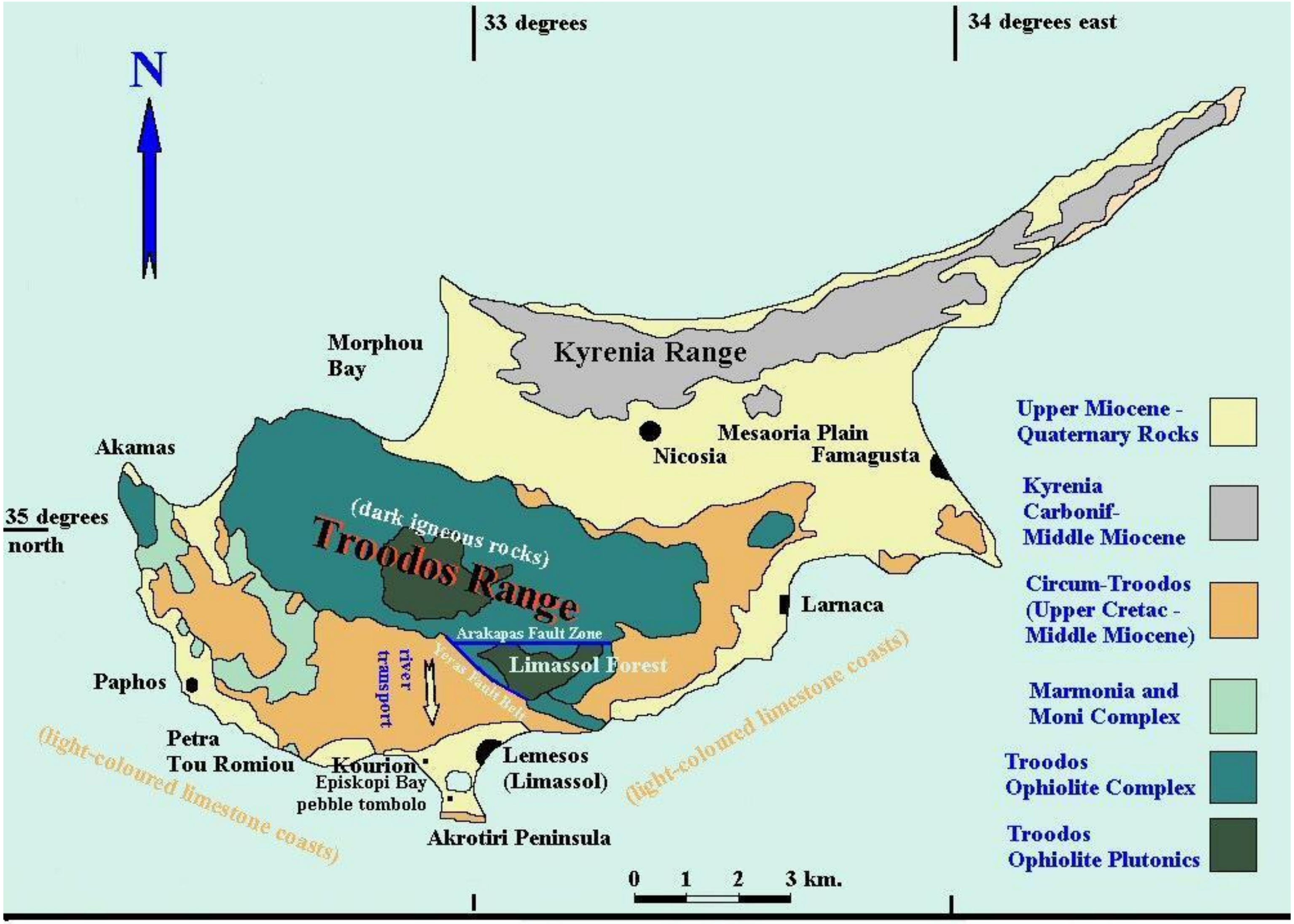
When compared with previous NA projects (cf. Miller et al, 2000), CNAP was focussed on one main objective, namely:

- **assessment of long-term bentonite reaction in leachates from low alkali cements**

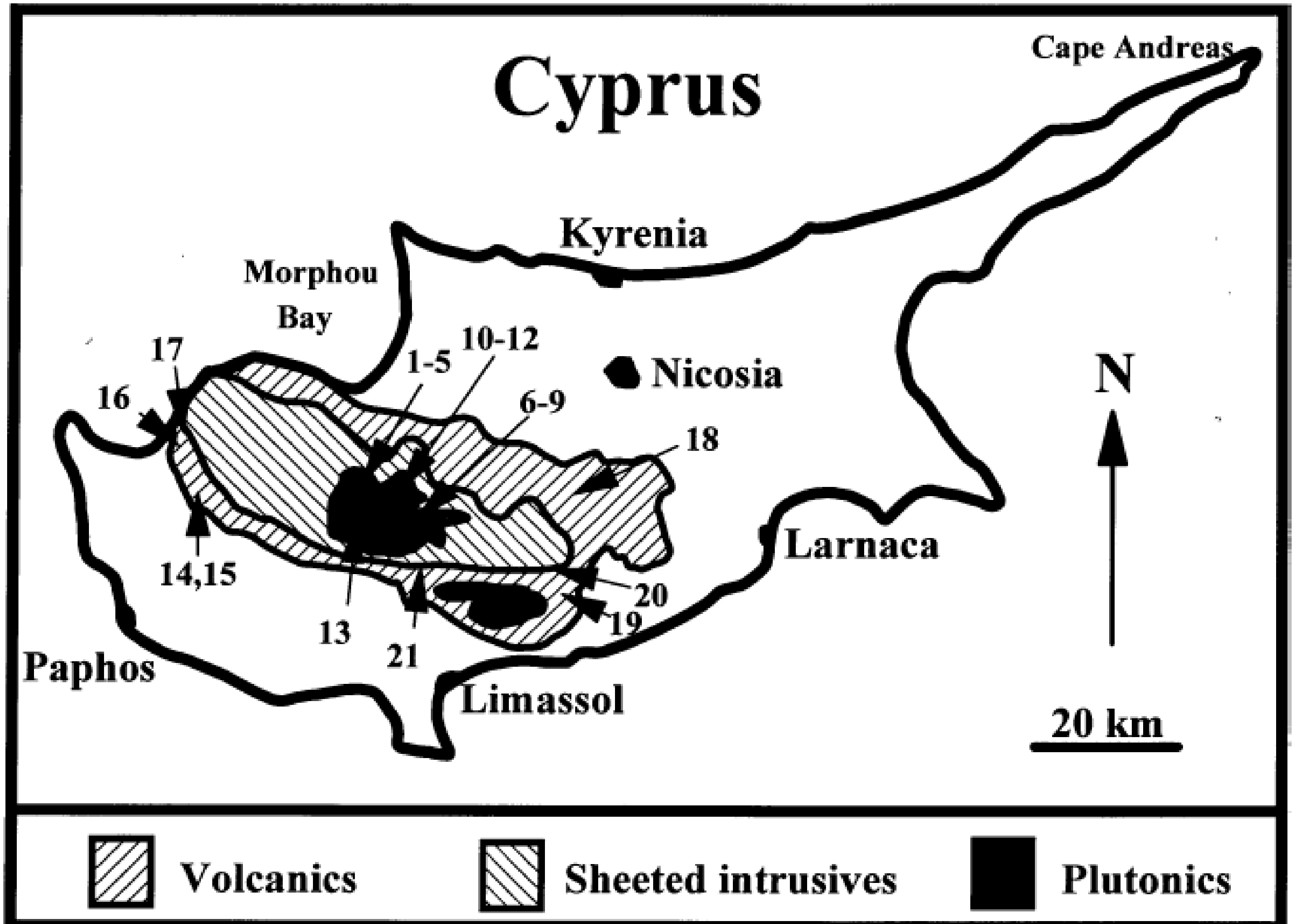
The aim was to assess the degree of bentonite reaction, where possible define the reaction products and assess how any reaction would impact bentonite's well established favourable properties for isolation and containment of the waste

