

(zircons, apatites et monazites) de la granodiorite. La mise en place de la partie ouest du massif de Lausitz s'est donc faite lors de l'orogénèse calédonienne ou hercynienne, ce qui est en accord avec les mesures d'âge du groupe de SCHÜRMAN. La question de savoir si l'est du massif a le même âge ou est plus âgé pourrait être résolue par la même méthode.

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### Summary

By a quantitative study of pleochroic haloes in biotite, the haloe age of the Lausitz granodiorite, in comparison with the granite age of the Elba Isle, was estimated to  $280 \pm 150$  M.Y. The granodiorite is either caledonian or hercynian.

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## Tetracalcium Hydrogen Triphosphate Trihydrate, a Constituent of Dental Calculus

In a large number of dental calculus specimens from Copenhagen, and a small material from Alaskan Eskimos, we have found the major crystalline inorganic constituents of dental calculus to be brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), apatite, and a magnesian whitlockite (or  $\beta\text{-Ca}_3(\text{PO}_4)_2$  with some 7 atomic % of calcium replaced by magnesium)<sup>1</sup>. Brushite is found only in the mandibular region because mandibular, but not parotid, saliva is supersaturated with this compound<sup>2</sup>. Magnesian whitlockite and apatite are common also in concretions from the salivary glands and ducts<sup>3</sup>. In contrast, brushite was found only in one such salivary calculus out of 30 examined.

As a minor constituent, we have recently found another calcium phosphate in dental calculus: crystalline tetracalcium hydrogen triphosphate trihydrate ( $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ ). It was found in 48 out of 124 calculus specimens collected from Copenhagen patients in 1955. This compound, the existence of which has been alternately claimed and disclaimed since BERZELIUS, was first obtained in the pure crystalline state by BJERRUM<sup>4</sup>. He determined its solubility product, from which it follows that its solubility over a wide range of pH lies between that of brushite and that of a hydroxyapatite of moderate particle size (about 600 Å). Its presence was long overlooked in our X-ray diagrams of dental calculus, because it is, as a rule, only present in minor quantities, and many of its strongest diagram lines lie close to those of whitlockite and apatite. Its presence as a minor component in a mixture of calcium phosphates

is best ascertained by a powder diagram line at  $d = 18.6$  Å which coincides with no apatite, whitlockite or brushite lines but unfortunately lies outside the range of ordinary Debye powder cameras. The line is strong in Guinier diagrams.

The historical elusiveness of the compound might suggest that it is only a short-lived intermediate in the hydrolysis of acid calcium phosphates. This is not true, however. We have now found it in nature, and we know it is quite stable in the dry state. A twenty-year-old preparation of the compound has been found in this laboratory to give the same X-ray diagram as a newly prepared specimen.

We should suspect it of being present also in some specimens of certain calcium phosphate minerals, such as are catalogued under the names collophanite, zeugite, monite and martinite. A number of such minerals has already been examined with X-ray powder methods by FRONDEL<sup>5</sup>, who found them to contain only the expected compounds: apatite and in some cases whitlockite. The lines of tetracalcium hydrogen triphosphate trihydrate may, however, have been overlooked, as in the case of dental calculus diagrams and for the same reasons.

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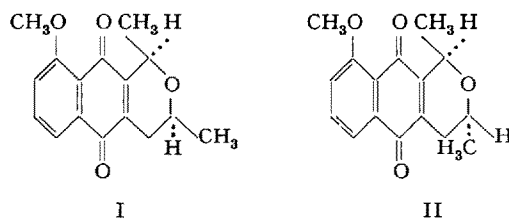
### Zusammenfassung

Die überwiegenden Bestandteile des Zahnsteins sind Apatit, magnesiumhaltiger Whitlockit mit rund 7 Atomprozent Magnesium und (nur in der Mandibularregion) Brushit. Als untergeordneten Bestandteil haben wir in 48 von 124 untersuchten Zahnsteinproben auch Tetracalcium-hydrogen-triphosphat-trihydrat gefunden.

<sup>5</sup> CL. FRONDEL, Amer. Min. 28, 227 (1943).

## Synthese der razemischen Eleutherin-Chinone

Den Chinonen aus *Eleutherine bulbosa* (Mill.) Urb. (Iridaceae) wurden auf Grund von Abbaureaktionen die nachfolgenden Formeln zugeteilt<sup>1</sup>, in denen höchstens die Lage der Methoxylgruppe noch etwas unsicher war.



(+)-Eleutherin Smp. 175°      (-)-Isoeleutherin Smp. 177°  
(±)-Eleutherin Smp. 156°      (±)-Isoeleutherin Smp. 153–154°

Wir haben nun auf dem nachstehenden, eindeutigen Wege (±)-Eleutherin und (±)-Isoeleutherin synthetisch

<sup>1</sup> H. SCHMID, TH. M. MEIJER und A. EBNÖTHER, Helv. chim. Acta 33, 1751 (1950). – H. SCHMID und A. EBNÖTHER, Helv. chim. Acta 34, 561, 1041 (1951).

<sup>1</sup> A. TOVBORG JENSEN and M. DANØ, J. dent. Res. 33, 714 (1954). – A. TOVBORG JENSEN and S. L. ROWLES, Acta odont. scand. 15, 121 (1957), and unpublished results.

<sup>2</sup> A. TOVBORG JENSEN and M. DANØ, J. dent. Res. 33, 714 (1954).

<sup>3</sup> A. TOVBORG JENSEN and M. DANØ, J. dent. Res. 31, 620 (1952).

<sup>4</sup> N. BJERRUM, Selected papers (Munksgaard, Copenhagen 1949), p. 245; Mat. Fys. Med. Dan. Vid. Selsk. (to be published).