Meilanov *et al.*[15] in their attempt to verify the semiconductor model of photosynthesis, found a relatively high quantum efficiency (12–20%) for bulk photoconductive effects in metal-sandwiched dry Chl layers (0.3–2 μm thick) across which a high voltage (30–250 V) was applied. Our system is essentially different in that the photocurrent is produced by a direct electronic coupling between an excited Chl and the conduction band of SnO_2, not by an accelerating effect of the electric field across the Chl layer.

An extension of the present experiments to the construction of biomimetic membranes on SnO_2 OTE by incorporating other photosynthetically important compounds into the Chl *a*–DPL mixed monolayer would be highly promising in view of the *in vitro* simulation of the photosystem II in plant photosynthesis.

We thank Dr K. Iriyama for useful discussion, and Tien-Kai Li for technical assistance. This work was supported in part by a grant-in-aid from the Ministry of Education of Japan.

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Received 30 October 1978; accepted 16 January 1979.

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Enhanced CO_2 greenhouse to compensate for reduced solar luminosity on early Earth

CURRENT models for the evolution of the Sun require an increase in solar luminosity by 25% since the formation of the Solar System[1]. Such an increase in the solar constant should have profound effects on the terrestrial climate, but there is no evidence from the fossil record of a corresponding change in the Earth's global mean temperature[2]. This apparent conflict cannot be explained by the apparent inability of solar models to account for the low observed neutrino flux[3]. Even models that are forced to fit the neutrino data require a similar increase in the solar luminosity. As Newman and Rood[1] state: "a faint young Sun is one of the most unavoidable consequences of stellar structure considerations". We discuss here whether CO_2–H_2O in a weakly reducing atmosphere could have caused this change in the early Earth's temperature by the so-called greenhouse effect.

Sagan and Mullen[4] suggested that the solution must lie in a more efficient atmospheric greenhouse effect on Earth during the period when the solar luminosity was low. To increase the greenhouse effect, it is necessary to change the atmospheric composition, or density, or both. Sagan and Mullen[4] postulated that the atmosphere was reducing during the early history of the Earth and found that a small amount of ammonia in the atmosphere (mixing ratio 10^{-5}–10^{-6}) would provide the necessary opacity to outgoing infrared (IR) radiation to increase the mean surface temperature. In this model, the transition from reducing to oxidising conditions with the replacement of the NH_3–H_2O greenhouse by a CO_2–H_2O greenhouse comes about as a result of the development of widespread green plant photosynthesis 1,000–2,000 Myr ago. A similar route was invoked by Hart[5], who developed a more detailed model for the evolution of the atmosphere.

We agree that an enhanced greenhouse effect caused by a change in atmospheric composition is a good solution to the solar constant dilemma, but we think the NH_3–H_2O model is unrealistic. Current thinking about the early atmosphere of the Earth is shifting away from the traditional view that called for a highly reduced mixture of methane, ammonia and hydrogen, for reasons summarised by Walker[6]. More recent data have simply added strength to Walker's conclusions. As the noble gases on Mars show the same pattern of relative abundances as they do on Earth and in the 'planetary component' of the meteoritic gases, whatever fractionation process caused this pattern must have occurred before planet formation[7]. This being the case, the cosmic abundance ratio of 1.6×10^4 for H/Ne[8] gives the maximum amount of hydrogen available for a 'captured' primitive atmosphere. Using the present atmospheric partial pressure of Ne (12.7×10^{-6} bar), the maximum hydrogen partial pressure on the primitive Earth from this source was 10 mbar. As Walker[6] has pointed out, such an atmosphere would have dissipated in $<10^4$ yr. The partial pressure of ammonia in this atmosphere would have been comparable to that of neon, but its lifetime against photodissociation would have been short and it would have been out of equilibrium with crustal rocks.

