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Herbert's Quarry, South Wales – an analogue for host-rock alteration at a cementitious radioactive waste repository?

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ABSTRACT

Cement in radioactive waste repositories will produce leachates of pH > 10 which may alter the host rock, affecting its ability to act as a barrier to radionuclide migration. To complement the many laboratory and modelling studies of rock alteration in cement leachates, analogue sites have been investigated to understand reactions at time scales relevant to geodisposal. However, analogue site histories may be poorly constrained and these systems may be influenced by site specific factors. Therefore increasing the number of sites studied is important to minimize uncertainty in the applicability of results. Herbert's Quarry has been characterized and assessed as a potential anthropogenic analogue. Streamwater sampling at the site identified Ca-rich fluids, ≤ pH 12, analogous to cement leachates. However, rock and sediment samples exhibited extensive $CaCO_3$ precipitation in these fluids and no reaction of silicate rock. The streamwaters were also found to be oxidizing, unlike the reducing conditions expected at a repository, and temperatures were 15–25°C below those predicted for repositories. Therefore, Herbert's Quarry is believed to have limited applicability as an analogue in this context.

Keywords: hyperalkaline, analogue, geodisposal, C–S–H, carbonate, streamwater.

Introduction

The internationally preferred method for higher level radioactive waste disposal is burial within a deep Geological Disposal Facility (GDF) (OECD-NEA, 2008). The use of large quantities of cementitious materials is proposed in generic designs for the UK, Switzerland, France and Canada (DEFRA, 2008; NDA, 2010*a*; NAGRA, 2014; Andra, 2012; Nuclear Waste Management Organisation, 2010). In cementitious facilities, after groundwater resaturation, cement components will dissolve and produce high-pH leachates. Initially the leachate will be KOH- and NaOH-dominated (pH ~13) but will evolve over 10^4 to 10^5 years to be $Ca(OH)_2$-dominated and fall in pH from ~pH 12.5 to 10.5 (Atkinson, 1985; Berner, 1992). The alkaline leachate will migrate into the geosphere forming a Chemically Disturbed Zone (CDZ) in which the host rock may be altered, and its ability to act as a barrier to radionuclide migration may be affected.

Generally, laboratory studies have found that CDZ conditions cause the dissolution of silicate minerals and precipitation of C–S–H phases. However, these studies are necessarily short in

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timscale with few lasting longer than 1–2 years (Gaucher and Blanc, 2006; Fernandez *et al.,* 2010; Moyce *et al.,* 2014). To improve understanding of the potential mineral alteration processes at longer timescales, high-pH systems in the natural and anthropogenic analogues have also been studied (IAEA, 1989; Miller *et al.,* 2000; Savage, 2011). Pertinent to this study, examination of cements in historic structures and natural systems, such as Maqarin in Jordan and a number of saline lakes, have been studied as analogues for high-pH mineral alteration (Tinseau *et al.*, 2006; Techer *et al.,* 2012; Hodgkinson and Hughes, 1999; Milodowski *et al.,* 1998; Surdam, 1977; Taylor and Surdam, 1981, in Savage, 2010; Chermak, 1992, 1993). These studies have also shown high pH causes silicate mineral dissolution and secondary C–S–H phase formation but also suggest that over long timescales (10 s to 10^6 years) C–S–H may evolve to K-feldspars or zeolites (Savage, 2011). However, analogue systems are generally poorly constrained and increasing the number of sites studied is important to increase confidence in their applicability to CDZ scenarios (McKinley and Alexander, 1992). Typically, analogue site characteristics should be representative of a cementitious GDF such as those outlined in Table 1.

This study aims to characterize Herbert's Quarry and assess its potential as an analogue site. The Quarry encompasses disused limestone workings and lime kilns operated over the past 200 years and contains high pH streamwaters (>pH 11) (Andrews *et al.,* 1997) resulting from water percolating through CaO-rich waste on site.

Herbert's Quarry background

Herbert's Quarry is located on the Black Mountain at (National Grid Reference SN73531 18971). The site is underlain by the Dowlais Limestone Formation which is comprised of tabular, thick-bedded limestones with shale interbeds and some local basal sandstones (British Geological Survey, 2014). Limestone was worked and calcined to produce lime (CaO) for over 200 years at the now disused site (workings extend for ~0.14 km^2) and at least five streams flow northwards from the site (Calch, 2014).

Streamwaters of pH >11 have been identified at Herbert's Quarry attributed to residual CaO at the site forming $Ca(OH)_2$ in aqueous solution and raising streamwater pH (Andrews *et al.,* 1997). However, $Ca(OH)_2$ reacts with CO_2 under ambient conditions and reverts to $CaCO_3$, reducing solution pH. $CaCO_3$ deposits at Herbert's Quarry have been studied previously (Andrews *et al.,* 1997), indicating that some carbonation of $Ca(OH)_2$ has occurred, potentially minimizing the high-pH zone at the site.

