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ORGANOMINERALIZATION

Synonyms

Organomineral formation

Definitions

Organomineralization. Processes of mineral formation mediated by organic matter (OM), independently of the living organisms which it derives from. The organic compounds may be excretion products or detached parts of living organisms, or relics and by-products of dead organisms, that have been released in waters or incorporated in soils, sediments or rocks. Abiotic OM may also induce the formation of minerals in nature or in the laboratory.

Organominerals. The mineralic products of organomineralization. They should be distinguished from minerals precipitated through inorganic processes, among which some may contain OM entombed or complexed during crystal growth, from organic minerals such as graphite, and from biominerals produced by living organisms.

Genesis of the organomineralization concept

The term *Organomineralization* was introduced in 1993 by Trichet and Défarge (1995) at the 7th International Symposium on Biomineralization. It aimed to designate the processes of mineral formation that are similar to biomineral formation by living organisms, because induced by organic templates, compartments and compounds (*Biomineralization*, qv), but distinct because occurring in waters, soils, sediments or rocks, independently of the living organisms which the mineralizing OM derives from. The substantive *Organomineral* was also introduced at the same symposium to designate the mineral products of organomineralization, to be distinguished from the biominerals produced by living organisms (Défarge and Trichet, 1995). These definitions were supported by illustrations of organomineral formation processes including (Défarge and Trichet, 1995; Trichet and Défarge, 1995): diagenetic calcification of gastropod fecal pellets; post-mortem encrustation of cyanobacterial filaments, fish organs, and soft tissues of trilobites by calcium carbonate (CC), calcium salts of fatty acids, or pyrite; formation of CC bodies and phosphate pellets under the influence of sedimentary OM; intervention of soil organic compounds in the crystallization of aluminium and iron oxides and hydroxides; precipitation of metal oxides and sulfides following the demixion of organo-metallic complexes submitted to geothermal heating; and laboratory formation of CC ooids in the presence of OM rich in acidic groups.

The first hypotheses on the role of sedimentary OM in the precipitation of minerals in natural environments, believed to be analogous to that played by organic templates in biomineralization, were published in the 1960s in papers on the formation of calcareous microbial deposits, oolites and coprolites (Trichet, 1967, 1968; Mitterer, 1968; for later references see Morse et al., 2007). These hypotheses were founded on the similarities in composition of the organic fraction of these carbonate bodies with that of biomineral matrices, which are both rich in acidic amino acids, and on earlier work evidencing that dissolved organic compounds can favour CC precipitation from waters (see references in Mitterer, 1968; Trichet, 1968; or Trichet and Défarge, 1995).

A decisive step in this research and in the genesis of the concept of organomineralization was made thanks to studies on carbonate formation in the modern lacustrine *microbialites* (qv) of Pacific atolls (Défarge and Trichet, 1995): The mineral fraction of these sediments was shown to be principally composed of magnesian calcite micrite clusters that had precipitated within the alveoli, on the wall surfaces of an organic honeycomb-like network formed by the reorganization of *extracellular polymeric substances* (*EPS*, qv) secreted by *cyanobacteria* (qv). These organic templates of precipitation thus had the same origin as those of CC biomineralization in cyanobacteria, which is associated with the cell sheath (Merz-Preiβ, 2000). In addition, it was demonstrated that this OM fixed divalent metallic cations at acidic sites, whose affinities with calcium ions explain why they act as nucleation sites for CC biomineralization (Addadi and Weiner, 1992; Gilbert et al., 2005). When they can be individually observed, the magnesian calcite crystals were shown to grow with their *c*-axis perpendicular to the organic template (*e. g.*, Défarge et al., 1996, Fig. 5C), as is frequently observed in epitaxial CC biomineralization (Addadi and Weiner, 1992), *e. g.* on algal cell surfaces (Weiner and Dove, 2003). This process of micrite precipitation thus appeared analogous to carbonate biomineralization, although distinct because mediated by nonliving, sedimentary OM. These micrite organominerals were accompanied by tubular ones, resulting from the post-mortem encrustation of cyanobacterial filaments, which thus controlled the final mineral shape, and by biomineralized cyanobacterial sheaths (Défarge and Trichet, 1995). These carbonate microbialites thus revealed a continuum of mineralizing organic-mineral interactions in nature, from biomineralization through organomineralization processes (Défarge and Trichet, 1995; Défarge et al., 1996).

Organomineralization *vs.* biomineralization

The existence of such continua among biomineralization processes *sensu stricto* had already been established: Lowenstam and Weiner (1989) distinguished ‘biologically controlled mineralization’, characterized by cellular controls on crystal nucleation and growth, delineated spaces of mineral formation, and specific habits of the biominerals produced, and ‘biologically induced mineralization’, which designates biotic processes that are not specifically designed for mineralization, but result in mineral being formed. However, in these latter cases too, organisms exercise some control on mineral formation (Lowenstam and Weiner, 1989; Weiner and Dove, 2003).

