References and Notes

1. The SRXL resin, used to obtain the data for this report, is no longer commercially available from the Ionac Chemical Co., Birmingham, N.J. A resin reportedly identical is available from the Ayalcn Water Conditioning Co., Ltd., P.O. Box 586, Haifa, Israel, under the trade designation of Srafion NMRR. Trade names and company names are used in this report for identification only and do not imply endorsement by the Bureau of Mines.
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Olivines: Revelation of Tracks of Charged Particles

Abstract. *A one-step, three-component aqueous etchant was developed for revealing the tracks of charged particles in olivine. The etchant reveals tracks of small cone angle, which are equally well developed in all the crystallographic directions. The scope of fossil cosmic-ray track studies in extraterrestrial samples has thus been increased, because olivine is often an abundant constituent and because it has a higher threshold ionization for track registration and has lower uranium, thorium, and trace element concentrations as compared with pyroxenes and feldspars. The etchant does not attack any of the principal rock-forming minerals in normal etching time, which allows a nondestructive study of fossil tracks in thin-section mounts. The study of fossil cosmic-ray tracks in olivine is particularly valuable for investigations of very, very heavy cosmic-ray nuclei and for highly irradiated samples such as those found in the lunar regolith.*

The existence of cosmic-ray and spontaneous fission records in meteoritic and terrestrial minerals has demonstrated the usefulness of these solid-state detectors for the study of the cosmic-ray prehistory, the age, and the thermal history of minerals (*1*). For most of the rock-forming minerals in terrestrial and extraterrestrial samples, a suitable acid or alkali etchant exists (*2, 3*). However, for olivine, $(Mg,Fe)_2SiO_4$, which is usually abundant in most extraterrestrial samples (*4*), no satisfactory etchant has yet been reported. It has been claimed that etching with KOH and HF reveals tracks on the (100) face (*5*). No informative data based on studies of the (100) face have yet been reported, since such studies are time-consuming and applicable only in limited cases when large crystals are available. In this report we describe an etchant for satisfactorily revealing tracks in olivine, regardless of the crystallographic orientation.

The etchant described here was developed after we had made systematic studies of the shapes of tracks and the extent of development in a large number of randomly oriented crystals, both for cosmic-ray tracks in meteoritic olivines and for fission-fragment tracks in terrestrial and meteoritic olivines. On the basis of such studies and also on the basis of the observation of the tracks revealed on a given crystallographic plane by different chemicals, we were finally able to make up a compatible multicomponent etchant that showed little or no preference between different crystallographic directions in the revealing of tracks. The results of this study are discussed in detail elsewhere (*6*); the salient features of the olivine etch, designated as "WN," are described here.

The WN etchant is prepared by successively mixing 1 g of oxalic acid, 1 ml of orthophosphoric acid (85 percent), and 40 g of the disodium salt of EDTA