TABLE 1. Characteristics representative of a cementitious GDF.

Parameter	Range	References
Cement leachate chemistry and pH	KOH- and NaOH- or $Ca(OH)_2$-dominated fluid pH 10.5–13	Atkinson (1985); Berner (1992)
Groundwater chemistry	Site specific but salinity = 1000 ds mg l^{-1}	Lagerblad and Trägårdh (1994); NDA (2010*a*)
Redox conditions	Reducing	NDA (2010*b*)
Temperature	40–50°C	NDA (2010*a*,*b*)
Reaction timescale	10s–1,000,000s years	Savage (2011)
Rock type	High strength (e.g. granite), lower strength sedimentary (e.g. clay) or evaporate	NDA (2010*b*)

Methodology

Two streams were sampled at low flow in summer 2013. The streams originated in spoil heaps (stream 1, grid ref. 273829, 218971; stream 2, grid ref. 273459, 219133) predominantly composed of angular limestone blocks ≤20 cm. Three minor streams also joined stream 1 (Sites X, Y and Z).

Eh, pH, temperature, total dissolved solids (TDS) and conductivity were measured along each stream. Salinity and dissolved oxygen were also measured and GPS coordinates recorded. At selected locations solution samples were taken. A 2 ml sample was taken for anion analysis (CO_3^{2-}, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) by Ion Chromatography. An additional 10 ml sample was taken and acidified in 2% nitric acid for cation analysis by ICP-AES (Ca) and ICP-MS (Fe, Mn, Mg, S, Al, Si, Mg, K, Na, Sr, Ba, Ti, Zn, Co, Cr, Cu, P, Ni and Pb).

Rock samples from the stream beds at each sample point and blocks of siliceous rock, cemented into tufa at the base of an ephemeral stream, were taken. The ephemeral stream was approximately 60 m west (approx. 273396, 219185) of stream 2. The rock samples were sectioned, resin embedded and examined under a Scanning Electron Microscope (SEM).

Results

Fluid chemistry

Stream temperatures varied between 15–24°C during sampling depending on time of day measured. Eh varied between 9–286 mV, indicating oxic conditions in both streams (Fig. 1 and Table 2). Both streams were of alkaline pH at source, ≤pH 12.0 (Fig. 1 and Table 2), in agreement with the findings of Andrews *et al.* (1997). However, pH was elevated in stream 2 for only 20–80 m (to site 3) and in stream 1, although pH varied significantly as high-pH tributaries joined the main stream, pH remained elevated for only 180–240 m (to site 14). It was also noted that at stream 2 a freshwater source (stream 2, site 1; pH 7.94) joined and mixed with the high-pH stream (stream 2, site 2; pH 11.0). The difference in pH was indicated visually by white/grey suspended particles in the high-pH waters (discussed further in the following section on stream 2).

TDS measurements varied with pH by an order of magnitude between the highest pH areas and those below pH 10.5, mirroring a similar trend in conductivity (Fig. 1, Table 2). Streamwater chemistry showed that in the highest pH samples, Ca concentration was elevated to 100 s mg l^{-1} but fell markedly to <50 mg l^{-1} in both streams as pH fell (Fig. 2*a*). Conversely, CO_3 concentration in solution rose in both streams as pH fell from tens to hundreds of mg l^{-1}, attributed to streamwater equilibration with atmospheric CO_2 (Fig. 2*b*). Aluminium concentration fell with pH from several hundreds of µg l^{-1} to 100–200 µg l^{-1} (Fig. 2*c*) while Mg concentration rose with falling pH from <50 µg l^{-1} to hundreds of µg l^{-1} (Fig. 2*d*). It was also noted that Si concentration was <9 mg l^{-1} in all samples, with no discernible trend relative to pH.

Solid phase characterization

Stream 1

Round to sub-angular, 1–3 cm 'pebbles' with friable surfaces formed the first 100 m of the bed of stream 1 (Fig. 3*a* and *b*). SEM examination showed these were fossil rich, angular limestone fragments ≤20 mm in size coated in highly porous $CaCO_3$ (Fig. 3*c*–*e*). Interestingly, the $CaCO_3$ coatings exhibited distinct growth layers <10 µm thick, parallel to the underlying limestone surfaces (Fig. 3*e*). These $CaCO_3$ coatings have been interpreted as precipitates formed as a result of the equilibration of atmospheric CO_2 with Ca^{2+} in solution, mediated by limestone surfaces. Minor occurrences of quartz particles up to 200 µm in size were also identified entrained in the $CaCO_3$ coatings (Fig. 3*f*). Solid samples were not taken in the lower pH region of the stream, as non-hyperalkaline conditions are not analogous to the scenario considered.

