Proceedings of the 12th International Conference on Environmental Remediation and Radioactive Waste Management
ICEM2009
11-15 October, Liverpool, UK

ICEM09-16276

REACTION OF BENTONITE IN LOW ALKALI CEMENT LEACHATES: PRELIMINARY RESULTS FROM THE CYPRUS NATURAL ANALOGUE PROJECT (CNAP)

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ABSTRACT

Bentonite is a key component in many designs for radioactive waste repositories. The plasticity, swelling capacity, colloid filtration, low hydraulic conductivity, high retardation of key radionuclides and stability in relevant geological environments all make bentonite an ideal barrier/buffer material. However, bentonite is chemically unstable under higher pH conditions and this is a potential problem for repository designs which mix cement and concrete with bentonite barriers. The hyperalkaline (pH~13) leachates from the cement are expected to cause alteration of the bentonite. Low alkali cements produce lower pH (around 10-11) leachates and it is expected that this will slow bentonite reaction (or even stop it altogether) over the timespan of relevance to repository safety. Unfortunately, it has proven extremely difficult to study these very slow reactions in the laboratory so an alternative approach, that of studying natural analogues of the reaction process, has begun in Cyprus. In this paper, preliminary details of this new investigation of long-term bentonite reaction in the natural hyperalkaline groundwaters of the Troodos ophiolite in Cyprus are presented. Here, groundwater pH values of 10.0 to 11.9 have been reported, falling into the range typical of low-alkali cements that are presently being developed for use in radioactive waste disposal. The aims of this stage of the project were to identify likely sites of hyperalkaline groundwater/bentonite reaction and assess the relevance of the current site conceptual model. Preliminary groundwater and petrographic data for one group of related sites where hyperalkaline groundwaters are present are also discussed.

INTRODUCTION

Bentonite is a key component of the engineered barrier system in the disposal concepts developed for many types of radioactive waste. The choice of bentonite results from its favourable properties (including plasticity, swelling capacity, colloid filtration, low hydraulic conductivity, high retardation of key radionuclides) and its stability in relevant geological environments. In addition to bentonite, significant amounts of cement and concrete will also be used in a repository, either in construction or as part of the engineered barrier system. Cementitious materials will react with groundwater to produce hyperalkaline leachates, initially with with pH >13 but later falling to around pH 12.5; see, for example, Haworth et al., 1987). However, bentonite is unstable under hyperalkaline conditions and may react with the hyperalkaline leachates. This has driven recent interest in low alkali cements, because the pH of the leachate is somewhat lower than standard OPC (Ordinary Portland Cement), lying around pH 10-11(see U.Vuorinen et al., 2005, for example). It is hoped that this lower pH will reduce, or even eliminate, bentonite degradation, so allowing the use of low alkali cements in close proximity with bentonite.

Assuring the long-termed stability of bentonite in contact with such hyperalkaline fluids under conditions representative of a deep geological repository requires complementary laboratory, modelling and *in situ* studies. In particular, to build a robust safety case, it is important to have supporting natural analogue data to confirm understanding – and validate models – of the likely long-term performance of bentonite (see discussion in Miller et al., 2000).

In general, natural analogue studies can:

- Provide information on alteration rates, the products of such alteration and their safety-relevance to the performance of the engineered barrier system
- Allow testing of current models and databases used to assess such alteration
- Provide input to a range of supporting documents for safety cases

However, due to the extremely slow reaction kinetics of bentonite reaction in low alkali cement leachates (see the discussion in Metcalfe and Walker, 2004), in this particular case, natural analogues would appear to be the only viable method of studying bentonite reaction. As a result of a review of the available literature (e.g. Neal and Shand, 2002, Christidis, 2006) and recent geological investigations by the authors, several sites in Cyprus were selected as particularly promising for this purpose; preliminary field investigations this year confirmed the presence of hyperalkaline springs (with a pH of 10-12) in the vicinity of bentonites and clay-rich soils at a wide range of sites in Cyprus (see Figure 1).

Here, the overall concept is presented and hydrochemical and petrographical data from one related suite of sites where hyperalkaline groundwaters have been identified are presented. Data on bentonite reaction will be presented elsewhere (Alexander et al., 2009) following analysis of representative samples.

NATURAL ANALOGUE CONCEPT

Although systems representative of leachates from both OPC (i.e. groundwaters with pH 12.5 and above) and low alkali cements (groundwater pH of 10 to 11) have previously been examined as natural analogues of cementitious repositories, neither produced data of relevance to the questions now being posed with regard to low alkali cements. For example, the natural cements in Jordan are closely representative of OPC-based materials (see Alexander, 1992; Linklater, 1998; Smellie, 1998; Pitty, 2009), so the pH is too high for the current purpose. An appropriate low alkali water chemistry was studied in Oman (McKinley et al., 1988), but this project did not include any investigation of bentonite/leachate reaction.