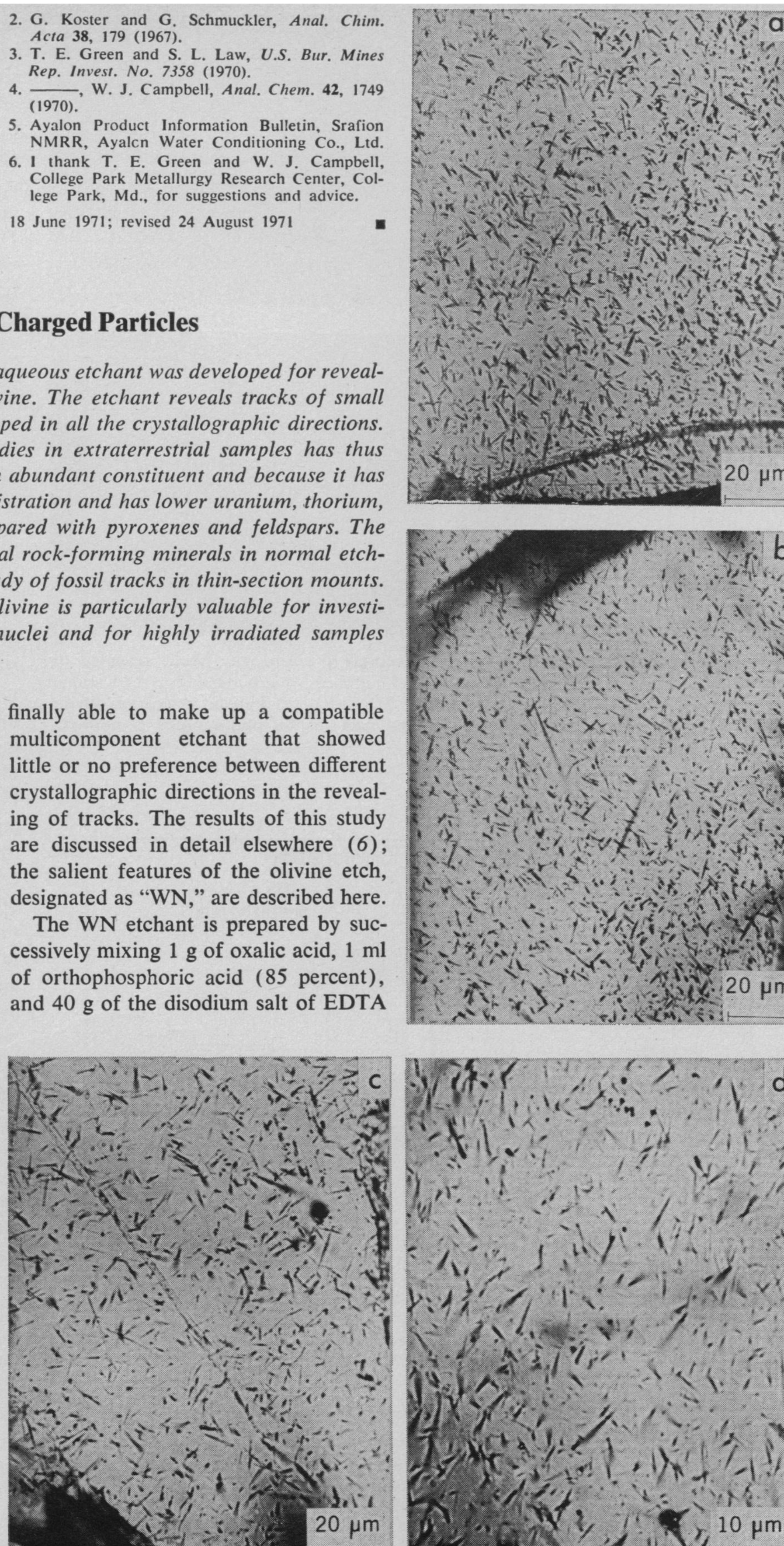

Fig. 1. Fossil cosmic-ray tracks due to iron-group nuclei in olivines: (a and b) from the Patwar meteorite; (c and d) in lunar regolith grains from the Apollo 12 mission. Part c shows sample 12028,68 (double core); part d shows sample 12041,11 (surface scoop). Tracks were revealed by etching with WN at its boiling point for 5 hours. Tracks were decorated with 0.25 unit of silver (*8*).