Stream 2

At the head of stream 2, clear non-hyperalkaline water occurred for ~30 cm (stream 2, site 1) before mixing with cloudy high-pH water containing fine grained white/grey suspended particles (stream 2, sites 2 and 2*a*; see Table 2 and Fig. 4*a*). The cloudiness at sites 2 and 2*a* occurred across a 3 m × 4 m pool and the stream bed in this high-pH zone was comprised of friable 'pebbles' (Fig. 4*a*). Downstream, where pH remained >pH 8.5, the stream bed was cemented with a layer of $CaCO_3$ tufa (Fig. 4*b*). The 'pebbles' at sites 2 and 2*a* were shown via SEM to be identical to the $CaCO_3$ 'pebbles' in stream 1. However, at stream 2 these were coated in a fine grained, white material similar to the suspended particles in the waters in this area. The fine grained coating and suspended material was isolated, analysed by SEM and found to be sub-rounded/angular, 50–100 µm, $CaCO_3$ particles (Fig. 4*c* and *d*). This indicates that $CaCO_3$ formation is rapid in the zone where high-pH, Ca-rich water mixes with CO_3-rich freshwater.

Rock samples

To assess silicate mineral alteration at Herbert's Quarry, two silicate rocks were extracted from a dry stream bed ~60 m west of stream 2 (no silicate rocks were identified in streams 1 or 2). This stream bed was comprised of blocks of rock cemented within $CaCO_3$ tufa (Fig. 5*a*). Because of the presence of tufa, anticipated to have formed from high-pH, Ca-rich streamwaters, it was inferred that high-pH waters would have affected these samples at periods of high flow. The first was a conglomerate, ~15 cm in all dimensions, containing quartz pebbles and likely to have originated in the

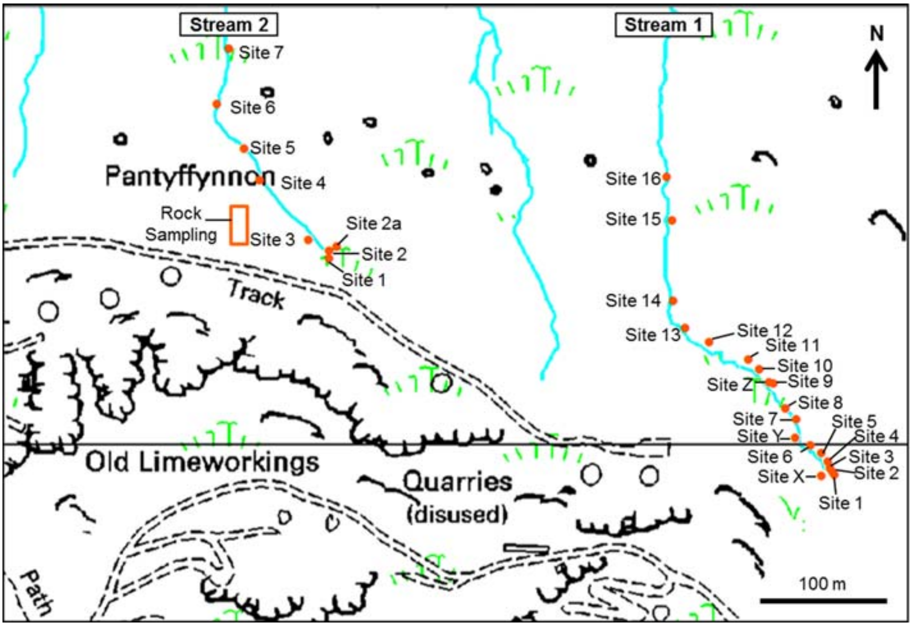

FIG. 1. Ordnance Survey map of Herbert's Quarry with sample locations overlain ©Crown Copyright/database right 2014. An Ordnance Survey/(Datacentre) supplied service.

Honeycombed Sandstone Member or the Twrch Sandstone Formation (British Geological Survey, 2014; Fig. 5*a*). A white/grey coating, limited in extent was noted on the conglomerate shown in section via SEM and EDX analysis to be up to 1 mm thick, porous and pure $CaCO_3$. No dissolution features attributable to high-pH alteration were identifiable on the conglomerate because it would have been weathered before entering the stream.