Supporting project aims included estimating the time of reaction and integrating the results with ongoing laboratory and URL projects (LCS) and modelling studies

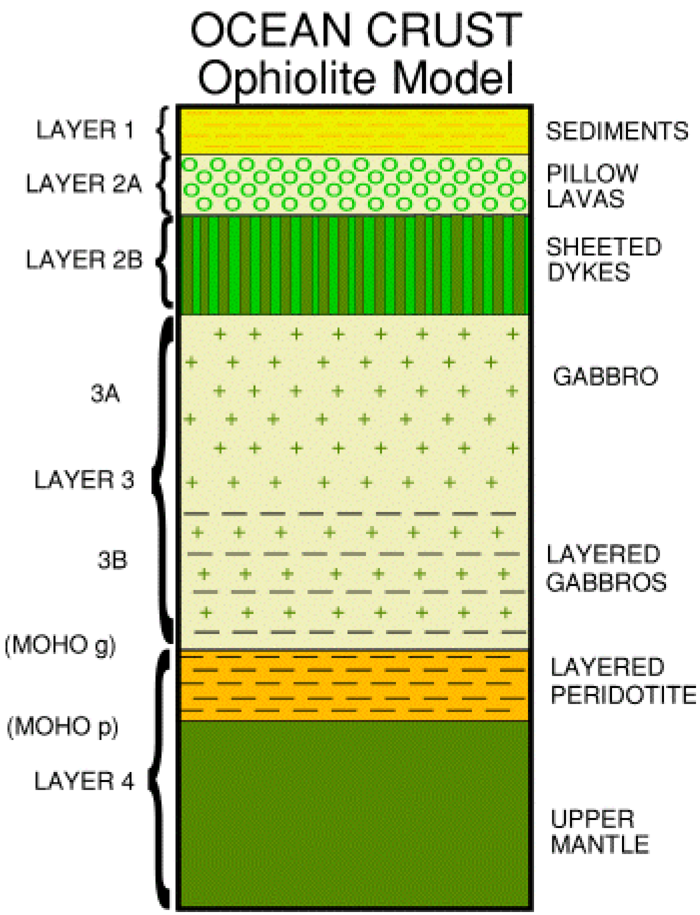
Overview of the geology of Cyprus



Alkaline groundwater sources



Background – model ophiolite



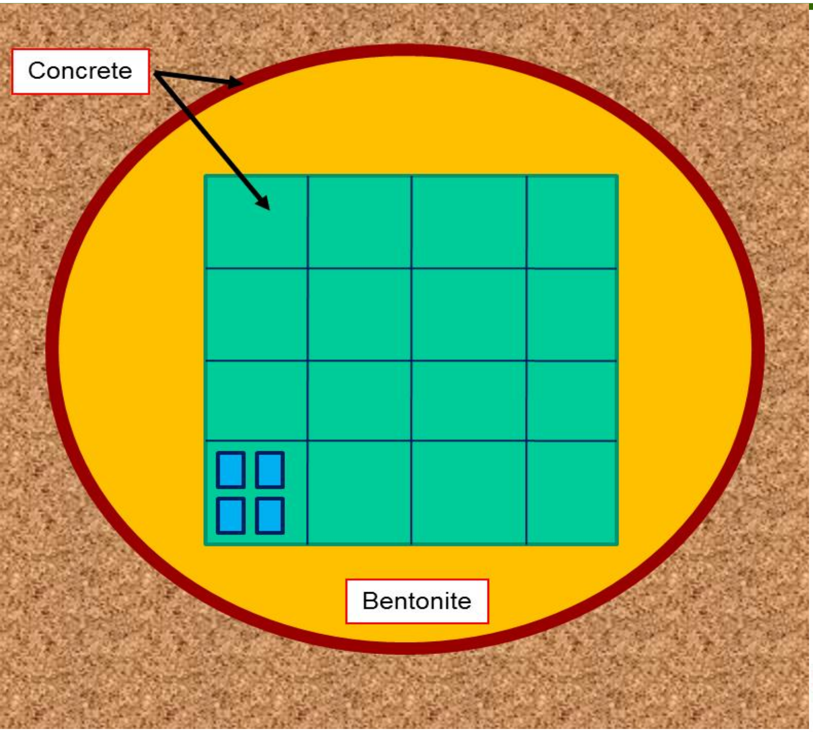
Main reaction pathways to serpentine involve olivine ($(Fe,Mg)_2SiO_4$)* interaction with $CO_2 \rightarrow$ serpentine ($Mg_3Si_2O_5(OH)_4$)

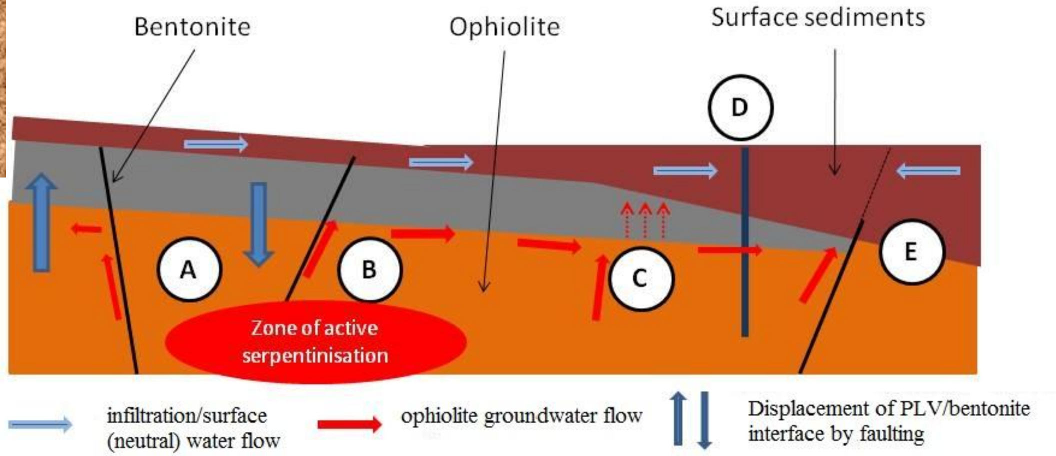
Additional products can include:

- 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

What’s the analogy?





