

technologique le permettra. De même, la microsonde moléculaire devrait permettre d'étudier les agrégats cristallins observés dans les urines lithogènes et pratiquement absents des urines normales, de déterminer la composition des cristaux et particules microscopiques présentes dans les divers échantillons; tout cela devrait contribuer à une meilleure connaissance des sédiments urinaires et ouvrir sur une

différenciation efficace des urines normales et pathologiques. D'importantes applications médicales pourraient en découler comme par exemple un dépistage précoce des sujets potentiellement lithiasiques ou encore l'instauration de traitements protecteurs adaptés à chaque situation.

Bibliographie

- (1) M. Daudon, M. F. Protat et R. J. Reveillaud., Analyse des calculs par spectrophotométrie infrarouge. Avantages et limites de la méthode, *Ann. Biol. Clin.*, 1978, **36**, 475.
- (2) M. Delhayé et P. Dhamelin-court., Raman microprobe and microscope with laser excitation, *J. Raman Spectrosc.*, 1975, **3**, 33.
- (3) W. H. Boyce, Organic matrix of human urinary concretions, *Am. J. Med.*, 1968, **45**, 673.
- (4) R. S. Malek et W. H. Boyce, Intranephronic calculosis: its significance and relationship to matrix in nephrolithiasis, *J. Urol.*, 1973, **109**, 551.

- (5) C. Y. C. Pak, Physicochemical basis for the formation of renal stones of calcium phosphate origin: calculation of the degree of saturation of the urine with respect to brushite, *J. Clin. Invest.*, 1969, **48**, 1914.
- (6) E. L. Prien Jr., Calcium oxalate renal stones, *Am. Rev. Med.*, 1975, **26**, 173.
- (7) C. Y. C. Pak, O. Waters, L. Arnold, K. Holt, C. Cox et D. Barilla, Mechanism for calcium nephrolithiasis among patients with hyperuricosuria: supersaturation of urine with respect to monosodium urate, *J. Clin. Invest.*, 1977, **59**, 426.

Analysis of archaean microfossils by the laser molecular microprobe

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Analyse de microfossiles archéens par la microsonde moléculaire à laser

La preuve de l'existence de microfossiles dans des roches archéennes est basée sur trois critères principaux. L'inclusion découverte doit évidemment montrer des structures d'organisme. Ensuite, il est nécessaire de s'assurer que cette inclusion est un composant primaire de la roche et non une contamination des temps ultérieurs. Cela limite l'étude aux lames fines ou polies de la roche qui montrent les inclusions découvertes dans leur position originale à l'intérieur de la matrice minérale. Troisièmement, il faut prouver que l'inclusion est une substance organique qui peut être ainsi différenciée des cristallites et des pseudofossiles inorganiques semblables. Dans la pratique, cette preuve devient un problème. La plupart des techniques d'analyse classiques nécessitent le broyage et le lessivage des échantillons de la roche. Les résultats obtenus sont représentatifs du bitume de la roche entière mais non spécifiques des microfossiles inclus.

L'analyse non destructive et individuelle des microfossiles dans la roche

est devenue possible avec la microsonde moléculaire Mole. Des microfossiles trouvés dans le Swartkoppie chert (Afrique du Sud, 3 400 millions d'années) et dans la Isua quartzite (SO Groenland, environ 3 800 millions d'années) ont été analysés ainsi. Des lames minces, non montées, de la roche ont été utilisées pour cette technique. Nos études montrent que les inclusions découvertes sur les roches archéennes renferment une variété de composés organiques qui sont manifestement d'origine biologique. Ils sont présents dans une forme fossilisée qui est en accord avec la forme métamorphique de la roche environnante.

Les résultats combinés des analyses morphologiques et chimiques montrent que des témoins de la vie sont présents dans les plus vieux sédiments connus sur terre. Ainsi, la vie doit remonter à beaucoup plus que 3 800 millions d'années.

