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DEVELOPMENTS IN HYPERALKALINE NATURAL ANALOGUE STUDIES AROUND THE ZAMBALES OPHIOLITE, PHILIPPINES

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ABSTRACT

Past studies have identified ophiolites as potential sources of hyperalkaline waters that can be considered analogues of the leachates produced by cementitious materials in repositories for radioactive waste. The Zambales ophiolite in the Philippines has been determined to undergo widespread active serpentinisation, resulting in hyperalkaline springs at several locations. Measured pH values range up to 11.1, falling into the range typical of low alkali cements that are presently being developed to minimise geochemical perturbations resulting from use of concrete. A key goal is to examine the alteration of natural bentonite in contact with such waters to determine if, indeed, pH values in this lower range eliminate the problems seen at the high values (>12) associated with conventional concretes.

Evidence has been accumulated to support the conceptual model of hyperalkaline groundwater flow in fractures underlying bentonite deposits in the Mangatarem area of the Zambales ophiolite. Drilling and trenching has exposed a direct contact between bentonite and pillow lavas of the ophiolite and several generations of hyperalkaline groundwater flow within fracture zones have been identified. As yet, water samples have not been obtained from this contact, but analysis of reacted bentonite is ongoing. Preliminary data are reported here for the first time.

INTRODUCTION

As noted in Milodowski et al (2009; this session), bentonite is one of the most safety-critical components of the engineered barrier system for the disposal concepts developed for many types of radioactive waste. However, bentonite – especially the swelling clay component that contributes to its essential barrier functions – is unstable at high pH. This led to some repository designs (especially for disposal of high-level vitrified waste, HLW or spent fuel, SF) that exclude use of concrete from any sensitive areas containing bentonite, due to the fact that it reacts with groundwater to produce leachates with an initial pH of up to about 13 (cf. Haworth et al., 1987).

Such an option of avoiding the problem by constraining the design was considered acceptable during early, generic studies but, as projects move closer to implementation, it is increasingly recognised that constructing extensive facilities underground without concrete – a staple of the engineering community – would be difficult, expensive and potentially dangerous for workers. This last point is especially important given the extreme sensitivity of most stakeholders towards even 'conventional' accidents at nuclear sites (see discussion in Alexander et al., 2007). This is especially the case in countries like Japan and the UK, where a volunteering approach to siting a repository means that repository construction could be in a technically challenging host rock.

A further area of concern involves transuranic wastes (TRU, or other high toxicity/long half-life intermediate-level waste, ILW), particularly if this is co-disposed with HLW/SF. TRU waste contains large inventories of cementitious materials and hence, in principle, could pose a risk to the engineered barrier system (EBS) of HLW/SF, even if concrete was excluded from the HLW part of the repository (e.g. scenarios discussed in Nagra's Projekt Entsorgungsnachweis; Nagra 2002). Indeed, some designs of the EBS for various kinds of low- and intermediate level waste (L/ILW) include a bentonite layer, which is planned to act as an external barrier around concrete structures To date, there has been no comprehensive demonstration that the performance of such a barrier can be assured for relevant periods of time.

Recently, therefore, there have been extensive efforts to better understand the interactions of hyperalkaline fluids with bentonite, coupled with studies aimed at reducing the risk by development of low alkali cement formulations. The greatest challenge is bringing the information produced by laboratory (conventional and underground rock laboratories, URL) and modelling studies together to form a robust safety case. This is complicated by the inherently slow kinetics of such reactions and the commonly observed persistence of metastable phases for geological time periods (for a good overview of the issues involved, see Metcalfe and Walker, 2004). Clearly, this is an area where natural analogues could play a valuable role – bridging the disparity in realism and timescales between laboratory studies and the systems represented in repository performance assessment (see also discussion in Alexander et al., 1998). The natural analogue approach to study bentonite/hyperalkaline interaction is discussed in detail in Milodowski et al., 2009; this session) and so will not be covered further here.

There are a number of locations worldwide where such an analogue might be found, including Cyprus (see Milodowski et al., 2009), Oman, California, Bosnia, Papua New Guinea, Japan and the Philippines. Based on a multi-attribute analysis, considering factors such as probability of finding suitable locations, relevance to Asian programmes, opportunity for training, low risk of disrupting calls for volunteer sites in Japan and cost-effectiveness, the Philippines was chosen as the focus for this new study. After preliminary field studies investigated several potential sites across the Philippines (Alexander et al., 2008), the Zambales ophiolite in Luzon (Figure 1) was chosen as the focus of the new study.

