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# Microprobe studies of space weathering effects in extraterrestrial dust grains

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[Plate 1]

A new microprobing procedure is used to characterize both the physical and chemical surface properties of individual grains on a microscale. In this procedure the same sub-micrometre sized area of a given grain is successively analysed with a high voltage electron microscope, an Auger microprobe and a field emission scanning electron microscope. This analytical technique has been applied to study lunar weathering effects and to tentatively infer the irradiation history of a $^{22}$Ne-rich fraction of the Orgueil meteorite.

## 1. Introduction

Mineral grains exposed on the surface of atmosphereless and magnetic field free bodies like the Moon, the asteroïdes, etc. suffer a complex alteration (space weathering) resulting from the combined interactions of various active parameters of the interplanetary medium (solar wind, solar flare and galactic cosmic rays, meteoritic flux). The characterization of such space weathering effects requires the physical and chemical analysis of individual grains on a microscale. For this purpose a new microprobing procedure has been developed in which the same sub-micrometre sized area of a given grain is successively analysed with a high voltage electron microscope (h.v.e.m.), an Auger electron microprobe and a field emission scanning electron microscope (f.e.s.e.m.).

We first describe the different steps involved in this analytical method, and we then present preliminary results concerning lunar dust grains and exotic particles extracted from carbonaceous chondrites. Finally we discuss possible improvements of our technique and we list a few of its future applications to other areas of sciences.

## 2. Outline of the microprobing procedure

At the present time, there is no unique instrument which can fully characterize both the physical and chemical properties of micrometre sized grains on a microscale. It is thus necessary to perform a sequence of analysis with different instruments which generally operate with primary beams of electrons. As such beams can possibly alter the grains it is necessary to define the right analytical sequence which will minimize the beam effects.

### 2.1. *Electron microscope preparations*

The grains are first dispersed on special electron microscope substrates that are fixed on numbered gold grids. Therefore the position of a given grain can be quickly found. In addition as the substrates are remarkably stable, the grains can be exposed to various treatments intended to characterize or simulate natural processes (heating up to 1000 °C, chemical etching, heavy ion irradiation, low energy ion implantation, metallic coating, etc.).

### 2.2. *H.v.e.m. run*

A selected grain is then observed with the h.v.e.m. which can potentially help in analysing its following 'physical' features: ultrathin coatings; latent tracks; degree of lattice ordering from the centre to the edge of the grain; exsolution lamellae; inclusions and microfracturing. In addition an electron spectrometer (h.v.e.s.) has been recently attached to the microscope which can be used to 'chemically' characterize several of these features by measuring the energy losses suffered by the primary electron beam.

### 2.3. *Indium replication*

The next analytical step involves the use of the Auger microprobe. In this instrument beam charging and heating effects are minimized by imbedding the insulator grains in a conductive matrix. This is simply obtained by pressing the electron microscope preparation against an indium foil. An indium 'replica' of the grid is thus obtained in which the grains are fixed while still keeping their coordinates as defined by the replica of the numbered grid (figure 1, plate 1).

### 2.4. *Auger microprobe run*

In the conventional Auger electron spectroscopy applied to lunar samples (Gold *et al.* 1974), a large beam (*ca.* 1 mm) of low energy electrons ($\lesssim 2000$ eV) is used and no single grain analysis can be performed as a great number of grains are required to get signals above background. This severe limitation is suppressed in the Auger microprobe which is a special type of scanning electron microscope equipped with an electron spectrometer. This instrument has the following characteristics:

(1) The primary electron beam has an energy of 10 keV (which can be increased up to 30 keV), an intensity of $10^{-7}$ A and a diameter of 0.5 μm.

(2) Two different modes of operation can be used: in the punctual mode, the complete electron spectrum of a given grain can be obtained which in turn yields the chemical composition of the most superficial layers of the grain up to a depth of 2 nm; in the scanning mode, a secondary electron picture of the grains is obtained with a resolution which is good enough to both identify the grain coordinates and detect possible alteration of the grain during the analysis. This picture can be obtained either with the total secondary beam or with electrons of a selected energy which thus reflect the repartition of a given element in the preparation.

