OXYGEN ISOTOPES IMPLANTED IN THE LDEF SPACECRAFT

J M Saxton, I C Lyon, E Chatzitheodoridis, P Van Lierde[*], J D Gilmour
and G Turner

Department of Geology, University of Manchester, MANCHESTER, M13 9PL, UK
Phone 44-(0)61-275-3842 Fax 44-(0)61 -275-3947

[*]also VG Isotech, Aston Way, Middlewich, Cheshire, UK

SUMMARY

We have used secondary ion mass spectrometry to study oxygen implanted in the surface of copper from LDEF. Oxidation that occurred in orbit shows a characteristic oxygen isotope composition, depleted in ^{18}O. The measured depletion is comparable to the predicted depletion (45%) based on a model of the gravitational separation of the oxygen isotopes. The anomalous oxygen was contained within 10nm of the surface. Tray E10 was calculated to have received 5.14×10^{21} atoms of oxygen cm^{-2} during the LDEF mission[1] and so there is sufficient anomalous implanted oxygen present in the surface to obtain a reliable isotopic profile.

INTRODUCTION

The atomic oxygen to which LDEF was exposed in orbit is expected to be depleted in ^{18}O in comparison with ground level atomic oxygen due to gravitational separation of the oxygen isotopes above the turbopause (about 110km). Below this altitude the isotopes are well mixed but above it the scale heights for ^{18}O and ^{16}O differ by a factor of 18/16. Oxidation that occurred in orbit should therefore show a characteristic oxygen isotopic composition. We have used an ion microprobe to study the oxide layer on a sample of copper grounding strap from tray E10 on LDEF in order to determine the oxygen isotopic composition of the atmosphere at LDEF orbital altitudes.

EXPERIMENTAL TECHNIQUE

The sample was studied by SIMS (secondary ion mass spectrometry) using a VG Isolab 54 ion probe. A Cs^+ beam (of total energy 18keV on the target) was used to sputter oxygen from the sample surface; secondary O^- ions were then analysed in a double focussing mass spectrometer. We measured ^{16}O and ^{18}O simultaneously using different detectors: a Faraday cup for the ^{16}O beam and a microchannel plate detector for ^{18}O. This multicollection facility was a vital feature of the experiment, since the anomalous oxide layer on the LDEF samples was very thin and the signal short lived (typically of the order of a few minutes). A primary ion beam of 2 nA focussed to a spot size of approximately 100 μm reduced the sputtering rate sufficiently that consistent and reproducible isotopic depth profiles were obtained, even in very near surface layers where the oxygen abundance and isotopic ratio were highly variable. The beam was held static on the surface as we did not have the facility for rastered depth profiling. Undoubtedly this reduced the depth resolution and contributed significant edge effects when the ion beam had sputtered through the anomalous layer, but the near surface profile is thought to be quite accurate. We are in the process of improving our depth resolution by using Köhler illumination to give uniform ion beam density across the primary beam and we will re-examine the samples to improve the isotopic depth profiles.

The ease with which the surface layer was sputtered meant that no ion beam imaging, peak centring or beam optimisation could be performed on any part of the surface which was to be analysed. The experimental procedure adopted therefore was to first obtain high precision and consistent $^{18}O/^{16}O$ ratios from ordinary copper sheet or an area of the LDEF copper sheet which had already been analysed, peak centre and optimise the ion beams, and just at the point at which software starts to measure isotopic ratios, move the sample under the primary ion beam to an area which had not been analysed. The LDEF copper always showed large depletions of ^{18}O near the surface, rising up to

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'normal' terrestrial ratios as the beam sputtered away near surface layers. When the Cs^+ beam was defocussed to greater than $100\mu m$ spot size to reduce the sputtering rate, consistent values of the most extreme surface depletions were recorded. We also used identical experimental procedures on ordinary (non-LDEF) copper sheet and unexposed LDEF stainless steel surfaces, but no experimental artifacts were ever observed which could have produced the observed isotopic profiles.