A - active serpentinisation of the ultramafics both locally and at depth producing alkaline groundwater and hydrogen and methane
B - high pH groundwater under bentonite, neutral groundwater above it with diffusive transport of both into the bentonite
C - interaction of high pH groundwaters with the base of the bentonite and diffusion of high pH front into the bentonite with ongoing cation exchange
D - borehole P1 through bentonite and into PLV, borehole P3 at PLV/bentonite interface, boreholes P2, P4 and P5 in the surface sediments
E - dispersed release of high pH groundwaters into deeper sediments

Hyperalkaline groundwater sources

CNAP hydrochemistry – Phase II and III

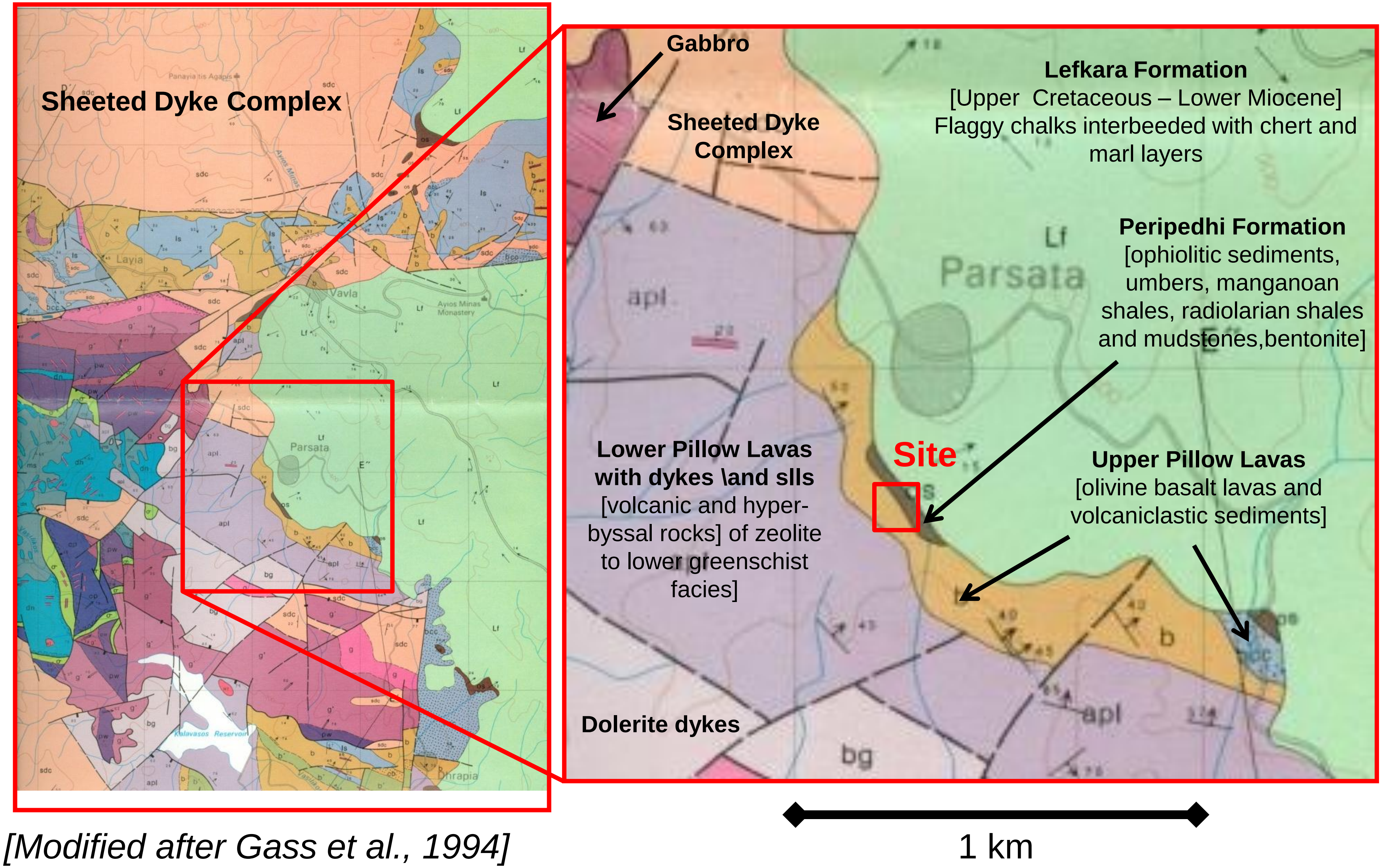
Sample	Field pH	Lab pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}
P1-2010a	nd	11.1	48.3	0.11	96.5	1.34	5.40	nd	80.9	149	<0.200
P1-2010b	nd	11.1	50.1	0.11	97.2	1.39	7.20	nd	85.6	159	<0.200
P1-2010c	nd	11.1	48.8	0.10	95.0	1.35	9.00	nd	85.1	158	<0.200
P1	11.42	10.3	36.5	0.021	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

Bentonite in Cyprus

Mineral phase	MX-80 %	Kunigel VI %	Parsata %
montmorillonite	87	46-49	17-40
Quartz	3	0.5-0.7	trace
Biogenic silica	-	-	18-53
Chalcedony	-	37-38	-
Feldspar	3	2.7-5.5	1-2
Mica and chlorite	4	-	3-4
Carbonate	-	4.1-5.4	1-2
Analcime	-	3.0-3.5	-
Heavy minerals	0.2	0.5-0.7	-

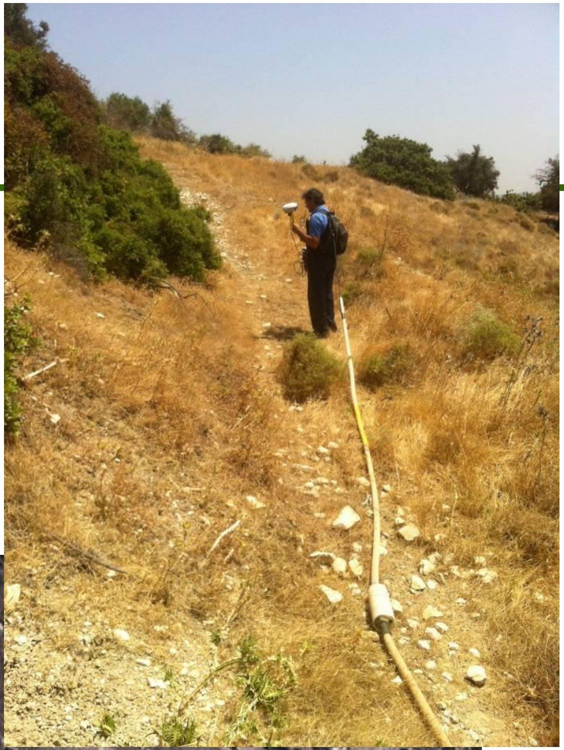
Sampling site - Parsata abandoned village


Geology of the Parsata site



[Modified after Gass et al., 1994]

