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Paleopedogenic palygorskite from the basal Permo-Triassic of northwest Scotland

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Abstract

X-ray diffraction, scanning-electron microscopy, and chemical analysis show the presence of palygorskite across an unconformity of New Red Sandstone on Torridonian sandstones in northwest Scotland. An expansion of the mineral on glycollation is attributed to the replacement of zeolitic water present in channels in the mineral structure. The origin of the palygorskite is thought to be due to neoformation within a basal Permo-Triassic soil profile, the mineral occurring as coatings on fossil ped surfaces. A semi-arid to arid climate at the time of formation is inferred.

Introduction

A recent paper in this journal (Singer and Norrish, 1974) described the occurrence of palygorskite in some Australian soils, and stability fields were produced for the mineral to suggest its pedogenic origin by neoformation within the soil profiles. It is intended here to relate these observations and findings to the presence of palygorskite across an unconformity at Gruinard Bay, northwest Scotland (British National Grid Ref. NG 900929).

The unconformity, which occurs as a natural arch, and which was illustrated as long ago as 1856 (Nicol, 1856) consists of gently dipping Permo-Triassic New Red Sandstone conglomerates resting on moderately steeply dipping Torridonian sandstones (Fig. 1).

At and below the junction the Torridonian is severely brecciated, with calcite veins and staining from the overlying red conglomerates penetrating down to a depth of about 1 meter. The overlying New Red Sandstone consists of a thickly-bedded conglomerate, partly cemented by calcite, and erosively truncated by a later conglomerate.

Fresh samples of this conglomerate, and of the brecciated Torridonian, reveal a white shiny film (which does not effervesce with acid) along internal fissures.

Experimental

Five fresh samples were collected across the unconformity on a profile 90cm long (Fig. 1). Samples for X-ray diffraction were ultrasonically disaggregated, treated for 5 hours with buffered NaOAc (at pH 5), and repeatedly washed with distilled deionized water to obtain a suspension. The fraction less than 2 microns ($<2\mu$ fraction) was separated by sedimentation and a portion deposited on an unglazed ceramic tile under vacuum. X-ray diffraction patterns were obtained from air-dried tiles using a Philips PW 1380 horizontal goniometer, Cu$K\alpha$ radiation with a Ni filter, and with a scanning speed of 1°/minute. Further patterns were obtained after glycollation (using a vapor pressure method) and after heating to 400°C, 550°C, and 800°C for one hour at each temperature. Additional separations of the $<0.2\mu$ and 2μ–63μ fractions were made, and diffraction patterns obtained as above.

Samples of fissure surfaces and of freshly-split surfaces were sputtered with gold and examined using a Bausch and Lomb SEM II scanning electron-microscope.

Finally, samples of the white film were carefully scraped off further fissures, avoiding contamination from neighboring material; and SiO_2, Al_2O_3 total iron, TiO_2, P_2O_5, and MnO were determined colorimetrically using a Technicon Auto-analyser. CaO, MgO, Na_2O, and K_2O were determined by atomic absorption spectroscopy on a Perkin-Elmer PE 403 Atomic Absorption Spectrometer (analyses by S. Malik and D. Bungard).

Results

X-ray diffraction

With the exception of sample *a*, all the samples were dominated by a mineral characterized by *d*-spacings of 10.5, 6.44, 5.42, 4.48, 4.13, 3.36, 3.18, 3.04, and 2.59 (in Ångstroms), corresponding closely to those of palygorskite (Powder Diffraction File); the appearance of a peak at 9Å after heating to

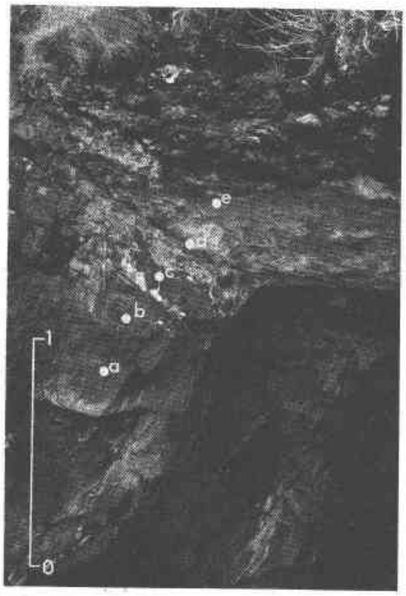

FIG. 1. Eastern side of the arch at Gruinard Bay showing the position of samples *a-e*. The plane of the unconformity passes just below *d*. (Scale in meters.)

400°C adds further support for the mineral being palygorskite (Nathan, 1969). The mineral collapses slighty to 10Å on heating to 400°C, and fully at 550°C; it is destroyed at 800°C.

It is worth noting, however, that on glycollation there is a definite shift in the peaks (with the exception of those at 5.42Å and 3.04Å), most of which show an expansion, but one of which shows a collapse (at 4.48Å) (Fig. 2).