1. Problem

Proof of microfossils in archaean rocks is mainly based on three criteria. The find must, of course, show organismic structures. Secondly, it must be made sure that the find is a primary constituent of the rock and not a contaminant of later times. This restricts the study to thin or cut sections of the rocks exhibiting the finds in their original position within the mineral matrix.

Thirdly, it must be proved that the find consists of organic substance, and is thus distinguished from crystallites and similar inorganic pseudofossils. In practice, this proof becomes a problem. Most of the conventional analytical techniques require powdering and leaching of the rock samples. Consequently the results obtained are representative for the whole-rock bitumen but not specifically for the enclosed microfossils.

Individual and non-destructive analysis of microfossils in rocks has proved possible by combined application of the electron microprobe

analyser, the X-ray microscope and the heating microscope. The results help decide whether a find consists of fossil organic substance or not, however, they give no information on the molecular species present in the microfossil body. The molecular microprobe Mole seems to fill that gap.

2. Occurrences

The discoveries described stem from two different localities of different ages. The microfossil *Ramsaysphaera* (Plate 1) occurs in the Swartkoppie chert of the Swaziland system in the Barberton mountain land (South Africa). According to the available radiometric data, the age of the chert is probably close to 3 400 million years (2). A still older fossil called *Isuasphaera* (Plate 2) has recently been detected in cherty layers of a quartzite, which are part of the Isua series in SW-Groenland, about 150 km north-east of Godthaab (8). The known radiometric data indicate an age of about 3 800 million years for the rock sequence. These sediments are the oldest known on earth.

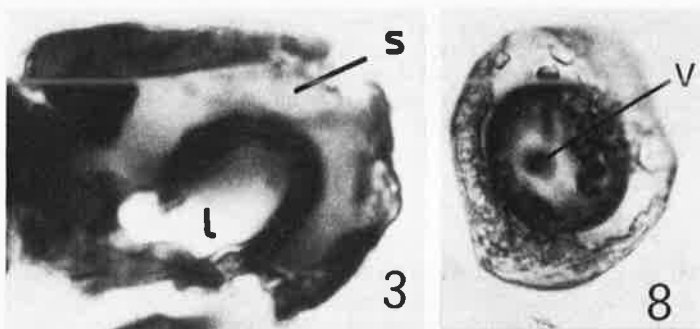


Plate 1.

Plate 2.

Plate 1. The microfossil *Ramsaysphaera*

Plate 2. *Isuasphaera isua* Pflug from Isua quartzite SW-Greenland

Our observations were made from thin and cut sections which show the finds in their primary positions within the rock matrix. The material used is compact and unweathered. No maceration, etching, impregnation, or other methods which might produce artifacts were applied.

Analysis of whole rock samples showed that both occurrences of the Swartkoppie chert as well as the Isua quartzite contain hydrocarbons (9). Analysis of the carbon isotopes yielded indications that the organic material present in both these rocks is at least partly derived from organisms. (12).

3. Results

3.1. Raman spectra of *Isuasphaera* (Isua quartzite, Greenland)

Two different types of spectra were obtained. The one (curves *b* to *f*, Plate 3) is typical for the dark brownish substance composing cell wall and cell filling, the other one (Plate 4) for the so called « gas vacuole ». This is a spherical vesicle characterized by a low light refraction and a bright yellowish colour. Usually, the vesicle is wrapped in the cell lumen, but a few of them were found isolated as inclusions in quartz grains.

Most of the spectra obtained from cell walls and fillings are found to coincide with those of asphaltites (compare curves *a* to *d*, Plate 3). Several spectra vary from this type by developing a stronger intensity at $1\ 360\ \text{cm}^{-1}$ (curves *e* and *f*, Plate 3). Such patterns are known from amorphous carbon produced by charring of plant material.