The second sample was of slate ~5 cm × 5 cm × 1 cm (Fig. 6*a*). This was friable, indicative of weathering, and white material occurred on the surface that had been below the tufa surface. In section, a 100–250 µm porous layer (~30% porosity) with pores up to 20 µm was visible on the surface that had been below the tufa (Fig. 6*b* and *c*). The increased porosity indicates dissolution and it was limited to the sub-tufa side of the sample, suggestive of dissolution by the high-pH streamwater, as suggested by similar studies (e.g. Gaucher and Blanc, 2006; Mäder *et al.,* 2006; Hodgkinson and Hughes, 1999; Braney *et al.,* 1993; Savage *et al.,* 1992; Ramirez, 2005). However, some weathering prior to the slate entering the stream cannot be precluded. It was noted that locally the higher porosity layer was coated with a blocky material up to 30 µm thick which also filled some pores (Fig. 6*b* and *c*). EDX analysis identified this as $CaCO_3$. Material was also identified within cleavage planes as layers up to 20 µm thick and sub-rounded particles up to 100 µm, also identified as $CaCO_3$ via EDX analysis (Fig. 6*d*). This $CaCO_3$ is attributed to precipitation from high-pH Ca-rich, streamwaters nucleating on slate surfaces/voids/pores.

Discussion

Hyperalkaline zones were identified in two streams at Herbert's Quarry. However, pH and Ca concentration fell rapidly downstream, attributed to $CaCO_3$ precipitation removing Ca from solution and consuming OH^-, thereby lowering the pH. This was corroborated by the presence of $CaCO_3$ particles/surface coatings in both streams. $CaCO_3$ precipitation also sequesters CO_2 but in both streams CO_3 concentration increased with decreasing pH. This is attributed to the equilibration of lower pH streamwaters with atmospheric CO_2 where lower Ca concentration minimized $CaCO_3$ precipitation. As pH decreased the Mg concentration in solution also increased while Al concentration decreased, thought to be to the result of the change in solubility of these species with pH. For example, the precipitation of brucite ($MgOH_2$) above pH 10 (Pokrovsky and

TABLE 2. Stream 1 and stream 2 fluid chemistry, pH, redox, TDS and temperature measurements (to 3 significant figures; 2 standard deviations error shown).

Sample site	pH	ORP (mv)	Temp (°C)	Conductivity (μs/cm)	TDS (ppm)	Ca	Si	Na	K	Mg	Al	Fe	Sr	Sulfate	Nitrate	Chloride	Carbonate
						mg l^{-1}				μg l^{-1}				mg l^{-1}			
Stream 1																	
Site 1	11.8	9	15.6	1540	1078	147 ± 3.16	4.84 ± 2.58	4.49 ± 0.02	7.93 ± 0.09	36.7 ± 3.90	664 ± 11.84	19.3 ± 2/09	176 ± 0.73	13.3	2.97	30.1	n.a.
Site 2	11.8	107	16.8	1590	1461.5	152 ± 0.67	4.13 ± 0.08	4.03 ± 0.03	3.50 ± 0.01	35.5 ± 0.25	655 ± 7.36	9.00 ± 0.38	172 ± 1.58	12.1	2.53	7.66	2.51
Site 3	11.7	65	22.2	1300	770.75	132	4.43	3.69	2.03	37.4	699	19.3	169	12.6	2.15	5.37	26.9
Site 4	8.51	208	21.9	115	28.855												
Site X	8.40	193	15.5	211	133.15	47.3	3.08	3.04	0.59	941	308	7.86	84.4	4.93	1.82	4.99	134
Site 5	10.7	227	15.8	344	199.4	21.4 ± 0.68	5.16 ± 2.82	3.81 ± 0.08	1.59 ± 0.01	538 ± 2.25	390 ± 4.37	11.5 ± 0.38	104 ± 0.61	9.53	2.29	5.34	31.4
Site 6	8.72	209	18.9	198	120.2												
Site Y	11.3	95	17.6	724	432.25												
Site 7	9.68	138	16.3	173	99.2	38.7	7.84	3.92	1.60	566	209	11.4	86.6	7.99	1.66	4.87	95.0
Site 8	11.2	103	19.9	439	259.65												
Site 9	9.19	133	20.4	189	106.8												
Site Z	11.7	63	16.0	1220	741.8												
Site 10	11.4	63	19.7	579	339.15	69.5 ± 4.67	8.66 ± 0.77	3.47 ± 0.14	1.11 ± 0.01	174 ± 7.55	348 ± 7.43	41.2 ± 1.37	106 ± 2.93	11.2	2.28	5.02	71.2
Site 11	10.7	83	20.7	223	127.1												
Site 12	9.99	105	20.5	151	85.345												
Site 13	9.56	111	19.3	157	89.35												
Site 14	9.31	114	20.3	162	92												
Site 15	8.29	129	18.0	199	113.4	42.2	6.59	3.85	1.41	606	169	28.2	81.2	7.10	0.65	4.86	123
Site 16	8.21	134	16.4	196	112.55												

(continued)

TABLE 2. (*contd.*)