RESULTS AND DISCUSSION

We have studied copper grounding strap from position E10 (near the forward edge). The exposed side of the copper (ie facing along the velocity vector) was visibly darkened whilst the unexposed side appeared bright and shiny. Figure 1 shows the ^{16}O signal as a function of time for the darkened (exposed) side of the E10 copper in which the depth scale was determined by using a Talystep 1 (manufactured by Rank Taylor and Hobson with a depth resolution of 50Å). Oxygen is clearly concentrated within 10nm of the surface. Unfortunately the depth measurement proved very difficult to perform accurately due to the surface roughness of the copper. (Figure 2 shows a back scattered SEM image of the surface illustrating the micron sized irregularity of the surface.) The surface roughness also makes simple models of implantation of oxygen in the surface questionable and the depth profiles difficult to interpret. The depth calibration is assumed to be linear with time since we have no way at present of obtaining a more accurate depth calibration. Indeed we were only able to obtain a depth calibration by sputtering a crater for an hour and measuring the final crater depth ($1\mu m$). The Talystep profile of this crater is shown in figure 3 along with surface irregularities.

Figures 1 and 4 show the variation of $\delta^{18}O$ with time (and hence depth) for the exposed and unexposed sides, respectively, of the E10 copper. The ratio is expressed as permil variation from 'normal' oxygen (i.e., the isotopic composition at sea level calibrated by obtaining an isotopic ratio from the bulk copper when the depth profile reached a constant isotopic value - which agreed with the value obtained from copper gently oxidised by a heat gun in the laboratory).

The variation of $\delta^{18}O$ with depth is different for the two sides but several spots on both sides yielded consistent profiles for each side. The exposed side appears to have a layer of isotopically more normal material at the surface. Viewing the sample optically whilst the darkened surface was sputtered showed that the minimum isotopic value for this side occurred when the primary beam just sputtered through this dark layer to reveal bright copper underneath. Although the exposed side profile appears to have a shallower gradient than the unexposed side, this is probably an artifact produced by a lower primary beam density. One of our objectives in the near future is to improve the precision of depth profiles for both sides of the copper.

The oxygen in the LDEF surface is clearly depleted in ^{18}O with respect to normal oxygen. The exact value of the depletion is difficult to determine precisely due to a variable admixture of normal oxygen from the bulk copper. Extrapolation of a graph of $^{18}O/^{16}O$ vs $1/^{16}O$ (Lyon et al.[2]) suggests a value for $\delta^{18}O$ of -450 ± 50 $^o/_{oo}$ (though a single value as low as -550 $^o/_{oo}$ has been recorded, see fig. 4). The ^{18}O and total oxygen signal decrease with time as we begin to sample the residual (impurity) oxygen in the bulk copper. We have calculated the expected depletion in $\delta^{18}O$ over the whole of the 6 year mission to account for solar cycle variations in the atmosphere using data from the MSIS86 model[3]. The oxygen density and calculated $\delta^{18}O$ value at a particular height and time were integrated over the spacecraft's orbit for the six year mission and a total integrated $\delta^{18}O$ value for the implanted oxygen determined. LDEF received most of its atomic oxygen exposure between days 2000-2106 of the mission during a rapid descent from 400km to 300km, so we took the isotopic and density parameters every 6 months for the first 5 years and every 1 month for the final year. The average $\delta^{18}O$ value integrated over the whole mission was $-450^o/_{oo}$ but this value is probably uncertain by $\pm50^o/_{oo}$. This uncertainty arises mainly from having to assume hydrostatic equilibrium in calculating the $\delta^{18}O$ values (an assumption we know to be not strictly true) and partly from uncertainty in the height of the turbopause. The calculation of $\delta^{18}O$ as a function of height is a subject we intend to study in more detail.

An obvious implication of the difference in isotopic depth profile between the outward and inward facing surfaces is that the contamination layer was deposited on surfaces very late in the LDEF mission, a conclusion which runs contrary to expectations from other experiments. Such a novel

conclusion must therefore be treated with caution. Other studies have shown that atomic oxygen reacts with surfaces in a complex fashion[4], some surface contaminants proving much more resistant to erosion than normal surface materials and considerable sub-surface erosion occurring as atomic oxygen penetrates through microscopic pin pricks in resistant surfaces. The surface roughness of the copper also makes simple models questionable.

The observation of anomalous profiles on both sides of the copper requires scattering of oxygen atoms behind the copper. We are now studying how profiles vary with distance from edges of the copper and it is clear that extensive further work is required to understand the measured profiles and predict the effects of space exposure on materials.

FUTURE WORK

We are in the process of extending our measurements to ^{17}O, to see if the ^{17}O depletion is also that expected by simple theory. In order to provide an accurate calibration at these extreme depletions, we have also prepared samples of copper, oxidised on the surface with a known amount of ^{16}O enriched oxygen. In addition to calibrating isotope ratios these should allow us to quantify the dose of atomic oxygen received by the samples of copper from LDEF. We will also study copper strap from other trays; we have samples from D07 (close to the RAM atomic oxygen vector) and E02 (from the trailing side of LDEF which should have received a very small flux of anomalous oxygen). We also intend to study the effect of LDEF surface contamination on our measurements.