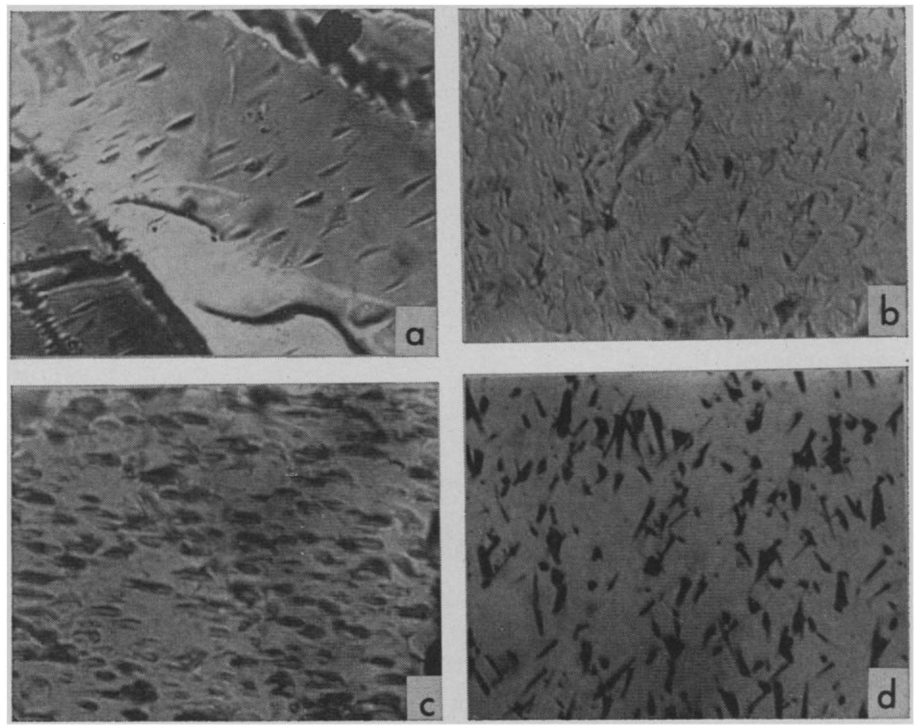

Fig. 2. Solid-state damage patterns in olivines exposed to cosmic-ray nuclei revealed by etching with NaOH or HF. (a) Apollo rock 10017 etched with NaOH (*2*, *3*). (b and c) Patwar meteorite olivines etched with ($HF + H_2SO_4$) (*9*). (d) Patwar meteorite olivine etched with NaOH (*2*, *3*). The field of view in each of the photographs is approximately 30 by 50 μm.