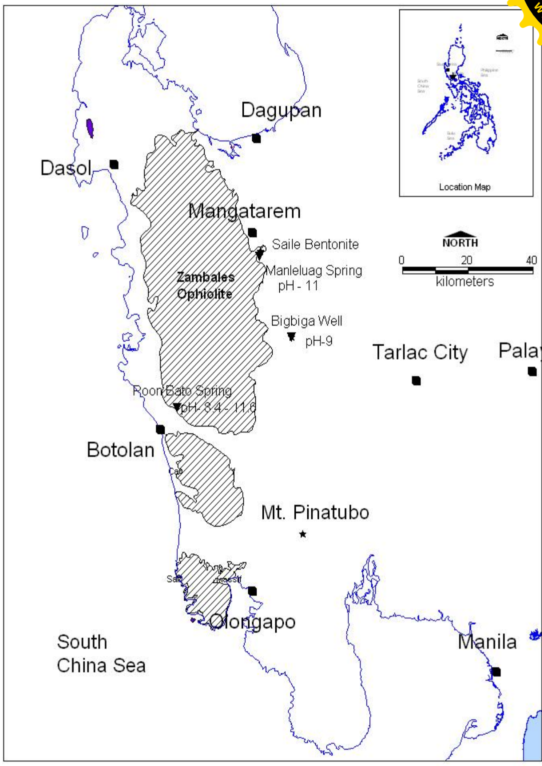

FIGURE 1: THE ZAMBALES OPHIOLITE AND THE MANGATAREM AREA, LUZON.

Currently, the technical focus is on:

- 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?
- BPM (blind predictive modelling – see Pate et al., 1994) of the chemistry of safety relevant elements (eg Se), including *in situ* speciation
- colloid filtration
- microbiology of the system (cf. McKinley et al., 1988)
- staff training, including mentoring by experienced (in radioactive waste disposal) international staff

GEOLOGICAL SETTING

All hyperalkaline groundwaters studied so far in the Philippines originate from the 20 or so known ophiolite bodies, which are widely scattered throughout the archipelago. The definition of an ophiolite used here is presented in Milodowski et al., 2009) and, briefly, includes:

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deep (abyssal) marine sediments (including bentonites)

pillow lavas (basalt)

sheeted dyke complex

high level/isotropic gabbro

layered mafic cumulates (gabbro)

layered ultramafic cumulates

transition zone dunites and residual peridotites

If any of the above lithologies is missing, it should be called an ophiolite *complex*, but this term is frequently misused in the literature. The hyperalkaline pH values (generally between pH 10 and 11) observed in the groundwaters are a product of the serpentinisation of the ophiolites, a reaction which is discussed in detail in Milodowski et al. (2009)

The serpentinite mineral assemblages are very strongly reducing and the hyperalkaline waters in the Philippines are generally effervescent with H_2 and/or CH_4 gas (Figure 2). Some of the reaction pathways are also strongly exothermic, frequently producing hydrothermal groundwaters (which are often used as therapeutic springs in the Philippines).

FIGURE 2: MANLULUEG HOT SPRING, ZAMBALES OPHIOLITE, SHOWING GAS (H_2±CH_4) EMANATING FROM A FRACTURE IN GABBRO (FROM YAMAKAWA ET AL., 2009).

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 both the Zambales opholite and at the Troodos ophiolite in Cyprus (cf. Milodowsk et al., 2009) and means that drilling and/or trenching is require to access the site of hyperalkline groundwater/bentonite interaction.

SITE DESCRIPTION

The site is situated at the eastern edge of the Zambales ophiolite and the northwestern periphery of the Central Luzon Valley. The main areas of interest are

- the Sailes Industries bentonite quarry (E120°18', N15°43'), near the lone, conical 700 m high volcanic plug called Mt. Malabobo (Figure 4). Mt. Malabobo is the most westerly volcanic plug of the Central Luzon Valley.
- the Manleluag Hot Springs (Figure 2), about 2.5 km southwest of the quarry (E120°16'52", N15°42'16"), siuated in the gabbro of the Zambales ophiolite (Figure 4).

The site lithology may be described as (younging upwards):

Quaternary Alluvium
Andesite plugs
-----------------------(Unconformity)-----------------
Early to Middle Miocene Moriones Formation
-----------------------(Unconformity)-----------------

Zambales Ophiolite (a complete Eocene to Late Oligocene ophiolite)
a. Aksitero Formation (including bentonites)
b. Pillow Lava Basalt (and autobreccia)
c. Diabase-Diorite Dyke Complex
d. Gabbro

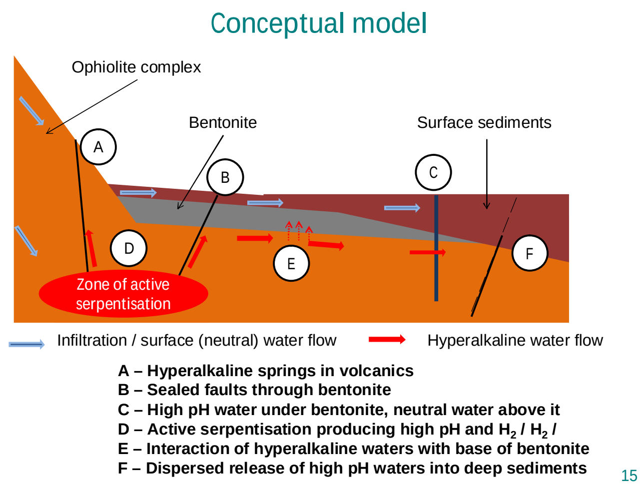

FIGURE 3: CONCEPTUAL MODEL OF THE HYPERALKALINE GROUNDWATER/BENTONITE INTERACTION IN THE MANGATAREM AREA (FROM ALEXANDER ET AL., 2008)

