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ORGANIC GEOCHEMISTRY PROVIDES EVIDENCE FOR A LAGOONAL ORIGIN OF LARGE ATOLL PELOIDAL PHOSPHORITES

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ABSTRACT

The study of the organic content of insular peloidal phosphorites was undertaken in order to get the same kind of information as those obtained through organic geochemical studies on the origin of marine peloidal phosphorites. i.e.information on the sedimentological and diagenetic environments in which phosphorites were formed. The content in total organic carbon (T.O.C.) (from 0.5 to 6 %, in 27 samples studied), the high proportion of labile organic carbon (acido-soluble and humics) (> 60 % of T.O.C.), Rock-Eval pyrolysis results and the molecular composition of hydrocarbons, fatty acids and amino acids, all suggest an algal (essentially cyanobacterial) origin for the organic matter associated with insular phosphatic peloids. Such a result confirms the abundance of cyanobacteria in the phosphatogenic milieu which had been already suggested by the coating of peloids.Phosphatogenesis took place in closed lagoons where important cyanobacterial biomasses accumulated phosphorus. Such environments are known in recent atolls, for example in Niau atoll (French Polynesia). The source of phosphorus can vary : sea water vary inputs, leaching of biogenic phosphorus from the aerial and sub-aerial parts of the reef, avian guano or endo-upwelling processes transfering deep (ca. 500 m) marine waters from outside the reef into the lagoon through the porous body of the reef.

INTRODUCTION

From the beginning of this century (Power 1905) approximately to its end (ca. 1990) , the main problem discussed about the genesis of atoll phosphorites was that of the source of phosphorus which was considered to come from avian guano deposited on the emerged parts of the reefs. Those guano inputs were supposed to provide all types of atoll phosphorites i.e. soil-related, phoscrete-type phosphorites or some meters-thick large peloidal deposits. Arguments were of oceanographic, paleogeographic, climatic (Hutchinson 1950, Veeh 1985) and isotopic (Aharon and Veeh 1984, Ayliffe et al. 1992) nature. If superficial phoscrete formations turned out definitely to derive from guano-P and form in pedological conditions (Stoddart and Scoffin 1983, Rodgers 1994 a,b), the environment of formation of meters thick deposits of peloidal phosphorites remained uncertain. In 1990, Piper et al. and Rossfelder, respectively, drew attention on the place where phosphatic-rich solutions, considered by those authors to derive from the leaching of guano deposits, could react with carbonate rocks to form calcium phosphate : respectively in the phreatic zone at the sub-top part of the reef for Piper et al. (1990) and in lagoonal sand deposits for Rossfelder (1990).

Organic geochemistry, i.e. the search of information on the origin and on the nature of the organic matter associated with the phosphorites at the end of diagenetic processes has been used to provide independent evidence on the environmental, sedimentological and diagenetic conditions in which peloidal phosphorites formed.

RESULTS

Before presenting the information provided by organic geochemical methods, let us recall two data which will be useful for the following discussion (1) 25 insular peloidal phosphorites studied by Fikri (1991) contain organic carbon in the range 0.5 to 6.4 % (1.7 % as mean value).Those 25 samples were collected in Nauru, Mataiva (low atoll) (2) the peloids in insular phosphorites are very often coated. The petrographic study of such coatings suggests that they resulted essentially from the accretion of blue-green algal remains (Piper et al. 1990 ; Fikri 1991) i.e. that the formation of peloids happened in humid, or water-rich, environments.

The study of the organic matter involved the following approaches : Rock-Eval analysis, separation and analysis of labile (acido- and alkalinosoluble organic fractions), hydrocarbon, fatty acid and amino acid analysis.

Rock-Eval analysis

The points representative of samples in a (Hydrogen Index - T°max) diagram (Espitalié et al. 1985) are localized in the type II organic matter's domain (i.e. algal domain, ibid.) and, more precisely, in the domain in between type II and type III organic matter's domains (Fikri 1991). This shows that the organic matter proceeded from algal (sensu lato) biomasses and that this organic matter underwent a certain oxidation.

The fact that the peak representative of the kerogen fraction susceptible to crack under increasing temperature (peak P2, ibid.) is divided in two sub-peaks indicates a poorly transformed, non polymerized organic matter. This is in agreement with the cenozoic age of the studied sediments as well as with the superficial conditions in which they stayed and evolved since they were deposited.

Acido-soluble and humic fractions

The acido-soluble organic fraction was obtained by treating finely powdered phosphorites by 2N HCl, at room temperature. The humic fraction was thereafter obtained by treating the residue of the previous acid attack by 0.1N NaOH at room temperature. The term humic is used to designate organic fractions which are soluble in alkaline solvents, whatever the origin of the organic matter (higher plants or algae).