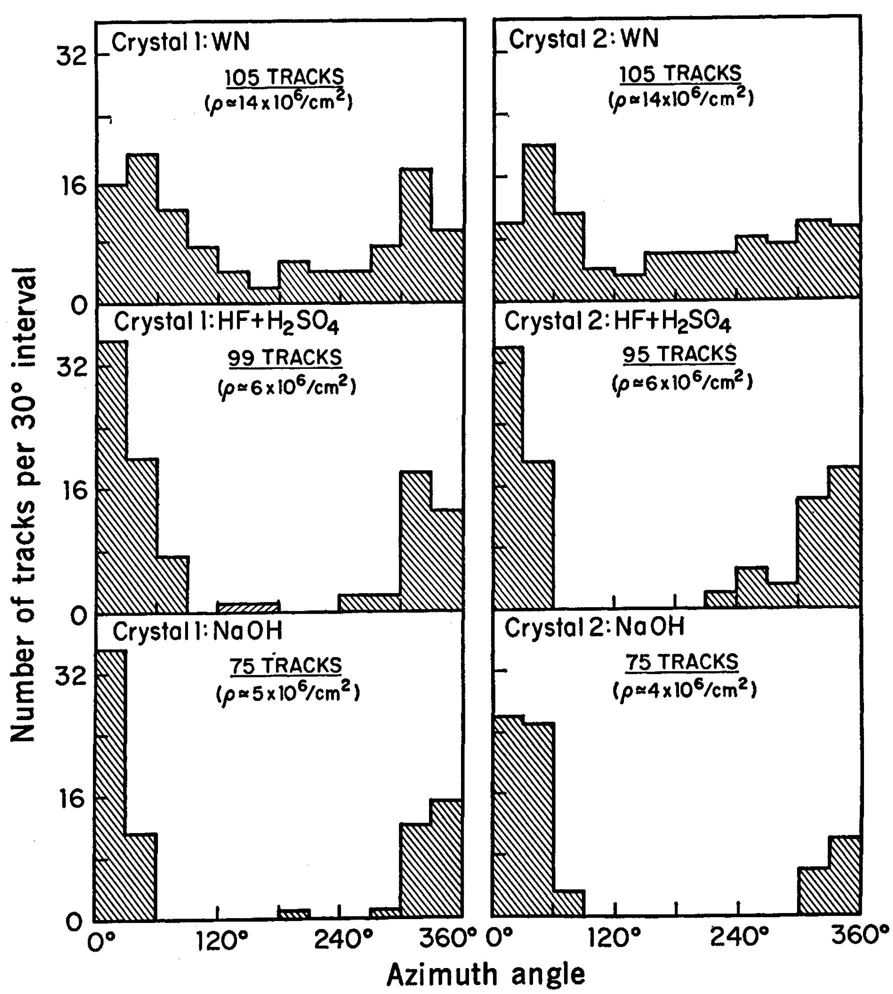

Fig. 3. Histograms showing distribution in projected angles for fossil tracks in Patwar meteorite olivines etched with WN, ($HF + H_2SO_4$), and NaOH. Results are for two crystals, designated 1 and 2.

(ethylenediaminetetraacetic) acid in 100 ml of distilled water; the *p*H of the solution is adjusted to 8.0 ± 0.3 by adding NaOH pellets. A part of the disodium salt of EDTA remains undissolved at room temperature but most of it dissolves when heated. Olivine is etched (*7*) at the boiling point of WN (105°C) by using a reflux arrangement adopted by Lal *et al.* (*3*) for etching feldspars and pyroxenes with alkali solutions. The time of etching is typically 4 to 5 hours for observing tracks optically; for electron-microscope replication (*8*), 2 to 3 hours is sufficient.

Figures 1 and 2 are photomicrographs of fossil tracks in meteoritic and lunar olivines. The samples were mounted and polished according to techniques discussed earlier by Lal *et al.* (*3*). Tracks etched by WN on a polished surface are shown in Fig. 1; these tracks are primarily due to cosmic-ray iron-group nuclei in olivine crystals from the Patwar meteorite and the Apollo 12 lunar regolith. For comparison, we include in Fig. 2 the types of formations resulting from the etchants commonly employed: NaOH or HF, or a mixture of HF and H_2SO_4 (*9*). With these etchants, etch figures, slits, and pits are normally revealed, but, on favorable crystallographic planes, tracks (albeit of large cone angles) are also revealed; these tracks are usually confined, within rather limited directions, to a projected angle of $\leqslant 20°$. Figure 2d is an example of a very favorable revealing of tracks by use of NaOH, HF, or ($HF + H_2SO_4$).

We studied the extent of isotropy with the WN etch (that is, the relative development of tracks in different directions in relation to the crystallographic axes) by examining both the track densities ρ (number of tracks per square centimeter) and the angular distributions of tracks in artificially irradiated (to fission fragments of ^{252}Cf) olivines and in extraterrestrial samples exposed to cosmic-ray nuclei. The results of this study are given in Figs. 3 and 4. That the WN etch reveals tracks in all directions can be seen in Fig. 3, where data are presented for two typical crystals (*10*). In the same crystals, on a fresh, internal but parallel surface exposed by grinding down 30 to 40 μm, tracks demonstrating anisotropy were revealed (Fig. 3), when

NaOH or ($HF + H_2SO_4$) was used as the etching solution. The other independent source of information on the isotropy in etching rests on observations of track densities (Fig. 4). A peak in track densities is observed only for the WN etch (see data in the top row of Fig. 4); the observed spread is consistent with expectations based on statistical and observational errors in the case of ^{252}Cf fragments and with expectations based on theory in the case of cosmic-ray tracks in the Patwar meteorite (*11*). The wide spread in track densities for etchings with HF, NaOH, or ($HF + H_2SO_4$) relates to the anisotropy of tracks revealed in different track and crystallographic directions. Only in the case of WN etch are proper tracks seen. In other cases, the data include slits, large cone angle tracks, and patterns that could be counted as single events.

These data clearly establish the unbiased etching of tracks in olivines regardless of crystal orientation or track direction when WN etch is used, in contrast to the preferential and imperfect etching with NaOH or HF. The WN etch is satisfactory for olivines in the wide compositional range commonly found in terrestrial and extraterrestrial samples [15 to 30 percent Fe_2SiO_4 (fayalite)]. For a lower content of fayalite, such as in the Norton County meteorite, and a higher content of fayalite, such as in the Angra dos Reis meteorite, larger percentages of oxalic acid and phosphoric acid, respectively, improve the etching of tracks.