The gabbro and diabase dyke complex are located at the western end of the study area. The pillow basalt and overlying pelagic Aksitero formation (bentonite-containing) are in the central area (Figure 4). The Neogene Moriones Formation and the volcanic plugs are found at the eastern part of the study area, occuring as isolated hills running in a N-S line (Mt. Malabobo is the only plug in the detailed study area). Quaternary alluvium covers much of the older formations.

Structurally, at least 3 prominent trends exist (see Figure 4):

- Northwest (NW)
- North-South (N-S)
- Northeast (NE)

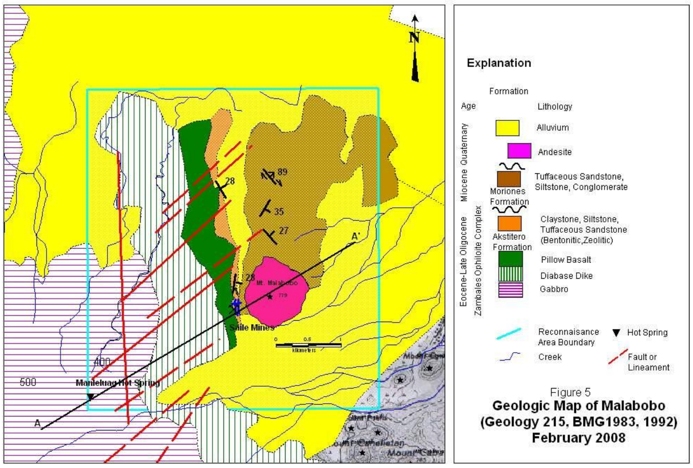

FIGURE 4: MAIN GEOLOGICAL ELEMENTS OF THE FIELD AREA. THE BENTONITES ARE LIMITED TO THE AKSITERO FORMATION

In the Manlulueg area, two faults measured in the gabbro trend N50E and N-S with steep dips. Sense of movement is right-lateral and the fault surface is brecciated and altered with calcite and/or tufa filling. The N50E trending system appears to be controlling the movement of the deep-flowing hyperalkaline groundwater. East-West trending dykes are also observed cutting through the gabbro and show themselves as prominant 'steps' in the stream sections.

SAMPLING AND ANALYTICAL METHODS

Sampling methods are presented in Arcilla et al. (2009) and include details of the groundwater sampling and preservation. Data for three samples are currently available: M1 and M2 from the Manleluag Hot Springs and S4, from a fracture in the pillow lavas exposed just north of the bentonite quarry. Rock samples were collected by a mixture of small diameter drillcores and shallow trenching with a mechanical digger. Sub-samples were collected in the trenches with a small, portable drill or by hand. A sample depository, with an associated online database for use by the project partners, has been set up at and will be maintained by the University of the Philippines. The main sample site of interest is trench ST1, from the northern end of the quarry (see Figures 5 and 6).

All solid samples taken were analyzed by XRD and XRF at the University of the Philippines to determine the mineralogy and chemistry, respectively. Samples were partially dried at 60°C. An attempt was made at 150°C, but the samples rapidly resorbed water due to the 80-90% relative humidity in the laboratory. XRD analysis was carried out qualitatively on a Shimadzu Maxima XRD-7000 while XRF analysis was

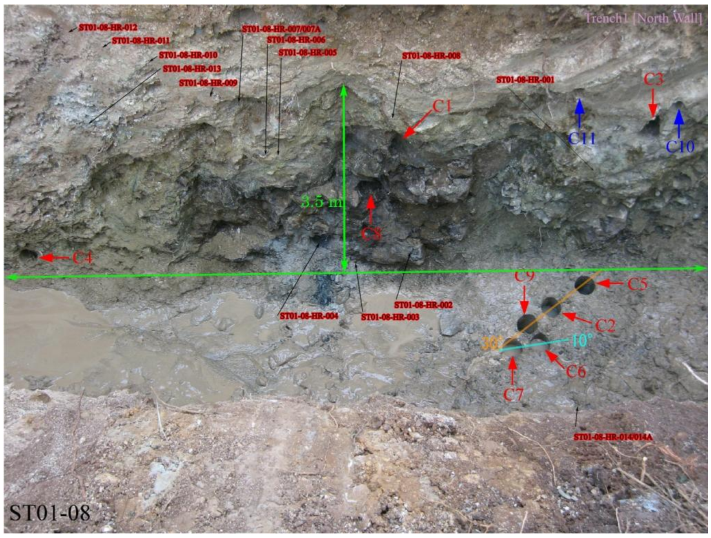

FIGURE 5: PHOTOGRAPH OF THE FLOOR AND SOUTH WALL OF TRENCH ST1 SHOWING THE SAMPLING SITES AND POSITIONS OF THE BOREHOLE SAMPLES. THE POSITION OF THE SAMPLING COORDINATES ORIGIN (SEE FIGURE 6) IS ON THE WALL ABOVE BOREHOLE C5.

