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FIRST OBSERVATION OF ETCHED URANIUM FISSION TRACKS IN NEPHELINE BY HERMANN TRAUBE (1895)?

by

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Zusammenfassung

In Jahr 1895 hat Hermann TRAUBE über die Beobachtung anomaler Ätzfiguren auf Prismenflächen von Nephelin berichtet. Diese Ätzfiguren wurden mit HCl erzeugt, hatten eine dreieckige Gestalt mit einer trichterförmigen, exzentrischen Vertiefung. Ihre Achsen waren regellos orientiert, d.h. ohne jeglichen Bezug zu kristallographisch indizierbaren Richtungen. Daher gehorchen diese anomalen Ätzfiguren nicht den bekannten Regeln der chemischen Auflösung von Kristallen. Stattdessen ist eine inhärente Ursache ihrer Exzentrizität anzunehmen. Höchstwahrscheinlich wurden sie durch nukleare Partikelspuren infolge der spontanen Kernspaltung von ^{238}U verursacht. Letztere war im Jahr 1895 noch unbekannt.

Ätzversuche durch den Autor dieser Arbeit ermöglichen eine Größenabschätzung von ca. < 20 μm für die gewöhnlichen und anomalen Ätzfiguren, die von TRAUBE (1895) beobachtet wurden. Die These, es könne sich um geätzte Spaltspuren gehandelt haben, gewinnt dadurch an Wahrscheinlichkeit. Der Versuch, induzierte Spaltspuren in Nephelin mit verdünnter HF sichtbar zu machen, ist allerdings gescheitert, da die Ätzrate von HF auf Prismenflächen deutlich größer als jene von HCl ist.

Abstract

In 1895, Hermann TRAUBE has reported the observation of anomalous etch figures on prism faces of nepheline. These etch figures were produced with HCl, had a triangular shape with a funnel-like, eccentric extension into the crystal. Their axis had a random orientation without any relation to crystallographic directions. Thus, these anomalous etch figures are not compatible with the principles of normal crystal dissolution and should have an inherent reason for their eccentricity. Most probably they were caused by nuclear particle tracks origination from the spontaneous fission of ^{238}U which was unknown in 1895.

Etching experiments by the author of this article provide a length estimation (ca. $< 20\ \mu$m) for the ordinary and anomalous etch figures observed by TRAUBE (1895) and thus support the assumption that they were fission tracks. However, the attempt to reveal induced fission tracks in nepheline with diluted HF has failed because of a higher bulk etching rate compared to that of HCl.

Key words: nuclear fission, nuclear particle tracks, chemical etching, enantiomorphism

1. Introduction

The discovery of radioactivity was mainly provoked by experiments of BECQUEREL (1896, a, b, c) who had observed that a piece of uranium salt placed for several hours on layers of opaque papers enwrapping a photographic plate produced a silhouette on the plate which became visible by chemical development. After several experiments with both phosphorescent and non-phosphorescent uranium salts, he concluded that a penetrating invisible radiation is emitted by the uranium itself, and is not produced by insolation or another external energy source.

Radioactive decay of atomic nuclei can be classified in several processes, as for example alpha (α) decay by emission of a helium nucleus, beta (β-) decay by emission of an electron, electron capture, and others. Compared to alpha and beta decay, spontaneous fission of very heavy atomic nuclei is a rare event. The α decay frequency of ^{238}U is 1.8×10^6 times higher than its spontaneous fission which produces two atomic nuclei with nucleon numbers of about 140 and 95, plus two or three free neutrons (cf. WAGNER & VAN DEN HAUTE, 1992, and references cited therein).

First experimental evidence for neutron induced uranium fission was obtained by chemical detection of one of the fission products which was a radioactive barium isotope (HAHN & STRASSMANN, 1939).

Electrically charged particles produced by nuclear decay can be detected in a cloud chamber, in a bubble chamber or by chemical etching of insulating solids which were exposed to nuclear radiation. The passage of ionizing nuclear particles through insulating solids creates linear tracks of radiation damage on the atomic scale. These tracks can be enlarged by chemical etching and thus become visible under an optical microscope (cf. FLEISCHER, PRICE & WALKER, 1975; HEJL, 2000). Particle tracks produced by nuclear fission are called fission fragment tracks or simply fission tracks. Naturally occurring fission tracks in minerals are almost exclusively produced by the spontaneous fission of ^{238}U.