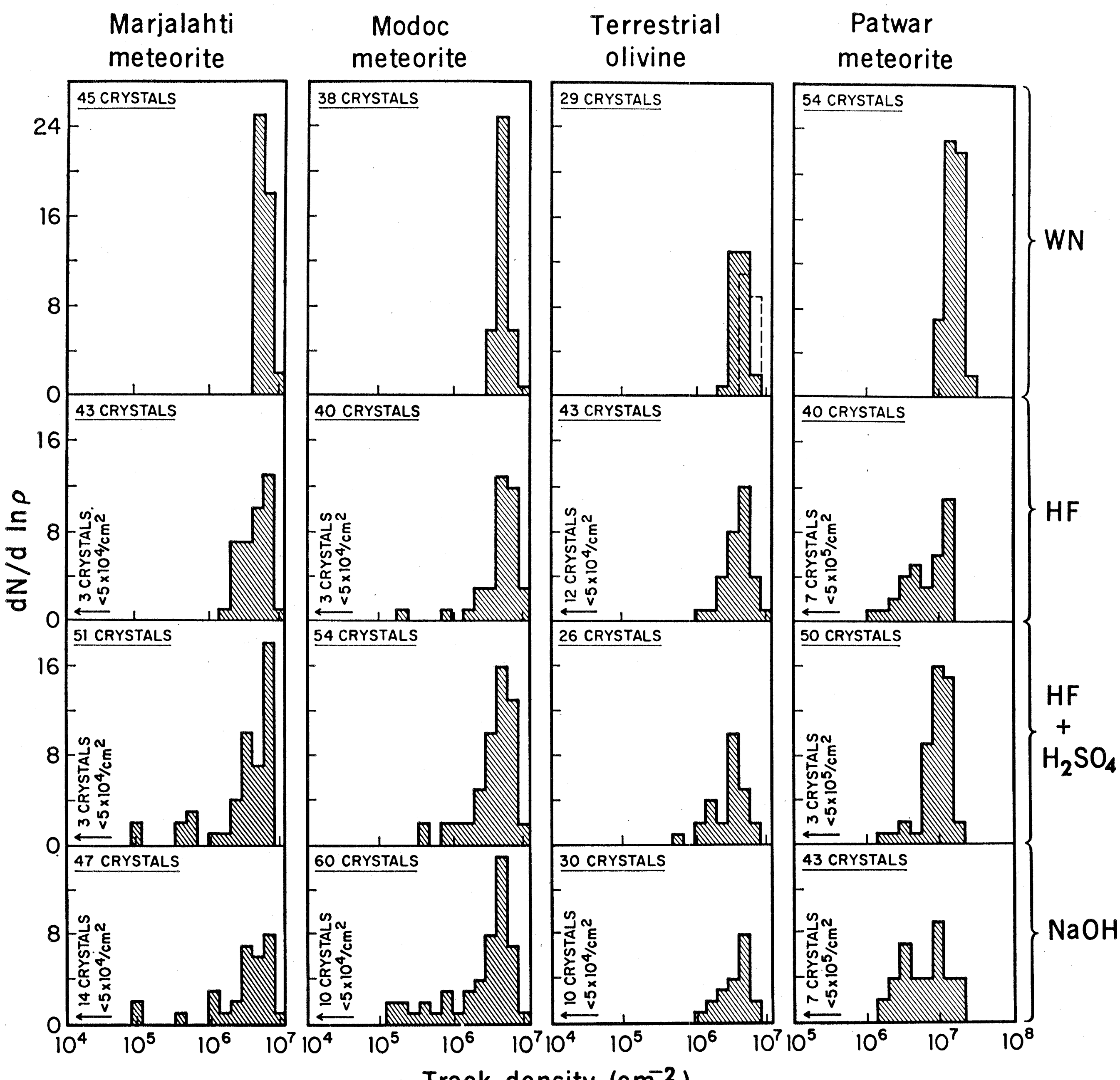

Fig. 4. The observed distribution in the density of tracks (and also, for HF and NaOH etches, marks such as etch slits and large cone angle tracks) in terrestrial and meteoritic olivines. The etchant marked on the right was used for all samples in a given row. Tracks in the Patwar meteorite are due to cosmic-ray nuclei. In other cases, they are due to fission fragments from a ^{252}Cf source. Crystals were irradiated under identical conditions. The dotted-line histogram in the top row, third inset, refers to tracks observed in an irradiated terrestrial enstatite crystal etched with NaOH (*2, 3*).

