

# Travertine-cemented screes on the serpentinite seacliffs of Unst and Fetlar, Shetland

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## Abstract

Screes on high serpentinite sea cliffs in Shetland have been internally cemented by deposits of brucite, hydromagnesite and aragonite since the last glaciation. These minerals have been deposited from solutions originating as rain (often contaminated with salt spray), which fell on the serpentinite screes and dissolved Mg and minor amounts of Ca from the more finely divided and powdery scree components. As the solutions filtered down through the screes they deposited cements in the form of spherulitic layers of brucite and hydromagnesite with minor amounts of aragonite. At sea level the Mg-rich solutions mingled with sea water impregnating the scree and there cementation within the scree took place by the crystallization of plush-type layers of aragonite on the serpentinite fragments.

KEYWORDS: brucite, hydromagnesite, aragonite, calcite, travertine, serpentinite, Shetland.

## Introduction

TRAVERTINE (including tufa) is widely distributed in the British Isles and has, until now, always been found associated with older carbonate-bearing rocks (Pentecost, 1993), although none has previously been reported from Shetland. The deposits described below are exceptional in their association with the ophiolitic serpentinites of Unst and Fetlar, Shetland.

Three types of lithified breccia of post-glacial origin occur within the outcrop of the ophiolitic serpentinite of Unst and Fetlar, but not elsewhere in Shetland. Types A and B are travertine-cemented and occur only on high serpentinite sea cliffs. Type A are scree breccias cemented by brucite and hydromagnesite with lesser amounts of aragonite and calcite, while Type B are aragonite-cemented scree breccias occurring just above high-tide level. Type C are consolidated/lithified till resting on the serpentinite bed rock, but which show no visible trace of a cementing component. In all localities these three rock-types are currently subject to erosion.

## Field occurrence of travertine

*Type A.* Serpentinite sea cliffs reaching heights of between 100 and 200 m occur in north-east Shetland at Hill of Clibberswick in Unst and East Neap in Fetlar (Fig. 1). The cliffs slope at 40 to 50° seaward, are mostly faced with coarsely jointed, fresh serpentinite and plunge steeply beneath the sea. In several places screes occur due to large cliff falls. One such fall occurred at Clibberswick (Fig. 1, locality A0) in the last few years, resulting in a cone of debris with its apex a few tens of metres below the cliff top and which passes without interruption below sea level, completely burying the bed-rock cliff face below it. The scree is composed of serpentinite fragments varying in size from fine powder to blocks 10 m or more in diameter, the fine material being especially evident in the upper parts.

On the East Neap cliff in Fetlar there are the remains of several much older screes of this type, formed sufficiently long ago for them to be much reduced in size by cliff erosion so as no longer to