Fission tracks could be observed in mica by transmission electron microscopy (SILK & BARNES, 1959). Few years later, fission tracks could be revealed in various minerals by chemical etching, and were used for dating of hornblende and apatite (FLEISCHER & PRICE, 1964; WAGNER, 1968). On the other hand, chemical etching of mineral surfaces was not a new analytical method of the second half of the 20th century. At the end of the 19th century, chemical etching of crystal faces was a standard method for the investigation of crystal symmetry. Thus, we may ask if etched fission tracks could have been observed previous to the formulation of the physical concept of nuclear fission. Indeed, WAGNER & VAN DEN HAUTE (1992, page xii, Fig. 1) gave an example of a photomicrograph taken from an ancient textbook of BAUMHAUER (1894) which shows some anomalous etch figures having a lower symmetry than the etched face. WAGNER & VAN DEN HAUTE (1992) have argued that some of these anomalous etch figures are etched fission tracks.

The present article deals with anomalous etch figures in nepheline observed by TRAUBE (1895), i.e. one year earlier than the „discovery" of radioactivity by BECQUEREL (1896, a, b, c). Most probably, these etch figures are fission tracks too.

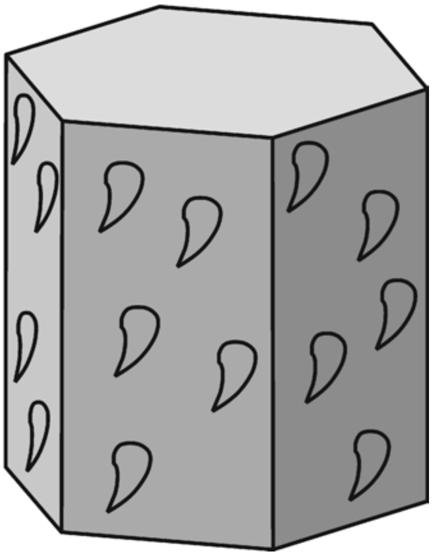

Figure 1
Single crystal of nepheline with typical asymmetric etch figures produced by exposure to strongly diluted hydrofluoric acid (HF).

2. First evidence of nepheline's enantiomorphism by etching experiments of H. BAUMHAUER (1882)

The enantiomorphism of nepheline was first recognized by BAUMHAUER (1882, 1891) who had studied etched figures of nepheline produced by strongly diluted hydrofluoric acid at room temperature, and alternatively by warm diluted hydrochloric acid. Etch pits on prism or pyramid faces of nepheline are highly asymmetric but with the same orientation and shape as other etch pits on the same face (BAUMHAUER, 1882, 1891). On the other hand, their orientation is symmetrical to those on a corresponding face of a twin partner.

BAUMHAUER (1882) concluded that the etch figures of nepheline are incompatible with the highest hexagonal symmetry, but indicate a minor hexagonal symmetry without mirror planes parallel and normal to the crystallographic c-axis (in german: *„Hemiedrie in Verbindung mit Hemimorphismus nach der Hauptaxe"*; BAUMHAUER, 1882, p. 216). These results were confirmed in a later article of BAUMHAUER (1891). Afterwards and even nowadays, such etch figures of nepheline are often reproduced in textbooks as an example for crystal faces with minor symmetry (Fig.1).

3. Confirmation of nepheline's enantiomorphism and observation of anomalous etch figures by H. TRAUBE (1895)

TRAUBE (1895) repeated BAUMHAUER'S etching experiments and could mainly confirm the former results. TRAUBE used nepheline crystals from Mount Vesuvius (Italy). These crystals were nearly transparent, up to 5 mm in size, and had grown in druses of noncognate calcareous ejecta together with green augite, biotite and few sanidine. With diluted hydrofluoric acid, TRAUBE could reveal asymmetrical etch figures on prism faces, very similar to those described by BAUMHAUER (1882, 1891).

Etching of prism faces with a rather high concentration of hydrochloric acid also produced asymmetric etch pits but with different shape than those revealed with HF. Apart from compact, rather shallow etch pits, also some needle-like, eccentric cavities were observed and described as follows (in german): *„Nicht selten trat auch der Fall ein, dass die Figuren bei längerer Dauer der Ätzung ihre geradlinig dreieckige Gestalt beibehielten, sich aber trichterförmig vertieften und so einen dreiseitigen Kegel darstellten. Die Spitze des Kegels lag jedoch nicht über der Mitte der Ätzfigur, sondern stark seitlich daran, meist ausserhalb derselben. Diese Kegel waren oft so tief in den Krystall eingesenkt, dass es u. d. M. einer verschiedenen Einstellung bedurfte, um ihre Gestalt deutlich zu erkennen.“* (TRAUBE, 1895, p. 469). In english translation: *„Quite often was the case that the figures preserved their triangular shape after prolonged etching, but became deeper and funnel-shaped, thus forming a trilateral cone. The peak of the cone was not located in the middle of the [superficial] etch figure, but strongly at the side, mostly outside of it. These cones often extended so deep into the crystal that a modified focus of the microscope was necessary in order to recognize clearly their shape."*

Ordinary and anomalous etch figures are depicted in Fig. 2 (redrawn after TRAUBE, 1895, p. 469). Except of the small triangular etch figures (type a), all types of etch pits are clearly asymmetrical, i.e. without a mirror plane parallel to the c-axis. Those of type e and f extend deeper into the crystal and exhibit a conical shape with a very eccentric lower end. Such etch pits are not compatible with the principles of normal crystal dissolution and must have an inherent reason for their eccentricity. Tiny spicular inclusions would have been recognized by TRAUBE (1895) and thus can be excluded. On the other hand, the etch pits of type e and f have a close resemblance with etched fission tracks originating from the spontaneous fission of ^{238}U, which was not yet discovered in 1895.