Parsata sampling site



Parsata sampling sites

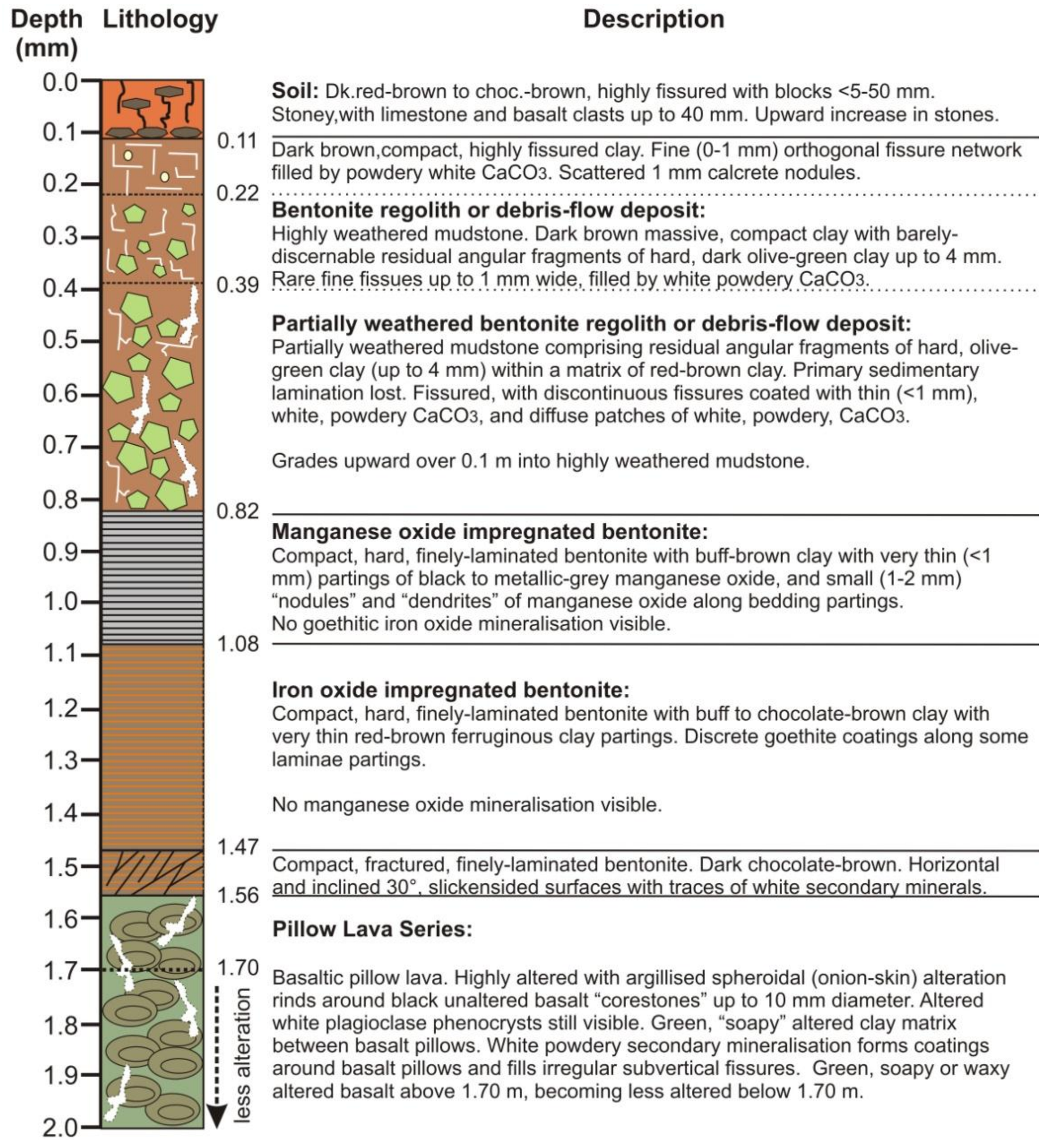
Parsata sampling sites

Parsata sampling sites

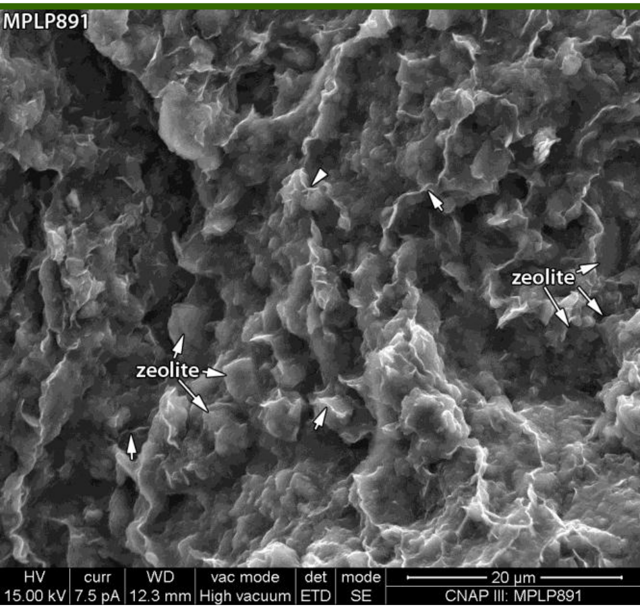
Trench 4, sampling transect T4-2

Trench 5, background bentonite

Parsata trench – lithological sequence

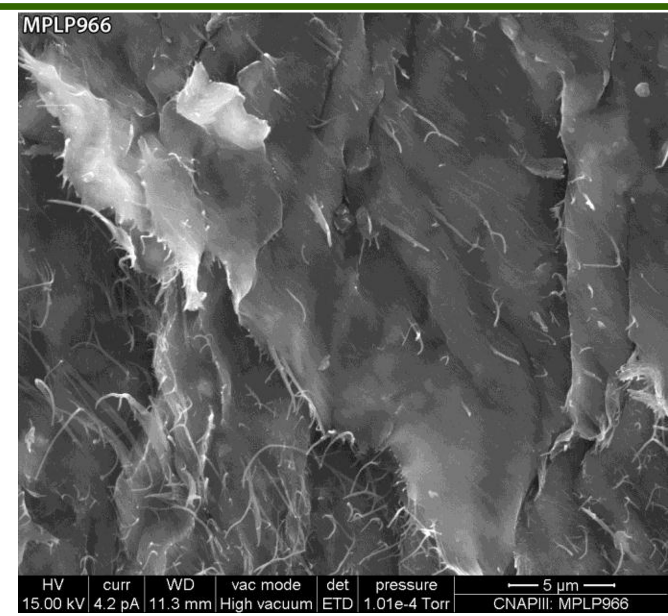


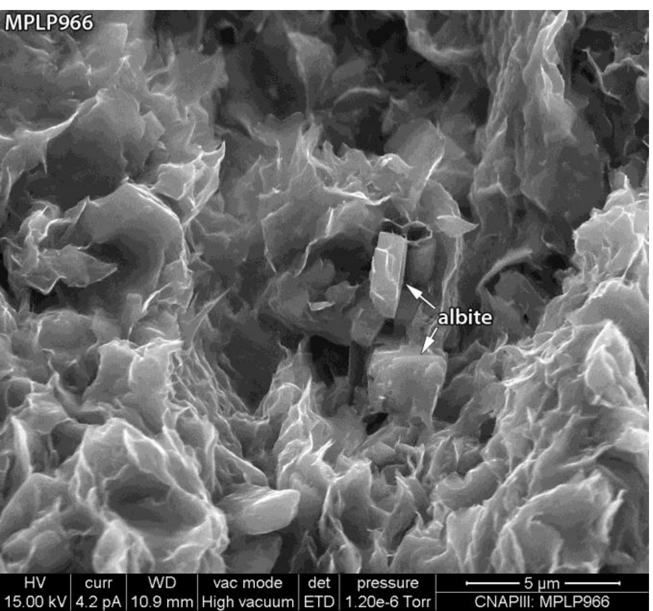
Petrography – bentonite reaction



LEFT: Subhedral authigenic zeolites coated with fine secondary smectite

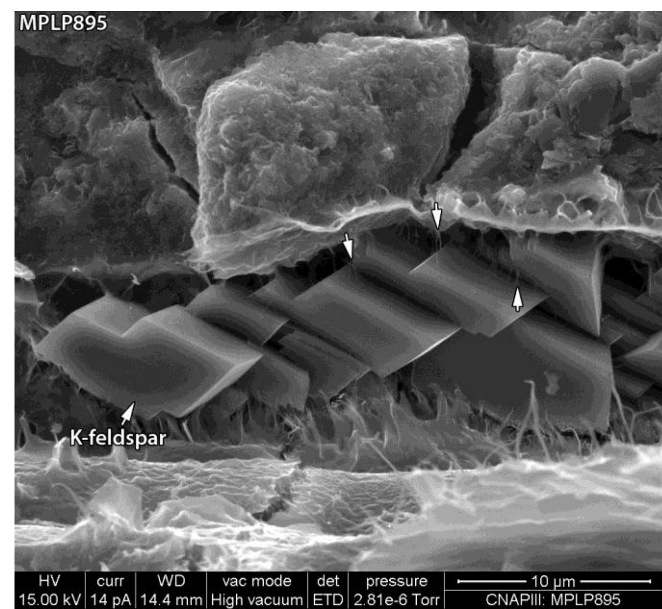
RIGHT: Sheets of smectite with fibrous palygorskite growing from smectite edges and surfaces





