

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 of 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

par P. Dhamelincourt *, J. M. Beny **, J. C. Dubessy ** et B. Poty **

(* CNRS, Université des Sciences et Techniques de Lille, U.E.R. de Chimie, Laboratoire de spectrochimie infrarouge et Raman, 59650 Villeneuve d'Ascq et ** Centre de recherches sur la géologie de l'uranium, B. P. 23, 54500 Vandœuvre, France]

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

inclusions rich in CO₂ (Bournac, Massif Central and Camperio, Tessin). Quantitative analyses for CH₄, C₂H₆, C₃H₈, CO₂, N₂ and H₂S were obtained. An isotopic analysis (¹³C) of CO₂ from Camperio has been attempted.

The solid phases of small size contained in three fluid inclusions were determined: calcite in Bitsch quartz (Valais), nahcolite in Bancroft quartz (Ontario), and hematite in a dolomite from Rabbit Lake (Saskatchewan). The sensitivity of the instrument and its limits for mineralogical purposes are discussed.

Neuf inclusions fluides ont été analysées de manière non destructive à la fois par microthermométrie et par spectroscopie Raman à l'aide de la microsonde Mole.

Les phases solides de petite taille contenues dans trois inclusions fluides ont été déterminées : calcite dans un quartz de Bitsch (Valais), nahcolite dans un quartz de Bancroft (Ontario) et hématite dans une dolomite de Rabbit Lake (Saskatchewan). La sensibilité de l'appareil et les limites de son utilisation en minéralogie sont discutées.

L'effort a porté principalement sur la phase gazeuse dans quatre inclusions riches en hydrocarbures (Remuzat, Drôme; Lastourville, Gabon; Vermutfluh, Berne et Val d'Illicz, Valais) et dans deux inclusions riches en CO₂ (Bournac, Massif Central et Camperio, Tessin). Des analyses quantitatives pour CH₄, C₂H₆, C₃H₈, CO₂, N₂ et H₂S sont données. L'analyse isotopique (¹³C) du CO₂ de Camperio a été tentée.

L'article complet a été publié dans le *Bulletin de Minéralogie*, 1979, 102, (n° 5/6), 600.

Applications de la microsonde moléculaire à laser Mole en micropaléontologie : étude du test des foraminifères

par M.-T. Venec-Peyre * et H. Jaeschke-Boyer **

(* Institut de Paléontologie, Muséum National d'Histoire Naturelle, L.A. n° 12 C.N.R.S., E.P.H.E., 8, rue Buffon, Paris 75005 et

** Laboratoire d'applications, ISA Jobin-Yvon, 16, rue du Canal, Longjumeau, France)

Applications of the microprobe Mole in the study of foraminifera

Foraminifera are unicellular animals whose protoplasm is protected by a shell usually mineral in nature. The size of individual specimens varies from a few hundred microns to a few millimeters, and the thickness of the shell rarely exceeds several tens of microns. Those dimensions make it difficult to study these organisms, requiring the use of advanced technology. Because of its performance, the laser molecular microprobe, Mole has found an application in micropaleontology. Its powers of resolution and the possibility of quick, in situ, analysis have enabled the mineralogical characterization of the different layers contained in the shells of two species, one « calcitic » the other « aragonitic », thereby raising some doubt concerning the mineralogical nature of these two species. The use of the Mole has also allowed the solution of a problem concerning the classification of Foraminifera by

revealing the calcitic nature of one species attributed to an aragonitic family; for this type of study the method has proved invaluable because it does not destroy the sample, which is very important, if not indispensable, when rare or reference specimens are being examined. The examination of the sample requires neither the use of a vacuum nor special preparation of the specimen thereby avoiding a tedious, detailed job when such small and fragile organisms are to be handled. Knowing that the present number of species of Foraminifera both living and fossilised is over 21,000, that have been in existence since the Primary era and that the shell is susceptible to modification during diagenesis through geological periods, one can easily imagine the interest generated in the use of the Mole in micropaleontology.

En raison de ses performances la microsonde moléculaire à laser Mole s'est révélée un outil précieux adapté à l'étude du test des Foraminifères. Avant de donner les principaux résultats obtenus, il me semble judicieux de présenter ce groupe zoologique et de donner quelques renseignements qui aideront à la compréhension de l'exposé.

b) chez les espèces pluriloculaires elle peut être :

- non-lamellaire et se fait par juxtaposition de loges successives ;
- lamellaire: lors de l'adjonction d'une nouvelle loge, du carbonate de calcium est sécrété sur les loges préexistantes; il en résulte un épaissement progressif de la paroi de la dernière loge vers la première loge, et l'aspect lamellaire du test (Pl. 1, Figure 1).

Les Foraminifères sont des organismes unicellulaires dont le protoplasme est protégé par une coquille appelée test. Ce test est composé de une ou plusieurs loges dont l'arrangement varie selon les espèces. Ces loges communiquent entre elles par une ouverture ou foramen. La composition du test est également fonction des espèces : les plus primitifs sont constitués d'une membrane flexible et transparente, mais le plus souvent le test s'enrichit en matières minérales qui peuvent être, soit empruntées au milieu (micas, magnétite, spicules d'éponges, etc...) et soudées par un ciment élaboré par l'animal, soit sécrétées par le protoplasme (dans ce cas il est le plus généralement calcaire, quelquefois siliceux). La croissance s'effectue suivant plusieurs modalités :

Les individus entiers mesurent de quelques dizaines de microns à quelques centimètres et l'épaisseur de la paroi des loges varie de quelques microns à quelques centaines de microns. Ces dimensions en font un matériel difficile à étudier. La microsonde moléculaire à laser Mole a permis de résoudre quelques problèmes concernant le test de ces organismes. Les résultats obtenus apportent des éléments nouveaux dans trois des grands axes de recherche sur l'étude de ces Protistes : la systématique, la biominéralisation et l'écologie.

1. Application de la microsonde Mole en systématique

Comme tous les groupes animaux et végétaux, les Foraminifères sont répartis suivant des critères bien définis, dans une classification dont