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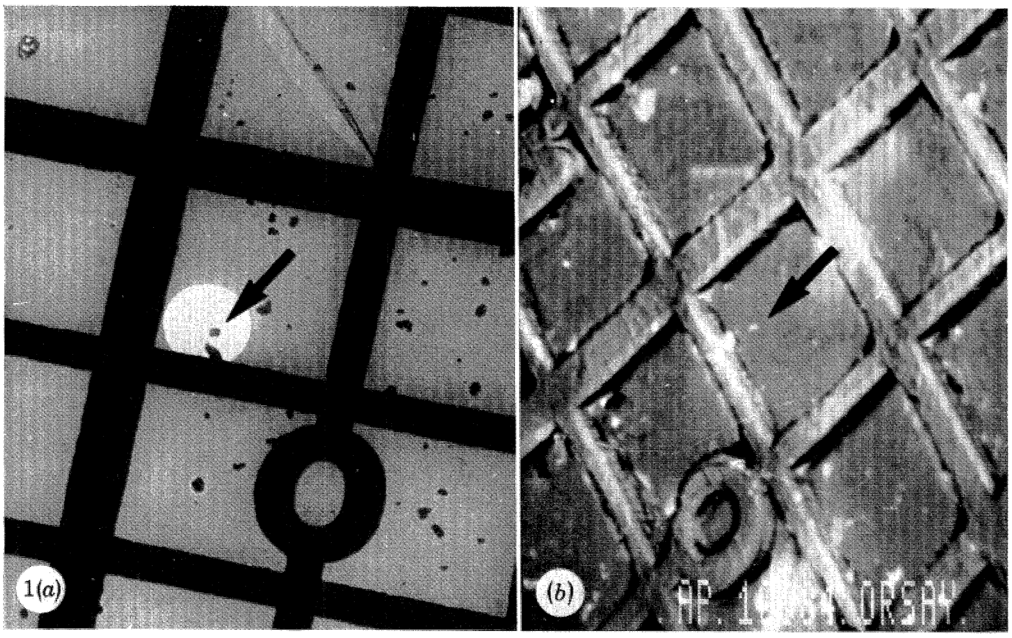
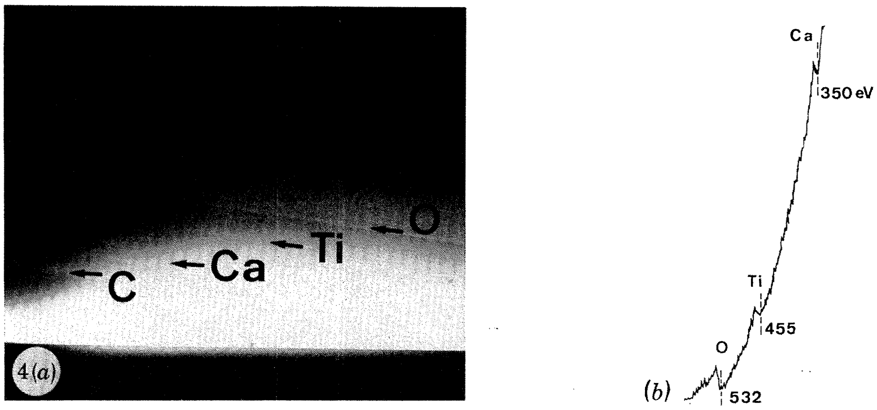
### DESCRIPTION OF PLATE 1

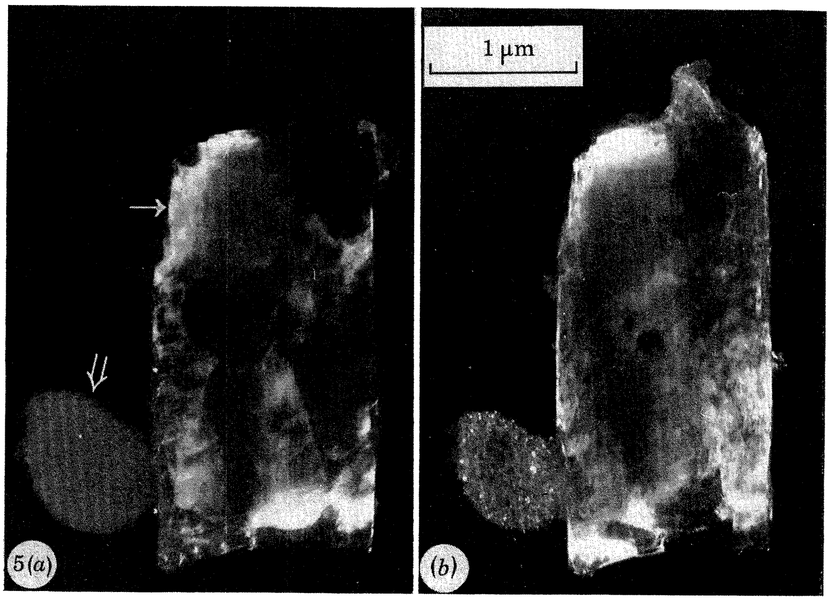
FIGURE 1. Analytical procedure. The same grain is first observed with the h.v.e.m. (*a*), then imbedded in indium for a subsequent Auger microprobe analysis which can yield a secondary electron picture (*b*).

