

Formation and Transformation of Clay Minerals: the Role of Bacteria

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INTRODUCTION

Bacteria are the most abundant forms of life we know on our planet that can be able to survive in a variety of habitats, from hot to cold springs, from soils to deep sedimentary rocks, in radioactive wastes and in living organisms. It has been estimated (Whitman *et al.*, 1998; Lipp *et al.*, 2008) that the prokaryote number is $3.5 - 5.0 \cdot 10^{30}$ and although global seafloor sedimentary microbial abundance has been recently reduced to $2.9 \cdot 10^{29}$ (Kallmeyer *et al.*, 2012), number of these single-celled organisms remain truly impressive and their mass exceeds that of all plants and animals on Earth. Therefore to modelling mineral equilibria it is imperative to take into account the presence of bacteria in geological environments.

It is ascertained that bacteria can use inorganic compounds as sources of matter and energy to interact with rock-forming minerals and may play a role in mineral formation and transformation processes. This is especially true in the case of clay minerals because they are ubiquitous in soils and sediments and have peculiar physical and chemical characteristics.

This lecture will not be an exhaustive close examination of the role of bacteria in formation and transformation of clay minerals but intends to illustrate a few examples on the influence of bacteria on the genesis of clay minerals and possible “active” role of clay minerals on bacteria and organic matter.

Excellent reviews in geomicrobiology have been published by the Mineralogical Society of America (*edited by Banfield and Kenneth, 1998; Dove et al., 2003; Banfield et al., 2005*) or by Wiley (*Konhauser, 2006*). These books provide a detailed documentation on several geomicrobiological issues and anyone who is interested in what

effects bacteria may exert on our planet should give a look at them.

SCIENCE AT CUTTING EDGE

Up to the eighties, two obstacles hindered the progress in this field at the border - should such a border exist- between biotic and abiotic:

- microbial ecologists and biologists on the one hand, and mineralogists and geochemists on the other, tended to downplay mineralogically and biologically driven processes respectively. An obstacle, not secondary, is that related to the incomplete knowledge of the reciprocal progresses. Fortunately, the availability of electronic journals is filling this gap, but a lot of efforts are needed to manage and to fully understand data coming from other scientific fields;
- the complexity of the world of bacteria seems without limits! Knowledge about these organisms is still incomplete, and in some cases, it is decidedly poor. It is enough to think that sometimes is difficult, or well nigh impossible, to even identify a species. The metabolism and the activities of many taxa are unknown and, consequently, their role in abiotic processes are unknown. However, also in this case, the enormous progresses of techniques based on DNA and RNA approaches are leading, and will lead, to significant progress in this area.

When one think of bacteria, one think of something that has always existed. Surely, it is not so, but bacteria are among those ancestral forms still living today and are continuously renewed. It has been estimated (Whitman *et al.*, 1998) that a soil contains a biomass of $2.6 \cdot 10^{29}$ bacterial cells with a turnover time of about 900 days.

Bacteria morphology is variable. Normally they are some micrometres in length and assume the form of rods, spirals, spheres and other shapes; the commonest on the earth surface are ovoidal, rather like potato croquettes.

Microbes and clay minerals have extraordinary similarities: both have i) micrometric dimensions ii) a very high specific surface and iii) a surface electric charge (negative or positive). Can we say that bacteria are living clays? For sure these two “micro-objects” may interact and influence their behaviour and evolution in a given environment.

However, knowledge concerning the role played by bacteria on the genesis of clay minerals is poor. And still scarce is our knowledge on the influence that clay minerals exert on bacteria, something that we may define as the “biotic role of clay minerals”. As we will briefly see, clay minerals may have played -and likely are playing- a role on the fate of the basic constituents of bacteria: DNA and RNA.

Looking at the role of bacteria in forming clay minerals, the first question to answer is: how do bacteria synthesize them? The knowledge we have today on the genesis of clay minerals mediated by bacteria -which I believe should be distinguished by the use of the prefix “bio”- comes from observations carried out both on natural systems (rocks, soils, water suspended matter) and in laboratory experiments.

BACTERIA; IRON & CLAY MINERALS

There are a number of studies documenting the role of microbes in forming clay minerals in geological environments mainly related to the presence of iron since this element is essential for their life (*e.g., Folk and Lynch, 1997; Fortin et al., 1998; Konhauser and*

palabras clave: Formación, transformación, arcillas, bacterias.

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Urrutia, 1999; Konhauser, 2007; Konhauser et al., 2002; Ueshima and Tazaki, 2001).