Characteristic spectra were obtained from two cell vacuoles (Plate 4). In these Raman spectra, we find the typical lines of organic functional groups. A stretching vibration of the carbonyl group $\text{C}=\text{O}$ appears at $1\ 745\ \text{cm}^{-1}$. This high wave number corresponds to

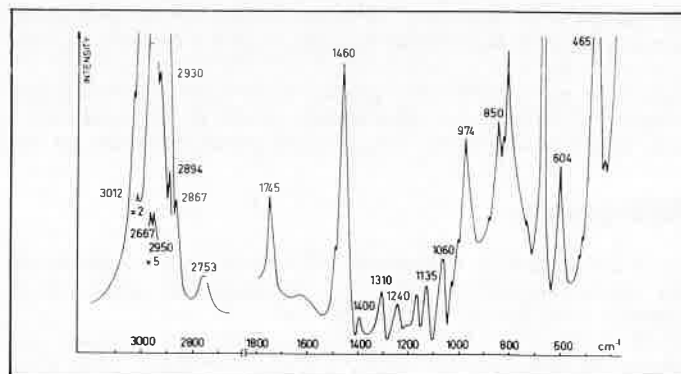


Plate 4. Raman spectrum obtained from the cell vacuole of *Isuasphaera*

that of an ester carbonyl. An intense line at $1\ 460\ \text{cm}^{-1}$ shows that a great amount of aliphatic hydrocarbons is present. The line corresponds to the deformation vibration of CH_3 and CH_2 groups. The same groups are responsible for the broad, intense signal at about $3\ 000\ \text{cm}^{-1}$. It is a region in which the $\text{C}-\text{H}$ stretching vibrations appear. The highest peak is a doublet at $2\ 950$ and $2\ 967\ \text{cm}^{-1}$; this high position is typical for $\text{C}-\text{H}$ vibrations in an electronegative environment corresponding to that of an ester function. Between $1\ 460$ and $1\ 745\ \text{cm}^{-1}$, no significant lines for $\text{C}=\text{C}$ double bonds are found.

3.2. Raman spectra of *Ramsaysphaera* (Swartkoppie chert, South-Africa)

The spectra obtained proved to be well reproducible. They all are similar in their principal features. The examination indicates that cell and sheath consist of organic material of a certain composition (Plate 5).

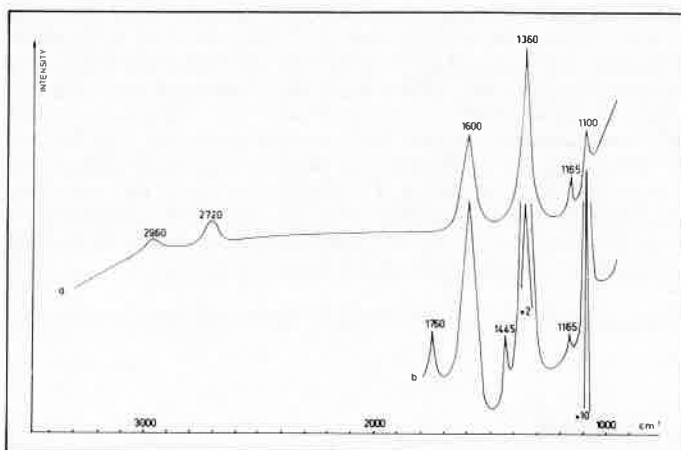


Plate 5. Raman spectra obtained from the cell material of *Ramsaysphaera*

Curve *a* : from cell, Curve *b* : from sheath

Raman lines appear at $1\ 360$, $1\ 600$, $2\ 720$, $2\ 960\ \text{cm}^{-1}$ within the organic range of the spectrum (curve *a* on plate 5). Additional lines might be present in the range below $1\ 200\ \text{cm}^{-1}$, but this is not certain, since diffusion effects of the quartz matrix and other minerals disturb this part of the diagram. The strong line at $1\ 360\ \text{cm}^{-1}$ may be attributed to a symmetric $\text{N}-\text{O}$ vibration of the NO_2 group, the weaker line at $1\ 600\ \text{cm}^{-1}$ is characteristic of aromatic double bonds $\text{C}=\text{C}$.