FIGURE 4. Analysis of artificial metal deposit by high voltage electron spectroscopy. (*a*) Electron energy loss spectra obtained for a feldspar grain coated with 1 nm Ti. (*b*) Corresponding densitometer recording. The Ti line is clearly visible in this grain whereas it is absent in feldspars extracted from mature soils. The other lines are due to the major constituent elements of the crystal (Ca, O) and to the substrate (C).

FIGURE 5. Dark field micrographs of grains from the Ne-E separate of Orgueil. Before heating (*a*) the grains are either crystalline (single arrow) or completely amorphous (double arrow). After heating (*b*) at a low temperature (500 °C) the t.c. are only observed in the amorphous grains. The crystalline grains show t.c. only when they have been artificially irradiated with heavy ions, and then heated at 500 °C.







Figures 1, 4 and 5. For description see opposite.

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### 2.5. *F.e.s.e.m. run*

If necessary the selected grain in the indium replica can be further characterized by using a f.e.s.e.m. with its non dispersive X-ray spectrometer (EDX). This instrument provides a high resolution picture of the surface topography as well as the chemical composition of major elements in a volume of ~ 1 μm³.

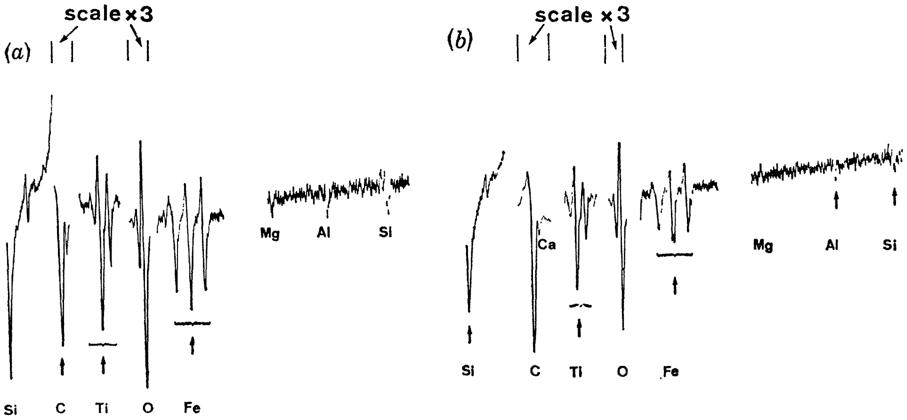

FIGURE 2. Auger microprobe search for accretionary particles on a 10084 ilmenite grain. (*a*) Punctual mode (0.2 μm²) (*b*) Scanning mode (100 μm²). No increase in intensity of the Ca, Mg, Al and Si peaks can be detected when going from the punctual to the scanning mode, and this indicates that silicate particles accreted on the grain, do not markedly alter its surface composition.

## 3. STUDY OF WEATHERING EFFECTS IN LUNAR DUST GRAINS

### 3.1. *Physical alteration*

#### 3.1.1. *Amorphous coating*

We already reported the existence of amorphous coatings of solar wind radiation damaged material (s.w.a.c.) on micrometre sized feldspars and pyroxenes extracted from mature soils (Bibring *et al.* 1972). The thickness distribution of the s.w.a.c. has already been used to infer the thermal properties of the ancient solar wind (Borg *et al.* 1974), and the proportion F of feldspar grains with an amorphous coating was defined as an index of solar wind maturity (Bibring *et al.* 1975). In addition by running both an ilmenite and a feldspar separate from the 5 μm residue of the 10084 soil, we observed s.w.a.c. on about 100 % of the feldspars but not on any one of the 11 ilmenites so far analysed. Therefore we first deduce that in mature soils only the feldspars but not the finest ilmenites show solar wind saturation effects. Furthermore our simulation experiments (Bibring *et al.* 1974) indicate that the solar wind exposure time, $T_{\text{s.w.}}$, required to develop s.w.a.c. on feldspars and ilmenites are of about 2000 and 20000 years respectively. By combining this observation to the previous one we can then set the following experimental limits on the effective $T_{\text{s.w.}}$ values attached to the constituent 1 μm grains of mature soils: $2000 < T < 20000$ years. This $T_{\text{s.w.}}$ experimental value has been used to check the validity of a Monte Carlo statistical model intended to describe the dynamical evolution of the lunar regolith (Duraud *et al.* 1975) at very shallow depths ($\lesssim$ 1 cm).