We will now describe some salient features of the successful etching of olivine crystals by our method. Let us first consider the sensitivity of the olivine with particular reference to cosmic-ray iron-group and heavier nuclei [see also (*6*)]. We find that, compared with the two principal mineral groups of feldspars and pyroxenes, olivines are the least sensitive; that is, the threshold ionization required for track registration in olivines is the highest. In contrast to pyroxene, in which iron-group nuclei have a mean etchable length of 11.5 ± 0.5 μm, the corresponding length for olivine lies between 8 and 10 μm. Comparisons of surface track densities in coexisting samples of pyroxene and olivine from the interior of lunar rocks and meteorites show that, owing to the higher threshold, the track densities in olivine are lower by a factor of about 2. This lower sensitivity is of crucial importance in studying crystals exposed on the lunar surface in which track density is high; most of the olivine crystals can now be studied optically.

For this reason, olivine is an ideal mineral for studying low-energy particle irradiation in gas-rich meteorites and in lunar samples, both of which have high radiation doses in the border zones. In several of the more primitive extraterrestrial materials such as the carbonaceous chondrites, olivine is the only crystalline material useful for track investigations. Furthermore, since olivines are relatively free of trace elements, including the fissionable nuclides, there will be fewer tracks produced by spontaneous fission. This should help in accurately deducing cosmic-ray spectra, even from data obtained at great depths in meteorite samples (where cosmic-ray contributions become small). In addition, since the etchant is chemically inert toward the other common minerals like feldspar and pyroxene, and since the surface loss due to etching is very small in olivines, it permits nondestructive study of thick sections. Since the sensitivities for track registration in feldspar, pyroxene, and olivine are different, comparison of their tract data should result in an understanding of cosmic-ray composition.