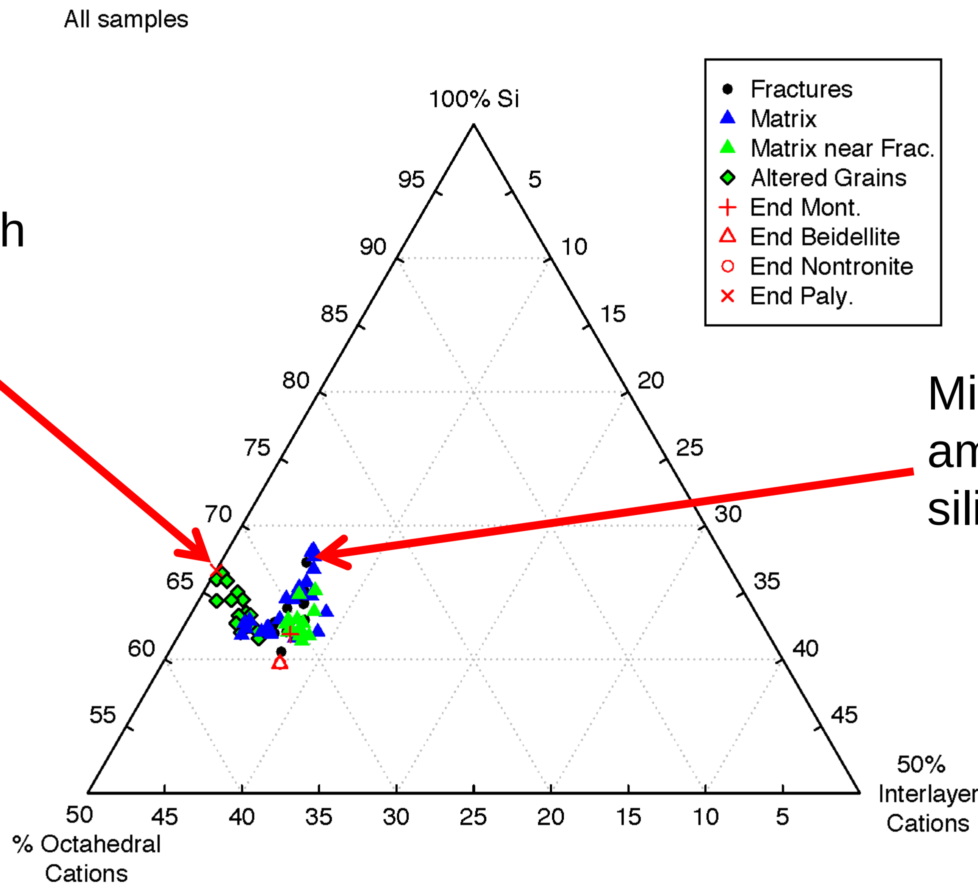
LEFT: Wispy smectite flakes with secondary fibrous projections of palygorskite

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



Clay mineral compositions - 1

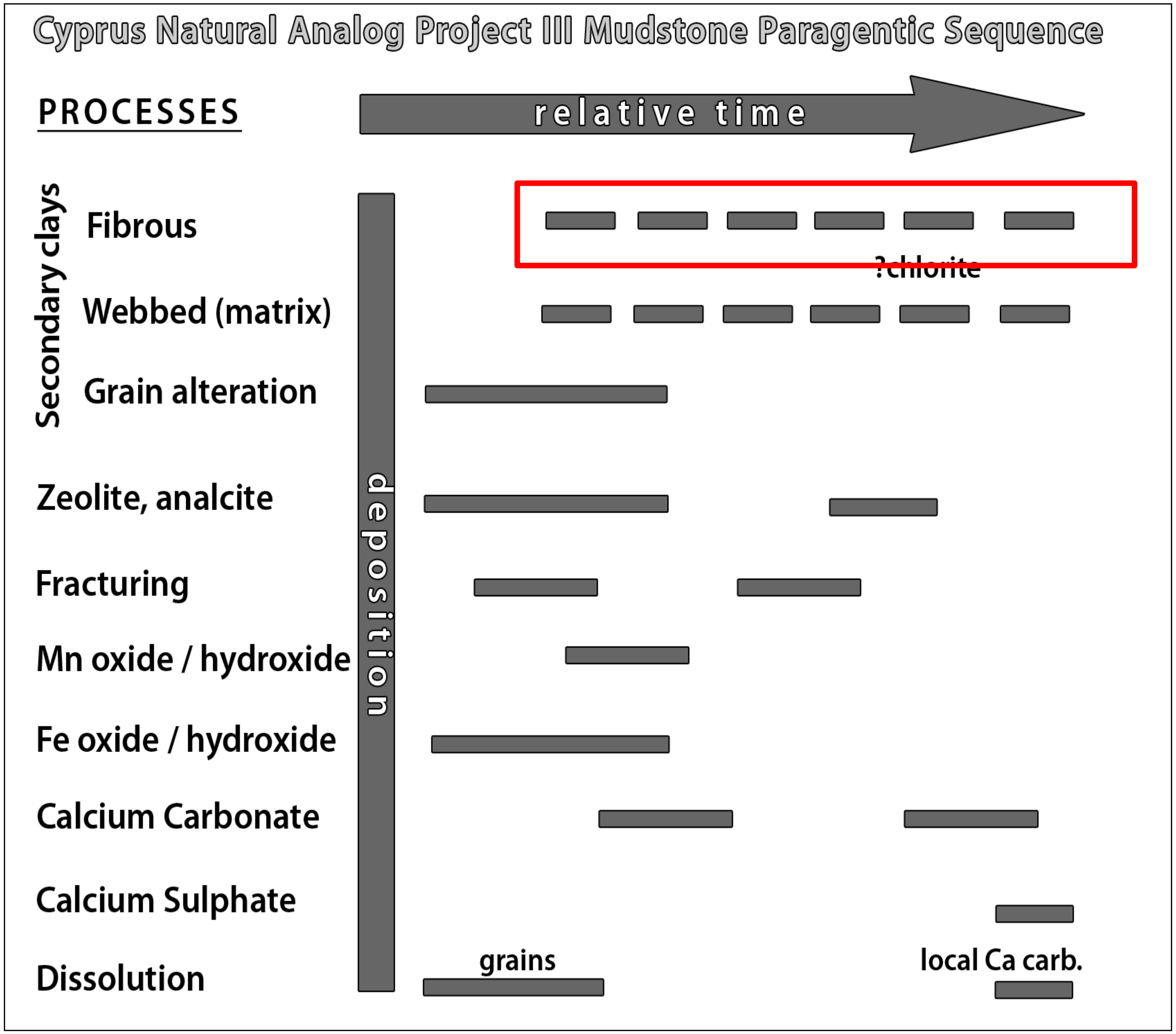
Triangular compositional plot of EDXA-EPMA data for *Si-octahedral cations-interlayer cations* for all clay in the bentonite



