Table 1. RESULTS OF POTASSIUM-ARGON DATING

Material	K_2O (per cent) Average of 5 determinations	Volume of argon (mm.^{3}) / Weight of sample (gm.)	Atmospheric contamination present	δV_R	δt	Age in millions of years
96388 (coarse). Old Lizard Head Series. Pen Olver	9·03	0·1206	2·7	0·4	3·25	357
96388 (fine)	9·01	0·117	1·6	0·2	3·21	352
96391 (fine). Old Lizard Head Series, nr. Life-boat station, Polperro	9·11	0·130	8·4	0·4	3·27	359
96391 (coarse)	9·17	0·121	2·0	0·2	3·20	355
						Mean = 356
96392 Kennack Gneiss, Kennack Sands	6·97	0·1188	14·1	0·5	3·58	397
96393 Kennack Gneiss, Polgwidden	5·98	0·0874	3·8	0·6	3·47	384
						Mean = 391

$\lambda_e = 0·584 \times 10^{-10}$ yr.$^{-1}$. $\lambda_\beta = 4·72 \times 10^{-10}$ yr.$^{-1}$.
δV_R = Percentage standard deviation in volume of radiogenic argon due to uncertainty in isotope ratios of specimen.
δt = Error in age (in millions of years) due to a 1 per cent error in proportion of K_2O or volume of radiogenic argon.

grade metamorphism during the late (? Hercynian) thrusting.

In order to check the figures yielded by the Old Lizard Head series, determinations are to be made on hornblendes from the Landewednack hornblende schist and from hornblende granulites in the metamorphic aureole of the peridotite.

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CRYSTALLOGRAPHY

Epitaxial Growth of Crystals on One-Degree Orientated Substrates

DURING the oxidation of one-degree orientated metals, an unexpected variation in the dispositions of oxide crystallites was observed which appears to be similar to epitaxial growth[1] of crystals on single crystal substrate. In this process, the growing crystals (overgrowths) aligned themselves in a certain manner depending on the arrangement of atoms or ions of the substrate and more correctly on the potential energy configuration at or near the surface layers. Consequently a definite orientation relationship is established between their crystal axes, and the overgrowths are said to develop a two-degree orientation such that two axes of theirs are parallel to two of the substrate. This is more often expressed by a plane and axis of each. Single crystal substrates thus greatly influence the orientation of the overgrowths at least in the initial stage of their growth[2]. On different faces of the substrate, the deposit orientation would normally be different, provided the growth condition is not too drastic or temperature not too high. The same orientation may, however, be induced on different faces of the substrate, but is again determined by the substrate structure. Numerous illustrations of such epitaxial growth of crystals are cited in the literature (see Pashley[3]).

On polycrystalline and amorphous substrates, this type of orientated overgrowths is not observed, simply because there is no regular order in the disposition of crystallites of the substrates in the former and no regular periodicity in the atomic arrangement in the latter. In one-degree orientated substrates, however, there is some partial order in distribution of crystallites in the sense that they have a common and parallel axial direction (or plane), known as orientation axis (or plane); but otherwise they are all randomly disposed. No result is yet published which suggests the influence of such substrate on the growing crystals. In view of my observation mentioned earlier, orientated metal substrates were oxidized slowly in air and the nature of the oxide crystals studied by electron diffraction.

Nickel electro-deposits of {100}, {110}, {210} and $\{10\bar{1}0\}$ + {211} orientations (one-degree) and cobalt of {110} were prepared by electro-deposition[4]. These were then heated in air in an electric furnace to a temperature of about 320° C. for about an hour and the surface layers examined by electron diffraction both before and after oxidation in the usual way[2,4].

Table 1

Substrate orientation (1-*d*)*	Oxide orientation (1-*d*)*
Ni {100}	NiO {100}
Ni {110}	NiO {110}
Ni {210}	NiO {210}
Ni $(10\bar{1}0)$ + {211}	NiO {111}
Ni {Poly}	NiO
Co {110}	Co_3O_4
Co {110} †	CoO {110}

* 1-*d*: one-degree orientation.
† At about 10^{-2} mm. mercury pressure of air.

Nickel metal was oxidized to nickel monoxide (NiO) only, whereas cobalt to cobalto-cobaltic oxide (CO_3O_4) in air, but to cobaltous oxide (CoO) only at low pressure ($\simeq 10^{-2}$ mm. mercury) of air. The surface layers on nickel substrates consisted not only of orientated polycrystalline monoxide but also of unreacted metal. Nickel monoxide (NiO) crystallites developed different orientations depending on the nature of initial substrate orientation (Table 1). But under the same conditions, polycrystalline nickel was oxidized to unorientated nickel monoxide. On further heating, however, entire surface layers, whether of orientated or unorientated nickel, consisted of polycrystalline nickel monoxide only. Further oxidation would lead to nickel monoxide, having preferred orientation determined entirely by the oxidation conditions similar to cuprous and cupric oxides on copper[5]. For better orientation the oxidation should be carried out at mild conditions. On cobalt {110} surface under milder conditions of oxidation at low pressure, again {110} orientated cobaltous oxide was observed.

These results clearly show that the overgrowth orientations can also be influenced considerably by substrates orientated one degree, at least in the initial stage of growths, and the process closely resembles the epitaxial growth on single crystals.