The most accredited hypothesis is that the process of bioclay formation start with bacteria fixing iron on the cell wall - better is to say on the sheaths. Initial Fe, Al-silicate phases precipitated directly when dissolved silica and aluminum reacted with cellularly bound iron via hydrogen bonding between the hydroxyl groups.

Microscopic techniques are surely the most used ones in the geomicrobiological studies. An examination of contributions occurring in the literature indicates that the most frequent bio-clay minerals observed contain iron. A very interesting example on a cell encrusted in (Al, Fe)-silicate amorphous phases (occurred in tephra from Kilauea volcano) can be found in Konhauser et al. (2002). Fortin et al. (1998) reported a thin section of a rock coating showing crumpled sheets growing on totally mineralized bacteria. EDS analyses showed an identical chemical composition for the sheets and the amorphous core material, with an Fe and Si content similar to nontronite. Clay minerals, possibly nontronite, sometimes appears as crumpled sheets and it seems that they are rooted in the bacterial wall.

Minerals also have been found in the extracellular polymeric substances (EPS) thus indicating that EPS facilitate nucleation and formation of clay minerals. Presence of amorphous and poorly ordered clay on a cell wall, and within the extracellular polymers, has been reported by Konhauser & Urrutia (1999).

As suggested by Chan et al. (2004) the cells extrude the polysaccharide strands to localize FeOOH precipitation in proximity to the cell membrane. Scanning (SEM) and transmission (TEM) electron microscopic observations revealed the presence of FeOOH-mineralized filaments and nonmineralized fibrils. No crystalline cores were present.

An analogous feature was previously observed in rocks (Fortin et al., 1998): bacterial extracellular polymers occurring as thin filaments of Fe-oxides contained small amounts of Si and Al in a rock coating. The polymers appeared to trap small round nodules also composed of Fe-oxides.

Konhauser and Urrutia (1999) suggested that the clay minerals crystallization in

the presence of bacteria start with the formation of iron rich aggregates, followed by a progressive mineralisation that then leads to the partial and complete encrustation of some bacterial cells.

Several characteristic properties of these inorganic particles are indicative of an authigenic origin.

First, the vast majority of grains are amorphous to poorly ordered structures with chemical compositions that in general differ from the detrital material carried in suspension.

Second, the grain types on each individual bacterium have similar chemical compositions. For example, on any particular bacterium, all epicellular grains tend to have similar Fe, Si and Al ratios.

Third, most attached grains exhibit a tangential orientation around the bacterial cells. Detrital clays showed a preference for edge-on orientation with cellular surfaces.

Fourth, the generally small size of the particles suggests that the grains formed via chemical reaction with the organic ligands.

However, given the abundance of clay minerals in natural environments not all naturally occurring minerals associated to the cell surface are necessarily precipitated on the cell wall. We should also consider the ability of bacteria to use pre-existing clay minerals as substratum. As it was experimentally documented by Walker et al. (1989), cells of *Bacillus subtilis* and *Escherichia coli* may adhere to crystals of smectite and kaolinite, but they adsorbed onto the minerals with distinct efficiency, which implies that different species behaves differently.

It is just this aspect that was dealt with in a study (Glasauer et al., 2001) which documented that pre-existing iron oxyhydroxides particles were adhered to the surface of *Shewanella putrefaciens*, a gram negative bacteria, and that in some instances, the mineral crystals had even penetrated the outer membrane and peptidoglycan layers. If we had observed this in a natural sample, we would have concluded that the inner part of the membrane is able to synthesize Fe minerals. There is no doubt that biomineralization does take place in many environments. However we also should take into account that sorption of preformed nanosize minerals can also occur.

BACTERIA & FE-CLAY MINERALS

But, what about iron in clay minerals? Are bacteria able to remove iron from clay minerals and to transform them? A number of experimental studies were carried out on this subject as it has been recently reviewed by Dong et al. (2009). Some experiments indicated that reduction of Fe(III) to Fe(II) led to a partial dissolution of clay structure; others reported evidences for solid state reduction mechanism. The reasons of this inconsistency may be (Dong et al., 2009): *i*) the mechanism of Fe(III) reduction may be mineral specific; *ii*) the mechanism of reduction may be dictated by the extent of Fe(III) reduction; *iii*) the mechanism may depend on the type of medium, the presence or absence of organic matter, and the solution pH used for bioreduction experiments. In other words, although a number of information is available our current understanding of mechanisms of microbial reduction of ferric iron in clay minerals is far to be fully understood.