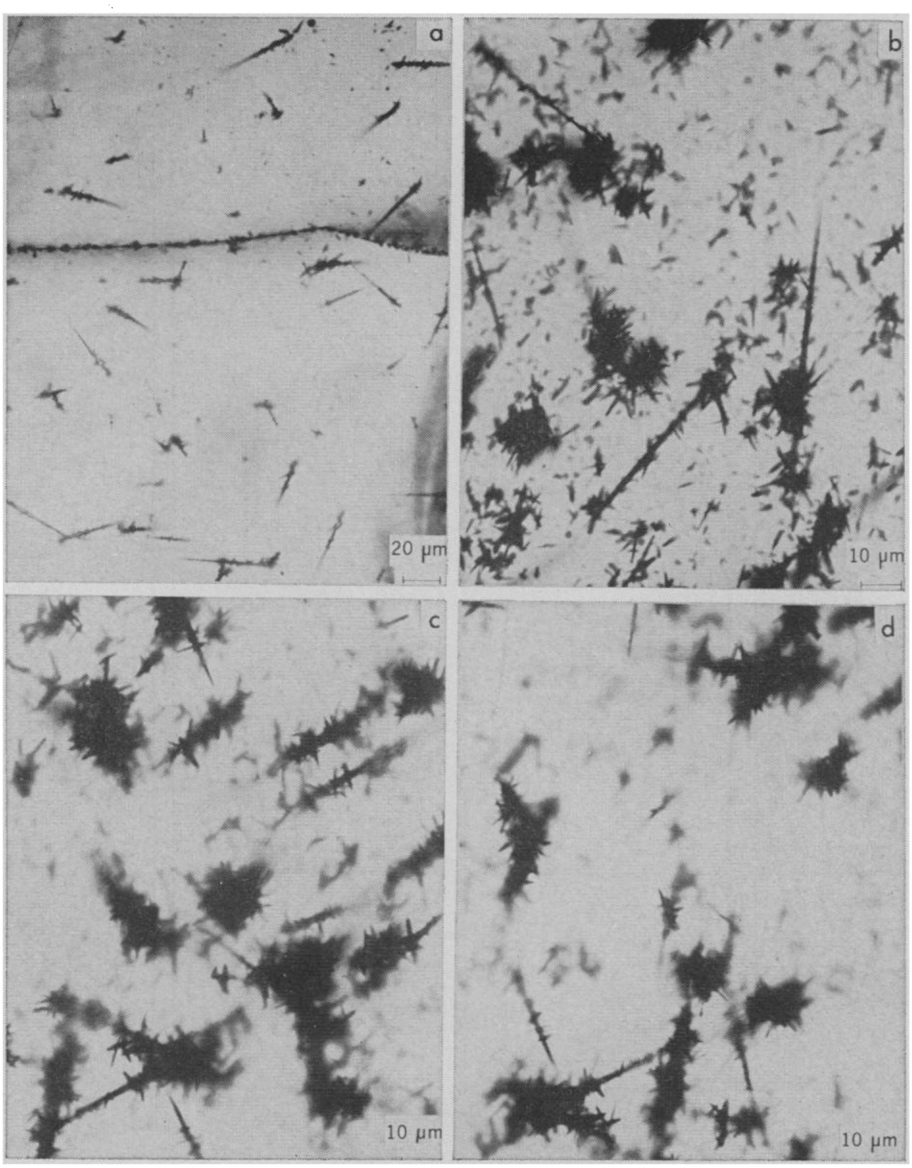

Fig. 5. Long fossil tracks due to VVH nuclei ($Z \geqslant 30$) in olivine crystal from the Patwar meteorite. (a) Tracks revealed by etching for 20 hours in WN. (b–d) Tracks revealed by etching for 50 hours in WN. A surface layer of 10 to 30 μm, which contained overetched tracks of iron-group nuclei, was removed to obtain a clear view of long tracks. Tracks were decorated with silver for optical contrast according to the method of Macdougall *et al.* (*8*).

Because the WN etch can be used at lower temperatures and does not attack other minerals, it has a particular advantage in the study of fossil tracks of high *Z* (atomic number) cosmic-ray nuclei [$Z \geqslant 30$, usually designated as very, very heavy (VVH) nuclei] in single crystals or in thick sections (*6*, *12*). An additional advantage is the fact that the cone angle of tracks is small, smaller even than the angle observed in pyroxenes (*3*). Consequently, the prolonged etching that is necessary to reveal the long tracks due to VVH nuclei does not result in any appreciable surface loss due to the etching of TINT tracks (*13*); TINT's (track-in-track events) represent deeper-seated tracks within the crystal etched via the canal of a surface track. With the WN etch, we have now been able to study the energy spectrum of VVH nuclei in irradiated grains from the lunar surface, as well as in meteoritic crystals. Previously it was possible only in rare cases to see long tracks in lunar pyroxene crystals of high track density ($\geqslant 10^8$ cm^{-2}) because of a marked "surface loss" in the time required to etch a track to a length of even 30 to 40 μm.

We have studied a few thousand tracks of VVH nuclei revealed with the WN etch. We present here photomicrographs (Fig. 5) of long tracks due to VVH nuclei in olivines from near-surface regions of the Patwar meteorite. The technique for observing long tracks is similar to that described earlier (*13*). The short intersecting spurs on long tracks are due to iron-group nuclei TINT's. Some of the bushlike clusters without a visible long track are due to steeply dipping long tracks.

The WN etch should introduce a sparkle in the work of trackologists who, to their disappointment, have discovered that the bulk of the mineral grains in an extraterrestrial sample is often composed largely of olivine, a mineral which has resisted previous attempts to reveal proper tracks.