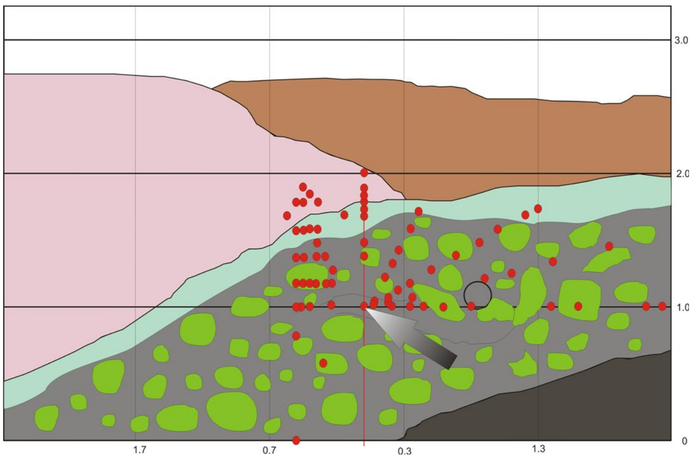

FIGURE 6: SKETCH OF TRENCH ST1 SOUTH WALL SHOWING THE SAMPLE LOCATIONS (RED DOTS). THE ORIGIN (COORDINATES 0,0) IS INDICATED BY THE LARGE ARROW. THE BLACK CIRCLE IS BOREHOLE ST01-08-C2-001. GREEN BLEBS ON GREY REPRESENT THE PILLOW LAVAS, THE LIGHT BLUE RIM AT THE TOP OF THIS AREA IS A GENERALLY FE AND/OR MN ENRICHED ZONE OF THE BENTONITE. PINK AREA IS BENTONITE, BROWN IS A WEATHERING ZONE. SCALE IS IN METRES.

performed using a Shimadzu ED-XRF, with a standard deviation of ±5%. Groundwaters were analysed at the

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laboratories of the British Geological Survey, UK using UKAS accredited methods and facilities (full details in Arcilla et al., 2009).

RESULTS AND DISCUSSION

The groundwater analyses are shown in Table 1. Note that due to limited funding, repeat analyses was not possible and so these data represent one analysis only and hence little can be said regarding data uncertainty. The data for M1 and M2 are remarkably similar for two parallel-trending fractures some 250m apart. This suggests that they have a similar source at depth in the gabbro.

TABLE 1: GROUNDWATER ANALYSES FOR THE MANLELUAG SPRINGS (M1 AND M2) AND THE SAILE QUARRY SAMPLE (S4)

Sample code	units	M1	M2	S4
pH		11.0	10.9	8.20
Ca^{2+}	mg L^{-1}	24.3	22.7	35.7
Mg^{2+}	mg L^{-1}	<0.050	<0.050	20.2
Na^{+}	mg L^{-1}	27.1	27.5	12.9
K^{+}	mg L^{-1}	<2.500	<2.500	<0.500
OH^{-}	mg L^{-1}	21.1	19.1	n/a
CO_3^{2-}	mg L^{-1}	5.52	6.15	n/a
HCO_3^{-}	mg L^{-1}	n/a	n/a	233
Cl^{-}	mg L^{-1}	18.9	18.9	1.90
SO_4^{2-}	mg L^{-1}	0.820	0.838	0.787
NO_3^{-}	mg L^{-1}	<0.020	<0.020	1.33
∑Cation	meq L^{-1}	2.39	2.33	4.01
∑Anion	meq L^{-1}	1.99	1.89	3.91
Balance	%	9.28	10.41	1.23
Br^{-}	mg L^{-1}	0.054	0.059	<0.020
NO_2^{-}	mg L^{-1}	<0.010	<0.010	0.046
HPO_4^{2-}	mg L^{-1}	0.458	0.419	<0.100
F^{-}	mg L^{-1}	<0.010	<0.010	0.084
NPOC	mg L^{-1}	0.679	0.761	1.11
Total P	mg L^{-1}	<0.050	<0.050	0.045
Total S	mg L^{-1}	<1.250	<1.250	0.417
Reduced S	mg L^{-1}	0.16	0.05	<0.01
S Diff	%	121.9	122.4	37.0
Si	mg L^{-1}	10.8	11.3	25.7
SiO_2	mg L^{-1}	23.0	24.3	55.0
Ba	mg L^{-1}	<0.010	<0.010	<0.002
Sr	mg L^{-1}	<0.025	<0.025	0.063
Mn	mg L^{-1}	<0.010	<0.010	0.028
Total Fe	mg L^{-1}	<0.050	<0.050	0.052
Oxidised Fe	mg L^{-1}	<0.050	<0.050	0.052
Al	mg L^{-1}	0.210	0.246	<0.010
Co	mg L^{-1}	<0.010	<0.010	<0.002
Ni	mg L^{-1}	<0.025	<0.025	<0.005
Cu	mg L^{-1}	<0.025	<0.025	<0.005
Zn	mg L^{-1}	<0.025	<0.025	<0.005
Cr	mg L^{-1}	<0.010	<0.010	0.011
Mo	mg L^{-1}	<0.075	<0.075	<0.015
Cd	mg L^{-1}	<0.010	<0.010	<0.002
Pb	mg L^{-1}	<0.050	<0.050	<0.010
V	mg L^{-1}	<0.075	<0.075	<0.015
Li	mg L^{-1}	<0.125	<0.125	<0.025
B	mg L^{-1}	<0.125	<0.125	<0.025
As	mg L^{-1}	<0.075	<0.075	<0.015
Se	mg L^{-1}	<0.075	<0.075	<0.015
$\delta^{18}O$	‰ VSMOW	-9.30	-9.22	-7.81
$\delta^{2}H$	‰ VSMOW	-62.70	-61.60	-53.50