Maybe we should consider that bacteria introduce several variables, mainly related to the biofilm and EPS they produce. For instance: chemical composition of solutions within biofilms may be different with respect to bulk solution (e.g., Lawrence et al, 1994); pH may change in the same culture (e.g., Vroom et al., 1999); pH, temperature and bacterial species control biofilm production (e.g., Ho.tack. et al., 2010). In a recent experiment aimed to evaluate the inorganic and biologic controls on clay formation by alteration of volcanic glasses (Cuadros et al., 2013) it has been documented that biofilms can exert a control on neofomed smectites.

And speaking again about clay minerals containing iron, I would like to call your attention to the results of an experimental investigation (Kim et al., 2004) on the most studied clay mineral: the interstratified illite-smectite (I-S).

Numerous studies have emphasized temperature, pressure, and time as geological variables in either solid-state or dissolution-precipitation I-S reaction mechanisms but the role of microbes has been disregarded. The results of such experiment are very important because, as you all well know, degree of conversion of smectite to illite is frequently used as a geothermometre to allow reconstructions of the thermal and tectonic history of sedimentary basins (e.g., Burst, 1969; Peacor, 1992; Pevear, 1999; Weaver 1960). Kim et al. (2004) incubated *Shewanella*

onidensis with nontronite for 14 days at room temperature and they found that the bioproducted Fe(II) concentration increased with time; the control, that consisted of solutions that containing death cell in place of living cells, did not show any reduction. Transmission electron microscope lattice fringe images of the non-reduced control samples showed typical 13 Å spacings, suggesting that smectite was the only clay phase present. However two clay phases were observed in the sample incubated with bacteria: smectite and illite, as well as newly formed iron rich minerals. Neoformation of illite was also detected by XRD.

More recently it has been documented that smectite-to-illite transition may be catalysed by the presence of organic matter in the interlayer of the smectite (Zhang *et al.* 2007b) as well as by thermophilic bacteria (Zhang *et al.* 2007a).

BACTERIA & KAOLINITE

Less information is available about another clay mineral which is frequently found in soils and sediments: kaolinite.

The presence of kaolinite in association with bacteria has been documented since 1980 but for specific studies on this mineral we have to refer to the studies of Japanese clay scientists. It should be stressed that we are talking about single nanoparticles -don't imagine seeing kaolinite booklets- and that they are all amorphous or have a very low crystallinity.

Non crystalline Al-Si-Fe materials have been found to grow on the cell surface in pore water of weathered volcanic ashes (Kawano and Tomita, 2001). Materials surrounding bacteria may appear as massive aggregates of granular minerals and as aggregates of flakes rich in Al, Si and Fe.

Halloysite, a possible precursor of kaolinite, was observed in microbial films from laboratory cultures derived from natural sediments (Tazaki, 2005) and it was also found on the surface of bacillus-type bacteria. The electron diffraction pattern with 2.9, 2.5, 2.2 and 1.5 Å d-spacing also supported the hypothesis of a 7 Å halloysite-like mineral. Tazaki hypothesised a suggestive mechanism for bio-halloysite formation: "Clay bubbles might serve as a precursor for spherical halloysite crystallization. The formation mechanism of the hollow-sphere morphology of bio-halloysite seems to be the inflation of clay bubbles by the degassing of H₂S gas into the cohesive materials of the bacte-

rial cell wall under the low redox conditions of the solution." As will be shown later, microscopic observations we carried out in 2007 do not support this hypothesis.

There are difficulties in the synthesis of kaolinite. The first report of the synthesis of kaolinite at room temperature dates back to over 40 years ago. Linares & Huertas (1971) documented, by XRD and IR the neoformation of kaolinite starting from a Si-Al rich solution, in presence of humic acids. This experiment was repeated many time from worldwide researchers but failed to synthesize kaolinite. There, therefore, springs to mind the question: what other factor lead to the formation of kaolinite? Bacteria? We found a high number of bacteria in the international standards of soil organic matter (Leonardite, Pahokee, Elliot). I can assure you, it is by no means easy to exclude bacteria from an experiment in the lab. Bacteria are everywhere... we are full of bacteria!