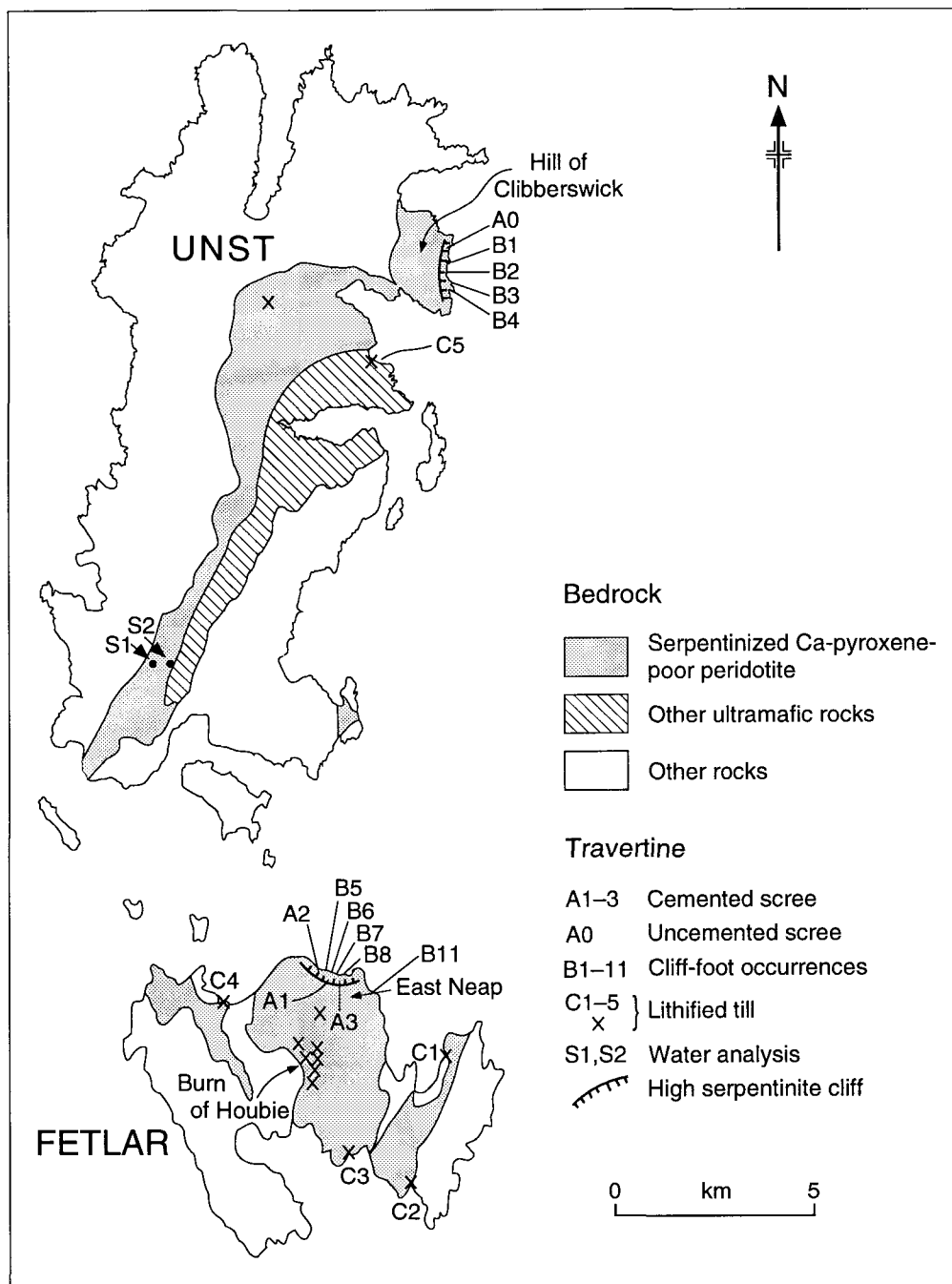


FIG. 1. The location of travertine deposits in Unst and Fetlar, Shetland.

reach sea level and to be partially overgrown by grass (Fig. 1, localities A1 to A3). Where the interior of these old screes has been exposed by recent cliff falls, they are seen to be composed of loosely packed blocks of serpentinite, which have been coated by a white, very fine-grained deposit of variable thickness up to 1 cm. As a result, the screes have been loosely cemented. The travertine cementing these screes is called Type A.

*Type B.* In a number of places at the foot of the cliffs at Hill of Clibberswick and East Neap, erosional relics of well cemented breccias formed of unsorted angular fragments of serpentinite ranging in size from millimetres to metres occur (Fig. 1, localities B1 to B11). The travertine cementing these breccias is called Type B.