Photochemical calculations by Kuhn and Atreya[9] indicate that ammonia would be irreversibly converted to N_2 on the primitive Earth in <40 yr if the mixing ratio were $\leq 10^{-4}$. Eugster[10] has investigated the stability of ammonia on the primitive Earth and concluded that a mixture of N_2 and H_2 will predominate over ammonia in a normal crustal environment. Outgassing of ammonia after the last phase of accretion (or after differentiation, choosing either an inhomogeneous or homogeneous model for planet formation) seems precluded by the lack of free iron in the upper mantle[6]. As life must have begun after this phase in the planet's history, it seems reasonable to agree with Eugster[10] that any initial ammonia in the atmosphere "was oxidised to nitrogen long before the origin of life". Small amounts of methane and ammonia may have been transiently present in later times as a result of meteoritic and cometary impact, but lunar evidence indicates that bombardment rates must have been close to their present low values ~3,600 Myr ago[11].

In fact, the idea that the chemistry preceding the origin of life must have occurred in highly reducing conditions supported the traditional view of the composition of the early atmosphere[12]. But there have been sufficient demonstrations that pathways towards the formation of essential pre-life compounds can occur only in weakly reducing conditions for this argument to have lost its original force. For example, Abelson[13] was able to produce amino acids from the UV irradiation of a mixture of CO_2, CO, N_2, H_2O and just 1–10% H_2. This seems a much more reasonable composition for the post-accretion (or post-differentiation) atmosphere of the primitive Earth[6,10]. It is especially unlikely that the ammonia-containing mixture invoked by Sagan and Mullen[4] (or ammonia plus methane suggested by Hart[5]) would last for 2,000–3,000 Myr after formation of the planet. But can this weakly reducing atmosphere provide the required greenhouse effect? The answer depends on carbon dioxide and water vapour, as the other gases are ineffective absorbers of IR radiation.

We have tested this possibility by assuming that the concentration of CO_2 in the early atmosphere was much higher than the present value. We have coupled the evolutionary model for the CO_2 abundance used by Hart[5] with a radiative–convective CO_2-climate model. (We used the model as in Augustsson and

0028–0836/79/0277—0640$01.00

Table 1 Predicted global surface temperature, T_s, throughout the evolution of the Earth's atmosphere

Time (10^9 yr BP)	S (W m^{-2})	P_{CO_2} (bar)	T_s (K)	
4.25	1,039	0.31	310	(284)
3.5	1,096	0.070	296	(284)
3.0	1,133	0.033	293	(284)
2.5	1,171	0.018	292	(286)
2.0	1,209	0.0086	290	(286)
1.5	1,247	0.0029	288	(286)
1.0	1,284	0.00065	286	(285)
0.5	1,322	0.00032	287	(287)
0	1,360	0.00032	290	(290)

The solar constant, S, is taken to be $S = 1{,}020$ W m^{-2} 4,500 Myr ago and is assumed to increase linearly with time. The CO_2 surface pressure, P_{CO_2}, is from Hart[5]. Temperatures listed in parentheses refer to deletion, within the model, of weak CO_2 bands at 9–10, 12 and 18 μm.

Ramanathan[14] except that we do not include the 7.6 μm pressure-induced band of CO_2 in the present analysis, because of the lack of band absorption data for the large amounts of CO_2 considered here.) Hart's model comprises a numerical simulation of the evolution of the Earth's atmosphere over its 4,500 Myr history, accounting for time-dependent outgassing, the Urey equilibrium, the onset of photosynthesis, and crude atmospheric chemistry to develop the time-history of the CO_2 concentration. Hart also presents NH_3 and CH_4 concentrations but we do not believe that these gases would persist within the early atmosphere. Moreover, even if CH_4 were present in the early atmosphere, this constitutes a very inefficient greenhouse gas. Quite obviously Hart's attempt contains many modelling uncertainties, but at least it produces a first estimate for the variability of atmospheric CO_2 over geological time.