ACKNOWLEDGEMENTS

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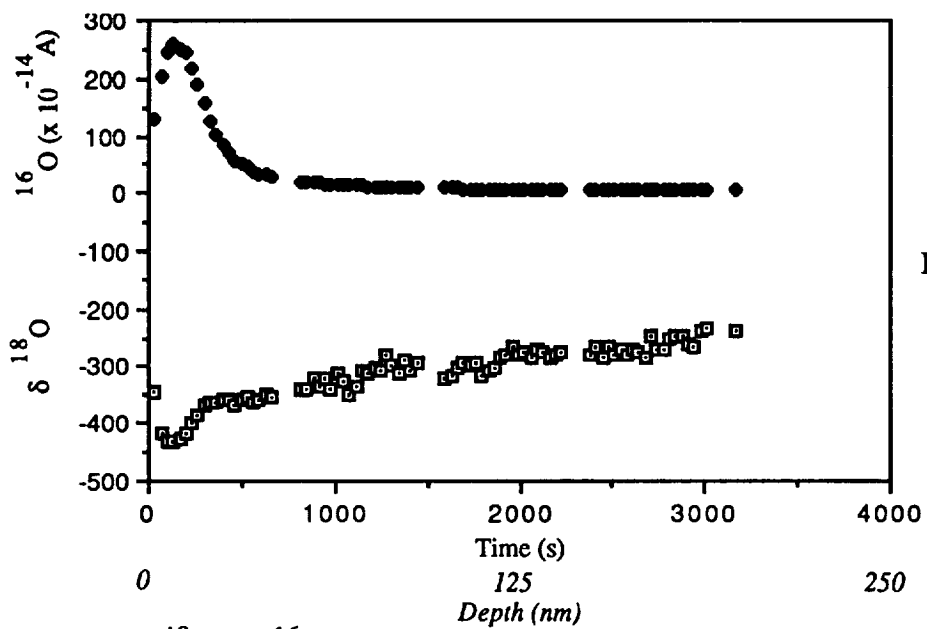4. LDEF Spaceflight Environmental Effects Newsletter. Vol 1, No2 12th April 1990

Figure 1

δ^{18}O and ^{16}O as a function of time for the exposed side of E10 copper
(depth equivalent estimated from final crater depth measured by a Talystep)

Figure 2.

A back scattered scanning electron photograph of the surface of the E10 copper showing micron scale roughness and an ion beam burn mark.
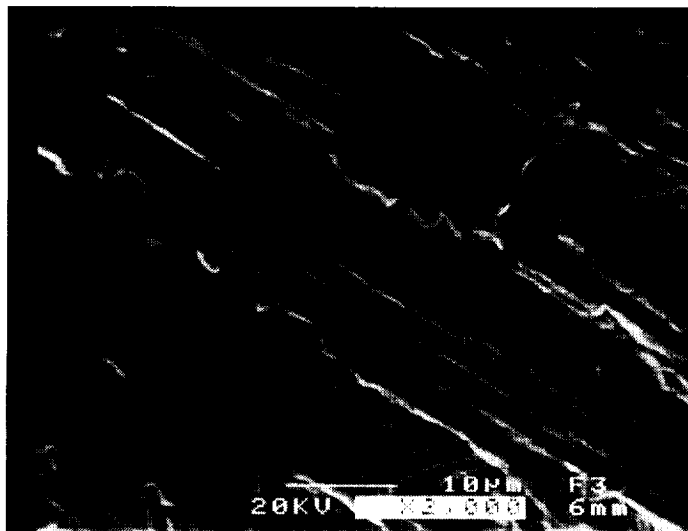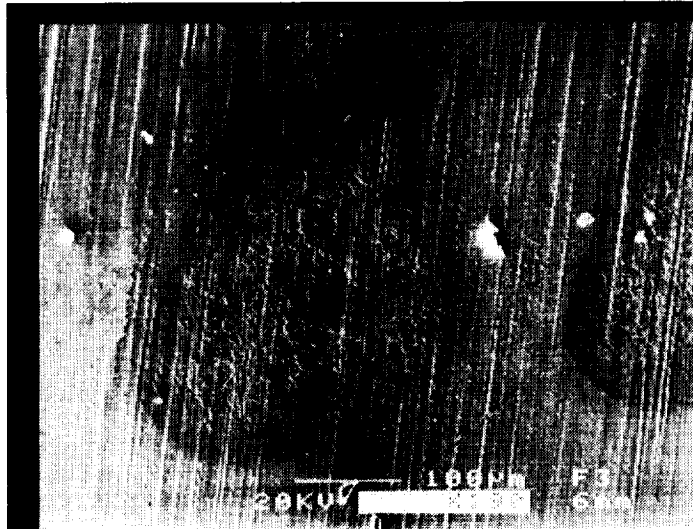
Figure 3