These patches of cemented serpentinite are generally only a few metres across and less than one metre thick. They occur only where the cliff face of bedrock forms a near-horizontal ledge just above high tide level. Similar ledges, lacking cemented deposits, occur elsewhere above sea level on the cliff face, and like those at sea level are of short horizontal extent, are not a part of an erosion terrace but merely the chance result of cliff collapse resulting from the marine erosion. The Type B deposits form patches of cemented serpentinite fragments adhering to the flatter parts of some, but not all, of the small ledges in the splash zone above high-tide level. They all occur in positions which, in the past, could have been covered by scree now removed by erosion and in several occurrences the remains of an old scree occurs on the cliff immediately above (Fig. 1, locality B6–A1). The Type B cement takes the form of a thin (< 1 mm) pale brown crystalline layer coating the serpentinite fragments so as to glue them together where the gaps between them are less than 1–2 mm. The patchy distribution of the cemented breccias on the individual ledges, and the fact that the cement is visible only in cross-section on broken surfaces and does not coat the present erosion surface, shows that the deposits are currently being eroded. It may be noted that in several places, along the same cliffs, but a metre or so lower, at mid-tide level, small beaches of very well rounded serpentinite pebbles occur, which show no signs of cementation.

*Type C.* These lithified breccias can be seen on cliff edges in several of the places where cliff retreat has exposed pockets of till overlying the serpentinite (Fig. 1, localities C1 to C5). In these places the base of the till is so lithified, generally up to a metre thick, that it stands out on the cliff face slightly proud of the unlithified till above and the serpentinite below, even, in one place, roofing a small cave formed by the serpentinite falling away (Fig. 1, locality C1). Exposures of otherwise indistinguishable Type C rock occur inland in Fetlar, in the valley containing

the Burn of Houbie, and rarely in Unst (Fig. 1), in the form of small patches, no more than 20 cm thick, resting directly on the serpentinite bedrock. Most occurrences of Type C breccia are exposed in the beds of streams, because elsewhere they tend to be hidden by the thin vegetation cover, but their occurrence appears to be unrelated to the streams, and they are currently being eroded by them. In two places, one in Unst (Fig. 1, locality C5), the other in Fetlar (Fig. 1, locality C4), Type C rock occurs on the coast in the splash zone, where the cliffs are no more than several metres high. The Unst occurrence locally exhibits Type B aragonite cementation lining small open spaces in the Type C breccia. Apart from this, Type C breccias show no visible cement.

### Mineralogy and lithology

*Type A.* In the old screes, on the cliff face above sea level, the white layers cementing scree fragments and coating surfaces vary in thickness from paint-like to approaching 1 cm. No two thin sections of such layers are precisely the same, but they are all composed of one or more crudely formed layers of spherulites of brucite with or without aragonite or of hydromagnesite, with scattered crystals of calcite replacing the other minerals. The minerals were identified by XRD, electron microprobe and optical examination, including staining with Feigl's solution. Polished thin sections of the coatings exhibited no cathode-ray luminescence.

The basal layer in contact with the serpentinite surface is usually 0.1 mm thick or less and composed of contiguous, perfectly formed hemi-spherulites of brucite (centres resting on the serpentinite) with close-spaced, prominent, very thin concentric laminations. Above this layer occur spherulites to hemi-spherulites up to 1 mm in radius of intergrown aragonite needles and brucite. Between and on top of these large spherulites are much smaller ones, rather coarsely crystalline, of hydromagnesite exhibiting radial slow-along extinction. The composition, in cation numbers, of the brucite as determined by electron microprobe is Mg 98.5% (and Al > Si > Na > Ca), and of hydromagnesite is Mg 98% (and Al > Na > Si > Ca). Aragonite occurs above the basal layer, associated with brucite, but small radiating bunches (crude hemi-spherulites) of pale brown aragonite crystals (the same colour as in Type B deposits) about 0.2 mm long occur within and on the surface of the hydromagnesite coating. On analysis these mostly register 100 % CaCO<sub>3</sub> though several showed traces of Al and/or Si. Calcite occurs as columnar crystals up to 0.5 mm long, sparsely distributed throughout the cementation layer replacing the other minerals. Compositions of 97 % CaCO<sub>3</sub> (and Mg > NA > Al > Si) were obtained.