Although Hart[5] has considered the greenhouse effect from enhanced CO_2, as well as other gases, he uses grey gas radiation modelling. But the realities of accounting for enhanced CO_2 require a more detailed radiation model[14,15]. Moreover, Hart has used a cloud radiation model which produces strong negative climate feedback, contrary to the findings of recent cloud–climate modelling studies[16,17]. This occurs as Hart relates global cloud amount to atmospheric water-vapour content, such that his cloud amount increases with increasing planetary surface temperature. But recent model predictions suggest that the reverse occurs (see ref. 16). Hart has additionally neglected the IR opacity of clouds. Thus, in his model, a warmer planet produces an enhanced planetary albedo due to increased cloudiness, but with no compensatory IR modification, and for this reason his model gives negative cloud feedback.

In the present study, we ignore climate-induced changes in cloud-cover fraction, following the suggestion that the cloud albedo and IR modifications are compensatory[17]. Moreover, we do not attempt to incorporate ice-albedo feedback, as the extent of the polar caps seems to depend on ocean advection and, in turn, the positions of the continents which have changed considerably over geological time[18]. Even without this effect, there are substantial uncertainties in modelling ice-albedo feedback[19]. Our model mostly predicts global temperatures greater than those at present; neglect of positive ice-albedo feedback will simply produce an underestimate of these temperatures. We further assume that the Earth's surface albedo is constant and equal to its present value, ignoring changes caused by mountain building and surface vegetation.

The results of our modelling are summarised in Table 1. We have simply assumed a total atmospheric pressure of 1 bar; the predicted global temperatures are not particularly sensitive to this assumption. The solar constant was taken to be 1,020 W m^{-2} (75% of the present value), 4,500 Myr ago.

The predicted global temperatures of Table 1 suggest that enhanced CO_2 concentrations could have been the sole mechanism for preventing glaciation of the Earth when there was reduced solar luminosity. Past global glaciation would be implied by climate models in the absence of an increased atmospheric greenhouse[20]. Within the confines of our model calculations, the Earth was never more than 4 K colder than at present. This, of course, does not account for glacial–interglacial oscillations which, on our time scales, comprise short-term climatic variability.

A detailed analysis of our model results revealed that some weak bands of CO_2, which have been neglected in previous studies of this problem[4,5], contribute significantly to the surface warming. These comprise two bands at 12 μm, two bands at 18 μm, and two bands in the 9–10 μm region. Predicted global surface temperatures, deleting these weak bands within the model calculation, are included in parentheses in Table 1. Clearly, these weak bands are important for large CO_2 concentrations. In this context, the neglect of the 7.6 μm band in the present model would produce an underestimate of the computed surface temperatures by about 5–10 K for CO_2 surface pressures of the order of 0.1–0.3 bar.

Our results are quite insensitive to events occurring from 4,500 to 4,250 Myr ago. For example, if there were an initial global glaciation during this time period, due possibly to limited outgassed CO_2, the CO_2 greenhouse effect at 4,250 Myr ago would be sufficient to melt the surface ice. To show this, taking the surface albedo for an ice-covered Earth to be 0.7, we estimate the corresponding global temperature 4,250 Myr ago to be 285 K, far too high for global glaciation to persist.

We conclude that there is no need for ammonia to be present in the early atmosphere to maintain moderate temperatures when the Sun's luminosity was low. Carbon dioxide alone is sufficient, provided the partial pressure of this gas approaches the values suggested by the evolutionary model of Hart[5]. In view of the huge amount of CO_2 that has been produced over geological time and our lack of knowledge about rates at which release and deposition occurred in primitive times, this does not seem an unwarranted assumption. In fact, more detailed calculations may permit us to place a limit on the amount of CO_2 that could ever have been present in the atmosphere at one time, as the full complement (some 70 bar) would have caused excessive warming of the Earth's surface. We are also pursuing applications to the atmosphere of Mars, where larger CO_2 abundances in primitive times might have provided a sufficient greenhouse effect to permit the flow of liquid water apparently required by the evidence for fluvial erosion on that planet's surface.