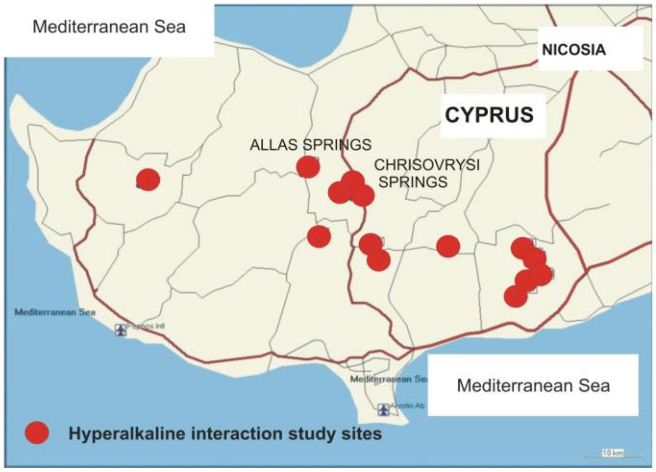

FIGURE 1: PRELIMINARY INVESTIGATIONS HAVE IDENTIFIED OVER A SCORE OF RELEVANT SITES IN SOUTHWEST CYPRUS.

There are a number of locations worldwide where such an analogue might be found, including Oman (e.g. Neal and Stanger, 1983; Anraku et al., 2009, this session), California (e.g. Barnes and O'Neill, 1969), Bosnia (e.g. Derkovic, 1973) Papua New Guinea (e.g. Barnes et al., 1978) and the Philippines (e.g. Alexander et al., 2008a,b; Vargas et al, 2009, this conference). Based on a multi-attribute analysis, considering factors such as probability of finding suitable locations with hyperalkaline groundwaters and bentonite together, relevance to European national radioactive waste disposal programmes, logistics (including ease of travel and cost-effectiveness) Cyprus was chosen as the focus for this new study.

Currently, the technical focus is on finding appropriate sites where the following items could be examined:

- long-term bentonite stability in contact with water analogous to low alkali cement leachates
- if possible, same system as above interacting with seawater/brines for a coastal repository
- if possible, same system as above interacting with a range of leachate chemistries as the precise situation in a repository will depend both on the site conditions and the composition of the cementitious materials – neither of which have been fixed as yet
- low alkali cement leachate/host rock interaction – is there any?

- can the gas (H_2 and CH_4) which is present in the groundwater/host rock system be studied as an analogy to repository gas transport?

GEOLOGICAL SETTING

All hyperalkaline groundwaters studied so far in Cyprus originate from the Troodos ophiolite or the Mamonia terrain (Figure 2). The term ophiolite was originally used by Brongniart (1813) for an assemblage of green rocks (serpentine, diabase) in the French Alps. Here, the nomenclature of the Penrose Conference of 1972 (Geotimes, 1972) has been adopted and, from top to bottom, consists of:

deep (abyssal) marine sediments (including bentonites)

pillow lavas (basalt)

sheeted dyke complex

high level/isotropic gabbro

layered mafic cumulates (gabbro)

layered ultramafic cumulates (herzbergites)

transition zone dunites and residual peridotites

If any of the above lithologies is missing, it should be correctly be called an ophiolite *complex*, but this term is frequently misused in the literature. The hyperalkaline pH values (generally between pH 10 and 11, but ~12 has been reported, see below) observed in the groundwaters are a product of the serpentinisation of the ophiolites, a reaction which has several possible pathways with the exact reaction pathway depending on Mg content of the precursor olivine/pyroxene or serpentine product, CO_2 fugacity, water-rock ratio, Ca^{2+} content of groundwater, etc.

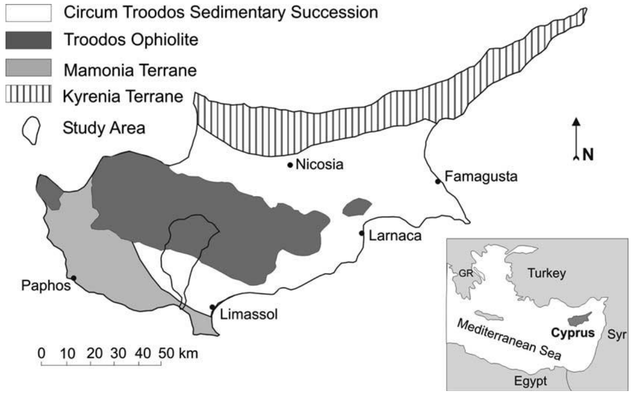

FIGURE 2: MAIN TERRAINS IN CYPRUS (FROM BORONINA ET AL., 2003)