Mixed analyses with palygorskite

Mixed analyses with amorphous/biogenic silica

Paragenesis



Palygorskite

Technical conclusions

- **the natural bentonite was shown to have undergone minimal reaction in the natural alkaline groundwaters (pH 11, dropping to pH 9 at a site of ongoing reaction due to pH buffering)**
- **it is difficult to estimate the degree of reaction because it can only be observed in very limited zones (i.e. at the base of the bentonite where the high pH groundwaters are in contact with it and along a few minor fractures), but it is a <u>maximum</u> of 1% of the total mass of the bentonite**
- **the secondary reaction product is palygorskite, a well known breakdown product of smectite when it is exposed to alkaline conditions (e.g. in soils, lakes etc)**
- **using two, independent methods, the high pH groundwaters have been shown to have been in circulation beneath and in contact with the base of the bentonite for a period of 10^5 years. This implies very limited reaction of the bentonite over repository-relevant timescales**

CNAP Benefits

Why ask?

CNAP Benefits

4.1 How has CNAP helped focus NDA-RWMD's R&D requirements?

- **4.1.1 Wasteform and container evolution**
- **4.1.2 Near-field evolution**
- **4.1.3 Geosphere and its evolution (4.2)**
- **4.1.4 Radionuclide behaviour**
- **4.1.5 Design development**
- **4.1.6 Public and stakeholder engagement (4.5)**

4.2 How has CNAP helped focus NDA-RWMD's Geosphere Status Report

4.3 How has CNAP helped focus HMG's MRWS process

4.5 Use for stakeholder communications

4.6 Scientific value: papers and reports

4.1 How has CNAP helped focus NDA-RWMD's R&D requirements?

overarching impact will be that any future studies on low alkali cement leachate reaction with bentonite will be able to use the CNAP data as a touchstone due to the fact that:

- **the system studied is highly representative of the repository environment, even if the nature of the natural bentonite is not exactly the same as the industrial bentonite in the EBS in some properties. It remains, nevertheless, highly analogous**
- **the chemistry of the natural groundwaters is analogous to low alkali cement leachates, especially in the OH^- and Ca^{2+} contents, two of the main drivers of reaction in the bentonite**
- **the timescales of bentonite/low alkali leachate reaction (in the order of 10^5 years) are directly repository relevant**

4.1 How has CNAP helped focus NDA-RWMD's R&D requirements?

- thus, although the observations of minimal change to the bentonite following some 10^5 years of reaction is a highly positive result, the importance is more that the above points engender confidence in the results

- more, they mean that CNAP acts as a boundary condition against which the relevance of future laboratory and modelling studies of low alkali leachate/bentonite reaction can be adjudged

4.1.1 Wasteform and container evolution

- CNAP has provided a clear indication that if low alkali cements are used for structural support and/or seals, any bentonite which is used as a container overpack or tunnel backfill should not degrade significantly due to interactions with cement leachates over the initial period of the repository evolution
- That so little of the bentonite at Parsata has reacted (much less than 1%) over a period of some 10^5 years, suggests that the bentonite overpack will protect the waste and canister for periods much greater than this timespan, so allowing wasteform and container design optimisation
- Indeed, depending on the specific wasteform and disposal design, this information could also be used to guide backfill optimisation where reaction with low alkali leachates is deemed likely

4.1.2 Near-field evolution

- **Bentonite CEC indicates presence of diffusion-driven high pH front some distance from the basal reaction zone**

- **Shows no relationship to mineralogy, suggesting that the bentonite buffer capacity is such that low alkali cement leachates have had little overall impact on the bentonite, indicating the system is robust over the 10^5 years timescales of the CNAP system**

- **Work from the open (and advective) system at Searles Lake reports different reaction products, may be a reflection of the very low solid/liquid ratio of this system and the massive flux of reactants. The repository environment would appear to be much better represented by the CNAP (and Philippine) study and so more weight should be placed on these results than from systems which are very far from representing the repository environment**

4.1.2 Near-field evolution: saline reaction

deep (abyssal) marine sediments, including natural bentonites

pillow lavas (basalt)

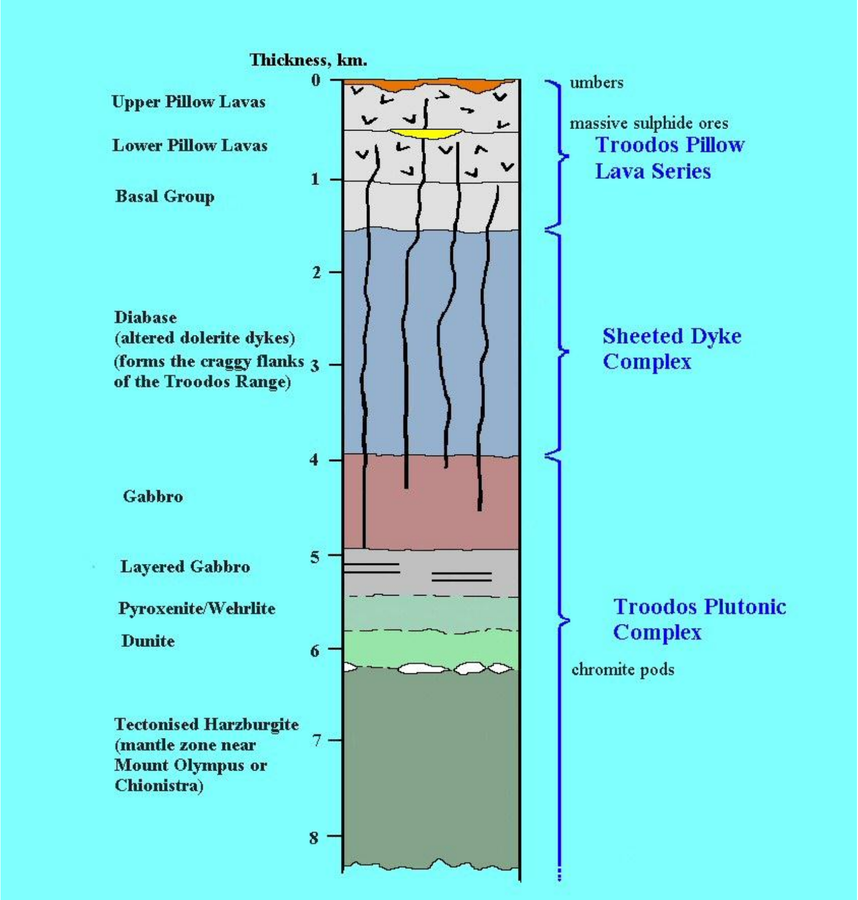
sheeted dyke complex

high level/isotropic gabbro

layered mafic cumulates (gabbro)