The transition to an oxidising atmosphere on Earth between 2,000 and 2,500 Myr ago, brought about by green-plant photosynthesis, is then not accompanied by a transition from an NH_3–H_2O to a CO_2–H_2O greenhouse, but rather represents a simple increase in free molecular oxygen with the concomitant disappearance of CO. The composition of the intermediate atmosphere, spanning ~2,000 Myr from the early escape of hydrogen to the onset of oxygen-producing photosynthesis, was probably very similar to the present atmospheres of Mars and Venus, two planets on which any living organisms (if present) apparently have not been able to influence atmospheric composition as they have on Earth[21,22].

This research was supported in part by NSF grant ENG-7682547 and NASA grants NAS-1-10493 and NGR 33-015-141. The National Center for Atmospheric Research is sponsored by the NSF.

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Received 15 November; accepted 13 December 1978.

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2,390 Myr Rb–Sr whole-rock for the Scourie dykes of north-west Scotland

THE Scourie dyke swarm intrudes the Lewisian Complex in north-west Scotland. The structural state of these basic dykes is used to subdivide the Lewisian into the pre-dyke 'Scourian' and post-dyke 'Laxfordian' complexes[1]. The ~2,700 Myr (refs 2–4) pyroxene-granulite facies Scourian gneisses of the Assynt area contain undeformed NW-trending dykes. Gneisses and dykes, which underwent the ~1,900 Myr (refs 5, 6) Laxfordian event, are now deformed and metamorphosed at amphibolite facies. Previous K–Ar measurements for the Scourie dykes in the Assynt area of the Lewisian gave a minimum age for dyke injection of 2,200 Myr (ref. 7). Younger K–Ar ages were thought to reflect later Laxfordian overprinting. I report here a Rb–Sr whole-rock isochron age of 2,390 ± 20 Myr (2σ) and an initial $^{87}Sr/^{86}Sr$ ratio of 0.7022 ± 0.0001 (2σ) for the Scourie dykes.

The Rb-Sr whole-rock method is in principle more suited to the problem of determining the emplacement age of the Scourie dykes. However, the range in Rb/Sr and measured $^{87}Sr/^{86}Sr$ ratios of the individual dykes is very small, and so any geological scatter in the data points will result in a large error in the 'fit of the isochron' and, hence, in the calculated age. Table 1 gives Rb–Sr whole-rock isotopic analyses for suites of samples from three Scourie dykes in the area of least post-2,700 Myr deformation and metamorphism at Scourie. The dykes at north and south Scourie Bay are fresh two-pyroxene dolerites[8], but the Kylesku Dyke contains amphibole replacement of pyroxene[6].

The ages and initial $^{87}Sr/^{86}Sr$ ratios of these three dykes, presented in Table 2, are all within 2 sigma error limits. Statistical tests (Student's *t*-test) show that the slopes of the isochrons are not significantly different at 95% confidence limits. There is no geological or petrological evidence to suggest that these dykes are not cogenetic or coeval. The 33 data points combined define an isochron (MSWD = 2.1) which gives an age of 2,390 ± 20 Myr (2σ) and an initial $^{87}Sr/^{86}Sr$ ratio of 0.7022 ± 0.0001 (2σ) (Fig. 1). This low initial $^{87}Sr/^{86}Sr$ ratio is within the range thought characteristic of rocks derived from upper mantle source regions at ~2,400 Myr (ref. 9). The age from this isochron is interpreted as being close in time to the primary igneous crystallisation of the dolerite dykes in the Scourie region. Combining the three sets of data has increased the range in Rb/Sr ratio and considerably reduced the calculated error on the time of emplacement. This low ±20 Myr uncertainty depends on the dykes being intruded at the same time and from the same source region. The combined Rb-Sr whole-rock age of 2,390 ± 20 Myr is considered the best estimate for the time of emplacement of the Scourie dykes investigated.