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

- high to medium temperature alteration
- low temperature precipitation

The former often shows itself in the form of pervasive serpentinisation of the entire mantle sequence (as is the case in much of Cyprus) 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 (1)

which fixes the upper temperature of serpentine formation at ~500°C (Moody, 1976). In addition, serpentinisation may occur at slightly lower temperatures (down to ~180°C at atmospheric pressure), but as this is associated with the original alteration on the seabed, it is considered no further here. Of more relevance to the conditions of meteoric groundwater circulation of interest here is low temperature serpentinisation (e.g. Barnes and O'Neil, 1969; Barnes et al., 1972). 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 groundwaters (see Table 1). The partial reactions may be expressed as (but see also alternatives in Moody, 1976):

olivine dissolution

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

forsterite serpentine (2)

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

fayalite (3)

pyroxene dissolution

$$2H_2O + 3MgSiO_3 \rightarrow Mg_3Si_2O_5(OH)_4 + SiO_2 \qquad (4)$$

$$H_2O + FeSiO_3 \rightarrow Fe(OH)_2 + SiO_2 \qquad (5)$$

$$H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2OH^- + SiO_2 \qquad (6)$$

precipitation

$$3(Mg^{2+} + 2OH^-) + 2SiO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + H_2O \qquad (7)$$

along with the groundwater components

$$Mg^{2+} + HCO_3^- + OH^- \rightarrow MgCO_3 + H_2O \qquad (8)$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O \qquad (9)$$

Of course, without full petrological details and kinetic information, the total reaction equation is always indeterminate. Nevertheless, from the viewpoint of the cement leachate analogy, it is worth noting that:

- the fluid output contains low Mg and SiO_2, regardless of the input water chemistry, so they are conserved within the system
- equation 7 involves a balance between Mg (from equation 2) and the input groundwater, with SiO_2 derived from equations 3 to 6 – so serpentine precipitation is buffered by differential olivine-pyroxene dissolution
- hydroxide is produced in equations 2, 3, 5 and 6, but the (Mg^{2+} + $2OH^-$) of equation 2 is consumed in equation 7, 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 in equations 8 and 9, giving rise to aragonitic, calcitic, dolomitic, magnesitic secondary carbonates and output groundwaters dominated by Ca-OH-Na-Cl compositions

TABLE 1: HYDROCHEMISTRY OF HYPERALKALINE GROUNDWATERS: EXAMPLES FROM AROUND THE WORLD FOR COMPARISON WITH THE CYPRUS GROUNDWATER DATA AND LOW PH CEMENT LEACHATES. ALL DATA IN PPM.

Location	pH	Na	K	Ca	Mg	Cl
Cyprus[1]						
Cyprus 3a	11.5	385	15.1	1.0	0.3	420.0
Cyprus 3b	11.2	163.0	1.2	93.0	0.5	190.0
Worldwide[2]						
Greece	11.3	24.0	1.0	34.0	0.3	15.0
Bosnia	11.7	35.0	1.5	29.0	7.0	20.0
Oman	11.5	132	4.8	34.0	1.3	127.5
PNG	10.8	15.0	3.0	14.0	2.3	22.0
Western USA	11.5	19.0	1.0	40.0	0.3	63.0
Philippines[3]						
Manleluag 1	11.1	28.0	0.5	18.6	0.2	17.4
Manleluag 2	10.4	20.6	0.4	18.1	---	15.8
Poon Bato	10.9	18.4	0.9	33.1	0.05	20.9
Narra 1	10.8	158	0.9	3.1	0.0	95.0
Narra 3	10.3	157	0.9	2.4	0.1	80.0
Cement leachate[4]						
ALL-MR f63	11.0	42	7.3	20	<0.5	52
OL-SR f63	10.0	4400	150	4300	0.56	13000

1: Neal & Shand (2002) 2: Neal and Stanger (1983) 3: Alexander et al. (2008b) 4: Vuorinen et al., 2005

The serpentinite mineral assemblages are very strongly reducing and the hyperalkaline waters are often effervescent with H_2 and/or CH_4 gas. Some of the reaction pathways are also strongly exothermic, frequently producing hydrothermal groundwaters in some ophiolite terrains (cf. Vargas et al., 2009), although this seems to be the exception in Cyprus. It is immediately clear from Table 1 that there is a significant range in water chemistries present from ophiolites worldwide. However, this is a positive aspect because the precise situation in a repository will depend both on the site conditions and the composition of the cementitious materials – neither of which have been fixed as yet.

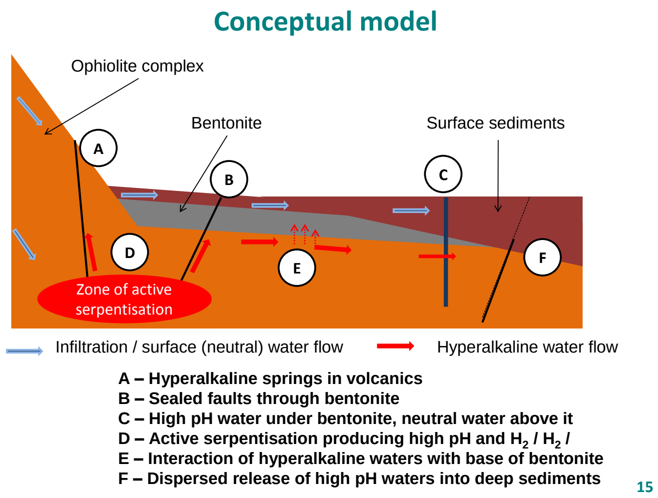

FIGURE 3: CONCEPTUAL MODEL OF THE HYPERALKALINE GROUNDWATER/BENTONITE INTERACTION (FROM ALEXANDER ET AL., 2008a)