### 3.1.2. *Accretionary particles on grains extracted from the* 10084 *soil.*

(*a*) *H.v.e.m. studies.* In mature soils most of the grains are in fact aggregates of welded dust. The central grain in an aggregate always shows a rounded habit with a s.w.a.c. Furthermore the density of secondary particles in the aggregate, $N_s$(nb/μm$^2$), varies from ~ 0.1 to 1, when the $F$ index of solar wind maturity increases from *ca.* 10 to 100 %. On the other hand ilmenites from the same soils have angular habits with no s.w.a.c., and their $N_s$ values are much smaller than those measured for the feldspars. These observations can be extended to coarser grains (~ 50 μm) by examining micrometre sized crushed fragments. In this way we detected two very different types of external surfaces on crushed fragments from 50 μm feldspars: frequently the surfaces are very clean and only show a rounded habit with a broken s.w.a.c. on which very few secondary particles are attached; occasionally 'dirty' external surfaces are observed where the s.w.a.c. is covered by large accretionary particles that look like the glassy matrix of the glassy agglutinates, and no evidence for a thermal metamorphism of the s.w.a.c. is found.

(*b*) *Auger microprobe run.* The presence of accretionary particles on the grains can be detected with the Auger microprobe. For this purpose we examined 100 μm ilmenites. By varying the analysed area from 0.2 μm$^2$ up to ~ 100 μm$^2$ we did not detect anything else than the characteristic major (Fe, Ti, O) and minor (Ca, Mg, Al, Si) transitions of ilmenite (figure 2). This strongly suggests that at least for ilmenites, the surface chemistry of lunar dust grains is not drastically altered by accretionary particles produced during lunar weathering.

(*c*) *F.e.s.e.m. run.* Although the complexity of the f.e.s.e.m. surface topography observed with a resolution of ≃ 5 nm on ilmenites, feldspars, and glassy agglutinates from sample 10084 now defies our understanding, 2 conclusions are clear: (i) there is no overlapping of accretionary particles on the grains; (ii) very shallow 'ring' structures with a 'thickness' of ~ 10 nm are frequently observed which could be the 'prints' of microscopic glass splashes now detached from the grains.

### 3.1.3. *High resolution stratification parameters*

By running micron-sized feldspars with the h.v.e.m. we currently define high resolution 'stratification' parameters which include:

(1) The proportion of grains showing tiny cristallites firmly imbedded into the grains that we attribute to radiation damage annealing (Dran *et al.* 1972). This parameter is also useful in deciphering the 'average' thermal metamorphic history of lunar soil samples.

(2) The proportion, $F$, of feldspar grains with an amorphous coating of solar wind radiation damaged material.

(3) The average 'non-corrected' track densities in the grains that we measure by counting the number of latent tracks that appear within a small circular reticule placed directly on the electron microscope plates.

(4) The average thickness of the solar wind amorphous coatings which is related to the average energy of the ancient solar wind.

(5) The average number of secondary particles attached to the micrometre-sized felspars, which can possibly reflect either the cycling of the grains through ejecta blankets or their incorporation into breccia from which they get subsequently released by erosional process.

(6) The proportion $G$ (< 5 μm), of tiny glassy grains as determined from electron diffraction patterns.

### 3.2 *Chemical alteration*

Several processes can potentially affect the surface chemical composition of lunar dust grains: condensation of lunar winds vapour phases; accumulation of solar wind implanted species; differential solar wind sputtering; chemical reduction by solar wind protons.

#### 3.2.1 *Metal enrichment in the surface layers of the grains*

Such enrichments have been postulated by others for Fe, Ti, K and Pb. Gold *et al.* (1974) even reported the existence of iron coatings on lunar dust grains. To check this hypothesis, we evaporated thin layers (1–5 nm) of iron and titanium on 1 μm feldspars obtained by crushing an internal chunk of lunar igneous rock (15475). We then performed a comparative analysis of these grains and mature lunar dust grains both with the Auger microprobe and the h.v.e.s. Our main results are:

(1) 1 nm thick layers of both Fe and Ti give Auger transitions which are at least 10 times greater than the corresponding ones observed either in feldspar blanks from rock 15475 or in feldspars from the mature 10084 and 60601 soils (figure 3).

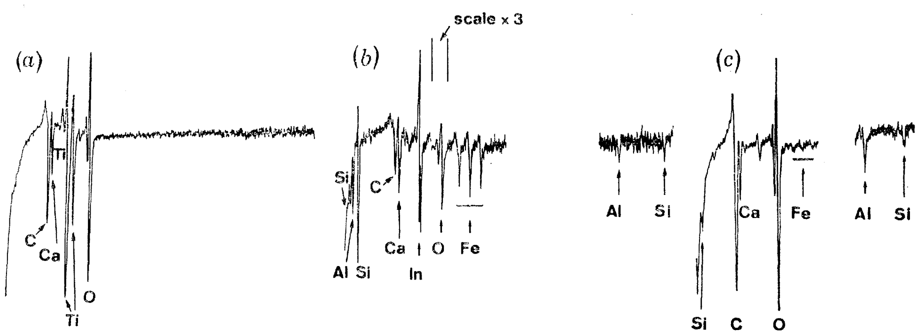

FIGURE 3. Analysis of artificial metal deposits on feldspar grains with the Auger microprobe. (*a*) and (*b*) lunar rock feldspar coated with 1 nm of Ti and Fe respectively. (*c*) Feldspar extracted from a mature soil (60601). Spectrum (*c*) shows Fe peaks at least 10 times smaller than the Fe coated sample and no Ti peak. Spectrum (*b*) clearly shows the Si and Ca peaks of the underlying crystal.