In 2004, Stefano Dumontet, Javier Huertas and myself began a series of experiments to try to synthesize kaolinite at room temperature using a water solution containing Si:Al=2:1 and oxalate in sterile conditions, with the addition of cold soil extract. The results were, in a certain sense, surprising (Fiore *et al.*, 2011). After 220 days of incubation, in sterile samples we detected the presence of hexagonal crystals of kaolinite (Fig. 1). In the sample containing bacteria it was observed the presence of filamen-

tous material, likely a biofilm, but we did not observe crystals of kaolinite. We cannot swear on it because in the samples containing kaolinite we observed only 4 crystals. The kaolinite formation has been seen as a bio-induced process through two steps. The first step is the formation and precipitation of the aluminosilicate gel, promoted by the presence of ligands as well as organic products (EPS, biofilm, metabolites, etc; at this step we have a mélange of gel, bacteria and their metabolic products). The second step is the formation of kaolinite within the gel as a consequence of the metabolic activity which changes the surrounding environment (pH, redox, ion concentrations) and causes local gel dissolution or its solid state re-arrangement towards a crystalline material. Although this experimental study provided the first evidence of the bioformation of kaolinite, the mechanism of its formation is still unknown.

In another experiment -the sample contained only the mother solution and cold soil extract- aged for 30 days, we observed several spheres having a Si:Al ratio close to 1 (Fig. 2) and many of them appeared blocked within the precipitated gel (Fig. 3). Many of them they were no bubbles and therefore we must conclude that the spheres are not the result of the inflation of clay bubbles by a degassing, no matter what the gas.

One should speculate that spheres formed as a consequence of gel contrac-

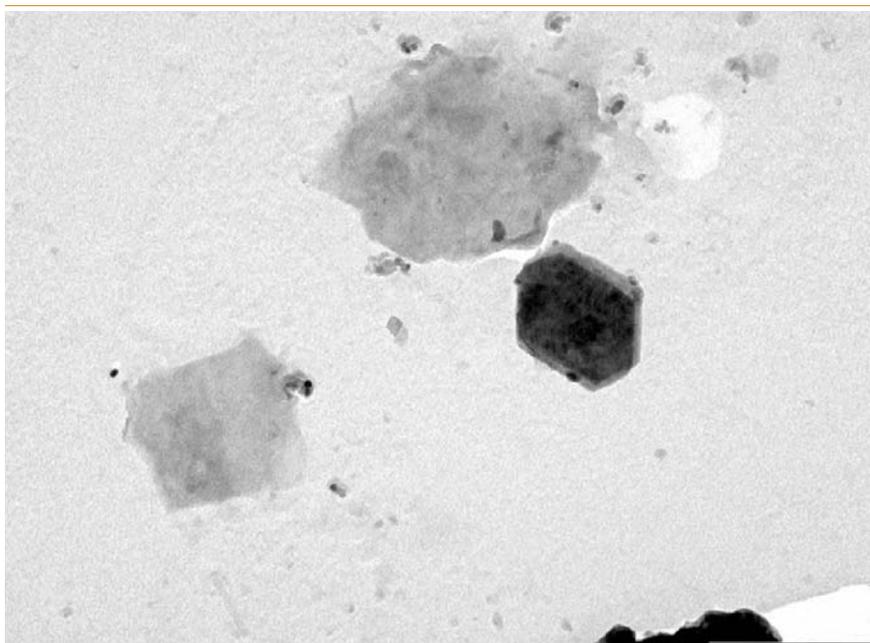


fig 1. Crystal of kaolinite formed after 220 days of incubation (Fiore *et al.*, 2011; unpublished). TEM image.

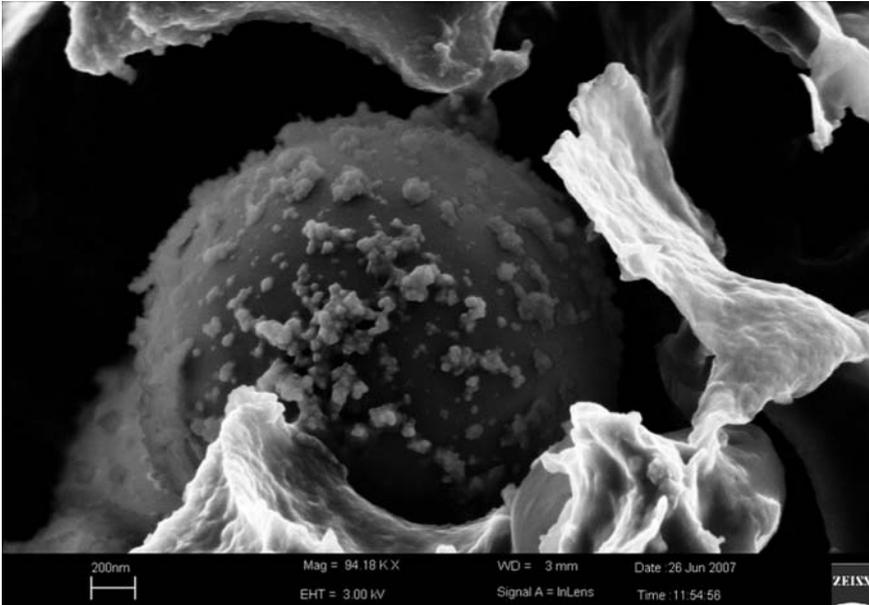


fig 2. Colonies of bacteria within the gel (Si/Al=1) precipitated from solution. SEM image.