Finally, it is worth noting that the bentonite layers at the top of the ophiolite can act as aquitards, isolating flow of deeper high pH waters from surface runoff (cf. Figure 3). This has been observed at the Zambales opholite in the Philippines (cf. Vargas et al., 2009) and, following two short field campaigns in Cyprus, would appear to be the same for the Troodos ophiolite. This means that drilling and/or trenching will be required in future to access most active sites of hyperalkline groundwater/bentonite reaction at the base of the bentonite layer.

SAMPLING SITES

Neil and Shand (2002) identified several sites with hyperalkaline groundwater and these data, supplemented by additional unpublished data of the Cyprus Geological Survey Department (GSD), were used to guide the preliminary site assesment and sampling campaign. As shown in Figure 1, 30 sites of relevance to low alkali cement leachate/bentonite reaction have been identified (and only lack of field time has prevented the identification of more). Of these, the hyperalkaline groundwaters in the vicinity of the Allas Springs area (sites 001 and 002 in Figure 1) are the most prolific. Here, the groundwater flow is fracture controlled and springs emit from both fractured harzbergites (from the layered ultramafic cumulates) and from the boundary of the harzbergites and the associated gabbros of the layered mafic accumulates. The springs themselves are easily discernable from the massive tufa deposits (Figure 4) which are produced when the Ca-saturated, CO_2-poor groundwaters equilibrate with the atmosphere, produced mixed calcium, magnesium and iron carbonates (calcite, aragonite, high-Mg calcite and pyroaurite).

In this area, 'true' bentonites are rare, but other clays and clay-rich soils which have been reacted with the hyperalkaline groundwater are currently under analysis (see Alexander et al., 2009, for details).

FIGURE 4: ALLAS SPRINGS, TROODOS OPHIOLITE, CYPRUS. THE SPRINGS ARE DISCERNABLE BY THE MASSIVE CREAMY-WHITE TO GREY TUFA DEPOSITS PRODUCED ON REACTION OF THE GROUNDWATERS WITH THE ATMOSPHERE (TREE IN THE BACKGROUND IS ~4M TALL). FROM ALEXANDER AND MILODOWSKI (2009)

RESULTS

Hydrochemistry

Groundwater analyses are now complete and a selection of the data is presented in Tables 2 and 3.

TABLE 2: HYDROCHEMISTRY OF SOME HYPERALKALINE GROUNDWATERS IN CYPRUS (FROM ALEXANDER AND MILODOWSKI, 2009)

Sample	Field pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}
A4-1	9.77*	3.20	58.7	747	31.4	152	1093	87.2
A4-2	9.90*	3.43	58.4	893	40.5	121	1342	106
A4-3	9.71*	3.37	58.8	921	40.7	154	1321	106
A5	9.8	1.34	64.2	224	9.76	307	346	27.7
A3	9.84	1.32	63.9	238	10.2	203	369	30.5
A2	9.69	1.61	65.5	172	7.33	232	254	22.8
A1-1	11.9	37.2	0.101	1435	63.1	272	2177	101
A1-3	10.01	12.2	0.554	1337	60.1	96.4	1926	114
A1-2	9.26	4.87	48.3	502	23.7	288	699	50.7
A1-4	9.78	11.2	5.73	1214	54.0	124	1748	78.5
A6	9.67	2.22	50.7	921	42.9	150	1383	97.0
C2	9.58	1.69	67.9	4.79	<0.5	255	8.361	3.207
C1	9.41	1.80	68.3	4.68	<0.5	309	8.486	3.272
C3	9.69	1.67	92.7	5.14	0.926	311	18.2	2.484

* Laboratory pH – field value likely to be at least 0.5 units higher

Two main groups of data are presented: those from Allas Springs (prefix A) and Chrisovrysi Springs (prefix C). Those from Allas Springs originate directly from spectacular, steep gulleys in harzbergite (i.e. the layered ultramafic cumulates part of the ophiolite) high on Mount Olympus and were sampled in the streams and thin soils downflow from the sources. There are a large number of samples from this area and they are grouped in related systems:

A4-1 to A4-3: This is the highest site, the spring (A4-1) emerging at the contact between the harzbergites and the overlying altered gabbros. The laboratory pH here is 9.77 (no functioning pH electrode was available during sampling), but by comparison with the other samples, the field pH is probably just >10. The water is not untypical for ophiolites (cf. Table 1), but the Na and Cl levels are somewhat high, possibly reflecting the presence of relict seawater in the host rock. Certainly the Br/Cl ration of this water is $2.2\text{x}10^{-3}$, somewhat lower than the seawater ratio of $3.3\text{x}10^{-3}$ (Kreitler and Bledsoe, 1993), but this may simply reflect loss of Br to microbial processes (e.g. Upstill-Goddard and Elderfield, 1988). Both Mg and K are somewhat higher than usual too. Samples A4-2 and A4-3 show indications of reaction along the flow path, both having lost Ca (presumably to the tufa precipitates), K, Na and Si and gained Mg. Interestingly, both also show significant gains of Cl, which might indicate other springs charging the stream from within the scree which covers much of the slopes (this could also explain the increased pH in A4-2). All three waters are oxidising, with the oxidant levels (e.g. NO_3^-) increasing with flow distance.

A5: This water seeps out of the scree/colluvium at the valley wall and so has presumably undergone some degree of reaction and chemical change from the original rock-buffered state. Nevertheless, the pH remains relatively high at 9.80 (field). It is a much less saline groundwater with lower concentrations of Ca and K, but higher Mg than A4-1.

A3: Is very similar to A5, but with a lower HCO_3^- concentration, presumably indicating less atmospheric interaction.

A2: Is very similar to A3, suggesting that their ultimate source under the scree is the same.

A1-1 to A1-3: A1-1 is the most saline sample collected yet and also has the highest pH at 11.9 (field value). This sample is collected immediately as it leaves a fracture in the harzbergite (see Figure 2.4) and is presumed to be correct as the electrode was set against pH 10 and 14 standards and the value is temperature corrected. The Ca is high and the Mg low, reflecting the fact that little atmospheric or sedimentary reaction has taken place. The Br/Cl ratio is 2.9x10, rather more close to the seawater ratio than any of the other Alles Spring samples, but the Na concentration is lower than seawater, reflecting reaction in the host rock. The chemistry of sample A1-3 reflects reaction in the soil and forest litter downhill from A1-1. Not surprisingly, the forest litter here is cemented with thick (20-30 cm) tufa deposits (see appendix 1 and comments in section 4.2). Sample A1-2, collected downflow of A1-3, shows signs of further reaction, including decreased pH, Ca, Na and K levels and higher Mg and bicarbonate. Interestingly, the overall chemistry of A1-2 is most similar to the A4 samples, clearly suggesting that they too have undergone interaction with the rock and scree.

A1-4: Is more saline (Cl=1748 mgL^{-1}) than A4-1 and has higher Ca, Na, NO_3^- and Br levels (although the Br/Cl ratio is the same as A4-1), possibly suggesting less reaction within the scree where it was collected. Compositionally, it lies between A1-2 and A1-3.

A6: Despite being collected the furthest away from the springs, sample A6 still shows clear signatures of its origin, with elevated pH, low Ca and high Cl concentrations. Interestingly, Schopka and Derry (2009) show that large rivers draining ophiolite ultramafics in the Philippines have consistently higher pH than those draining volcanic rocks in the area, hinting that these contributions may be important to defining water chemistry, at least on a local scale. Certainly, it proved possible to track down hyperalkaline seeps in the thickly forested slopes of the Zambales ophiolite in Luzon by following the pH trends in the small streams draining the area (Alexander et al., 2008a).

The Chrisovrysi Springs also originate in the same harzbergite as the nearby Allas Springs.

FIGURE 5: THE ORIGINAL SPRING AT SITE C2 (CHRISOVRYSI SPRINGS) IS UNDER THE OLD ROOF AND GROUNDWATER LOOKS TO HAVE FLOWED THROUGH THE SOILS AT THE SITE (NUMEROUS TUFA VEINS CAN BE SEEN THROUGH THE SOIL). FROM ALEXANDER AND MILODOWSKI (2009)

C1 to C3: Sample C1 is effectively the same as sample C2, so confirming the field observation that the C1 spring is probably supplied by the C2 cistern (see appendix 1). Both display high pH values (around 9.5) and low Ca concentrations, but these are likely to be due to storage for some time in the cisterns, so allowing some degree of atmospheric equilibration. The relatively high Mg concentrations imply some degree of reaction with the sedimentary cover before collection in the concrete cisterns and this is consistent with the original spring which seems to have flowed through the sediments and soils at the site before being captured by the cisterns in the 1960s (the cistern in the forefront of Figure 5 bears a 1962 date). Although physically close to the Allas Springs (only ~2 km apart), the high salinities which characterise the Allas area are absent in these waters.

Sample C3 is slightly removed from the cistern system and was collected from seeps into a stream. The water emerged from heavily altered serpentised harzbergite (serpentinite), so the chemistry and high pH (9.69 in the field) are not surprising. The chemistry is similar to that of C1 and C2, although the higher Mg may indicate more reaction with sediments at the sampling site. Interestingly, although the Cl concentration is low, the Br/Cl ratio (3.02×10^{-3}) is near that of seawater.