*Type B.* The cement forming this type of deposit takes the form of closely-packed needle-like crystals of pale-brownish aragonite with the *c*-axes oriented approximately normal to the serpentinite surfaces so as to form a plush-type coating. Although the *c*-axes of the crystals are approximately parallel there is no crystallographic continuity between the individuals, which average  $\sim 0.3$  mm long and 0.03 mm across. Many of the serpentinite fragments are no more than a millimetre apart so that the plush layers on adjacent fragments meet and the specimens are strongly cemented. However, in triple-junction areas the plush layers enclose a vug-type open space containing no other minerals. Electron microprobe analyses of these aragonites yielded  $\text{CaCO}_3$  98 % (Na > Mg > Al > Si).

*Type C.* Thin sections of this type of breccia are no different from those of unlithified till. No cementing material is apparent and specimens when treated with dilute acid do not effervesce. However, the restriction of their occurrence in all Shetland to the serpentinite of Unst and Fetlar and their association with the travertines points to a related origin.

#### Stable isotopes

Stable isotope data for the two travertines are listed in Table 1. The oxygen isotope data indicate considerable enrichment of  $^{18}\text{O}$  over meteoric waters and they stand at the upper range for travertines (Turi, 1986, records  $-29$  to  $+1$  ‰), and suggest that the most likely source is meteoric water which has undergone some evaporation thus concentrating the heavier isotope. The multiminerally and variable nature of Type A makes comparison with Type B difficult.

The travertines are also enriched with the heavier carbon isotope when compared with other British deposits, whose  $\delta^{13}\text{C}$  values average about  $-6$  ‰ with a range of  $-12$  to  $-2$  ‰ (Pentecost, 1993), and

which are associated with biogenic (soil atmosphere) carbon dioxide. The heavier values reported here indicate a lack of biogenic carbon input which agrees well with their location in soil-poor screes. The isotope compositions overall suggest a predominantly marine or atmospheric origin for the carbon.

#### Discussion and conclusions

This is the first time travertine deposits have been described associated with ultrabasic rocks in the British Isles, but they have been observed in the western USA and in the Middle East. Barnes and O'Neil (1971) and O'Neil and Barnes (1971) described post-glacial travertines (stream-bed conglomerate cements and crusts, and vein fillings) occurring on and near ultramafic rocks and serpentinites in a Mediterranean-type climate from the Coast Range of California. Minerals associated with calcite (including Mg-calcite) and dolomite include aragonite, hydromagnesite, nesquehonite and hydrotalcite. Stable isotope and chemical analysis of the travertine and associated water seepages led these workers to the conclusion that the deposits resulted from the mixing of Mg-bicarbonate (pH 8.9) groundwaters of meteoric origin with hyperalkaline (pH 12) Ca-rich solutions resulting from modern, low-temperature serpentinization of the ultramafic masses, and Ca-rich bicarbonate solutions (pH 8) derived from nearby non-ultramafic rocks. Reaction between the high-pH hydroxide waters and carbon dioxide originating in the soil, the Ca-bicarbonate solutions and epigene atmosphere produced carbonate ions leading to the precipitation of carbonate.

More recent studies (Clark and Fontes, 1990; Neal and Stanger, 1983) describe extensive deposits of travertine filling stream beds and veins in the outcrop of the ultramafic component of the Oman ophiolite. These deposits of Ca-carbonate (mineral unspecified), in a tropical region (temperatures up to  $45^\circ\text{C}$ ), were formed during both pluvial and dry periods due

TABLE 1. Stable isotope data (‰)

Spec. no.	Location and type	$\delta^{13}\text{C}_{\text{PDB}}$	$\delta^{18}\text{O}_{\text{PDB}}$	Minerals
83635b	A1	-1.05	-0.76	hydromagnesite, etc.
83635	A1	2.30	1.10	hydromagnesite, etc.
83647	B6	-0.67	-2.39	aragonite
83643	B8	-1.1	-2.4	
83628	B1	0.3	-2.5	aragonite

to hyperalkaline (pH 12) Ca-hydroxide waters, arising from low temperature serpentinization, issuing from springs and taking up CO<sub>2</sub> from the atmosphere (and from groundwater in pluvial periods).