The first overtone of the $1\ 360\ \text{cm}^{-1}$ line is observed at $2\ 720\ \text{cm}^{-1}$. The spectrum has the features of a resonant Raman spectrum. It is very often obtained with this type of product in which a large

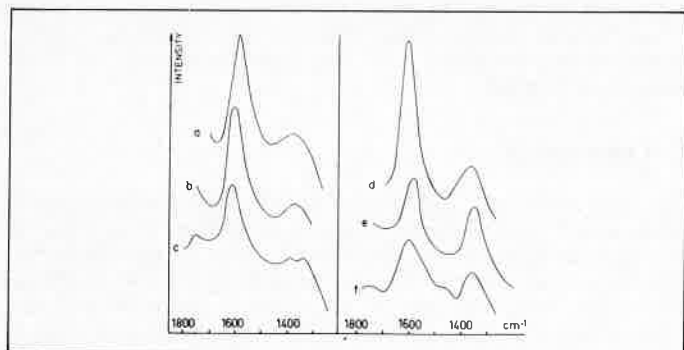


Plate 3.

Curve *a* : Raman spectrum from resinitic asphaltite.

Curves *b* to *f* : Raman spectra obtained from the cell material of *Isuasphaera*

delocalisation of π electrons is possible. In this case, the small intensity of the peak at 2960 cm^{-1} is also due to this effect, if it is attributable to C—H stretching vibrations.

Curve *b* on plate 5 shows the typical spectrum of the cell sheath. Dolomite is indicated by the lines at 1100 , 725 and 300 cm^{-1} . It can be concluded from the petrological studies that this dolomite is an alteration product derived from calcite. The calcite matter was apparently formed in a synsedimentary stage and became dolomitized subsequently, perhaps through diagenetic processes.

4. Conclusions

It must be regarded in the chemical interpretations that Ramsaysphaera (Plate 5) represent decomposed and fossilized remains of cell materials. Probably proteins, lipids, and carbohydrates were the main starting compounds involved in the post-mortem reactions. Recent studies show that upon death of cell, phenols, quinones, amino acids, and peptides are liberated which condense to form complex polymers of various molecular size (10). It is conceivable that mucopeptides are incorporated in the processes. Glucosamine also condenses with *p*-benzoquinone and may, therefore, act as the point of attachment of carbohydrates to the polymers. Phenols of the resorcinol type are characteristic substances that are formed by microbial fungi. Oscellinic acid is produced through their acetate metabolism. T.G. Felbeck (6) suggested that the central resistant core to which polymers and amino acids are bound is a polymer of four pyrene units linked together by methylene bridges at the 2,6-positions. Sulphur can be incorporated into the protobitumen by condensation reaction between thiols and quinones, aldehydes or sugars. The reaction products are relatively resistant against chemical and microbial attack and account for the high stability of the rock organic matter (G. Anderson, 1).

Probably the impregnating silica was additionally involved in the chemical reactions. Estermann et al. (5) found protein-silica complexes to be much more resistant against decomposition than protein-clay complexes. Leo and Barghoorn (7) suggested that penetrating silicic acid may interact with the cell carbohydrates through hydrogen bonding. The esters detected in the gas vacuole of *Isuasphaera* (Plate 4) are probably remains of metabolic products. The yeast cell contains large fat globules which commonly make up 30 to 40 % of the dry weight of the organism and reach 50 to 60 % in some genera. Additionally, copious amounts of lipids are stored in the extracellular cell sheath. Among the saponifiable lipids are fatty acids, the triglycerides, and other fatty acid esters, phospholipids and glycolipids. The unsaponifiable lipid materials are long-chained hydrocarbons and alcohols, phloroglucinal derivatives polynuclear quinones, terpenoids, and sterols (3). Many of the alcohols and sterols are bound with fatty acids to form esters. Compounds of the lipid fraction are relatively resistant to decomposition and can, under proper conditions, apparently last for long periods at time. Lipids are believed to be a main source material for the petroleum hydrocarbons.