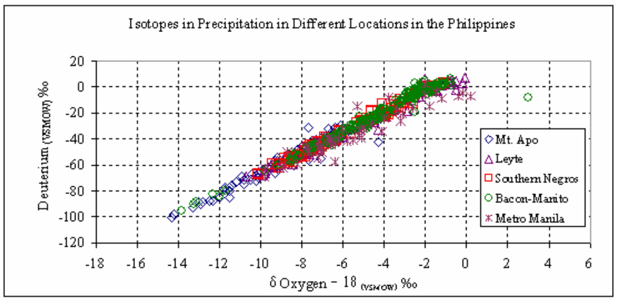


FIGURE 7: THE ISOTOPIC COMPOSITION OF RAINWATER: EXAMPLES FROM ACROSS THE PHILIPPINES (FROM GERARDO-ABAYA, 2005)

Although no age data are currently available, the groundwater is presumed to be relatively young from its highly dilute nature and the fact that the stable isotope data are similar to rainwaters across the Philippines (see Figure 7). With $\delta^{2}H = 6\delta^{18}O + 7$, they deviate slightly from the Philippine Meteoric Water Line as defined by Gerardo-Abaya (2005) of $\delta^{2}H = 8\delta^{18}O + 12$, but certainly plot within the range of reported precipitation.

Other aspects of the M1 and M2 waters are typical for those derived of serpentinisation of ultramafics, including very low Mg concentrations, high pH levels and high temperature. Generally, this suggests that the M1 and M2 waters are being produced by the serpentinisation of gabbros and that the source is very local. When additional data are available, it will be interesting to compare stable isotope data of the groundwaters with that of the gabbro and with the secondary materials present in trench ST1.

S4 was originally collected as it was flowing from a fracture in the pillow lavas below the bentonite and the water is significantly different from M1 and M2 in that it has a markedly lower pH and is much more mineralised than M1 and M2, suggesting a greater age and/or degree of rock-water reaction. The greatest differences from M1 and M2 include higher levels of Ca, Mg and Si and much lower Cl. The last point is important as it suggests that it is from a distinctly different source from M1 and M2. As do the stable isotope values, although it is of note that they still lie on the same Water Line of $\delta^2H = 6\delta^{18}O + 7$ as M1 and M2, i.e. with a slight deviation from the Philippines Meteoric Water Line. According to data presented by Gerardo-Abaya (2005), the differences in $\delta^{18}O$ between the two water types could be taken to indicate that both waters are representative of early rainy season (July) input, with M1 and M2 precipitating at around 1000 masl (i.e. from further west in the Zambales ophiolite) and S4 nearer 500 masl (i.e. locally, around the level of the Manleluag Spring). The slight deviation from the Philippine Meteoric Water Line may be no more than the local rainwater signature, but this needs to be confirmed with additional samples next field season.

The difference in the Cl content of the two water types may be significant, however. The low Cl content of the M1 and M2 waters is consistent with a short period of contact with the ophiolite, with some minor leaching of relict seawater in the rocks. The very low level of Cl in S4, a groundwater which appears to have undergone significantly more rock-water interaction than M1 and M2, suggests that it has not been in contact with the ophiolite – i.e. this groundwater has been moving through the alluvium above the bentonite.