Neither of these occurrences bears any resemblance in the field nor in mineralogy to the Shetland travertines. Nor are the origins attributed to them valid for Shetland. The Shetland occurrences are confined to sea cliffs in a cool, wet and stormy climate and thus formed in a very different environment from the other two. In Shetland the mean annual rainfall is about 100 cm, the mean annual temperature is 7.2°C (monthly average range 4.5–12.8°C), the annual mean wind speed is 24–27 km/h with gales (> 60 km/h) on 58 days (236 hours) (Berry and Johnston, 1980).

In Shetland, the ultramafic rock was almost completely serpentinized in the Caledonian orogeny and is coarsely jointed and unweathered. It is very extensively exposed with only a few centimetres of 'soil/glacial drift' over unexposed areas, especially in the neighbourhood of the two cliffs where the travertine occurs, though rare pockets of till occur elsewhere. Fourteen recent determinations of the pH of springs and streams on the serpentine outcrop in the area of Fig. 1 produced a range of values from 7.0 to 8.5. Eight determinations by the Institute of Geological Sciences (1978), carried out on the serpentine outcrop of Unst, gave results in the range pH 7.2, conductivity 330  $\mu\text{S cm}^{-1}$  to pH 8.8, conductivity 460  $\mu\text{S cm}^{-1}$ . Groundwater from the serpentinite obtained from a spring and a small pond fed by a stream arising within the serpentinite outcrop and flowing over it is very different in composition (Table 2) from the waters involved in the formation of the travertines described by Barnes and O'Neill, 1971; O'Neil and Barnes, 1971; Clark and Fontes, 1990 and Stanger, 1983.

The groundwater measurements are all taken from sites remote from the travertine occurrences, because no running water is available in the immediate neighbourhood of the occurrences. However, the sampling sites are all within the outcrop of the serpentinite. The great difference between these waters and those involved in travertine formation in the Coast Range of California and in Oman is obvious.

Both aragonite and brucite have been known to occur in Unst since the beginning of the last century (Brewster, 1823), but such occurrences are of coarsely crystalline material of hydrothermal origin, filling veins in certain localized areas well away from the travertine deposits and probably of Caledonian age.

The water which formed the travertine-cemented scree deposits of Shetland is rain water, (occasionally

TABLE 2. Water analyses

mg/l	S1	S2
Ca <sup>2+</sup>	0.65	0.65
Mg <sup>2+</sup>	19.0	22.5
Na <sup>+</sup>	19.5	20.5
K <sup>+</sup>	1.15	2.20
Cl <sup>-</sup>	44.8	59.0
PO <sub>4</sub> <sup>3-</sup> P	25.0	18.2
Si	2.35	1.75
Alkalinity as CaCO <sub>3</sub>	59.4	n.d.
pH	6.9	8.1
T°C	8	10

Analyst - Ms Paula Cocoran, Department of Oceanography, University of Liverpool.

S1 Spring water, grid reference HP5859 0232

S2 Loch water, grid reference HP5921 0257

Errors:- Ca, Mg, Cl  $\pm 1\%$ ; SiO<sub>2</sub>  $\pm 2.5\%$ ; alkalinity  $\pm 4\%$ ; Na, K  $\pm 5\%$ ; PO<sub>4</sub>  $\pm 6\%$ .  
n.d. not determined.

contaminated by sea spray), which fell directly on the screes resting on the cliffs. No springs occur on the cliffs and are very infrequent on the hillsides behind the cliffs, so that no groundwater has access to the screes. The high proportion of serpentinite fines in the screes provides ideal conditions for the rain water to dissolve up to its maximum content of Mg and Ca, at the prevailing temperature. The serpentinite forming the cliffs is highly serpentinized harzburgite, which contains about 40% MgO by weight, but only about 0.6 wt.% CaO (Thomas, 1980), present in the form of pyroxene altered to a variety of silicates, but not to carbonate.