Another continuum bridges biologically induced mineralization occurring through crystal nucleation on organic secretions outside of organisms (see Weiner and Dove, 2003, Fig. 4), and organomineralization on sedimentary organic substrates derived from EPS described by Défarge and Trichet (1995). The distinction between the two processes, however, is justified, as nucleating organic substrates may act remote in space and time from the organisms which they derive from, as in the examples documented by Trichet and Défarge (1995) for carbonate sediments or for metal minerals formed through geothermal heating of organo-metallic complexes.

In all cases of organomineralization, biotic processes (such as photosynthesis or sulfate reduction in the case of CC; Dupraz and Visscher, 2005) may also participate in solution supersaturation leading to crystal formation on the nonliving organic templates. However, the global process cannot be simply described as ‘biologically induced’ when these nonliving substrates appear to play a necessary role in crystallization, in particular crystal heterogeneous nucleation, or cessation or confinement of crystal growth. In introducing the concept of organomineralization, Trichet and Défarge (1995) aimed to point out that organic matrices and compounds inherited from living organisms may retain mineralizing properties after they have been released in waters and incorporated in soils, sediments and rocks.

Evolution of the organomineralization domain

The same year that Trichet and Défarge (1995) introduced the term *Organomineralization* at the 7th International Symposium on Biomineralization (1993), Reitner (1993), then Reitner et al. (1995) at the same conference, hypothesized that organic matrix-mediated processes were responsible for carbonate automicrite and peloid formation in modern microbialites and sponge tissues from reef caves. These processes appeared analogous to those postulated for the precipitation of CC organominerals in Polynesian microbialites (Défarge and Trichet, 1995; Trichet and Défarge, 1995), and have therefore been considered as organomineralization processes (Neuweiler et al., 1999; Reitner, 2004). Thereafter, a number of papers have documented CC organomineralization in natural environments or in the laboratory (see review in Défarge et al., 2009). New illustrations included for example automicrite formation in Lower Cretaceous carbonate *mud mounds* (qv; Neuweiler et al., 1999), or calcification of the housing tubes of modern and fossil polychaete worms (Fischer et al., 2000). Riding (2000) and Schlager (2003) identified organomineralization as one of the main processes of carbonate precipitation in *microbial mats* (qv) and *biofilms* (qv), or more widely in benthic marine sediments. Many in-vitro studies continued to demonstrate the control exerted by biological compounds on the crystallization of various mineral species (Davies et al., 2003). Thanks to experiments that induced the precipitation of carbonate bodies in the presence of OM extracted from the Murchison CM2 meteorite, Reitner (2004) pointed out that abiotic OM may also induce organomineral formation.

Dupraz and Visscher (2005) recently proposed distinguishing carbonate organomineralization mediated by crystal nucleation on recomposed EPS, as in the former examples documented by Défarge and Trichet (1995) in Polynesian microbialites, from carbonate precipitation following bacterial degradation of EPS: Bacterial degradation liberates EPS-bound ions such as Ca^{2+}, Mg^{2+}, or HCO_3^-, thus leading to outside solution supersaturation for Ca and Mg carbonates. The latter process is not considered by Dupraz and Visscher (2005) to be organomineralization *sensu* Trichet and Défarge (1995). However, sedimentary EPS may also concentrate ions independently of their living producers (Trichet and Défarge, 1995; Westall et al., 2000). In the case of carbonate precipitation induced by degradation of that sedimentary OM, since ion-binding by EPS is a prerequisite for mineralization, this process should be considered as a subcategory of organomineralization. The distinction between organomineralization induced by the liberation in solution of ions previously concentrated by sedimentary EPS, and organomineralization involving a nucleating role of EPS, corresponds to the distinction originally introduced by Trichet and Défarge (1995) between ‘organically-induced’ and ‘organically-supported’ organomineralization.

Geobiological consequences of organomineralization

Impact on present-day and past geological processes

Although difficult to evaluate, because frequently hard to distinguish from the direct role of biotic activity, and neglected by most geobiologists, the impact of organomineralization on sediment and soil formation is likely to be far from negligible. The works cited above (reviewed by Défarge et al., 2009) have already documented occurrences of organomineralization processes in the principal environments at the surface of Earth, from deep cold-water to shallow warm marine, through hyposaline to alkaline lakes, and terrestrial soils. They are involved in the formation of sedimentary calcareous build-ups such as microbialites, mud mounds, and reefs (qv). Organomineral products include micrites, ooids, peloids, and lithified cyanobacterial sheaths, worm housing tubes, animal tissues and fecal pellets. The rapid authigenic phosphatization of tissues after death, leading to the preservation of soft-bodied fossils, likely involves matrix-mediated organomineralization processes (see Briggs, 2003, 292). The principal mineral species forming biominerals (Weiner and Dove, 2003) are also represented by organominerals: Ca carbonates and phosphates, and metal sulfides, oxides and hydroxides; the silicification of EPS that occurs in biofilms independently of those of the micro-organisms (Westall et al., 2000) may also be regarded as an organomineralization.