Sample site	pH	ORP (mv)	Temp (°C)	Conductivity (µs/cm)	TDS (ppm)	Ca	Si	Na	K	Mg	Al	Fe	Sr	Sulfate	Nitrate	Chloride	Carbonate
						mg l^{-1}				µg l^{-1}				mg l^{-1}			
Stream 2																	
Site 1	7.94	286	20.0	198	108.75	32.3 ± 0.57	6.28 ± 0.09	3.76 ± 0.04	3.87 ± 0.12	1120 ± 23.67	204 ± 6.89	34.7 ± 18.67	73.9 ± 0.57	9.26	0.10	8.63	116
Site 2	11.0	160	23.2	391	238.7	206 ± 2.77	6.23 ± 0.02	3.84 ± 0.04	2.03 ± 0.00	51.0 ± 1.53	462 ± 7.34	13.9 ± 0.24	151 ± 2.23	13.5	0.76	5.25	26.0
Site 2a	12.0	85	23.9	2210	81.105	268	5.79	3.61 ± 0.05	1.75 ± 0.01	49.6 ± 1.53	181 ± 6.35	12.3 ± 1.07	148 ± 3.17	20.8	1.03	5.02	22.0
Site 3	9.61	163	23.0	143	1401.5	21.9	5.82	5.49	3.80	960	228	11.1	62.0	9.49	0.51	5.72	61.0
Site 4	8.39	154	19.8	196	112.8	42.0	5.68	3.44	0.86	1135	124	9.38	63.5	4.46	0.72	5.58	122
Site 5	8.15	274	20.4	188	108.05												
Site 6	8.45	260	20.9	175	100												
Site 7	8.49	211	20.3	181	103.55												

Phosphate was below detection limits in all samples. Dissolved oxygen concentrations were measured at between 5 and 18 ppm at all sites. Cr, Cu, Ni, Pb and Mo all below 10 ppb. Zn and Ba below 75 ppb.

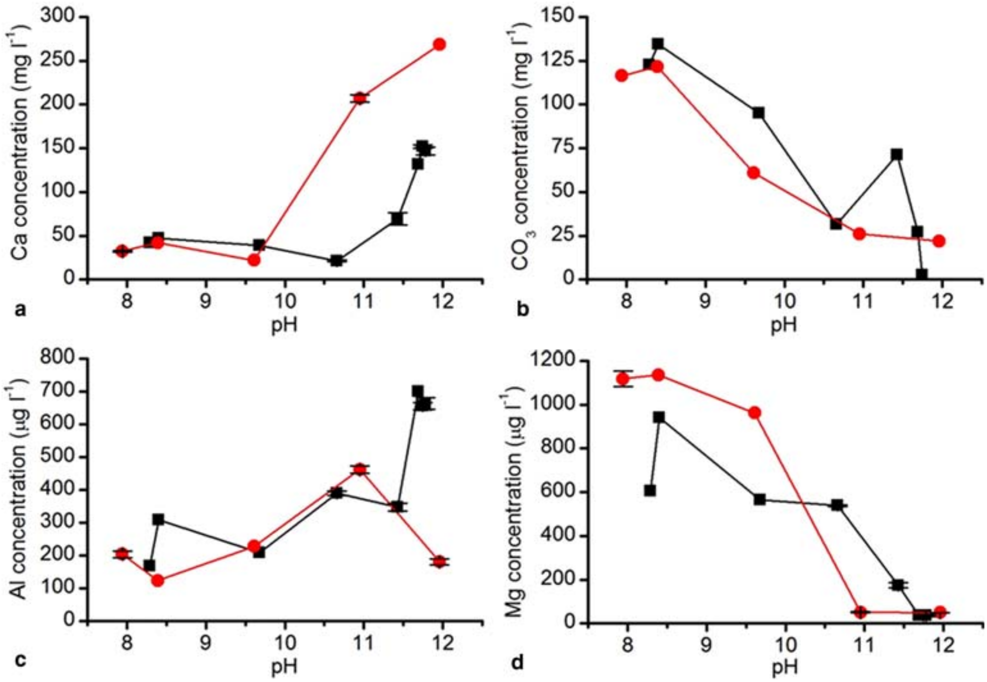

FIG. 2. Concentration of (*a*) Ca, (*b*) CO_3, (*c*) Al and (*d*) Mg in solution *vs.* pH in stream 1 (black) and stream 2 (red).

Schott, 2004) would limit Mg concentration in the highest pH zones, whereas gibbsite ($Al(OH)_3$) solubility increases with increasing pH above pH 6 (May *et al.,* 1979).

At Herbert's Quarry silicate rocks do not crop out in the vicinity of the streams and the low streamwater Si concentration indicated the absence of a significant Si source. Investigation of detrital silicate rocks cemented within stream bed tufa deposits indicated little dissolution directly attributable to reaction in high-pH fluid and no precipitation of secondary C–S–H phases as found in other studies of rock reaction in high-pH solutions (e.g. Gaucher and Blanc, 2006; Mäder *et al.,* 2006; Savage and Rochelle, 1993; Braney *et al.,* 1993; Ramirez, 2005) but provided further evidence of $CaCO_3$ precipitation.