The groundwater system at the site is currently underdefined i.e. no detailed mineralogical data exist for the gabbros, pillow lavas or the overlying bentonite, so there is little point in carrying out scoping calculations on potential sources of the waters until more mineralogical data can be obtained in the next field season.

The results of the XRD and XDF analyses are displayed next to each other for clarity. In Figure 8, sample transect 0° (i.e. moving away from the origin horizontally) is presented and there are several clear conclusions which can be drawn. The bentonite is clearly smectitic, but zeolite, serpentine and CSH phases are also present. A similar picture exists for sample transect 15°. Unfortunately, as XRD analysis is only qualitative, little can be said about the relative contents of these constituents.

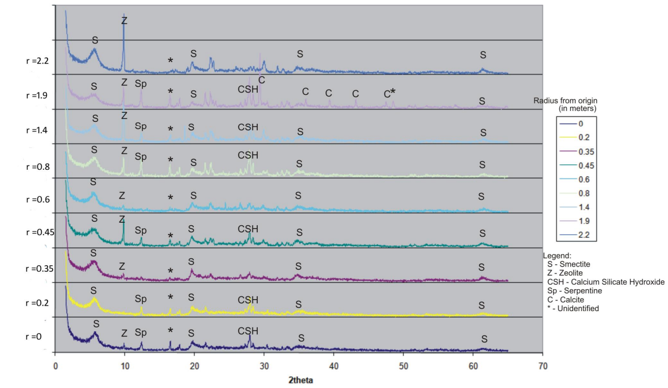
However, preliminary geochemical reaction modelling (using Geochemist's Workbench) suggests that the zeolites are formed from the reaction of the smectites with the hyperalkaline groundwater (Honrado et al., 2009). Here, analcime was used as a proxy for 'zeolites' and the smectite was reacted with a hyperalkaline water produced by reaction with the underlying basalts. Note also that CSH phases have been reported not only from 'thorough-going' OPC cement analogues such as Jordan (cf. Pitty, 2009), but also from other low alkali leachate analogies such as Oman (e.g. Bath et al., 1988).

Interestingly, the previously reported apparent association of Mn with the reaction pathways in the bentonite (Alexander et al., 2008) may be reflected in the Mn peaks at the outer end of the transect. The close correlation with Ca suggests the possibility of a mixed rhodacrosite/calcite phase, perhaps reflecting the gradual buffering of the $Ca(Mn)OH^-$ hyperalkaline groundwaters coming from depth by bicarbonate in the shallower groundwater (or porewaters: cf. Steefel and Lichtner, 1998a,b).

Transect 60° (and 30°) shows a similar mineralogical mix, but without the presence of serpentine (Figure 9). Once again, there is an almost 1:1 association of Ca and Mn. The peak in the Ca/Mn plot is similar to that seen in Figure 7, but without additional information on the samples, it is impossible to say if this represents a former flow channel or a vein in the rock produced by other means. However, by the foresight of the Univerity of the Philippines, this site has been preserved and it will be possible to return and carry out more specific sampling next field season.

Transect 90° (Figure 10) is much more dominated by smectite, with less zeolite present and very little CSH. This is possibly a reflection of the fact that the 90° transect actually penetrates the bentonite 'proper' and is not just seeing interclast bentonite in the pillow lavas, as is certainly the case in the other sample transects. Note also that the Fe/Mn enriched zone at the top of the pillow lavas is also very clear in the analytical results.

Thus it is clear that the predominantly pillow lava samples analysed to date nevertheless have enough bentonite associated with them for the smectite to show clearly in all analyses. Additionally, preliminary modelling suggests that the zeolites could have been produced as a product of smectite reaction in the hyperalkaline groundwaters. Although not included in this calculation to date, the CSH phases identified are completely consistent with reaction of clays and the basaltic pillow lavas with hyperalkaline groundwaters. Further data (e.g. stable isotope data for the gabbros, pillow lavas and bentonite) and calculations are required to assess if the S4 groundwater is a product of these reactions, but the low Cl concentration suggests that it has not reacted with the ophiolite *per se* and is indicative of the two-flow system (i.e. near-neutral, shallow groundwaters on top of the bentonite separated from the deep, hyperalkaline groundwaters below the bentonite – see Figure 3).