The sum of acido-soluble and alkalino-soluble fractions gives the labile, poorly-polymerized organic fraction. The extraction of this fraction out of 22 samples (Fikri 1991) and 2 other samples (Jehl 1995) led, respectively, to mean values of organic carbon of 61.7% (range 23.9-80.0%) and 89.9% (range 85.8-93.9%) of the total organic carbon.

Such significant quantities of labile organic matter within the bulk organic fraction of peloidal phosphorites are interpreted as the convergent result of three processes (1) low age (cenozoic) of the sediment (2) preservation at low (superficial) temperature (3) strong protection of the phosphate minerals against organic matter's condensation (polymerization). Such a protection has been demonstrated in other peloidal, much older, marine phosphorites (Cambrian; Sandstrom 1980 or Paleocene, Lower Eocene; Belayouni et al. 1990, Trichet et al. 1990).

The plotting of the points representative of the composition of extracted humic acids in an extended Van Krevelen diagram $[(H/C)_{at.}-(O/C)_{at.}-(N/C)_{at.}]$ shows the definitely algal and microbial origin of the organic matter associated with the peloids (Fig. 1). The domain of composition of higher-plant (terrestrial) derived humic acids is given after Debyser and Gadel (1977).

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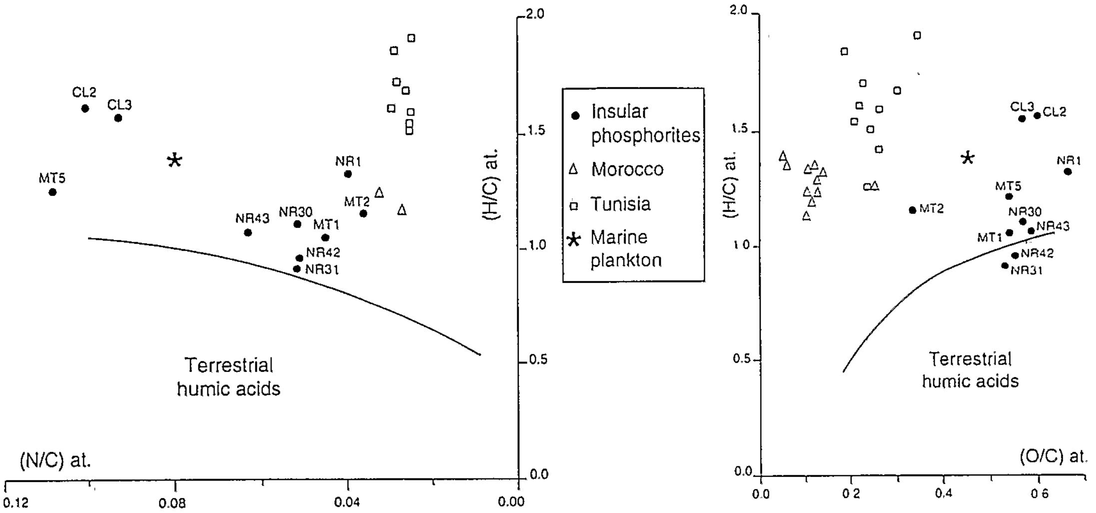

Fig.1: Diagram illustrating the composition of humic acids extracted out the organic matter associated with insular phosphorites. Comparison with that of humic acids extracted out of Moroccan and Tunisian phosphorites. After Fikri (1991). Domain of composition of terrestrial humic acids after Debyser and Gadel (1977). Composition of marine plankton after Pelet (1983). NR: Nauru, MT: Mataiva, CL: Clipperton.

Hydrocarbons

The analysis of hydrocarbons either in the bulk organic matter or in the separated humic compounds shows the presence of n-alkanes and cyclic alkanes. The n-alkane fraction contains almost always significant quantities of molecules in C_{17}, C_{18} (Fikri 1991) alkanes which are considered as being from algal origin, and, always, of heavier representatives (nC_{27} to nC_{29}, Fikri 1991 ; nC_{23} to nC_{35}, Jehl 1995). The origin of such heavy chains is still controversial. For most authors it results from microbial processes (Gassman 1982) whereas for Jehl (1995) it could result from the inheritance of heavy chains produced by cyanobacteria.

Hopanoids (hopanes and hopenes, pentacyclic hydrocarbons derived from the cell membrane of procaryotes) are present and often abundant (up to 0.54 mg/g rock in the two Mataiva samples analysed by Jehl 1995), suggesting an important contribution of microbial (bacterial and cyanobacterial) biomasses. Steroids (tetracyclic hydrocarbons mostly derived from eucaryotic algae) are strickingly poorly abundant (ratio of 1 to 5 of steroids to hopanoids in the samples of Mataiva analysed by Jehl 1995) suggesting that the biomasses having contributed to those insular phosphorites contained by far more cyanobacteria than eucaryotic algae. This contrasts strongly with the situation in marine peloidal phosphorites where steroids, derived from phytoplanktonic algae, are always abundant (Benalioulhaj 1989, Meunier-Christmann et al. 1989).