(2) The same result was also obtained from the h.v.e.s. run (figure 4, plate 1); a 1 nm thick Ti coating gives an observable transition line which is absent from the spectrum obtained with 10084 feldspar grain. Therefore we deduce that lunar weathering does not produce any thick (⩽ a few tenths of a nanometre) Fe and Ti rich coatings on lunar dust grains. Furthermore we also believe that this conclusion can be generalized to both K and Pb as we did not detect these elements on 100 μm ilmenite grains extracted from the same soil samples.

#### 3.2.2 *Search for solar wind implanted species*

Preliminary runs have been performed with the Auger microprobe in an attempt to detect solar wind implanted species. For calibration purpose known doses of low energy (~ 1 keV/n) ions ($^{15}N$, $^{20}Ne$, $^{32}S$) have been implanted in feldspar and ilmenite targets. The present sensitivity of the Auger microprobe is clearly not sufficient to detect any transition due to N, Ne, S, P, in ilmenites from 10084 samples. In feldspars artificially irradiated with doses of $5 \times 10^{15}$ ions/cm$^2$, we only detected S.

### 3.2.3 *Mineralogical composition of the* 5 *μm-residues of various soils*

With respect to grains from coarser size fractions, the finest grains show: (1) a much smaller proportion of glasses $G$ ($< 5\ \mu m$) $\lesssim 10\,\%$, which is not correlated to the glass content of the coarser size fractions. In particular with the exception of sample 15003,415 for which $G = 30\,\%$, 9 samples from section III of the Apollo 15 core tube have $G$ values smaller than $5\,\%$; (2) a much smaller content of pyroxenes with thin ($< 0.5\ \mu m$) exsolution lamellae; (3) a higher proportion of feldspars ($\sim 30\,\%$) in the mature soils and a corresponding depletion of Fe-Mg-rich grains such as pyroxenes and glasses, but the expected proportion of ilmenites. In addition most of the feldspars give weak Ti signals which suggest that accretionary particles on the grains are enriched in opaque grains. Such a feature could also partially account for the Auger spectroscopy results of Gold *et al.* (1974). The feldspar relative enrichment in the mature soils could reflect their contamination with anorthositic highland material.

## 4. STUDY OF EXOTIC COMPONENTS IN CARBONACEOUS CHONDRITES

Recent works have revealed the existence within carbonaceous chondrites of mineral fractions showing isotopic anomalies which were tentatively attributed to the admixture to meteoritic material of interstellar dust grains with isotopic composition different from the solar system average value (Clayton *et al.* 1973). In order to get further clues about the history of such exotic meteoritic grains, we have applied our analytical technique to a $^{22}$Ne-rich mineral separate (Ne-E fraction) extracted from the Orgueil meteorite (Eberhardt 1974). The most striking results of this study are:

(1) Before thermal annealing, about 50 % of the grains were completely amorphous and 50 % were crystalline (figure 5*a*, plate 1). In addition the amorphous grains presented the following characteristics: they were similar to the crystalline grains in their chemical compositions, showing strong Mg, Fe, Si EDX-signals; in contrast to the crystalline grains they were markedly 'rounded', looking very similar to dust grains artificially eroded by ion sputtering; and their morphologies were very different from both lunar soil 'glassy' grains, presumably formed by impact melting or glassy fragments found in heavily shocked meteorites such as Shergotty.

(2) Upon a low temperature annealing at 500 °C, very high densities of tiny crystallites (t.c.) similar to those produced during the annealing of latent tracks (Dran *et al.* 1972), were formed in the amorphous grains (but not in the crystalline ones) (figure 5*b*).

(3) After a laboratory irradiation in a flux of iron nuclei ($\sim 10^{11}$ Fe/cm$^2$) followed by a thermal annealing at 500 °C, the crystalline grains showed t.c. similar to those observed in the non-artificially irradiated amorphous grains.