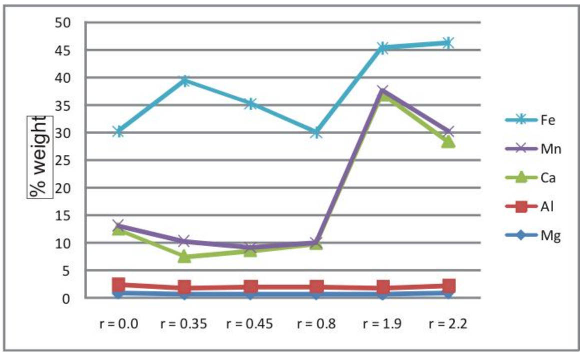
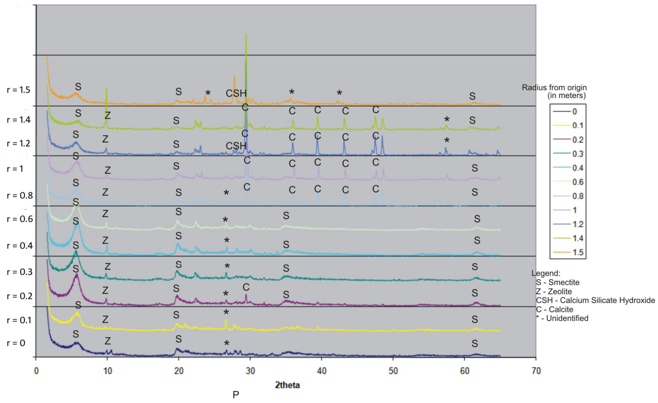


Figure 8: Mineralogy by XRD (left) and chemistry by XRF (right) of the material from trench ST1. Sample transect 0° (i.e. horizontally away to the right from the origin (0,0) in Figure 6). On the left hand figure x-axis, the distances represent the distance from the origin, stacked vertically for clarity.



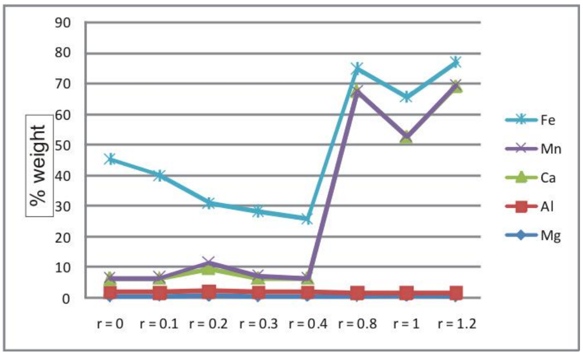
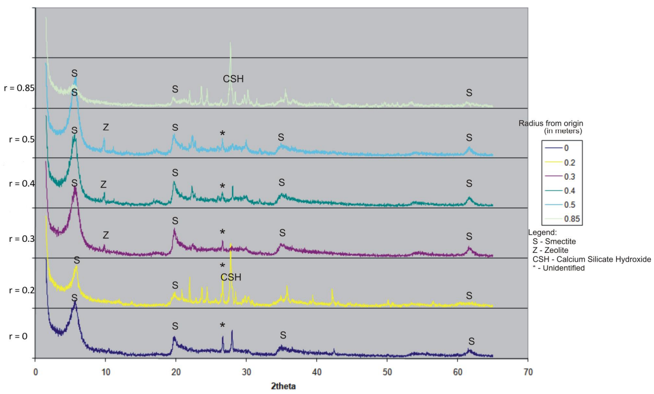


Figure 9: Mineralogy by XRD (left) and chemistry by XRF (right) of the material from trench ST1. Sample transect 30° (i.e. running at 30° to the horizontal and to the right from the origin (0,0) in Figure 6). On the left hand figure x-axis, the distances represent the distance from the origin, stacked vertically for clarity.



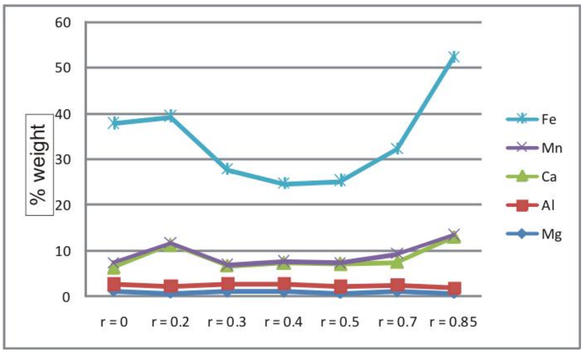


Figure 10: Mineralogy by XRD (left) and chemistry by XRF (right) of the material from trench ST1. Sample transect 90° (i.e. running at 90° to the horizontal and to the right from the origin (0,0) in Figure 6). On the left hand figure x-axis, the distances represent the distance from the origin, stacked vertically for clarity.

CONCLUSIONS

Although still preliminary, the results from the project indicate some degree of reaction of the bentonites in the analogue hyperalkaline cement leachates. Samples recovered from trench ST1 show that the bentonite is clearly smectitic, but zeolite, serpentine and CSH phases are also present. Preliminary geochemical reaction modelling suggests that the zeolites are formed from the reaction of the smectites with the hyperalkaline groundwater. Here, analcime was used as a proxy for 'zeolites' and the smectite was reacted with a hyperalkaline water produced by reaction with the underlying basalts.

Note also that CSH phases have been reported from other low alkali leachate analogies such as Oman but, as their stability field is at >pH10.5, this suggests they are the product of the earliest reaction with the hyperalkaline groundwaters. Unfortunately, no samples of 'pure' non-reacted bentonite have been analysed to date and this must be a priority for the next field season to allow further reaction modelling.