Expansion of palygorskite on glycollation has been noticed previously (G. Brown, personal communication), and has been attributed to the replacement of the zeolitic water in the internal channels of the mineral (Vanden Heuvel, 1966). I suggest that this is also the case here, and whether the amount of expansion is related to the number and size of the channels, and whether these are related to the mode of formation, is being investigated.

Other clays found in the samples include illite, montmorillonite, and chlorite, with kaolinite present as a trace in samples *b* and *c*. The distinction between chlorite and kaolinite was made by warming the material for 10 hours with 10 percent HCl; this usually destroys the chlorite. However, in some cases concentrated HCl was needed to destroy the chlorite completely, suggesting the presence of a more stable chlorite mineral; its increased abundance in the 2μ–63μ fraction suggests that this may be detrital. Illite was also concentrated in this fraction, whereas montmorillonite increased in the $<0.2\mu$ fraction.

Scanning electron microscopy

The fissure surfaces were seen to consist of a thin film (less than 0.5mm thick) of a fibrous mineral thought to be palygorskite. The mineral forms mats of well-orientated fibers, arranged in strips often at an angle to each other, and frequently having a wispy appearance. (Figs. 3 and 4)

These mats differ from those cited by Singer and Norrish (1974) only in the increased size of the fibers. Although some palygorskite was found in the larger channels of the rock, and also as thin coatings on the surfaces of some large grains, most of the grain-free argillans[1] *between* the fracture surfaces consist of montmorillonite.

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[1] Terminology of Brewer, 1964

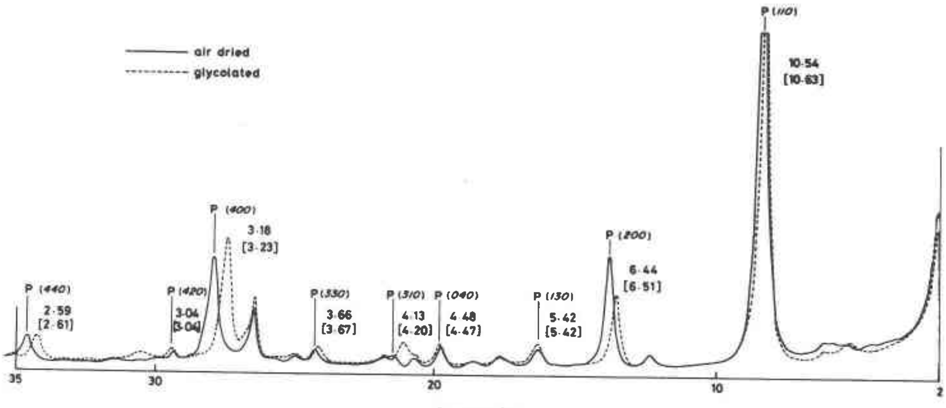

FIG. 2. Diffractogram obtained from $< 2\mu$ fraction of sample *e*, showing the effects of glycollation on the palygorskite (*P*) peaks. In italics is *hkl*; unbracketed—*d*-spacings under air-dried conditions; square brackets—*d*-spacings after glycollation.

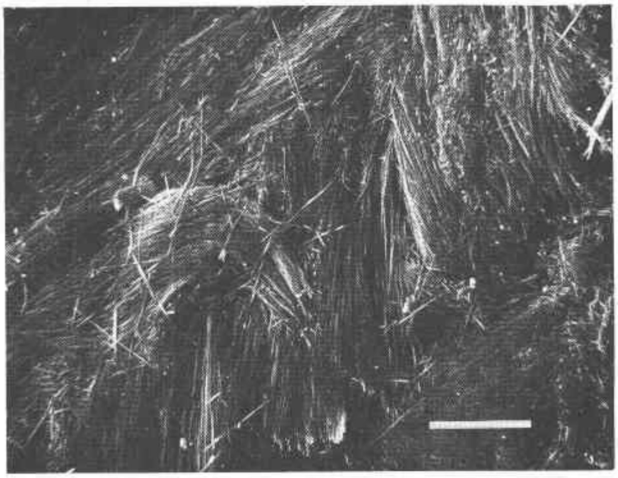

FIG. 3. Scanning electron micrograph of a coated fracture surface showing a mat of palygorskite fibers arranged in strips, the fibers within the strips having a near parallel orientation. Bar is 5μ long.

TABLE 1. Chemical composition of palygorskite crust scraped from a fractured surface *e*.*

	wt percent		wt percent
SiO_2	65.9	CaO	2.4
Al_2O_3	10.5	MgO	7.6
Total iron	1.3	P_2O_5	<0.1
TiO_2	0.2	K_2O	1.4
MnO	<0.1	Na_2O	<0.1
	Total 89.6		

*Dried at 110°C for two hours.