The stable isotope data (Table 3) tend to suggest that the precipitation altitudes are somewhat higher than the current springs and the all-sample regression line is $\delta D = 5.92 * \delta^{18}O + 4.99$ ($R^2 = 0.84$). In comparison, rainfall data for the Eastern Mediterranean show:

Kouris catchment, Cyprus (Boronina et al., 2005)
$\delta D = 6.6 * \delta^{18}O + 10.9$
Alexandria, Egypt (IAEA, 2005)
$\delta D = 6.56 * \delta^{18}O + 11.14$ ($R^2 = 0.90$)
Sidi Barrani, Egypt (IAEA, 2005)
$\delta D = 5.83 * \delta^{18}O + 10.10$ ($R^2 = 0.77$)

Jacovides (1979) and Boronina et al (2005) analysed 234 groundwaters from the Kouris catchment area in southern Cyprus and distinguished two water types:

- ophiolite samples with isotopically depleted groundwater
- overlying sediments with isotopically enriched groundwater

Within analytical uncertainty, they found that 52 % of groundwaters in the ophiolites and 10 % in the sediments fell on the local MMWL regression line. The rest of their samples were displaced below the local regression line around a line of a slightly smaller slope (m = 5.9), i.e. very similar to that observed for the all-sample line here.

TABLE 3: STABLE ISOTOPE AND TRITIUM DATA FROM THE SAMPLED GROUNDWATERS

Sample ID	$\delta^{18}O$	δ^2H	Tritium activity
	‰VSMOW	‰VSMOW	TU
A1-1	-6.99	-38.4	<1
A4-1	-6.80	-35.3	4.5 ± 0.4
C2	-7.59	-39.1	5.2 ± 0.4
C3	-6.56	-34.7	3.9 ± 0.4

The tritium data (Table 3) for sample A1-1 (sampled directly from a fracture in the harzburgite) suggests significant residence time for the hyperalkaline groundwaters. Unfortunately, directly relevant local data on the tritium content of precipitation are not currently available and these have to be accessed for a fuller assessment of groundwater residence times.

Petrography

Samples of host rock with conductive fractures and soil/sediment closely associated with hyperalkaline spring discharge sites were mineralogically and petrographically characterized by X-ray diffraction (XRD) analysis, optical petrography, secondary electron (SEM), and backscattered scanning electron (BSEM) microcopy supported by energy-dispersive X-ray microanalysis (EDXA).

Travertine deposits associated with the hyperalkaline spring discharge are composed predominantly of calcite with minor aragonite. They are characteristically finely laminated and microporous (Figure 6)

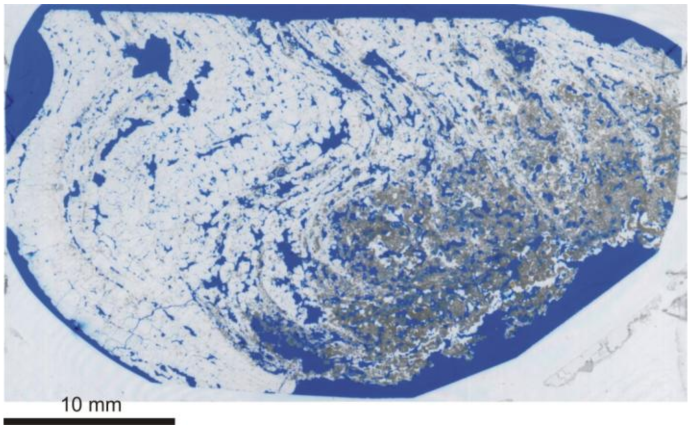

FIGURE 6: TRANSMITTED LIGHT PHOTOMICROGRAPH OF SECTION THROUGH TRAVERTINE FROM ALLAS SPRINGS (A1 SITE) SHOWING FINELY LAMINATED AND MICROPOROUS FABRIC.

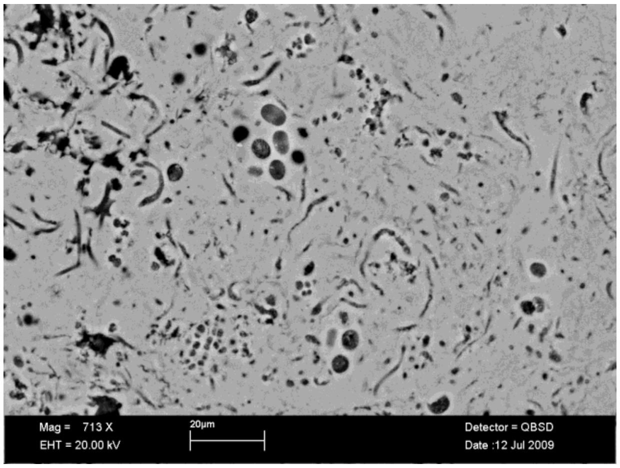

FIGURE 7: BSEM PHOTOMICROGRAPH ILLUSTRATING THE PRESERVATION OF BACTERIAL CELLS AND OTHER MICROORGANISMS WITHIN A1 SITE TRAVERTINE