Perhaps more important, however, is the fact that, despite evidence of reaction, the bentonite would appear to be still acting as an aquiclude, a result which is fully in agreement with the data from the Cyprus natural analogue project (see Milodowski et al., 2009). The groundwater system is currently underdefined, but two distinct waters have been sampled. The hyperalkaline groundwater would appear to originate from reaction with the gabbro and the young appearance of the M1 and M2 groundwaters may simply be a reflection of a localised, superficial flow regime, but the stable isotope data suggest an original height of precipitation of around 1000 m, which is some distance to the west in the Zambales ophiolite. This does not rule out other flow lines continuing at depth and reacting to a greater extent with the ultramafics, producing a hyperalkaline groundwater more characteristic of other ophiolites.

It also does not negate the concept of deep flow below the bentonite. Certainly the low Cl content of the S4 water suggests no contact with the ophiolite, other than at the top of the bentonite – i.e. a separate groundwater flow regime above the bentonite as proposed in the conceptual model. The groundwater system at the site is currently underdefined and there is need of detailed mineralogical and stable isotope data for the gabbros, pillow lavas and the overlying bentonite to allow more detailed modelling of both systems.

Although still provisional, the current would appear to suggest that sufficient bentonite survives reaction with the hyperalkaline fluids to maintain its crucial (in terms of repository performance) role as a barrier material. Further work is required this field season to better elucidate the degree and extent of reaction along with the mass of bentonite likely to have been lost to reaction over the lifetime of the current hyperalkaline groundwater flow system.

RECOMMENDATIONS FOR FUTURE WORK

Although the first priority of the project is the examination of bentonite stability under hyperalkaline conditions, the Mangatarem site (and several others in the Philippines) would make possible the following associated goals:

- Indicators of geological/hydrogeological stability (particularly for coastal sites). Surface samples could be analysed to define the uplift history of the site in an attempt to constrain the likely period of leachate/bentonite interaction (this will then be compared with the data from pristine and altered bentonites)
- Assessment of microbiological populations in the hyperalkaline groundwaters. There is evidence from the Maqarin site that microbes which are probably dormant in the pH 12.5 groundwaters are viable in solutions at pH 11. In this case, the degree of microbial activity in a repository containing significant amounts of low alkali cement could be considerably greater than in one with OPC. This should be fully integrated with the standard groundwater analysis
- At the Saile bentonite quarry, the close physical proximity of the volcanic plug to the bentonite quarry could be used to assess (plug) emplacement related impact on the bentonite backfill. Effects such as tectonism (e.g. changes in dip, fracturing) can be assessed by measuring and plotting fracture orientations and assessing the stress fields. The fractures should also be dated to define if they are in any way related to the plug emplacement. Hydrothermal alteration can be assessed by sampling for later mineralogical and isotopic analyses. The quarry may already be too far away from the plug to see appreciable changes, so a trench between the quarry and the plug could be dug to allow sampling progressively nearer the plug. It is acknowledged that current exclusion criteria make this an rather unlikely scenario, but this may be very useful in public communication of risk and might be needed for the sake of safety case completeness
- Gas samples for isotopic analysis (e.g. ^{14}C transport processes)
- Near-surface microbial utilisation of methane from the hyperalkaline groundwaters could be assessed to provide input to gas releases (^{14}C) to the biosphere
- Microbial populations in the bentonite: although most recent safety assessments (e.g. Ondraf, 2001; Nagra, 2002) claim that microbes cannot survive in (compacted) bentonite, actual data are very scarce. Study of samples from this site can be used to provide a base-case for any future laboratory studies
- Effects of active fractures: the presence of apparently active fracture systems in the quarry area should allow study of the impact of such an active system on the bentonite (and indeed could be tied in with the study of the faults in the bentonite noted above)

- Coastal repository related processes could be studied at several coastal ophiolites in the Philippines. Changes in radionuclide solubility and colloid populations in the hyperalkaline leachate/seawater mixing zone could be examined
- Gas: the influence of gas production within a bentonite barrier is a general area of interest and, in particular, understanding of gas production by TRU wastes and transport within the concrete/bentonite EBS system is a key open question. This could be a clear topic that could be studied at several of the sites
- Graphite: in Japan (and several other national programmes), significant quantities of irradiated graphite must be disposed of and there is much R&D ongoing on the benefits or otherwise of conditioning it for disposal. As graphite is reported to be present in the ophiolite complex, investigation of its stability under high pH conditions could contribute significantly to this debate.
- Training:
  - Involvement of younger staff
  - Joint teams with experienced "mentors"
  - Involvement of a range of international partners
- PR: exotic and interesting locations

Although these spin-off studies can all be directly assessed during main project work at the various sites, it is not possible for them to be funded by the main project budget. It may be more appropriate to look for additional partners who could focus specifically on one or other of the identified topics.

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