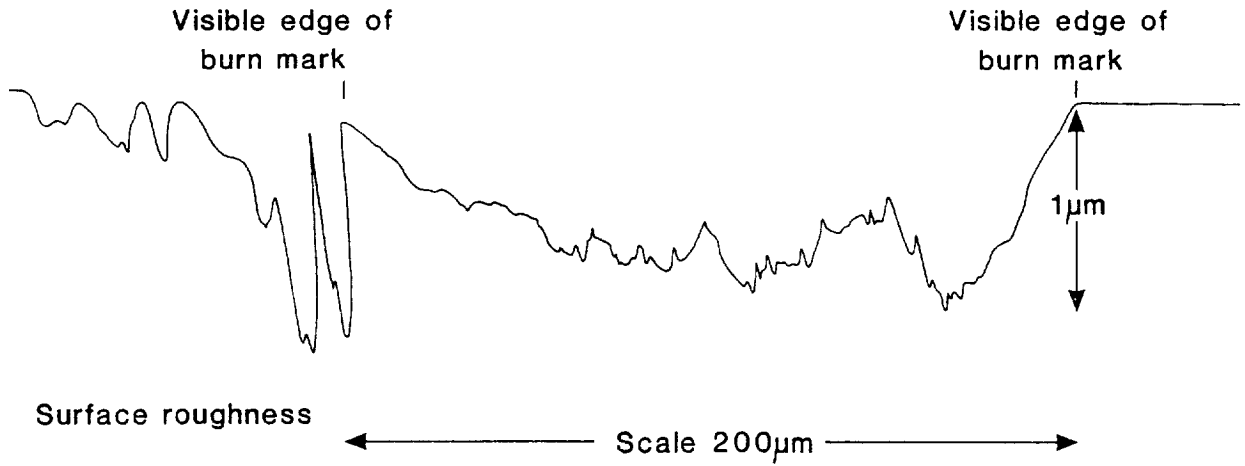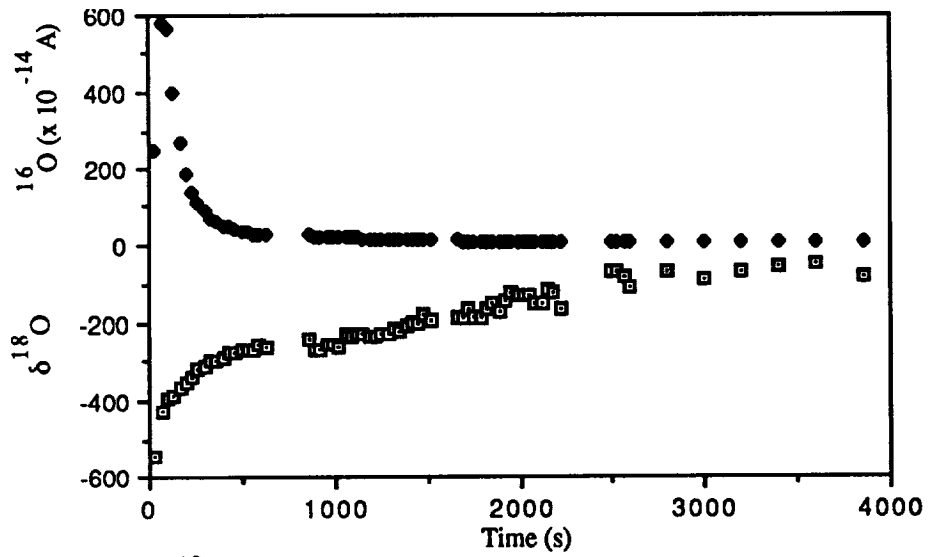### Talystep Profile of the Ion Beam Burn Mark

Figure 4

$\delta^{18}O$ and ^{16}O as a function of time for the unexposed side of E10 copper (no depth calibration for this side)