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GEOCHEMISTRY

Fossil Chlorins in a Triassic Sediment

Spectroscopic evidence for the presence of green chlorophyll-derivatives in ancient sediments and crude oils has been reported by Treibs[1] and by Blumer[2]. We have now succeeded in isolating and characterizing the green pigments responsible for the absorption band at about 640 mμ in the extracts of the porphyrin-rich Triassic oil-shale from Serpiano (Switzerland) (Fig. 1*A*). The pigments are isolated by first removing from the extracts the asphaltenes by iso-octane precipitation and extracting the ether solution of the pigment-concentrate with 6 *N* hydrochloric acid. Subsequent partitioning between ether and hydrochloric acid of increasing concentration removes the stronger bases deoxophylloerythroetioporphyrin (DPEP) and meso-etioporphyrin (MEP). The final purification of the green pigment is then accomplished by repetitive chromatography over partially deactivated alumina (Brockman III). The spectrum of the pure pigment (Fig. 1*B*) is characteristic of the chlorin (dihydroporphin) configuration, and the partial resolution of the band at 490 mμ in addition to the presence of a small band at 612 mμ is indicative of a meso-chlorin, a chlorophyll-derivative in which the vinyl-group in the 2-position has been hydrogenated to an ethyl-group[3]. The high chromatographic mobility of this pigment on alumina and on paper ($R_F = 0{\cdot}75$ on Whatman No. 3 paper, carbon tetrachloride–iso-octane developer, 7 : 3, see ref. 4) eliminates the possibility of the presence of acid-, ester- and other polar groups like —COH, —CO, —OH.

The pigment, which is thus characterized as a meso-etiochlorin, can be converted to the corresponding porphin by dehydrogenation with excess chloranil in boiling xylene. The reaction product (Fig. 1*C*) exhibits a typical porphyrin spectrum, intermediate between those of DPEP and MEP and identical with that of the DPEP/MEP-mixture present as uncomplexed pigments in the same sediment. This dehydrogenation product can be resolved by chromatography over alumina into fractions with the etio-spectrum of MEP and phyllo-spectrum of DPEP. Paper chromatography of these fractions confirms the spectroscopic evidence, the R_F-values agreeing within ±0·01 unit with those for pure DPEP and MEP.

For additional structural confirmation, the unknown dihydroderivative of DPEP was synthesized by hydrogenating with Raney-nickel a DPEP concentrate isolated from the oil shale. The spectrum of the hydrogenation product is identical to that of the fossil chlorin. A small difference in the R_F-values (0·68 for the synthetic compound, compared with 0·75 for the natural chlorin) is explained by the presence of a larger fraction of the more rapidly moving dihydro-MEP in the natural pigment.

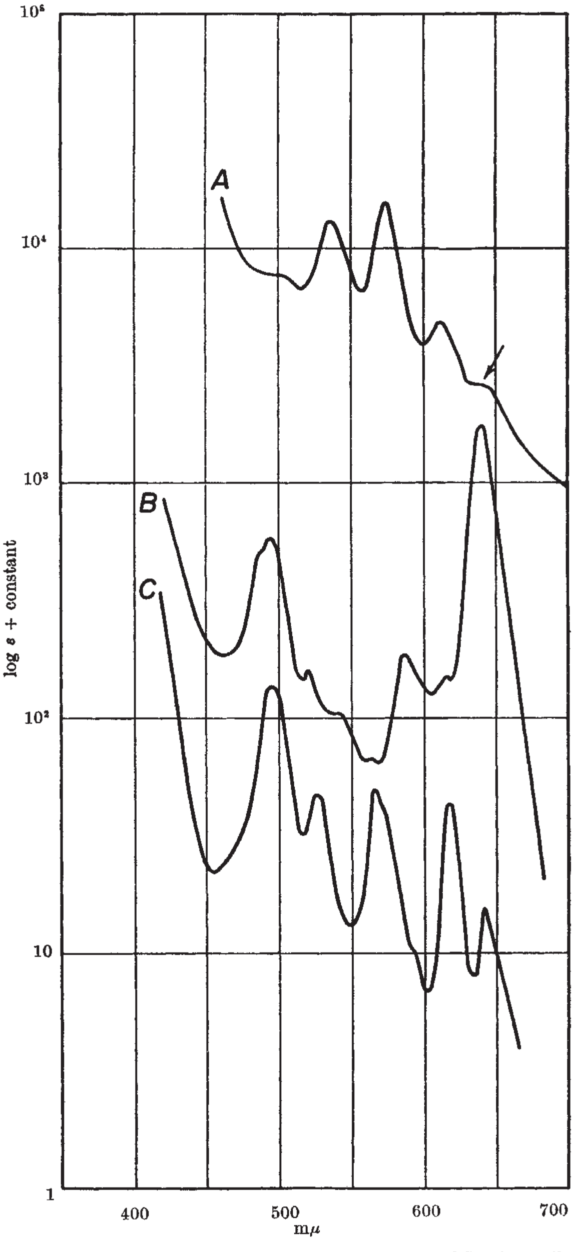

Fig. 1. Spectra. *A*, Benzene–methanol extract of Serpiano oil-shale; *B*, natural dihydro-DPEP containing some dihydro-MEP; *C*, porphyrin mixture obtained by dehydrogenation; the small peak at 641 mμ is a trace of residual chlorin

Thus, the fossil chlorin is characterized as a mixture of dihydro-DPEP (deoxo-meso-etio-pyro-pheophorbide *a*) with some dihydro-MEP (etiochlorin III). The etiochlorin must have been formed by intensive reduction from hæmin, protoporphyrin, mesoporphyrin and meso-etioporphyrin being intermediates. The chlorin structure of dihydro-DPEP is also more likely to be of secondary than of primary origin. The vinyl-group of the chlorophyll-pigments disappears early in geological history, probably by isomerization of the vinyl-chlorins to meso-porphyrins.