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Bacterial calcification as a possible trigger for francolite precipitation under sulfidic conditions

La calcification de bactéries peut-elle déclencher la précipitation de francolite en conditions sulfidiques ?

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ABSTRACT

Francolite (carbonate-fluor-apatite) is known to form in sediments where intense organic-matter decay occurs, but under oxic-to-suboxic conditions, because the alkalinity rise accompanying bacterial sulfate reduction (anoxic conditions) increases francolite solubility, hence preventing its supersaturation and precipitation. However, lagoonal, organic matter-rich, cryptalgal carbonates of Jurassic age located in the French Jura Mountains contain francolite that formed during early diagenesis, under anoxic-sulfidic and highly alkaline conditions. To explain this paradoxical situation, we propose the following "chain of reactions": the presence of abundant biomass in the sediment would supply the "raw material" to the reactional system, i.e., the initial P budget, released through organic decay. The development of cryptalgal, bacterial mats at the sediment–water interface would have limited exchanges between the water column and the pore space, hampering pore water renewal and favoring the early onset of sulfate-reducing reactions. The onset of sulfate reduction would increase pore water alkalinity, potentially preventing francolite precipitation. In addition, the presence of sulfide ions would induce organic matter sulfurization, resulting in a relative pH rise. Alkalinity and pH rises would trigger the development of conditions leading to carbonate supersaturation, inducing bacterial-structure calcification. The sudden fall in alkalinity induced by early calcification would allow francolite precipitation, despite sulfidic conditions.

RÉSUMÉ

La francolite (carbonate-fluor-apatite) se forme usuellement dans des sédiments où la libération de phosphate est provoquée par la dégradation de matière organique. Cependant, la précipitation de francolite ne peut se produire que dans des conditions faiblement réductrices (oxiques à suboxiques), car la sulfatoréduction se développant en conditions anoxiques provoque une augmentation de l'alcalinité des eaux interstitielles. Cet excès d'alcalinité augmente la solubilité de la francolite et empêche sa précipitation. Néanmoins, les carbonates stromatolithiques du Jurassique supérieur du Jura français, riches en matière organique, contiennent de la francolite qui s'est formée en conditions anoxiques et fortement alcalines. Nous proposons un schéma génétique pour expliquer ce paradoxe, reposant sur une chaîne de réactions. La décomposition de la matière organique

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sédimentaire initialement présente a fourni le phosphate dissous au milieu interstitiel. La présence de films bactériens à la surface du sédiment aurait agi comme une barrière limitant le renouvellement du milieu interstitiel et favorisant le développement précoce de conditions sulfatoréductrices. La sulfatoréduction aurait induit une augmentation de l'alcalinité des eaux interstitielles (s'opposant à la précipitation de francolite). La libération d'ions sulfure sous l'interface eau–sédiment aurait permis la sulfuration de la matière organique, ce qui concourt à augmenter le pH. L'accroissement de l'alcalinité et du pH ont provoqué la calcification précoce des bactéries ou de leurs substances extracellulaires, ce qui a fait chuter l'alcalinité. Cette chute d'alcalinité enfin a permis la précipitation de francolite. Cette précipitation s'est faite préférentiellement à partir de bioclastes et non pas en imprégnations diffuses dans le sédiment.

1. Introduction

Phosphorites form following a widely-accepted genetic scheme involving a massive flux of biomass to the sediments, the decay of which releases organic matter-linked phosphorus, and triggers carbonate-fluor-apatite (more specifically, francolite) precipitation (e.g., (Cha et al., 2005; Föllmi, 1996; Kim et al., 1999; Soudry, 2000)). The burial of phosphorus and the subsequent formation of phosphorites are typically observed in zones of the ocean with high surface productivity, such as modern suboxic to anoxic marine sediments of upwelling areas: off Namibia, Chile, Peru, in the Gulf of California and in the Arabian Sea ((Arning et al., 2009a; Arning et al., 2009b) and references therein). As authigenic phosphate enrichments originate from organic decay by bacterial activity, the role of microbes in the phosphogenesis has been much studied (Arning et al., 2008; Arning et al., 2009a; Arning et al., 2009b; Krajewski et al., 1994; Schulz and Schulz, 2005).

Francolite precipitation is generally considered as occurring under suboxic conditions (Cha et al., 2005; Föllmi, 1996; Froelich et al., 1988; Jarvis et al., 1994; Schuffert et al., 1998), that is, at the stage of denitrification and Fe-Mn oxihydroxide reduction, prior to the development of sulfate-reduction and fermentation reactions (anoxic conditions). However, the present study of Late Jurassic cryptalgal carbonate (the Laminites Bitumineuses Formation, Orbagnoux hamlet, Jura Mountains, France) yields several lines of evidence that francolite may have paradoxically precipitated under anoxic and strongly reducing conditions (concentrations in redox-sensitive trace metals, occurrence of sulfurized lipidic fractions of organic matter). Phosphatic stromatolites have already been observed (Martin-Algarra and Sanchez-Navas, 2000; Soudry, 2000) but the scenario of their genesis usually involves a multistep formation under contrasting redox conditions and with carbonate-fluor apatite precipitating during the non-anoxic stages. Here, to account for the paradox of francolite forming under anoxic conditions, we expose an interpretation grounded on early bacterial calcification induced by sulfate-reducing conditions, which lowered pore water alkalinity and triggered francolite formation.

2. An overview of phosphorus geochemistry in sediments

Phosphorus (P) is essential to all forms of life on Earth, as it plays a fundamental role in many metabolic processes and is a major constituent of skeletal material. Phosphorus is a structural element in DNA and RNA, as well as in many enzymes, phospholipids, and other biomolecules. Phosphorus is present with an average crustal abundance of 0.01%, but it shows a higher content in most marine sediments and sedimentary rocks (Föllmi, 1995; Föllmi et al., 2004; Mackenzie et al., 1993; Trappe, 1998). The main source of P to the sediments is the phytoplankton necromass that reaches the sediment–water interface, plus fish scales and bones. A further source of P is dissolved inorganic P that is transferred across the sediment–water interface (possibly with the help of microbial mats (Föllmi, 1996; Föllmi et al., 2005). Usually, P is released as PO_4^{3-} from decaying organic matter during oxic, suboxic and anoxic bacterial degradation at/or below the sediment–water interface. Largely, the P remineralized to pore waters can either escape from the sediment back to the water column or be precipitated and trapped within the sediment (Louchouarn et al., 1997; Sannigrahi and Ingall, 2005; Span et al., 1992). Under anoxic conditions, phosphorus then generally diffuses upward from the sediment and returns to the water column. This P cycling is very efficient: it has been estimated that only 1% of organic phosphorus escapes cycling and is trapped in sediments and sedimentary rocks (Benitez-Nelson, 2000).

However, if their escape from sediments is not possible, phosphate ions released by organic decay can reach pore-water concentrations high enough for authigenic phases, namely, francolite, to precipitate. Francolite may be represented by the formula:

$$Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_{x-y-z}(CO_3.F)_y(SO_4)_zF_2.$$

Francolite precipitation is conditioned by alkalinity, pH, Eh and bacterial activity (Benitez-Nelson, 2000; Reimers et al., 1996). Francolite can precipitate either rapidly (most probably replacing a short-lived and poorly crystallized precursor; (Föllmi, 1996)) or slowly (usually replacing calcite but possibly directly also (Föllmi, 1996; Jarvis et al., 1994; Piper and Perkins, 2004; Trappe, 1998). The P