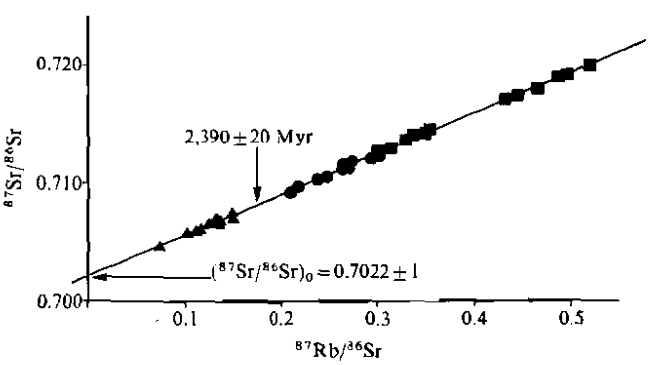

Fig. 1 Rb–Sr whole-rock combined isochron of samples from 'The Scourie Dyke' (■), Kylesku Dyke (●), and 'Scourie Graveyard Dyke' (▲). This isochron (MSWD = 2.1) gives an age of 2,390 ± 20 Myr (2σ) and an initial $^{87}Sr/^{86}Sr$ ratio of 0.7022 ± 1 (2σ).

Table 1 Rb–Sr whole-rock isotopic analyses for samples from three Scourie dykes

Sample no.	Rb/Sr (±2% ≤0.002)	Rb (p.p.m. ±10%)	Sr (p.p.m. ±10%)	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$
'The Scourie Dyke', north Scourie Bay (GR 151455–144458)					
MC 64	0.116	16.2	139	0.71395 ± 8	0.336
MC 65	0.103	14.9	145	0.71265 ± 4	0.299
MC 66	0.168	25.0	148	0.71901 ± 6	0.488
MC 67	0.121	18.3	151	0.71432 ± 6	0.350
MC 68	0.115	17.2	151	0.71363 ± 6	0.331
MC 69	0.180	25.8	144	0.71997 ± 8	0.520
MC 70	0.170	25.5	149	0.71923 ± 4	0.492
MC 71	0.108	16.4	152	0.71295 ± 6	0.313
MC 72	0.148	22.7	153	0.71717 ± 6	0.429
MC 73	0.154	22.7	147	0.71731 ± 4	0.445
MC 74	0.161	24.3	151	0.71806 ± 4	0.466
MC 75	0.122	18.0	148	0.71440 ± 4	0.352
Kylesku Dyke (GR 234330)					
MC 76	0.0920	15.3	166	0.71149 ± 6	0.266
MC 77	0.1025	17.1	166	0.71221 ± 4	0.297
MC 78	0.0930	15.2	164	0.71131 ± 4	0.269
MC 79	0.0725	13.0	179	0.70926 ± 4	0.210
MC 80	0.1030	18.1	176	0.71246 ± 3	0.298
MC 81	0.0855	12.1	141	0.71074 ± 8	0.247
MC 82	0.0930	13.1	142	0.71163 ± 4	0.269
MC 83	0.0745	12.5	169	0.70980 ± 4	0.216
MC 84	0.0810	13.4	166	0.71038 ± 4	0.234
MC 86	0.0915	15.2	166	0.71149 ± 4	0.265
MC 87	0.0935	15.1	161	0.71168 ± 6	0.271
'Scourie Graveyard Dyke', south Scourie Bay (GR 148448)					
MC 13	0.0385	7.3	185	0.70600 ± 6	0.111
MC 14	0.0395	8.5	215	0.70594 ± 6	0.114
MC 15	0.0255	4.1	160	0.70458 ± 4	0.074
MC 16	0.0460	6.9	150	0.70683 ± 4	0.133
MC 17	0.0520	7.9	151	0.70708 ± 4	0.150
MC 18	0.0515	7.7	149	0.70757 ± 8	0.149
MC 19	0.0460	6.7	146	0.70696 ± 8	0.133
MC 20	0.0420	7.3	173	0.70641 ± 6	0.122
MC 21	0.0460	6.5	142	0.70665 ± 6	0.133
MC 22	0.0350	5.7	164	0.70569 ± 4	0.101