Défarge et al. (1996) showed that organomineralization processes are probably commonly involved in microbialite calcification; this was thereafter confirmed in numerous cases (Défarge et al., 2009). The process of carbonate-fluorapatite precipitation mediated by dead bacterial cells, proposed by Sanchez-Navas and Martin-Algarra (2001) in phosphate *stromatolites* (qv) that are representative of microbial structures frequently encountered in pelagic sediments from Mesozoic Alpine-Mediterranean paleomargins, may also be considered as an organomineralization. The involvement of mineralizing OM remains the most plausible hypothesis for explaining the formation of magnesian calcite radial ooids composing numerous shallow marine carbonate sands (Morse et al, 2007). Neuweiler et al. (1999) provided evidence for the involvement of micrite organomineralization in the building of Lower Cretaceous mud mounds that are significant examples of calcareous build-ups, possibly originating in the Neoproterozoic, and common during the Phanerozoic. As EPS are essential components of microbial biofilms, which are widespread in nature and persistent throughout the history of life on Earth (Westall et al., 2000), EPS-mediated organomineralization has probably been active at least since the appearance of living organisms, and may represent a geologically early process of mineral production co-existing with, or even pre-existing, biomineralization.

Implications for astrobiological interpretations

Organominerals formed through the mediation of biologically-derived OM may serve as *biosignatures* (qv) in the search for evidence of life in the geological rock record or on extraterrestrial bodies devoid of fossils or bioconstructions. Westall et al. (2000) stressed that mineralized EPS could be used as markers of the presence of bacteria in terrestrial or extraterrestrial materials. However, these biotic EPS need to be distinguished from potential prebiotic EPS that might have the same abilities for fossilization (Westall et al., 2000). Laboratory experiments by Reitner (2004) have shown that OM, likely abiotic, extracted from the Murchinson CM2 meteorite, was able to precipitate CC organominerals similar to those known from terrestrial microbial sediments. More generally, organic molecules were proved to be able to precipitate, in sterile conditions, Ca carbonate or phosphate mineral products resembling biologically induced minerals, in particular those interpreted as fossilized ‘*nan(n)obacteria*’ (qv; Kirkland et al., 1999; Reitner, 2004; see other references in Défarge et al., 2009). Astrobiological studies for the search and the origin of life should keep in mind all this spectrum of potential prebiotic, abiotic, or biologically-derived organominerals in nature.

Potential engineering applications

Biomineralization processes have already inspired the design of new organic matrix-mediated materials by synthetic analogues of the matrices of natural biominerals (Davies et al., 2003). Such manufactured materials are artificial organominerals, although they can also be regarded, from a global geobiological perspective, as biominerals, because formed under direct biological, *i. e.* human, control. Similarly, organomineralization *sensu stricto* might in the future inspire further engineering processes based on the precipitation of minerals or the extraction of ions from solutions in sterile conditions, applied for example to water and wastewater treatment, soil remediation and improvement, protection and restoration of building stones, etc.

Summary and perspectives

The direct role of life in the functioning and the evolution of our Planet is beginning to be fully recognized, witness this encyclopedia. The geobiological impact of OM, however, which is in part included in the indirect role of biotic activity, but may also be due to prebiotic or abiotic processes, is far from being equally well acknowledged and studied. Since the mineralizing role of OM has now been proved in various environments and geological periods, it should be searched for and identified in other case studies, in particular in carbonate formation that took place before the rise of calcareous organisms. While organomineralization research has mainly been devoted until now to EPS calcification, studies on organomineralization processes leading to the formation of other common biomineral species, such as phosphates, metal sulfides and oxihydroxides, or silica, should be continued, and the case of other species like sulfates might be considered. The role of other types of sedimentary and soil OM needs also to be investigated. The possible involvement of abiotic OM in organomineral formation should be taken into account in astrobiological studies for the search of life on primitive Earth and on extraterrestrial bodies. In addition to materials applications based on biomineralization processes, other studies might be devoted in the future to organomineralization-inspired engineering.

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Cross-references

Biofilms

Biomineralization

Biosignatures

Cyanobacteria

Extracellular polymeric substances (EPS)

Microbial mats

Microbialites

Mud mounds

Nan(n)obacteria

Reefs

Stromatolites