At the A1 site, the travertine displays evidence of at least two distinct stages or types of calcium carbonate precipitation. The early stages of calcite was precipitated in close association with microbial activity and the development of biofilm. This appears to have partially desiccated and cracked, to be re-cemented by later calcite precipitation. The early-stage calcite preserves evidence of a microbial community comprising a variety of bacterial cells and other microorganisms (Figure 7) that appear to have been tolerant of the hyperalkaline environment at the A1 discharge site beneath the forest canopy.

Travertine from higher elevation at Allas Springs and at Chrisovrysi (A4, C2 and C3) show no evidence of microbial activity associated with the spring discharge site. This may reflect the absence of any soil development and consequently a lack of nutrients to sustain microbial activity in this area. However, the travertine from the A4 site contains occasional bands preserving fine spherical inclusions of altered aluminosilicate material (possibly smectitic) and spherical cavities after the dissolution of these features. These probably represent traces altered aerially deposited glassy volcanic ash particles that have been over the site possibly following following periodic volcanic eruptions within the Mediterranean area. These would appear to have largely dissolved by interaction with the hyperalkaline groundwater (Figure 8).

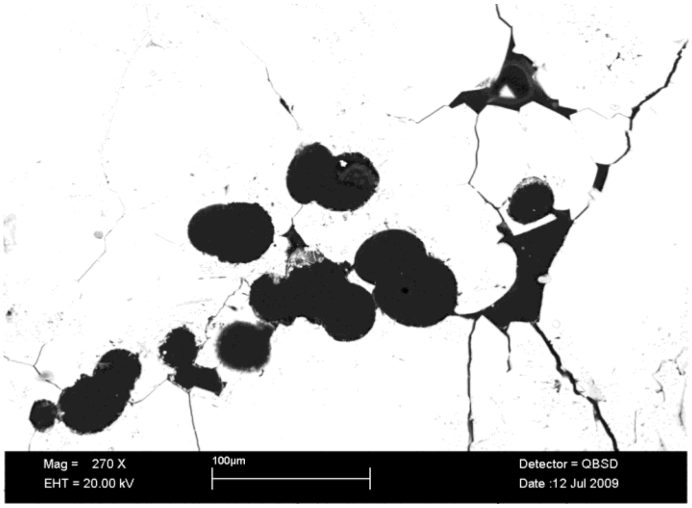

FIGURE 8: BSEM PHOTOMICROGRAPH ILLUSTRATING CAVITIES FORMED BY THE DISSOLUTION OF VOLCANIC GLASS SPHERULES INCLUDED IN THE A4 SITE TRAVERTINE

XRD and petrographical analyses of the altered fractured bedrock through which the Allas and Chrisovrysi springs discharge show that they are harzbergite, which has been virtually completely serpentinised. Only minor trace amounts of the primary orthopyroxene, olivine and garnet now remain, and the altered rock is composed largely of serpentine minerals (predominantly lizardite-1M and lizardite-1T). Although field observations suggested that the soils in contact within these groundwaters were clay-rich, subsequent XRD analysis has proved the “clay-grade” material to be largely composed of lizardite-1M and lizardite-1T. Little evidence of the presence of smectite or other clay minerals was found. The serpentine minerals are largely unaffected by the hyperalkaline groundwater, although occasionally the serpentine (lizardite) showed some minor exfoliation of the "clay" sheets, and minor dissolution cavities were observed in the fracture wallrock close to the surfaces in contact with the hyperalkaline groundwater. This suggests that some silicate mineral dissolution is actively occurring.

The most obvious mineralogical reaction with the hyperalkaline groundwater, observed within the associated fractured bedrock and within the soils and sediments (scree deposits), is the precipitation of carbonates. These are either forming as a result of interaction of atmospheric CO_2 with the hyperalkaline water, or through mixing of hyperalkaline water (from depth) with near surface bicarbonate-rich soil groundwater or porewater. Calcite is the principal secondary mineral present in these late fractures cutting the altered serpentinite surfaces The calcite may enclose or include euhedral crystals of an earlier Mg-Fe carbonate mineral (Figure 9) which can also be seen as fine crystalline coatings on the wallrock This Mg-Fe carbonate possibly corresponds to the small amount of pyroaurite identified by XRD in the bulk rock