*The origin of Type A deposits.* It is apparent that Type A deposits were formed by rain falling on newly-formed cliff-fall screes, like that at locality A0 (Fig. 1). The rain (at times contaminated by salt spray) percolated through the scree, dissolved Mg and Ca out of the fine powdery component of the scree and redeposited it as a cement composed of brucite and hydromagnesite with some aragonite on scree-fragment surfaces, especially where it enters empty spaces in the scree causing it to lose CO<sub>2</sub> and/or water. Considering the equable nature of the Shetland climate the temperature of the water within the scree cannot vary much from 6–7°C (the mean of the mean monthly temperatures weighted by the mean monthly rainfall).

Under these conditions, according to Lippmann (1973, figs 33 and 50), with low CO<sub>2</sub> content, Mg

would be expected to be deposited as stable brucite. At higher CO<sub>2</sub> content brucite and/or hydromagnesite would be deposited as metastable minerals (the high affinity of Mg for water would prevent the deposition of the stable mineral magnesite). Due to the relatively high concentration of Mg, Ca would be deposited in the metastable form, aragonite. The calcite found in the cementing layers grew later, evidently as a stable replacement mineral, possibly due to the action of low-Mg rainwater percolating through the already cemented scree.

It is apparent at locality B5 that the cementation still continues in the scree because the remains of an old scree continues down the cliff to about 10 m above sea level and the exposed bed rock between the scree and the sea has been 'painted' white by mineral deposition from water flowing from ephemeral springs at the base of the cemented scree. This water flows directly into the sea (over the remains of a B-type deposit) and is washed away immediately by the sea so that no aragonite deposition can take place.

*The origin of the Type B deposits.* Before the erosion of the scree at sea level had taken place the magnesium-rich water flowing down within it reached sea level, where the scree was impregnated with sea water. This sea water was thereby enriched in Mg, especially where the bedrock surface beneath the scree was flat, or better, concave upwards, thus ponding the sea water and protecting it from free circulation with the open sea. All the observed occurrences of this type of travertine are preserved in such situations, as described above. It is suggested that the enhancement of the Mg content of the sea water within the scree, possibly assisted by evaporation in times of drought and calm seas, was sufficient to reduce the solubility of the Ca and cause it to crystallize as the metastable mineral, aragonite, the precipitation of the stable mineral calcite being inhibited by the high content of Mg (Lippmann, 1973, p. 113). The exclusive deposition of carbonate indicates a higher content of CO<sub>2</sub> than in the scree above. This may have been due in part to waves breaking over the scree at sea level and continually forcing air, containing CO<sub>2</sub> through it.

Cementation must have taken place recently, since sea level has been rising in Shetland since the end of the glaciation and has risen at least 9 m in the last 5500 years (Hoppe, 1965) and the Type B deposits are still above sea level. The sea temperature rarely varies outside the range 7–12°C, and there is no evidence that it has done so in the recent past.

*The origin of the Type C deposits.* The occurrence of the Type C deposits in the same area as Types A and B, their superficially similar appearance and their restriction to the serpentinite outcrop point to a related origin. Their occurrence in valleys and in the bottoms of pockets of till may be

due to groundwater flowing through them, dissolving Mg from the serpentinite-flour component of the till and depositing it as sub-microscopic cement composed of brucite and/or hydromagnesite in the grain boundaries, the till being much more compact than the scree.

This is the first time that a marine-carbon source has been implicated in travertine formation. Travertines are frequently found on coastal cliffs, but in almost every case their origin can be traced to the degassing of a freshwater carbonate-rich aquifer. In Shetland, this is not the case. Unexplained occurrences of travertines in other non-carbonate areas are known, however. For example, in western Scotland, carbonate crusts occasionally develop on buildings near the coast (V. Lutz, pers. comm.) and in Norway crusts of calcite-travertine up to 8 cm thick have been observed on syenite sea cliffs with no obvious carbonate source (Hoeg, 1929).

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