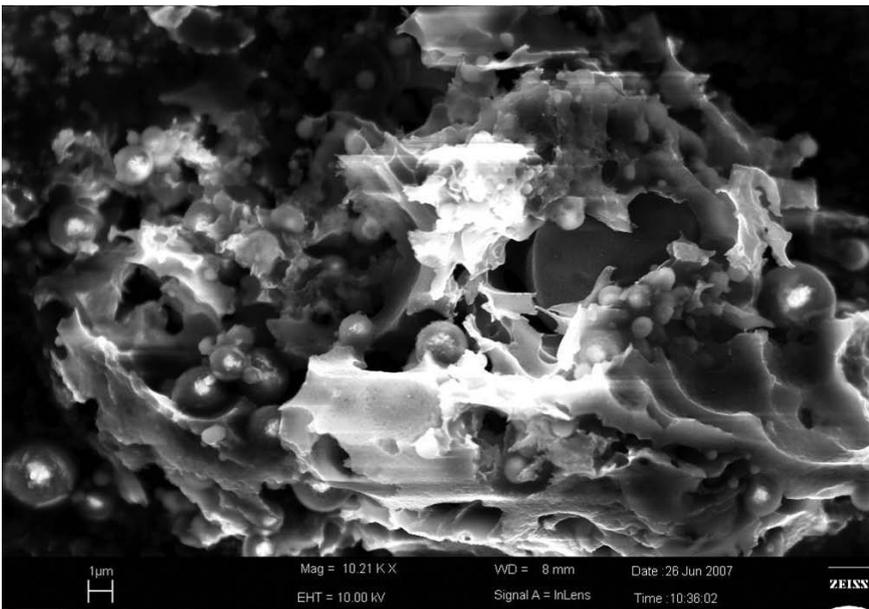


fig 3. Spheres formed in experiments (30 days) aimed to synthesize kaolinite at room temperature. Si/Al is close to 1 (from Fiore et al., 2007; unpublished). SEM image.

tion, that is a mechanism analogous to the one we showed to be at the basis of the formation of spherical kaolinite in hydrothermal conditions (Fiore et al., 1995; Huertas et al., 2004). However, in sterile experiment we did not observe spheres: in other words, the mechanism of formation must take into account the presence of bacteria. Bacteria might carry out a non-defined action within the gel and this would explain the reduced number of balls with respect to the millions of bacteria present in our experiment. There is not a handy explanation for these findings. Formation of vesicles has been observed in experiments performed using a

solution containing RNA, fatty acids, clay minerals and clay-sized minerals (Hanczyc et al., 2007). Higher number of spherical particles formed using an aluminosilicate substratum. There springs to mind a question: were the vesicles we observed formed by RNA or by bacteria fragments and covered by the aluminosilicate gel?

CLAYS AS BIOLOGICAL AGENTS

Silicon is an important element for microorganisms. It is able to enhance the growth and pathogenicity of some bacteria (Das and Chattopadhyay, 2000) and bacteria may, indeed, survi-

ve within the gel preserving their vital functions. Nassif et al. (2002) found isolated living bacteria trapped in silica gel and proved that more bacteria remain culturable in the gel than in an aqueous solution. We recently found active bacteria after 70 months of incubation (Dumontet et al., 2013; Fig. 4). Therefore the silica gel exerts an important role in determining the bacteria activity. They also suggested that the aggregate were not forming but our observations (Fig. 5; Fiore et al., 2011) did not substantiate this conclusion.

Fragments of bacteria may have an active role in “capturing” silicon. Vorokonov et al. (1975, cited in Malcov et al., 2005) found that nucleic acid of cow contains up to 0.31% of silicon as substituent of phosphorous. More recently, Hirota et al. (2010) documented the presence of Si in *Bacillus cereus* and in other *Bacillus* strains and concluded that Si layer enhances acid resistance. Another question springs to mind: may fragments of bacteria act as a template for crystal growth? This crazy idea is currently being investigated.

DNA, in turn, may be trapped and may change its conformation by interaction with phyllosilicates. Interactions between nucleotides and cleaved surface of chlorite have been successfully documented by Valdré (2007). He documented, by scanning probe microscopic observations, line-up of nucleotides along the edge of a brucite-like layer of a clinocllore.