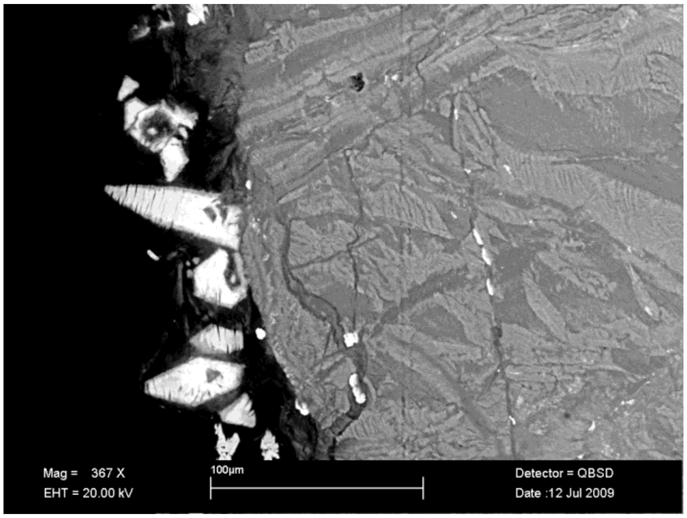

FIGURE 9: BSEM PHOTOMICROGRAPH SHOWING PYROAURITE NUCLEATED ON THE SURFACE OF A HYPERALKALINE GROUNDWATER-CONDUCTING FRACTURE IN SERPENTINITE FROM SITE C3.

DISCUSSION

The groundwater chemistries are fully relevant to the project aims, but it is clear that, in future, appropriate methodologies are required to obtain samples which have had no atmospheric contact. While simple sampling of springs and boreholes is appropriate for this reconnaissance study, it has the limitation that contact of the groundwater with the atmosphere induces rapid and widespread precipitation of secondary carbonates which can mask the more repository relevant mechanisms (for example, it may shield the host rock and bentonite from further reaction). Appropriate sampling is certainly not easy, but can be most suitably carried out downhole in dedicated boreholes. Nevertheless, the data from the Allas and Christovrysi Springs clearly indicate that groundwaters of relevant chemistries are being produced in the ophiolite and so will be available at more appropriate sites (such as in the Mamonia terrain – see Figure 2).

Somewhat surprisingly, mineralogical and petrographic analyses show that the active hyperalkaline groundwater-rock interaction and alteration of serpentinised harzbergite and lherzolite (serpentinite) at the Allas and Christovrysi Springs is dominated by interaction of the groundwater with serpentine minerals (principally 1M and 1T forms). There is little evidence of smectite or other relevant clays at these sites, by which reaction of bentonite can be studied. The principal alteration product of the interaction of the high-pH groundwater with the serpentinite is the formation of the complex Mg-Fe hydroxycarbonate mineral, pyroaurite ($Mg_6Fe_2(SO_4,CO_3)(OH)_{16}.4H_2O$). This phase is isostructural with "green rust" (Taylor and McKenzie, 1980) formed during the corrosion of steel, and also has significant ion-exchange properties and the potential to incorporate heavy metal cations (Seida et al., 2001). This phase may therefore have implications for the retardation of radionuclides in a repository environment, but this is currently outwith the scope of this study.

It appears that all of the solid materials (including soils and clay-sized material) at the Allas and Christovrysi Springs are dominated by serpentine minerals, making clear that almost complete serpentinisation of the original ophiolite lithology (in this area at least) has happened to a previously unsuspected degree. As such, further solid-phase studies at these sites would probably yield little repository-relevant relevant information.

CONCLUSIONS

Due to the extremely slow kinetics of bentonite reaction in low alkali cement leachates, natural analogues would appear to be the only viable method of studying bentonite reaction. The numerous hyperalkaline groundwaters and widespread bentonite deposits in Cyprus make it an excellent area to study the reaction of bentonites in low alkali cement leachates. The groundwater chemistry varies enormously, depending on the precise reaction path taken in the ophiolites, but at the moment, that is a positive aspect as the precise formulation of the low alkali cement to be used in any repository remains open (and hence variable; cf. Table 1). Although a range of sites have been sampled (see Alexander and Milodowski, 2009 for details), those discussed here are useful mainly for supporting the conceptual model of hyperalkaline leachate production and will not be included in any further examination of bentonite reaction.

Although the bentonite, clay-rich sediment and soil samples collected around the island are still being analysed in detail (see Alexander et al., 2009 for details), it is already clear that sufficient sites exist where both 'fossil' reaction fronts (i.e. they are now above the water table) and 'active', ongoing hyperalkaline groundwater/bentonite reaction can be studied. As such, a further field campaign will take place later this year to carry out a focussed study on the most appropriate sites identified in the reconnaissance campaign described here.

ACKNOWLEDGMENTS

The authors would like to express their thanks to the Project Funding Partners (Phases I and II) of the Cyprus Natural Analogue Project (CNAP), namely the NDA (UK), Posiva (Finland), SKB (Sweden) and, for Phase I only, Nagra (Switzerland). In addition, we would like to warmly thank all our colleagues at the Geological Survey Department of Cyprus (GSD), especially Dr Eleni Georghiou Morisseau (Acting Director), for their help and support. AEM, SJK and JCR publish with the permission of the Executive Director, BGS (NERC).

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