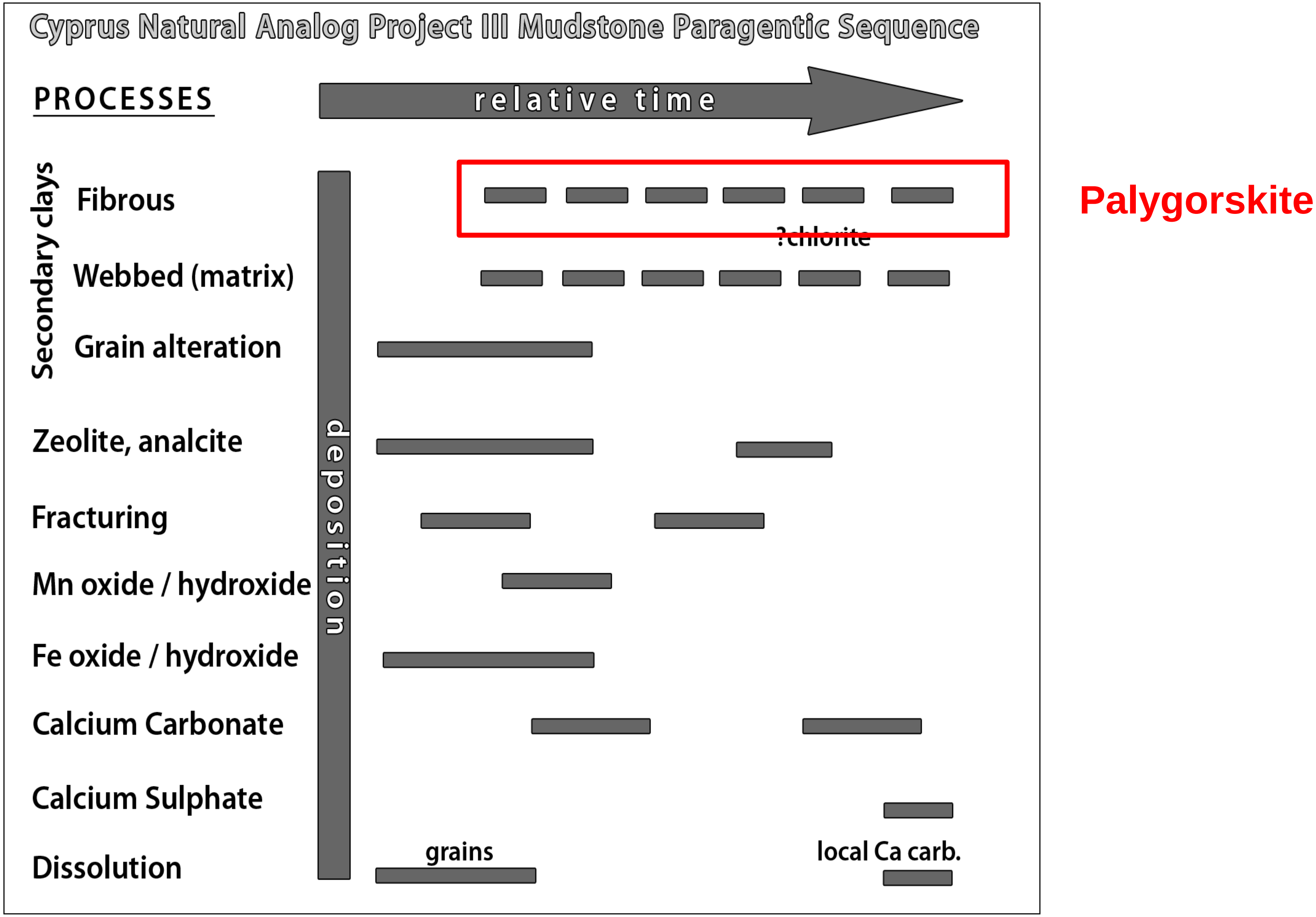
layered ultramafic cumulates

transition zone dunites and residual peridotites



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

4.1.2 Near-field evolution



Bentonite at the Parsata site is 90.4 Ma old

Age (Ma)			Formation	Lithology
2.0	Pleistocene		'Fanglomerate' Apalos Kakkaristra Athalassa	Conglomerates and Sandstones, Calcarenite, Sandstones, Conglomerates
5.2	Pliocene			
			Nicosia	Marls, Silts, Muds, Sandstones, Conglomerates
23.3	Miocene	Upper	Kalavasos	Evaporites
			Pakhna	Reefal and Bioclastic Limestone
		Middle		Pelagic Chalks, Marls, Calcarenites, Conglomerates
		Lower		Reefal and Bioclastic Limestone
35.4	Oligocene		Upper Lefkara	Pelagic Chalk and Marls
56.5	Eocene		Middle Lefkara	Massive Pelagic Chalks
65.0	Palaeocene			Pelagic Chalks, Replacement Chert
74.0	Maastrichtian		Lower Lefkara	Pelagic Chalks
83.0	Campanian		Kannaviou	Volcaniclastic Sandstones, Bentonite
90.4	Turonian		Peripedhi	Umbers, Radiolarites , Bentonites
Ophiolitic Basement				

4.1.4 Radionuclide behaviour

- ***"We need to understand how much radionuclides will be released into the water. This will depend on the chemistry of the near-field groundwater and the stability of the wasteform under these conditions. …R&D that we carry out …closely related to the area of wasteform research, where we study the stability and longevity of the wasteform"***
- **This being the case, the points noted in section 4.1.2 are relevant here too**
- **However, the results of indicate that, although the basic integrity of the bentonite has not been compromised by reaction with the alkali leachates, there has been some impact on the bentonite porewater chemistry (as reflected in the CEC changes) so any radionuclides retarded by exchange reactions could be impacted**
- **So assessment of radionuclide retardation on bentonite should take into account the changed cation occupancy when investigating repository designs which include low alkali cements**

4.2 How has CNAP helped focus NDA-RWMD's Geosphere Status Report - 1

- *"We have a good understanding of the expected mineralogical changes that will occur when …pH 12 water contacts the surrounding rock, such as formation of secondary CSH phases. …Our understanding of the effect of interactions between rocks and lower-pH water (in the pH range 10–11) is also less well-developed."*

- **What we clearly see is pore blocking with tufa – this will also happen with bicarbonate in fractures and porewaters at depth**

4.2 How has CNAP helped focus NDA-RWMD's Geosphere Status Report - 2

- ***"Modelling of the interactions between higher strength rocks and high pH waters has identified some circumstances in which the porosity in the ADZ may increase. …..Although these are thought to be minor short-term effects, it may not be possible to rule out localised short-timescale adverse effects."***

- **The results of CNAP would tend to suggest that such a scenario is irrelevant in the case of low alkali cement leachates, with pore clogging being much the likely reaction when bicarbonate containing groundwaters are present in the repository host rock**

4.2 How has CNAP helped focus NDA-RWMD's Geosphere Status Report – 3 - What next?

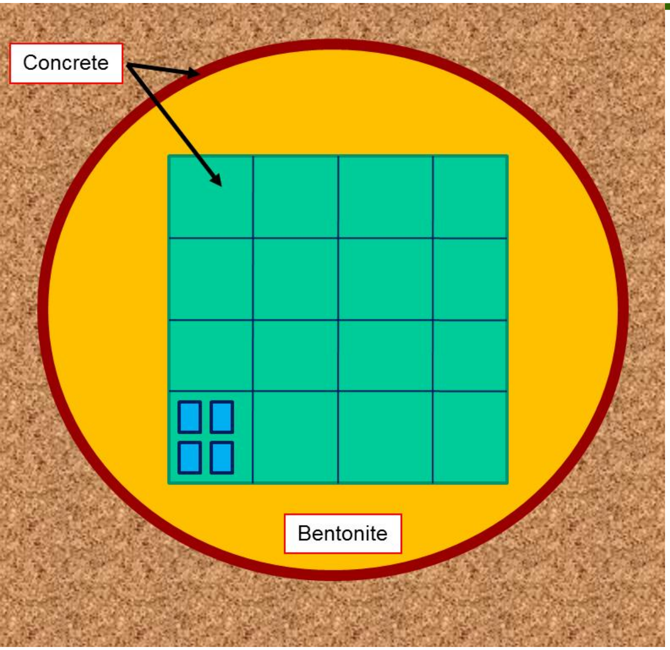
- **To date, no attempts have been made to conduct a detailed analysis of potential interaction between cement leachates and a repository host rock, but preliminary studies have been carried out by:**
- **Nagra: potential site at Wellenberg, assuming reaction with OPC leachates (Alexander and Mazurek, 1996)**
- **Posiva: ONKALO with OPC leachates (Alexander and Neall, 2007) and low alkali cement leachates (Soler, 2010; Soler et al. 2011)**
- **SKB: Forsmark, OPC leachates in detail, low alkali cement leachates in less detail (Sidborn et al., 2013)**