Rubidium and strontium were separated from the 3–5-kg samples by the standard techniques used in this laboratory[6,17]. Isotope analyses were made on a 12-inch solid-source mass spectrometer using single Ta filaments[18]. Sr blank was always better than 6 ng and Rb blank less than 2 ng. Rb/Sr ratios were determined by X-ray fluorescence using extended counting times (not less than 400 s) on both peaks and backgrounds. The precision on duplicate analyses was always better than 2% or ±0.002 (whichever is the greater) and were checked against isotope dilution analyses. The value of 1.42×10^{-11} yr^{-1} was used for the ^{87}Rb decay constant[19]. All errors are quoted at the 2 sigma level.

The main Scourian event formed granulite facies gneisses and NE–SW-trending structures. A later phase of NW–SE folding and associated almandine–amphibolite metamorphism has been recognised in the Assynt area[10–12]. This younger Inverian[10] event was synchronous with or occurred immediately before the intrusion of the Scourie dykes. The 2,390 ± 20 Myr date for the emplacement of the Scourie dykes provides a minimum age for this Inverian event. This is significantly older than the 2,200 Myr age previously quoted for this event[7,10–16] and perhaps indicates that the Inverian was a late phase of deformation and retrogressive metamorphism in the major Scourian event.

0028–0836/79/0277—0642$01.00

Table 2 Ages and initial $^{87}Sr/^{86}Sr$ ratios of three Scourie dykes

Locality	No. of data points	Age (Myr)	$(^{87}Sr/^{86}Sr)_0$	MSWD
North Scourie Bay	12	2,330±60	0.7025±3	1.4
Kylesku	11	2,380±150	0.7023±6	2.3
South Scourie Bay	10	2,580±220	0.7018±4	2.4
Mean (Fig. 1)	33	2,390±20	0.7022±1	2.1

The ~2,400 Myr age for the emplacement of the Scourie dyke swarm indicates that the Scourian tectonic episode had ceased by the beginning of the Proterozoic. This area of early continental crust then remained stable until the Laxfordian metamorphic and deformational event.

I thank Drs M. J. Bickle, S. Moorbath and P. N. Taylor for critical comments, John Luck for field assistance, and Roy Goodwin and Martin Humm for technical assistance. The work at Oxford is supported by the NERC.

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Geomagnetic intensity in Athens between 2000 BC and AD 400

MEASUREMENTS of the intensity in Athens of the geomagnetic field between 2000 BC and AD 400 are reported here. The material from which the intensity was determined consisted primarily of sherds from the Agora excavations. Some sherds, and a whole skyphos, from the collection of the Ashmolean museum at Oxford were also sampled. The ancient intensity of the Earth's magnetic field was inferred from stepwise thermal demagnetisation. This is essentially the technique developed by Thellier[1], with the modifications described by Walton[2].

The magnetisation was measured with a Squid magnetometer which was essentially that described by Walton[2]. Of the alterations to the apparatus the major change was to move the heating oven and field coils to a position below the magnetometer. The manipulations of the specimen were accomplished pneumatically. These were controlled by a small computer which also processed the signal from the Squid, printing out the components of the magnetisation, **M**.