According to FLEISCHER & PRICE (1964), etched fission tracks are straight (not curved), have a length of not more than 20 μm, and are randomly orientated, i.e. without crystallographic or other preferred orientation in a large number of tracks. Thus, the etch figures of type e and f revealed by TRAUBE (1895) could have been etched fission tracks. Unfortunately, TRAUBE has not indicated magnifications and did not insert scale bars in the figures of his publication. However, the comparison with the size of ordinary etch figures (without eccentricity) permits a rough estimation of track length, as will be explained below.

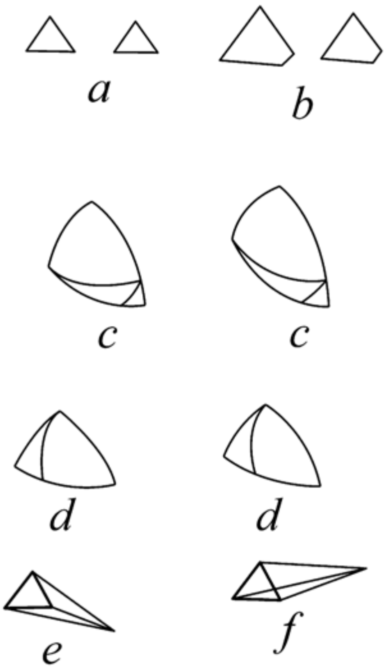

Figure 2

Ordinary (a, b, c, d) and anomalous (e, f) etch figures on prism faces of nepheline produced by exposure to hydrochloric acid (HCl) after TRAUBE (1895); redrawn after Fig. 2 (page 469) of the original publication.

4. A new attempt to reveal fission tracks in nepheline by chemical etching

WAGNER & VAN DEN HAUTE (1992, p. 161-186 and Appendix A) have listed more than 40 minerals suitable for fission-track dating, together with their specific etching conditions. Nepheline was never used for fission-track dating. Thus, appropriate etching conditions are unknown, but the ancient experiments of BAUMHAUER (1882, 1891) and TRAUBE (1895) may give an indication. Both authors agree that diluted HF is suitable for the revelation of crystallographic etch pits. TRAUBE (1895) has also successfully applied HCl for the revelation of asymmetric etch pits on prism faces – in contrast to BAUMHAUER (1882) who had concluded that HCl yields rather indistinct etch pits on basal faces, and no etch pits on prism faces. This discrepancy might be due to different HCl concentrations which were not indicated in the articles of both authors.

For the present investigation, nepheline crystals from druses of Mt. Vesuvius were embedded in various orientations in epoxy resin. These orientations include crystals with their basal faces or their prism faces parallel to both sides of the epoxy disk. The mounted short prismatic crystals with a size of up to 3 mm, were ground and polished, and were either attached to uranium doped glass IRMM-540 (1 sample mount; cf. DE CORTE et al. (1998) for the certified glass properties) or to polished surfaces of Durango apatite (2 sample mounts). These sandwich mounts were irradiated together with thermal neutrons in the FRM II Reactor (Forschungsneutronenquelle Heinz Maier-Leibnitz II, TU Munich, Garching, Germany) in order to produce a rather high areal frequency of nuclear particle tracks originating from the neutron-induced fission of ^{235}U. The thermal neutron fluence was 1.96 . 1015 cm^{-2} (thermal neutron flux of 1.15 . 1013 cm^{-2}s^{-1} for 170 seconds).

After irradiation, the nepheline sample attached to the IRMM-540 glass was step-etched at 20°C with 1 % HF and examined under the microscope after 30, 60, 90, and 120 seconds. After these 120 seconds, shallow etch pits first became visible. On prolonged etching, the etch figures became larger with a more distinct shape. They were examined after 3, 4, 6, 8, and 15 minutes. The other two nepheline samples that had been attached to Durango apatite during irradiation were etched for 10 minutes at 20°C with 1 % HF.

The main requirement for a proper revelation is that etched fission tracks must be distinguishable from other features such as etched screw dislocations, impurities or chatter marks. The etch figures visible after 15 minutes of etching (Fig. 3) resemble those described by BAUMHAUER (1882, 1891) and TRAUBE (1895) when diluted HF had been used for etching. They clearly display the asymmetry of nepheline's prism faces. Needle-like etch figures with random orientation as they could be expected for etched fission tracks were not observed at all stages of etching, and the observed etch figures are less frequent as would be the case for fission tracks produced by the specific irradiation parameters.