Ca concentrations of 80–800 mg l^{-1} and pH of 10.5–12.2 are representative of cement leachates in equilibrium with $Ca(OH)_2$/C–S–H phases (Atkinson, 1985). Therefore the Herbert's Quarry streamwaters of pH > 10.5 and Ca concentration up to 268 mg l^{-1} may be analogous to cement leachates predicted to form at a GDF (Atkinson, 1985). Also, as the high-pH streamwaters are likely to have existed at Herbert's Quarry for ~200 years (Calch, 2014) the site could extend laboratory studies. However, the prevalence of limestone and only minor occurrence of silicate rocks limits the applicability of the site for currently considered GDF host rocks. The restricted extent of high-pH solutions and resultant extensive precipitation of $CaCO_3$ also limit the potential for high-pH reactions as do the oxidizing streamwater conditions (GDF conditions are expected to be reducing) and temperatures 15–25°C below those anticipated at a GDF (NDA, 2010*a* and NDA, 2010*b*).

Summary and conclusions

In summary, high-pH, Ca-rich streamwaters were identified at Herbert's Quarry. Analysis of sediment and rock samples indicated extensive $CaCO_3$ mineralization as a result of the reaction of Ca^{2+} with dissolved CO_2. This precipitation of $CaCO_3$ reduces the lateral extent of the high-pH streamwaters and so limits the potential for rock alteration at high pH. The occurrence of silicate rocks was rare at the site. No formation of secondary silicate phases was observed in contrast to previous silicate rock alteration studies. Dissolution of silicate minerals was observed at the margins of slate clasts