These thermal annealing results show that the amorphous grains of the Ne-E fraction could have been produced by an irradiation in fluxes of v.h. nuclei that was sufficiently intense ($\geqslant\ \times 10^{13}\ \mathrm{cm^{-2}}$) to give a disordered (metamict) state in originally crystalline material. Our calculations have further shown that the associated proton flux could account for the $^{22}$Ne excess through the following spallation reaction: $^{25}\mathrm{Mg}\ (p, \alpha)\ ^{22}\mathrm{Na}\ (\beta^+)\ ^{22}\mathrm{Ne}$. Such an irradiation could possibly have occurred either during the T-Tauri phase of the Sun or in various extra solar system sites such as the expanding envelope of a supernova, etc.

## 5. Future trends

This microprobe analytical technique has already given some meaningful informations concerning space weathering processes affecting lunar dust grains as well as the irradiation history of meteoritic grains. However the sensitivity of the chemical analysis is not yet sufficient to detect solar wind species implanted in the surface layer of lunar dust grains. We expect that the following improvements will considerably increase the usefulness of this technique:

(1) The nuclear emulsion technique presently used in the h.v.e.s. runs will be soon replaced by an electronic detection system which will markedly increase the sensitivity (determination of trace elements) as well as the spatial resolution (up to 10 nm) of this method. It should then be possible to analyse tiny inclusions in the grains, as well as solar wind implanted species, etc.

(2) The present sample holder of the h.v.e.m. will be replaced by a new prototype specially designed to operate under a controlled atmosphere. This device will markedly reduce the formation of contamination layers on the grains that frequently perturb their subsequent Auger microprobe analysis.

(3) The Auger microprobe is also currently improved. By modulating the primary electron beam the signal to noise ratio has been already increased by a factor 100. It will therefore be soon possible to reduce considerably the beam intensity in order to avoid beam charging and heating effects on coarse grains.

(4) An all aluminium film substrate has been developed, which now allows the identification of carbon and/or nitrogen-rich grains in the electron microscope preparation.

When improved, the microprobing procedure we presented will be very useful in various fields of science connected with the analysis of tiny grains in natural environments and such as those present in terrestrial aerosols, in Antarctica dust, perhaps in the martian soil samples, etc. In particular we are currently trying to characterize tiny carbon-rich inclusions in a variety of meteorites including carbonaceous chondrites (type 1, 2 and 3), gas-rich meteorites, and enstatite achondrites.

This work would have been impossible without the active interest of B. Jouffrey of the Laboratoire d'Optique Electronique du C.N.R.S., Toulouse, and the superb technical assistance of C. Jouret and J. Sevely of the same institution, during the h.v.e.m. and the h.v.e.s. runs respectively. We are also deeply indebted to C. Legressus of Laboratoire de Chimie-Physique, C.E.N. Saclay for the Auger microprobe analysis.

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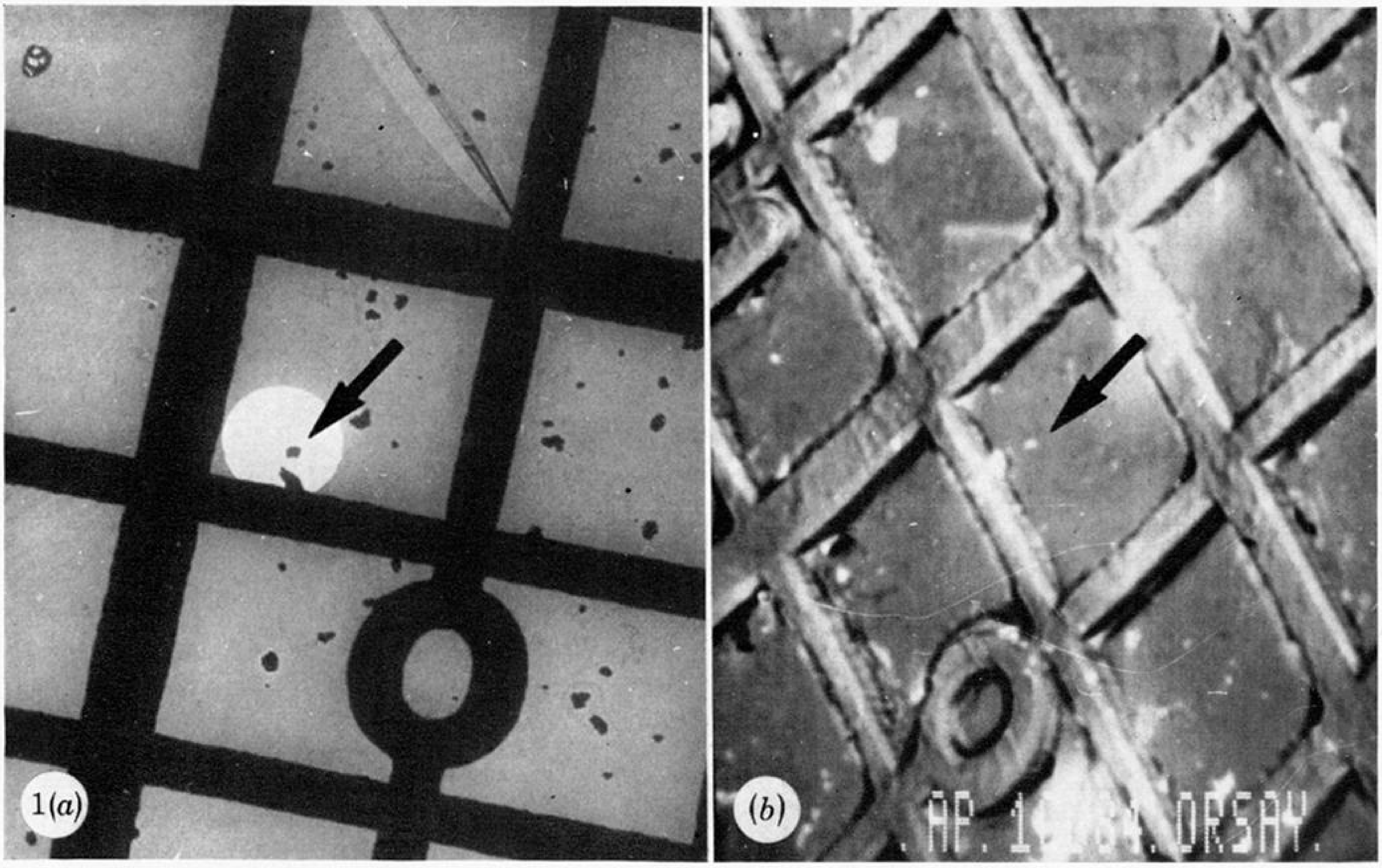