The size of the etch figures shown in Fig. 3 and that of etch figures on other prism faces are quite similar. The maximum length of the etch figures is about 20 μm which would be consistent with the expected length of etched fission tracks, but the parallel orientation of more than 10 visible etch pits is not compatible with the requirement of random orientation that would be expected for nuclear particle tracks produced by uranium fission. However, under the reasonable assumption that the magnification of the figures published by TRAUBE (1895) was the same for both kinds of etch pits produced with diluted HF and with diluted HCl, we obtain an indication for the approximate size of the anomalous etch figures depicted in Fig. 2 (type e and f).

Their length would be also in the order of about 20 μm or slightly less, which supports the assumption that they are etched fission tracks.

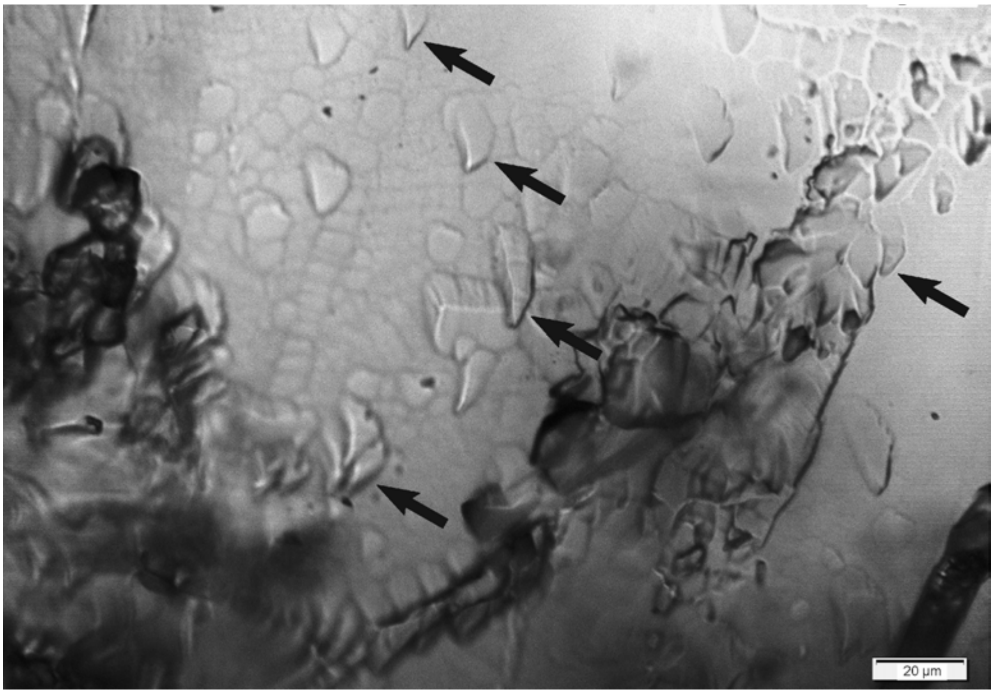

Figure 3
Prism face of nepheline in transmitted light after etching with 1 wt% HF at 20°C for 15 minutes. Some etch figures are clearly asymmetric (arrows), and very similar to those described by BAUMHAUER (1882, 1891) and by TRAUBE (1895). Eccentric etch figures with random orientation were not formed, in spite of thermal neutron irradiation together with an attached uranium doped glass IRMM-540.

5. Conclusions

The present investigation has shown that latent fission tracks in nepheline cannot be revealed properly by etching with strongly diluted HF. However, the etching experiments provide an indication for the size of some anomalous etch figures observed by TRAUBE (1895) on prism faces of nepheline after etching with HCl. These anomalous etch figures had an approximate size of < 20 μm, an eccentric shape and a random orientation. Therefore, I still support the assumption that TRAUBE (1895) has observed etched uranium fission tracks.

The failed attempt to reveal induced fission tracks with strongly diluted HF could be due to a higher bulk etching rate of HF compared to that of HCl. This assumption is supported by observations of TRAUBE (1895, p. 468): *„Die Prismenflächen widerstehen der Salzsäure viel mehr als der Flusssäure, daher empfiehlt sich die Anwendung einer concentrirteren Säure oder eine Temperaturerhöhung auf 50 – 60°C bei Einwirkung einer verdünnteren“.*

In english translation: „*The prism faces resist the hydrochloric acid much more than the hydrofluoric acid, therefore the use of a more concentrated acid or a temperature increase to 50 – 60°C in case of lesser concentration is recommended*". Such low bulk etching rate of nepheline's prism faces facilitates preferential etching of a linear radiation damage zone having a much higher linear etching rate.

Acknowledgments

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