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14. We thank W. F. Libby for placing the ^{252}Cf source at our disposal; R. S. Clarke, Jr., K. Fredriksson, and N. Grogler for making available to us the samples of Modoc and Marjalahti meteorites and terrestrial olivines; G. C. Chaterji and P. K. Chaterji of the Geological Survey of India, Calcutta, for providing us with samples of the Patwar meteorite; P. K. Talekar and A. Padhye for technical assistance; G. Arrhenius and J. D. Macdougall for assistance and helpful discussions; and J. R. Arnold and M. Honda for their invaluable suggestions on chemical aspects, without which this work could not have been accomplished. We are also indebted to the National Aeronautics and Space Administration for giving us the lunar samples.

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Duricrusts and Deep-Weathering Profiles in Southwestern Wisconsin

Abstract. *Numerous exposures in southwestern Wisconsin display the profiles of relict deep weathering. Crusts are mainly siliceous, but many are ferruginized to some extent. The occurrence of blocky silcrete, thought to be reported for the first time, recalls the profiles in the Australian belt of transition from silcrust to ferricrust. The humid-tropical kind of pedogenesis necessary to effect this transition may have operated as late as the mid-Miocene. In some localities, the action of groundwater has caused crusting, mottling, and reduction beneath the dolomite of former tower karst.*

Duricrusts and deep-weathering profiles (*1*) are exposed in numerous sections in southwestern Wisconsin, over an area of 13,000 km^2 (5,000 mi^2) or more. They transgress the local sedimentary succession, from not lower than the St. Peter sandstone, near the base of the Champlainian series (Ordovician), to well down into the Cambrian. The profiles include pallid zones in their lower parts, with mottled zones next above, and duricrusts at the top, being wholly comparable in their field characteristics and relationships to the profiles and crusts abundantly described from the Southern Hemisphere, notably Australia (*2*).

Total profile thicknesses exceed 30 m (100 feet) in places. Crusts, although mainly thin (depths of 0.25 to 1.0 m are common), exhibit the familiar range of variation in texture, from loose nodules through slaggy forms to coherent quartzites and blocky silcrete (*2, 3*). The mottled zones vary much in depth, some attaining 20 m, but usually the pallid zone constitutes the bulk of a given profile.

Ferruginized crusts range in color up to 7.5R 4/6, red on the Munsell scale; but thin-sectioning reveals that they consist primarily of sandstone, with the often hematitic iron coating the grains or filling the pore spaces. The silcrusts range from secondarily silicified arenites, wherein bedrock structures are perfectly preserved, to blocks identical in form, color, and texture with that of the gray billy of the Australian inland; silcrete blocks occur in association with highly reddened sandstone. The observed relationships recall those in part of the Australian transition zone between silcrusts and ferricrusts [see (*2*)].

The wide extent of the deeply weathered and duricrusted surface of southwestern Wisconsin implies pedogenesis under forest of the kind now called tropical in a climate probably belonging to the Aw type in Köppen's classification. We infer the affected surface to have been a pediplain (*4, 5*), some of the divides on which are represented by the highest ground of today. No date can yet be offered for the last operation of deep weathering in the area. Parham has referred kaolinitic weathering in Minnesota to Cretaceous times (*6*), but the paleoclimate appears to have been suitable, where a land surface was exposed, as late as the mid-Miocene (*5*).

Of particular interest is the relation between deep-weathering profiles in the St. Peter sandstone and overlying dolomites of the Galena-Platteville succession: at the outcrop boundary, the profile passes under the dolomite, not infrequently becoming compressed. Since deep weathering and regional crusting imply a general lowering of the affected surface, but since the underground surface of the St. Peter sandstone displays no sign of having suffered erosion, we conclude that the profiles have not been buried; that is, where they occur underground, they are not relict from Ordovician times but have been developed in place, beneath tower karst in the former tropical conditions. On this basis, the pallid and mottled zones developed in the normal fashion, under the control of perennial and seasonally fluctuating groundwater, respectively, while the encrusting iron was precipitated near the top of the groundwater table during wet seasons. This conclusion is strengthened by the observation that the basal dolomite bed is commonly ferruginized from below. A further implication is that the former tower karst was, like its present-day Caribbean analogs, sufficiently permeable to swallow surface moisture.

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