Fatty acids

In the samples studied by Fikri (1991), the fatty acid fraction comprises straight chain fatty acids (saturated, dominated by nC_{16} and nC_{18}, and unsaturated, dominated by $nC_{16:1}$, $nC_{17:1}$, $nC_{18:1}$, $nC_{18:1w9}$) and branched fatty acids (iso in the range C_{13} to C_{15}, anteiso in C_{15}-C_{17}, and branched on carbon 10).

If the straight chain representatives are present in many living organisms, the branched ones are essentially bacterial (Pond and Langworthy 1987). Their presence indicates important bacterial biomass in the phosphatogenic sediment.

Amino acids

The analysis by Fikri (1991) of the composition of the amino acids in the different fractions of the organic matter (acido- and alkalino - soluble fractions, residual fraction of the extraction of labile compounds) reflects that the bulk of organic matter comes essentially from (1) planktonic or benthic algal and blue-green algal populations and (2) probably important bacterial communities. For example, diaminopimelic acid, an amino acid specific of the cell wall of Gram- bacteria and of cyanobacteria can amount up to 4 % of the total amino acids (expressed in molecular abundance). Another example is the abundance of β-alanine and arginine which are supposed to derive respectively from aspartic acid and ornithine under microbial processes.

DISCUSSION

Table 1 shows the main geochemical properties of the organic matter associated with insular peloidal phosphorites and compares these properties with those of the organic matter associated with marine epicontinental peloidal phosphorites.

The geochemical data obtained on the organic matter associated with insular peloidal phosphorites show that this organic matter comes essentially from blue-green algae and bacteria. These data are convergent with that suggested by the coating of peloids by blue-green algae remains.

These data must therefore be taken into account in the reconstitution of atoll phosphatogenesis and replaced in its diagenetic history. Such a reconstitution is helped by the observation, in recent atolls, of ponds and sometimes whole lagoons (as in Niau atoll, French Polynesia) which are filled up with an organic matter resulting from the decomposition of blue-green algae and bacteria. This sediment is called «kopara» in the language of the Tuamotu Archipelago (Défarge et al. 1994). Such sedimentary lagoonal environments contain quantities of total (organic plus inorganic) phosphorus which have been proven to match those encountered in insular phosphorites (ca. 10^6-10^8t) (Tracey 1979, Jehl 1995) and the organic geochemistry of these kopara deposits has been proven to be strickingly similar to that of the organic matter associated with insular phosphorites (Fikri 1991, Jehl 1995, Rougerie et al. in press).

All these data and features strongly suggest that insular peloidal phosphatogenesis develops in lagoonal environments. This genesis involves the accumulation of important quantities of phosphorus through microbial-

Table 1 : Comparison of global and molecular organic data for insular and epicontinental phosphorites.

	Insular phosphorites (Fikri 1991) (a)	Epicontinental (Moroccan) phosphorites (Benalioulhaj 1989) (b)
Total organic carbon (T.O.C.)	0.5 - 6.0, %	1.0 - 4.0, %
Rock-Eval data and elemental analysis	algal origin, oxidation of org. matter (greater than in b)	algal origin, oxidation of org. matter (lesser than in a)
Acido-plus Alkalino-soluble organic carbon	23.9 - 80.0, % of T.O.C.	17.8 - 63.8, % of T.O.C.
Hydrocarbons	algal contribution microbial reworking hopanes >> steranes	algal contribution microbial reworking hopanes << steranes
Fatty acids	algal and microbial contribution	algal and microbial contribution
Amino acids	algal and microbial contribution	algal and microbial contribution

cyanobacterial and bacterial-biomasses which accumulate phosphorus. This stage of accumulation is followed by the liberation and precipitation of phosphoric ions during diagenetic pathways in highly organic sediments.

These conclusions corroborate the localization of peloidal phosphorites in atoll surface where they are to be found either under a present lagoon (as in Mataiva, French Polynesia) or at the site of ancient lagoons (as in Nauru or Makatea, French Polynesia). Possibilities of both reworking the phosphatic sediments and accumulating the phosphatic pellets in low, depressed, karstic areas of uplifted (Nauru, Makatea) or not uplifted (Mataiva) atolls are not ruled out.

The source of phosphorus is still debated. This element would be supplied to the lagoons either (1) through sea water inputs during irregular events (storms for example) or high sea level stands, (2) through the permanent lagoonward leaching of aerial or sub-aerial biologic constructions and soils of the reef rim (Rodgers 1994 a,b), (3) through avian guano inputs, or (4) through endo-upwelling processes i.e. through the flow of deep (ca. 400-500 m), phosphate rich (up to 2 mM/l P-PO_4), marine waters forced through the porous body of the reef under a thermal gradient due to temperatures being higher in the volcanic basement of the reef than in the reef surface (Rougerie and Wauthy 1986, 1993).

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