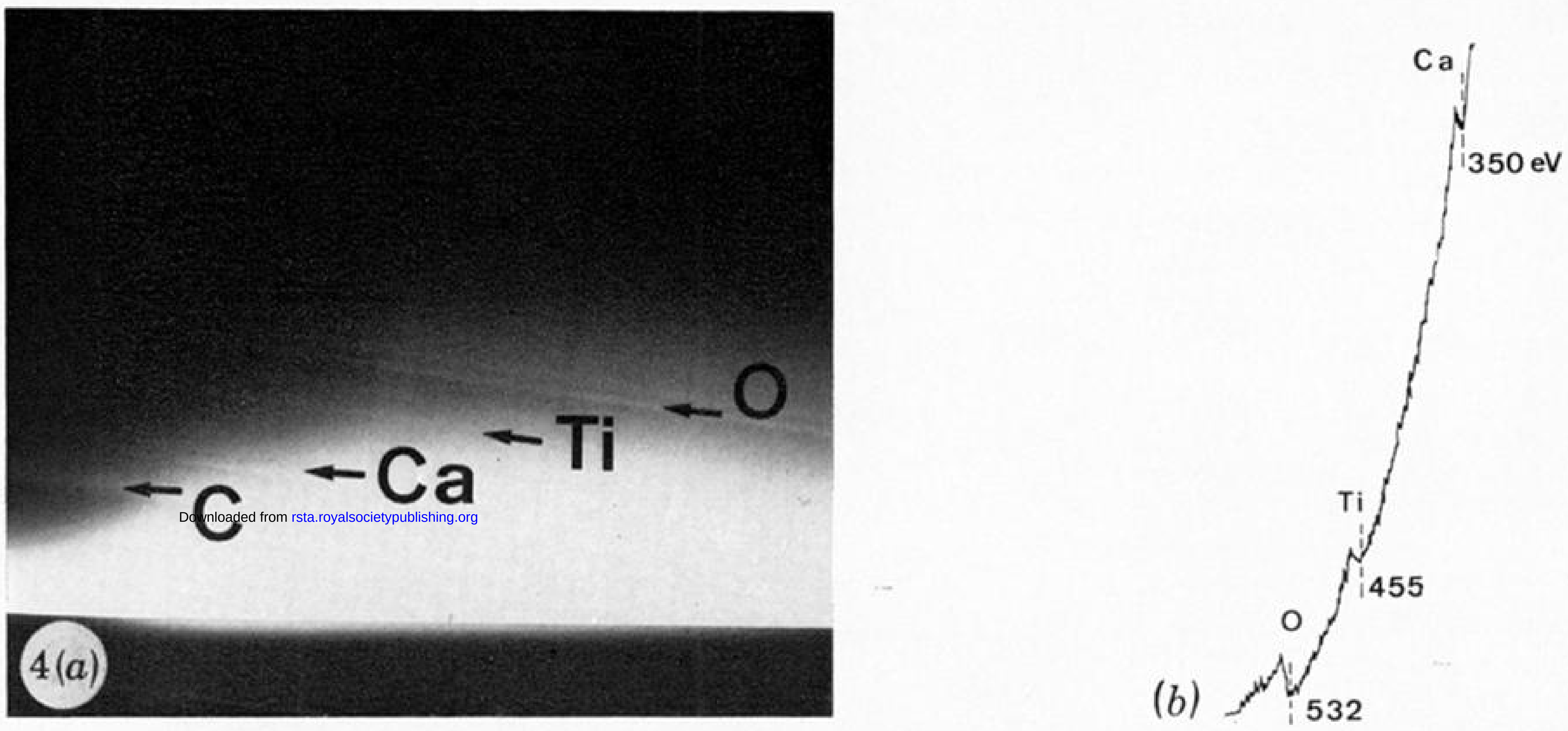

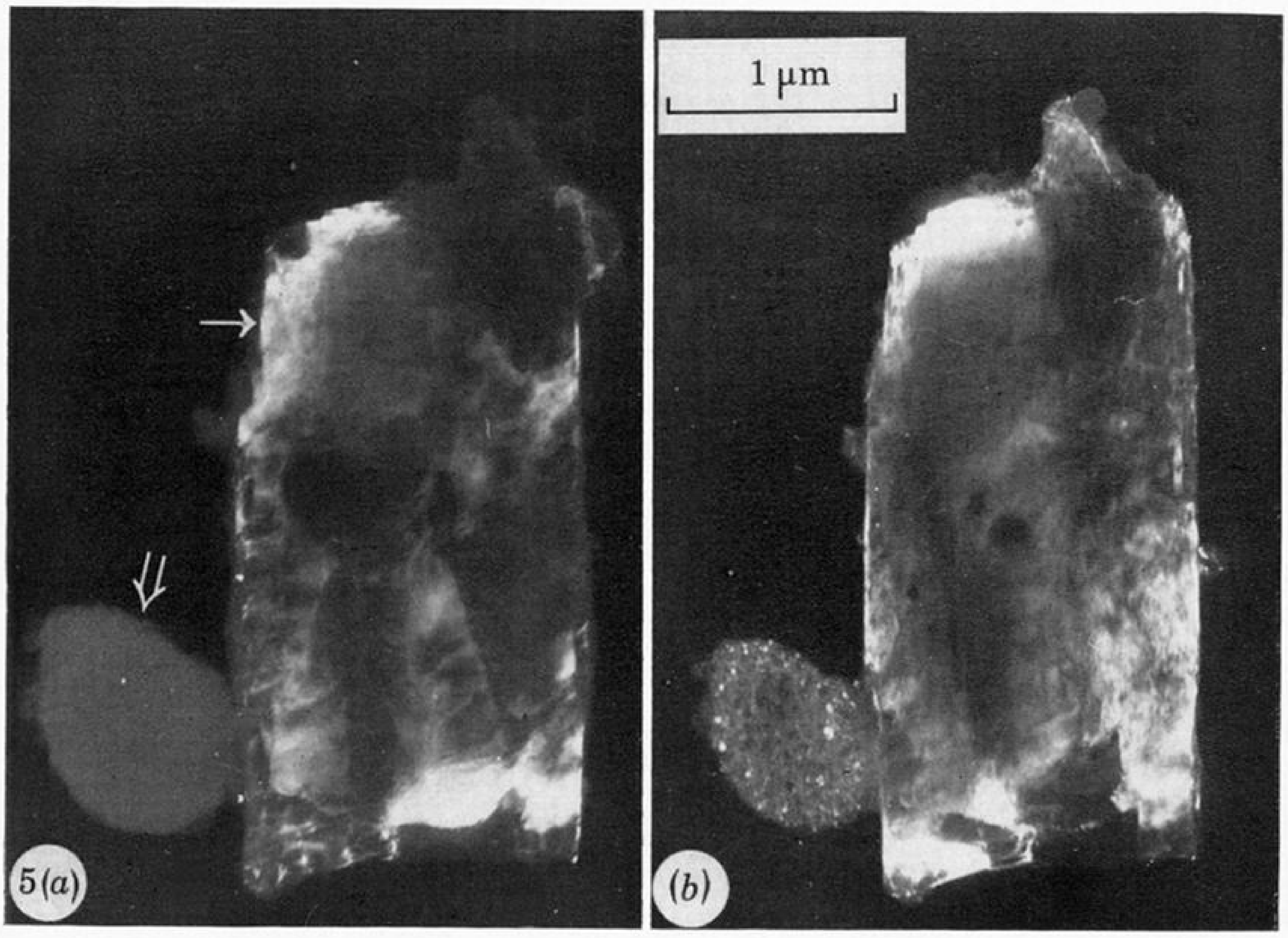

FIGURES 1, 4 AND 5. For description see opposite.