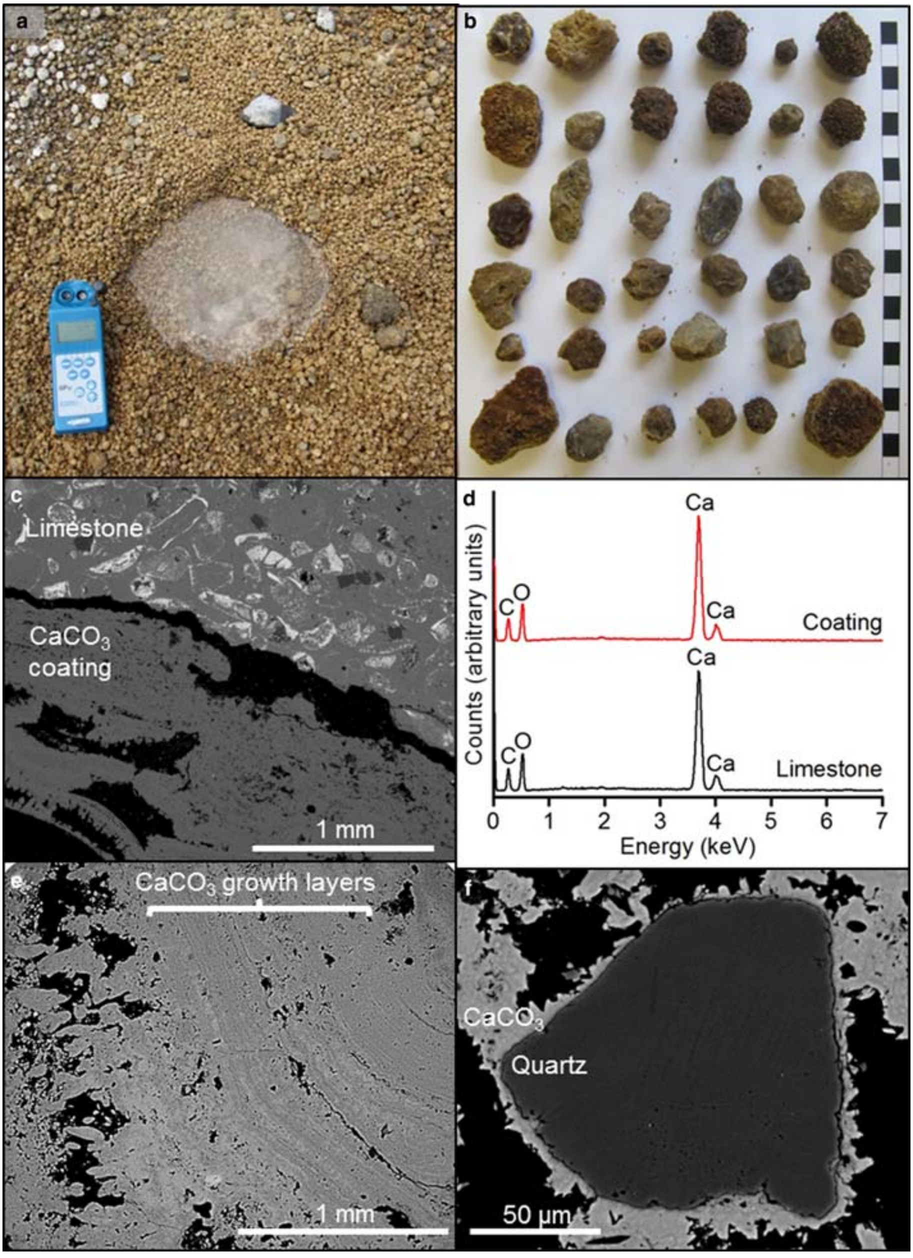

FIG. 3. (*a*) Stream bed (stream 1, site 1) comprised of $CaCO_3$ 'pebbles';(*b*) $CaCO_3$ 'pebbles' (scale shown in cm); (*c*) electron micrograph through a $CaCO_3$ 'pebble'; (*d*) EDX spectra of a limestone fragment with $CaCO_3$ coating shown in *c*; (*e*) electron micrograph of growth layers in $CaCO_3$ coating and (*f*) electron micrograph of quartz fragment entrained in $CaCO_3$ coating.

in contact with high-pH leachate streams. This resulted in enhanced porosity within the matrix of the clasts. Some of this alteration may be partly caused by weathering of these rocks prior to high-pH reaction. However, this alteration may be analogous to that expected from high-pH rock–water interaction in fractured silicate rocks, leading to enhanced matrix porosity in the fracture

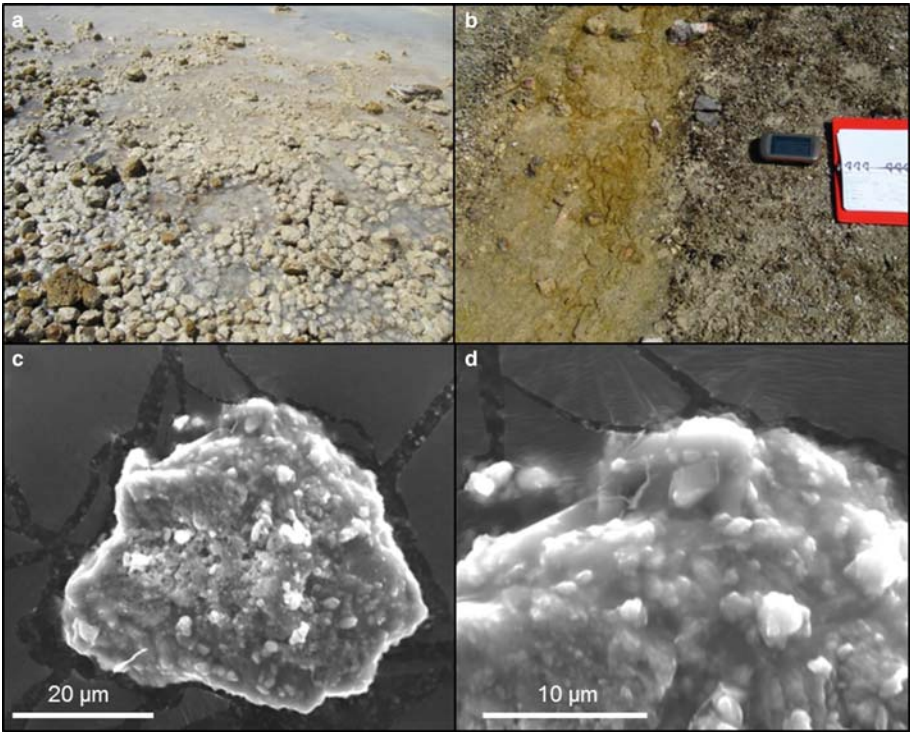

FIG. 4. Stream 2: (*a*) site 2 comprised of $CaCO_3$ 'pebbles' coated in fine grained white material; (*b*) bed of site 3 cemented by tufa deposit; (*c*) electron micrograph of $CaCO_3$ particle from streamwater suspension site 2; (*d*) higher magnification electron micrograph of *c*.

wallrock. This type of alteration may be important in regard to understanding rock–matrix diffusion processes influencing radionuclide migration within the CDZ.