Another recent contribution relatively to the active role of clay minerals, specifically montmorillonite, on nucleic acids has been given by Biondi et al. (2007). They documented that the presence of montmorillonite protected the RNA molecules against a specific degradation and increased the rate of cleavage kinetics by about one order of magnitude. In other words, clay-rich environments would have been a good habitat in which RNA or RNA-like molecules could originate and accumulate, leading to the first living cells on Earth.

Clay minerals really might be a mean for the building of genetic molecules, protection against degradation (by UV and X-ray radiation) and evolution toward increasing molecular organization.

Clays and bacteria represent an infinity of

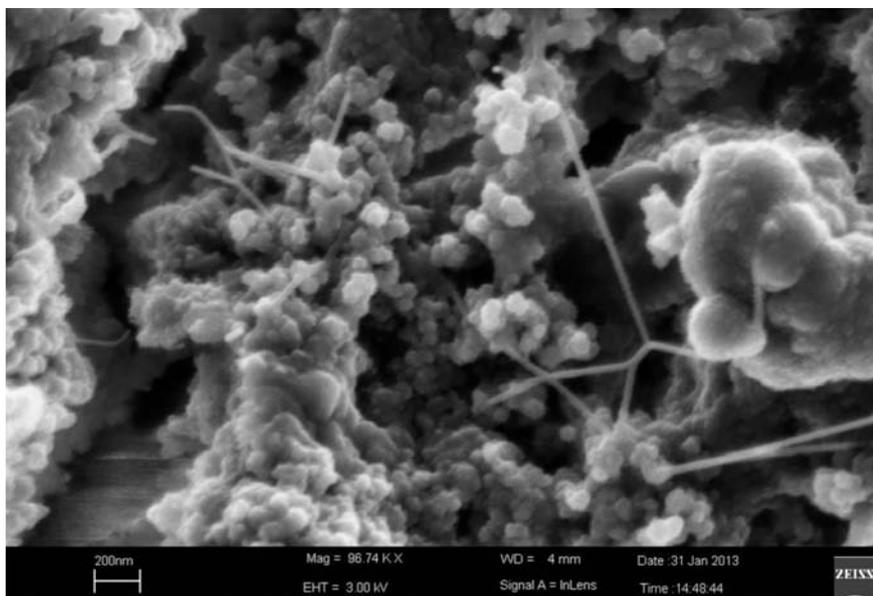


fig 4. Gel fragments exhibiting spherical humps on the surface. Si/Al is close to 1 (from Fiore et al., 2007; unpublished). SEM image.

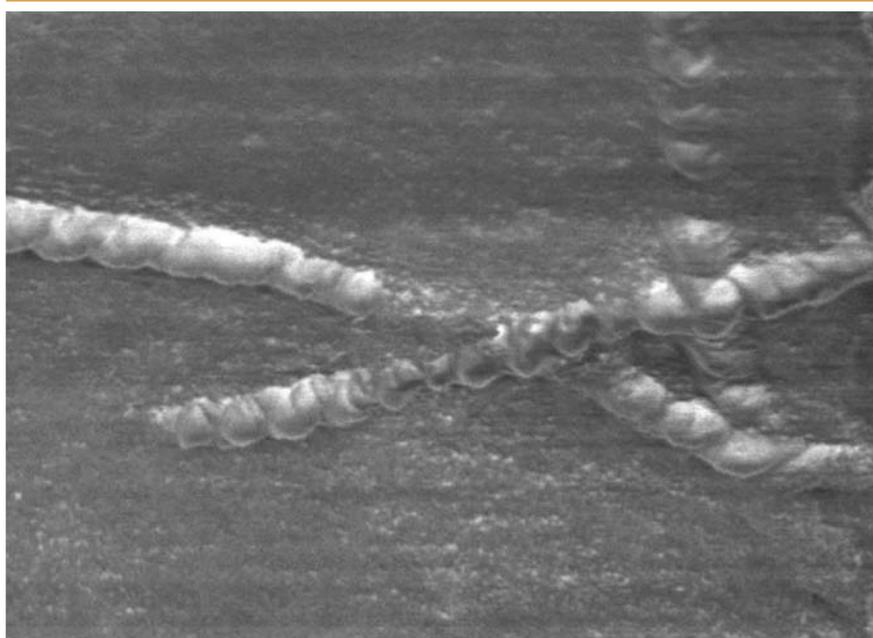


fig 5. Bacteria in gel matrix after 70 months of incubation. The bacterial filaments indicate that bacterial cells, even though heavily coated with amorphous minerals, are still metabolically active and able to produce filaments. From Dumontet et al. (2013; unpublished). SEM image.

little objects, living and non-living, that inhabit the surface of the Earth. It is almost obvious that they interact. It is up to us, mineralogists and geochemists, with biologists and microbiologists, to understand how extensive are these interactions.