The laboratory field, $\mathbf{H}_z$, was applied in the vertical direction and, as described by Walton[2], an attempt was made to minimise the change in the vertical component of **M**, $\mathbf{M}_z$. In practice, the choice of field was within 10–20% of the correct value. Accordingly, values of $\mathbf{M}_z$ were obtained both with a laboratory field applied, $\mathbf{M}_z^H$, and with no field applied $\mathbf{M}_z^0$. The values of $\mathbf{M}_z^H$ were then plotted against $\mathbf{M}_z^0$ and the laboratory field corrected to give that field which would have produced a stationary value of $\mathbf{M}_z^H$. Values were also obtained for the transverse component, $\mathbf{M}_y^H$ and $\mathbf{M}_y^0$. The values of $\mathbf{M}_y^0$ were plotted against $\mathbf{M}_z^0$, and the slope of the resultant line yielded the angle between **M** and **H**. By dividing the corrected laboratory field, **H**, by the cos of this angle the estimated value of the ancient field was obtained.

Measurements were made, using the above procedure at temperatures which were nominally 200, 250, 300, 400, 500, and 600 °C (the higher temperatures were often omitted if the sample had already demagnetised sufficiently at lower temperatures).

In addition, values of $\mathbf{M}_y^H$ and $\mathbf{M}_z^H$ were obtained at intermediate temperatures. $\mathbf{M}_z^H$ was then plotted against $\mathbf{M}_y^H$. As no component of **H** was present in the transverse direction, $\mathbf{M}_y^H$ provided a measure of the degree to which the sample had demagnetised. Thus the plot of $\mathbf{M}_z^H$ against $\mathbf{M}_y^H$ could also be used to correct **H**. Both plots were used, and the value of **H** which was used was an average of the two.

Finally, the angle between $\mathbf{M}_y^0$ and some arbitrary direction in the horizontal plane was monitored. The aim of this procedure was to identify the presence of possible additional components of **M** introduced by reheating the pottery in antiquity.

Attic pottery is, on the whole, quite strongly magnetised, a magnetisation density of 10^{-3} e.m.u. cm^{-3} being typical. Thus in principle a correction for demagnetising fields due to sample shape should be applied. However, this correction would not amount to more than the difference between the value for a disk with the field applied along a diameter, or at right angles to it. As the thickness of the sample was approximately equal to the diameter this correction was negligible.

A potentially more serious problem arises from demagnetising effects due to the shape of the vessel itself affecting the moment produced during firing in antiquity. In an attempt to estimate the magnitude of this effect, samples were taken from the base, sides and handles of an Attic skyphos which had been fired between 440 and 425 BC. However, before the results could be assessed a more serious source of error had to be considered.

Rogers (personal communication) has found that pottery is anisotropic: it is easier to magnetise in a direction parallel to the plane of the pot, than it is at right angles. It is possible to correct for this effect if the anisotropy ratio—the ratio of the moment produced in the hard direction to that in the easy direction—is known. The angle between the easy plane of magnetisation and **H** is known, and if the angle between this plane and the ancient field $\mathbf{H}^A$ is known, these two angles can be deduced from the changes in direction of **M** which occur on magnetisation in the laboratory field. The derivation of this correction factor will be detailed elsewhere. It turns out that the correction is simplified considerably if the sample is orientated so that **H** is either parallel or antiparallel to the laboratory field.

The results obtained from the Attic skyphos were corrected in this way. The anisotropy ratio was adjusted to yield the best agreement between samples taken from the base and those from the side, this amounted to 0.9. For these samples, the shape correction, if any, would be less than the scatter in the data. Hence, no shape correction was made. Unfortunately, the anisotropy correction of the results for the handles proved impossible because of instrumental difficulties, and these had to be discarded.

Having done this it was impossible to identify any shape effect, except possibly for the handles. Results for the latter, however, could not be corrected for anisotropy, so an unambiguous identification of a shape effect was impossible. In any case it seems that the shape correction is less than other sources of error for samples from the side and base, and all samples used came from these locations.

The anisotropy ratio obtained from these measurements on the skyphos was used to correct the values obtained from the rest of the material. This correction amounted to between 3 and 7% (obviously it could not be larger than 10%). The corrected values for the ancient field obtained from each sherd are plotted

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