Chemistry

The chemical analysis of the white film is given in Table 1. Concentrations are quoted to one decimal place only due to the small amount of material available for analysis. The results show a close similarity to published analyses of palygorskite (Isphording, 1973). The slightly high values of SiO_2 and CaO may be the result of some contamination by quartz and calcite; most of the remaining 10.4 percent is probably water. The 1.4 percent K_2O is unusually high and may be due to the presence of illite in the sample.

Discussion and conclusions

The results show that the white fibrous mineral coating the fissures across the unconformity is palygorskite. The variation in palygorskite concentration along the profile (Fig. 5), and its similar mode of occurrence to that described by Singer and

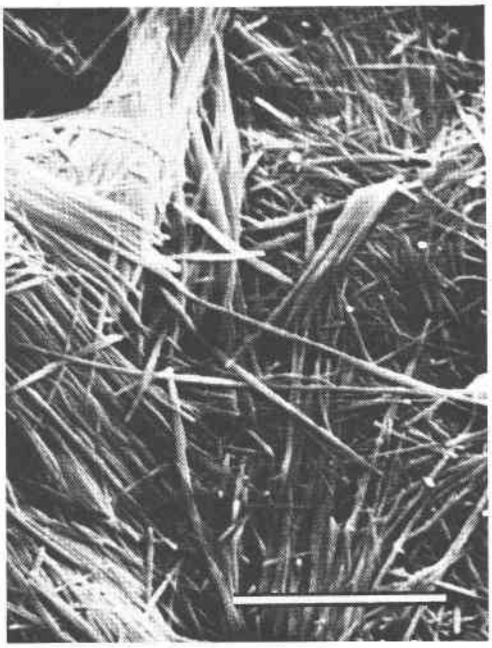

FIG. 4. Detail from Figure 3 showing palygorskite fibers at the junction of two strips. The strips generally consist of longer fibers (often > 3μ) becoming interwoven at the strip junctions, see top left of figure. Areas between the strips are occupied by poorly aligned smaller fibers (often <1μ in length). Bar is 2μ long.

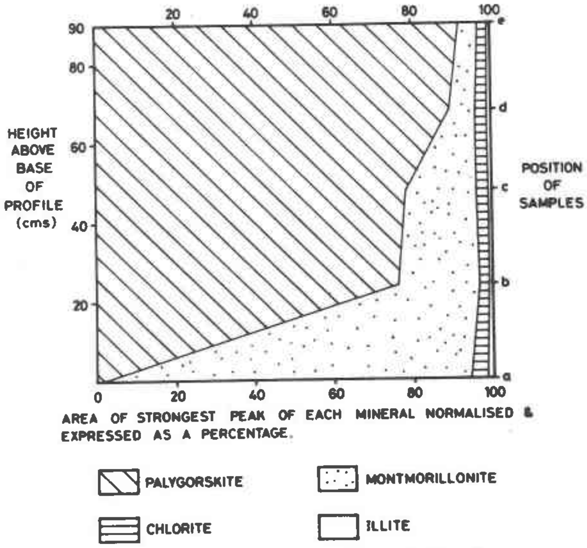

FIG. 5. Diagram to illustrate the variation in clay mineralogy along the studied profile. (<2μ fraction).

Norrish (1974), suggest its pedogenic origin. Although alteration of montmorillonite to palygorskite has been postulated in some cases (Sautereau, 1974), I believe that the palygorskite described here was neoformed within a soil profile. Drawing an analogy to the coated surfaces described by Singer and Norrish, I further believe that the shiny white films of palygorskite on the fissure surfaces are fossil ped coatings, the palygorskite being formed along these (and in some cases penetrating into the peds along large channels) after initial montmorillonite accumulation in the profile. The abundance of well-crystallized montmorillonite in sample *a* is also pedogenic, as this mineral is not common in Torridonian sediments.

It seems then that soil formation must have occurred after the deposition of the basal New Red Sandstone conglomerate, and that the resulting pedogenesis brecciated and disrupted the Torridonian to a depth of at least 50 cm. No A-horizon is seen and it is probable that this was removed before deposition of the overlying conglomerate which lies on an eroded surface.

Paquet and Millot (1972) have stated that palygorskite in soils is unstable and weathers to montmorillonite when the mean annual rainfall exceeds 300mm per annum, and indeed most examples of definitely neoformed palygorskite in soils occur in semi-arid environments (*e.g.* Millot *et al.*, 1969; Singer and Amiel, 1974; Singer and Norrish, 1974; Al-Rawi and Sys, 1967). It is generally accepted that the climate in Britain during Permo-Triassic times was semi-arid to arid (*e.g.* Audley-Charles, 1970); certainly the presence of well-developed calcretes (which also contain palygorskite—N. Watts, in preparation) a short distance above the unconformity at Gruinard Bay (Steel, 1974) is consistent with this.

It is hoped, therefore, that this short contribution is further evidence for use in Permo-Triassic reconstructions, and will provide a stimulus for closer work between soil scientists and geologists in the future.

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