REFERENCES

Banfield, J.F. & Nealson, K.H. Eds. (1998): *Geomicrobiology: Interactions between Microbes and Minerals. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America*, 35, 448 pp.

-, Cervini-Silva, J., Nealson, K.H. Eds. (2005):

Molecular Geomicrobiology. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, 59, 294 pp.

Biondi, E., Branciamore, S., Fusi, L., Gago S., Gallori E. (2007): Catalytic activity of hammerhead ribozymes in a clay mineral environment: Implications for the RNA world. *Gene*, 389, 10-18.

Burst, J.F. (1969): Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. *American Association of Petroleum Geologist Bulletin*, 53, 73-93.

Chan, C.S., De Stasio, G., Welch, S. A., Girasole, M., Frazer, B. H., Nesterova, M.V., Fakra, S., Banfield, J.F. (2004): *Microbial*

polysaccharides template assembly of nanocrystal fibers. Science, 303, 1656-1658.

Cuadros, J., Afsin, B., Jadubansa, P., Ardakani, M., Ascaso C., Wierzos, J. (2013): Microbial and inorganic control on the composition of clay from volcanic glass alteration experiments. *American Mineralogist*, 98, 319-334.

Das, S. & Chattopadhyay, U.K. (2000): Role of silicon in modulating the internal morphology and growth of *Mycobacterium tuberculosis*. *Indian Journal of Tuberculosis*, 47, 87-91.

Dong, H., Jaisi, D.P., Kim J. and Zhang G. (2009): Microbe-clay mineral interactions. *American Mineralogist*, 94, 1505-1519

Dove, P.M., De Yoreo, J.J., Weiner S., Eds. (2003): *Biomining, Reviews in Mineralogy and Geochemistry, Mineralogical Society of America*, 54, 381 pp.

Dumontet, S., Hlayem, D., Huertas, F.J., Lettino A., Pasquale, V., Fiore S. (2013): Kaolinite forming bacteria. A long-term experimental study. Abstract book 15th International Clay Conference, July 11-15, 2013, Abs-815.

Fiore, S., Dumontet, S., Huertas, F.J. (2007). *Clay Minerals and Bacteria*. In: Rocha F, Terroso D, Quintela A, Euroclay 2007 - Invited Lectures Book, p. 62-65, Aveiro, 22-27 Luglio

-, Huertas, F.J., Huertas, F., Linares J. (1995): Morphology of kaolinite crystals synthesized under hydrothermal conditions. *Clays and Clay Minerals*, 43, 353-360.

-, Dumontet, S., Huertas, F.J., Pasquale, V. (2011): Bacteria-induced crystallization of kaolinite. *Applied Clay Science*, 53, 566-571.

Folk, R.L., Lynch, F.L., (1997): The possible role of nanobacteria (dwarf bacteria) in clay mineral diagenesis and the importance of careful sample preparation in high magnification SEM study. *Journal of Sedimentary Research*, 67, 583-589.

Fortin, D., Ferris, F.G., Scott, S.D. (1998): Formation of Fe-silicates and Fe-oxides on bacterial surfaces in samples collected near hydrothermal vents on the Southern Explorer Ridge in the Northeast Pacific Ocean. *American Mineralogist*, 83, 1399-1408.

Glasauer, S., Langley, S., Beveridge, T. J. (2001): Sorption of Fe (Hydr)oxides to the surface of *Shewanella putrefaciens*: cell-bound fine-grained minerals are not always formed de novo. *Applied Environmental Microbiology*, 79, 5544-5550.