4.2 How has CNAP helped focus NDA-RWMD's Geosphere Status Report – 4 - What next?

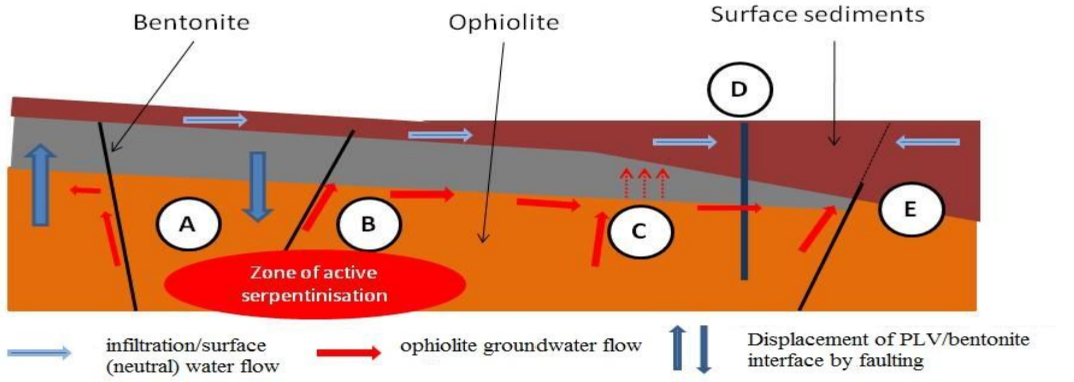
- **Although not a focus of CNAP, collateral information collected as part of the project confirms observation from the other sites noted above that porespace clogging, with the attendant impact of groundwater flow systems, is likely in some form**

- **scoping studies could be carried out in advance of site characterisation to produce likely scenarios of the types already produced in other national programmes to assess likely impacts on an UK host rock**

4.5 Use for stakeholder communications - 1



Simple concept, easier to get across to a non-technical and technical audience



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E - dispersed release of high pH groundwaters into deeper sediments

4.5 Use for stakeholder communications - 2

Also have the advantage of beautiful and intersting site and nice machines to play with...

4.5 Use for stakeholder communications - 3

And, if desired, site visits are easy (4-5 hours from UK) and cheap (out of season)

Talking of cheap, CNAP – how much?

Phase	Cost (€)	
I	15790	
II	107900	
III	163559	
IV	192305	
Total	479554	¥61.8 million
Per partner	~160k	~¥20.6 million

- From 2009 until present (final report under review)

Limitations of the analogy

- It must be emphasised that sites such as Parsata are no more than an analogy of a repository, not a copy, and hence certain differences are inevitable

- The natural bentonite is not a precise copy of the industrial bentonite: it cannot be as an industrial bentonite is a natural bentonite which has then been treated to a range of artificial enhancements (much like brown hair which has been bleached blonde)

- Nevertheless, the basic material is the same and should, in most circumstances, behave similarly

Last word - publications

For such a short-term, low budget project, CNAP has already produced a wealth of reports and scientific papers

- **W.R.Alexander and A.E.Milodowski (2008). Low-alkali cement leachate/bentonite interaction natural analogue study. Cyprus Natural Analogue Project (CNAP) Phase I. Bedrock Geosciences Technical Report BG08-01, Bedrock Geosciences, Auenstein, Switzerland.**
- **W.R.Alexander and A.E.Milodowski (2009). Cyprus Natural Analogue Project (CNAP) Phase II Reconnaissance Trip Report November-December 2008 Bedrock Geosciences Technical Report BG08-02, Bedrock Geosciences, Auenstein, Switzerland.**
- **A.E.Milodowski, W.R.Alexander, C.A.Constantinou, M.Rigas, C.Tweed, P.Sellin, P.Korkeakoski, S.J.Kemp and J.C.Rushton (2009). Reaction of bentonite in low-alkali cement leachates: Preliminary results from the Cyprus Natural Analogue Project (CNAP). Proc. ICEM'09 Conference, Liverpool, UK, October, 2009, ASME, Washington, USA.**
- **W.R.Alexander and A.E.Milodowski (*eds*) (2011). Cyprus Natural Analogue Project (CNAP) Phase II Final Report. Posiva Working Report WR 2011-08, Posiva, Eurajoki, Finland.**
- **W.R.Alexander, A.E.Milodowski and A.F.pitty (*eds*) (2011a). Cyprus Natural Analogue Project (CNAP) Phase III Final Report. Posiva Working Report WR 2011-77, Posiva, Eurajoki, Finland.**
- **W.R.Alexander, A.E.Milodowski, C.A.Constantinou, M.Rigas, C.Tweed, P.Sellin, P.Korkeakoski and I.Puigdomenech (2011b). Reaction of bentonite in low-alkali cement leachates: results from the Cyprus Natural Analogue Project. Proc. ICEM 2011 Conference, Reims, France, September, 2011, ASME, Washington, USA.**
- **W.R. Alexander, A.E. Milodowski, A.F.Pitty, S.Hardie, P.Korkeakoski, M.Rigas, P.Sellin and C.Tweed (2012). Reaction of bentonite in low-alkali cement leachates: results from the Cyprus Natural Analogue Project. Extended abstract *in* Proc. Conf. Geological Disposal of Radioactive Waste: Underpinning Science and Technology for Radioactive Waste 18 - 20 October 2011, Loughborough, UK. Mineralogical Magazine, December 2012, Vol. 76(8), pp. 149–152.**
- **W.R.Alexander and A.E.Milodowski (*eds*) (2013). Cyprus Natural Analogue Project (CNAP) Phase IV Final Report. Bedrock Geosciences Technical Report BG13-02, Bedrock Geosciences, Auenstein, Switzerland.**
- **W.R.Alexander and A.E.Milodowski (*eds*) (2013). Cyprus Natural Analogue Project (CNAP) Phase IV Final Report. Posiva Working Report WR 2013-XX, Posiva, Eurajoki, Finland (*in press*).**
- **W.R.Alexander, A.E.Milodowski, A.F.Pitty, S.M.L.Hardy, P.Korkeakoski, S.Norris, I.Puigdomenech, M.Rigas and P.Sellin (2013a). Bentonite reactivity in alkaline solutions: results of the Cyprus Natural Analogue Project (CNAP). Clay Mins (*in press*).**
- **W.R.Alexander, A.E.Milodowski and S.Norris (2013b). The contribution of CNAP to the understanding of bentonite reaction with low alkali cement leachates. Swiss Journal of Geosciences (*in prep*).**

Lastly, little friend…..