The presence of Ca-rich, high-pH streamwaters at Herbert's Quarry is balanced by the the widespread $CaCO_3$ precipitation through interaction with atmospheric CO_2, paucity of silicate rock, pervasive oxic conditions and low water temperature, which limits the site as an analogue for a cement leachate plume in the CDZ around a cementitious GDF. However, the site may hold

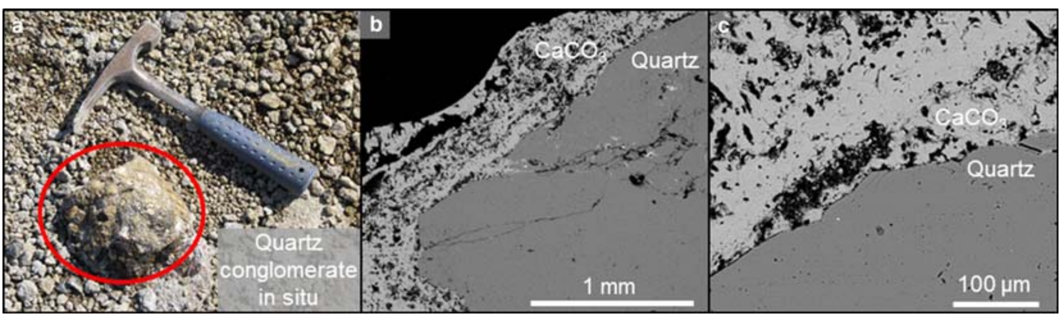

FIG. 5. (*a*) Quartz conglomerate cemented in tufa in dry stream bed *in situ;* (*b*) electron micrograph of $CaCO_3$ formed around quartz in conglomerate; (*c*) higher magnification electron micrograph of $CaCO_3$ formed around quartz in conglomerate.

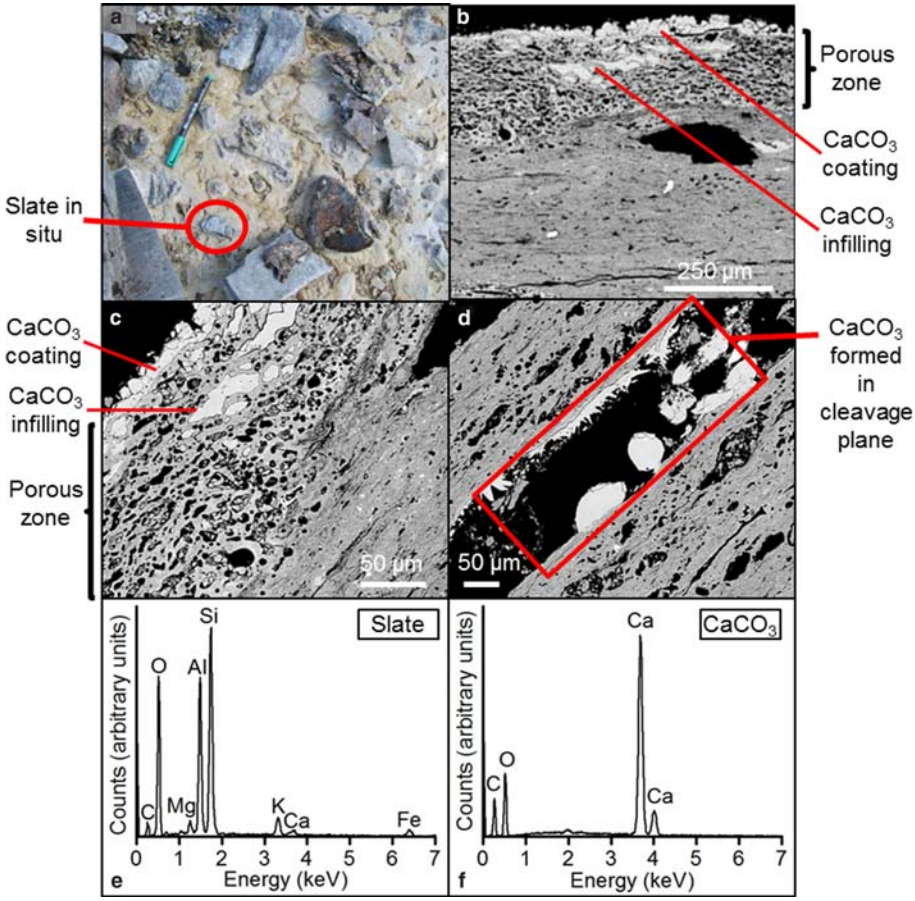

FIG. 6. Slate cemented in tufa (*a*) *in situ*; (*b*) in section via SEM exhibiting increased porosity at surface with $CaCO_3$ infilling; (*c*) higher magnification electron micrograph of increased porosity with $CaCO_3$ infilling; (*d*) electron micrograph of $CaCO_3$ in slate cleavage plane; (*e*) EDX spectrum of slate and (*f*) EDX spectrum of $CaCO_3$.

interest for microbial studies at high pH as alkaliphilic bacteria may be present which are starting to be recognized as important components for deep disposal (Rizoulis *et al.,* 2012; Bassil *et al.,* 2014; Williamson *et al.,* 2013) and further, targeted studies may be warranted.

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