Hanczyc, M.M., Mansy, S.S., Szostak, J.W. (2007): Mineral surface directed membrane assembly. *Origins of Life and Evolution of Biospheres*, 37, 67-82

Hirota, R., Hata, Y., Ikeda, T., Ishida, T.,

- Kuroda, A. (2010): The Silicon layer supports acid resistance of *Bacillus cereus* spores. *Journal of Bacteriology*, 192, 111-116.
- Huertas, F.J., Fiore, S., Linares, J., 2004. In-situ transformation of amorphous gels into spherical aggregates of kaolinite: a HRTEM study. *Clay Minerals*, 39, 423-431.
- Kallmeyer, J., Pockalny, R., Adhikari, R.R., Smith D.C., D'Hondt, S. (2012): Global distribution of microbial abundance and biomass in subseafloor sediment. *Proceedings of the National Academy of Sciences USA*, 16213-16216.
- Kawano, M. & Tomita, K. (2001): Microbial biomineralization in weathered volcanic ash deposit and formation of biogenic minerals by experimental incubation. *American Mineralogist*, 86, 400-410.
- Kim, J., Dong, H., Seabaugh, J., Newell, S.W., Eberl, D.D. (2004): Role of microbes in the smectite-to-illite reaction. *Science* 303, 830-832.
- Konhauser, K.O., Schiffman, P., Fisher, Q.J. (2002): Microbial mediation of authigenic clays during hydrothermal alteration of basaltic tephra, Kilauea Volcano. *Geochemistry, Geophysics, Geosystems*, 3, 1-13
- , Urrutia, M.M. (1999): Bacterial clay authigenesis: a common biogeochemical process. *Chemical Geology*, 161, 399-413.
- Lawrence, J.R., Wolfaardt, G.M., Korber, D.R. (1994): Determination of diffusion coefficients in bBiofilms by confocal laser microscopy. *Applied and Environmental Microbiology*, 60, 1166-1173
- Lipp, J.S., Morono, Y., Inagaki, F., Hinrichs, K.U. (2008): Significant contribution of Archaea to extant biomass in marine subsurface sediments. *Nature*, 454, 991-994.
- Malcov, S.V., Markelov, V.V., Polozov, G.Y., Sobchuk, L.I., Zakharova, N.G., Barabanshikov B.I., Kozhevnikov, A.Y., Vaphin, R.A., Trushin, M.V. (2005): Antitumor features of *Bacillus oligonitrophilus* KU-1 strain. *Journal of Microbiology, Immunology and Infection*, 38, 96-104.
- Nassif, N., Bouvet, O., Rager, M.N., Roux, C., Coradin T., Livage, J. (2002): Living bacteria, in silica gels. *Nature Materials*, 1, 42-44.
- Peacor, D.R. (1992): Diagenesis and low-grade metamorphism of shales and slates. In P.R. Buseck, Ed., *Minerals and Reactions at the Atomic Scale: Transmission Electron Microscopy*, 27, p. 335-380. *Reviews in Mineralogy, Mineralogical Society of America*.
- Pevear, D.R. (1999): Illite and hydrocarbon exploration. *Proceedings of National Academy of Science*, 96, 3440-3446.
- Tazaki, K. (2005): Microbial formation of a halloysite-like mineral. *Clays and Clay Minerals*, 53, 224-233.
- Ueshima, M. & Tazaki, K. (2001): Possible role of microbial polysaccharides in nontronite formation. *Clays and Clay Minerals*, 49, 292-299.
- Valdré, G. (2007): Natural nanoscale surface potential of clinocllore and its ability to align nucleotides and drive DNA conformational change. *European Journal of Mineralogy*, 19, 309-319
- Vroom, J.M., De Grauw, K.J., Gerritsen, H.C., Bradshaw, D.J., Marsh, P.D., Watson, G.K., Birmingham, J.J., Allison, C. (1999): Depth penetration and detection of pH gradients in biofilms by two-photon excitation microscopy. *Applied and Environmental Microbiology*, 65, 3502-3511
- Walker, S.G., Flemming, C.A., Ferris, F.G., Beveridge, T.J. and Bailey, G.W. (1989): Physicochemical interaction of *Escherichia coli* cell envelopes and *Bacillus subtilis* cell walls with two clays and ability of the composite to immobilize heavy metals from solution. *Applied Environmental Microbiology*, 55, 2976-2984
- Weaver, C.E. (1960): Possible uses of clay minerals in search for oil. *American Association of Petroleum Geologists*, 44, 1505-1518.
- Whitman, W.B., Coleman, D.C., Wiebe, W.J. (1998): Prokaryotes: The unseen majority. *Proceedings of the National Academy of Sciences USA*, 95, 6578-6583.
- Zhang, G., Dong, H., Kim, J.W., and Eberl, D.D. (2007a) Microbial reduction of structural Fe³⁺ in nontronite by a thermophilic bacterium and its role in promoting the smectite to illite reaction. *American Mineralogist*, 92, 1411-1419.
- , Kim, J.W., Dong, H., and Sommer, A.J. (2007b) Microbial effects in promoting the smectite to illite reaction: role of organic matter intercalated in the interlayer. *American Mineralogist*, 92, 1401-1410.