It must be taken into account with the interpretation of the Raman spectra that the analysed rocks have suffered metamorphism, the Isua quartzite more, the Swartkoppie chert less. Consequently, the organic substances present in the rocks must have been subjected to intense alterations.

Our results obtained from the Mole analysis generally coincide with these findings. The compounds detected in the *Ramsaysphaera* cells (curve *a*, Plate 5) can be interpreted as products of an advanced bituminization resulting in condensed aromatic clusters. Apparently, the *Isuasphaera* material is partly in a charred condition, partly close to a final stage of graphitization (Plate 3).

However there are samples in our collections the metamorphic rank of which is considerably below average. Apparently, the geologic heat flows have not reached all regions of the rock formations with the same intensity.

Bibliography

- (1) G. Anderson, Sulfur in soil organic substances. In: J. E. Gieseking (Edit.): Soil Components 1, 333. Springer-Verlag, Berlin-Heidelberg-New York (1975).
- (2) C. R. Anhaeusser, The evolution of the early precambrian crust of Southern Africa., *Phil. Trans. Roy. Soc. Lond.* 1978, A 273, 359.
- (3) O. C. Braids and R. H. Miller, Fats, waxes and resins in soil. In: J. E. Gieseking (Edit.): Soil Components 1, 343, Springer-Verlag, Berlin-Heidelberg-New York (1975).
- (4) P. R. Carey, Resonance Raman spectra of biological materials: Approaches to interpretation. Internat. Conf. Raman Spectrosc., Bangalore/India, 1978, 1, 105.
- (5) E. F. Estermann, G. H. Peterson and A. D. Mac Laren, Digestion of clay-protein, lignin-protein and silica-protein complexes by enzymes and bacteria, *Proc. Soil Sci. Soc. Amer.*, 1959, 23, 31.
- (6) T. G. Felbeck, Studies on the high pressure hydrogenolysis of organic matter from a muck soil, *Proc. Soil Sci. Soc. Amer.*, 1965, 29, 48.
- (7) R. F. Leo and E. S. Barghoorn, Silification of wood., *Bot. Mus. Leaflet. Harvard University*, 1976, 25, 1.
- (8) S. Moorbath, R. K. O'Nions and R. J. Pankhurst, The evolution of early precambrian crystal rocks at Isua, West Greenland, Geochemical and isotopic evidence. *Earth Planet. Sci. Lett.*, 1975, 27, 229.
- (9) B. Nagy, Organic chemistry of the young Earth. *Naturwiss.* 1975, 63, 499.
- (10) J. W. Parsons and J. Tinsley, Nitrogenous substances. In: J. E. Gieseking (Edit.): Soil Components 1, 263, Springer-Verlag, Berlin-Heidelberg-New York (1975).
- (11) H. D. Pflug, Yeast-like microfossils detected in oldest sediments of the earth. *Naturwiss.* 1978, 65, (12), 611.
- (12) M. P. Schidlowski, W. U. Appel, R. Eichmann and C. E. Junge, Carbon isotope geochemistry of the 3.7×10^9 yr old Isua sediments, West Greenland: implications for the archaean carbon and oxygen cycles, *Geochim. Cosmochim. Acta*, 1979, 43, (2), 189.

Analyse d'inclusions fluides à la microsonde Mole à effet Raman

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Analysis of fluid inclusions with the Raman microprobe Mole

Nine fluid inclusions have been analyzed non-destructively by spectroscopy with the Mole microprobe and simultaneously by microthermometry.

The effort was principally directed on the gaseous phase in four inclusions rich in hydrocarbons (Remuzat, Drome; Lastourville, Gabon; Vermutfluh, Berne and Val d'Illiez, Valais) and in two