

The Fe-Rich Clay Microsystems in Basalt-Komatiite Lavas: Importance of Fe-Smectites for Pre-Biotic Molecule Catalysis During the Hadean Eon

Alain Meunier · Sabine Petit · Charles S. Cockell ·
Abderrazzak El Albani · Daniel Beaufort

Received: 21 October 2009 / Accepted: 11 January 2010 /

Published online: 7 March 2010

© Springer Science+Business Media B.V. 2010

Abstract During the Hadean to early Archean period (4.5–3.5 Ga), the surface of the Earth's crust was predominantly composed of basalt and komatiite lavas. The conditions imposed by the chemical composition of these rocks favoured the crystallization of Fe-Mg clays rather than that of Al-rich ones (montmorillonite). Fe-Mg clays were formed inside chemical microsystems through sea weathering or hydrothermal alteration, and for the most part, through post-magmatic processes. Indeed, at the end of the cooling stage, Fe-Mg clays precipitated directly from the residual liquid which concentrated in the voids remaining in the crystal framework of the mafic-ultramafic lavas. Nontronite-celadonite and chlorite-saponite covered all the solid surfaces (crystals, glass) and are associated with tiny pyroxene and apatite crystals forming the so-called “mesostasis”. The mesostasis was scattered in the lava body as micro-settings tens of micrometres wide. Thus, every square metre of basalt or komatiite rocks was punctuated by myriads of clay-rich patches, each of them potentially behaving as a single chemical reactor which could concentrate the organics diluted in the ocean water. Considering the high catalytic potentiality of clays, and particularly those of the Fe-rich ones (electron exchangers), it is probable that large parts of the surface of the young Earth participated in the synthesis of prebiotic molecules during the Hadean to early Archean period through innumerable clay-rich micro-settings in the massive parts and the altered surfaces of komatiite and basaltic lavas. This leads us to suggest that Fe,Mg-clays should be preferred to Al-rich ones (montmorillonite) to conduct experiments for the synthesis and the polymerisation of prebiotic molecules.

Keywords Fe-clays · Basalt-komatiite · Prebiotic · Molecule synthesis · Hadean

A. Meunier (✉) · S. Petit · A. El Albani · D. Beaufort
HydrASA University of Poitiers, Bât. Sciences Naturelles—FRE 3114 INSU-CNRS,
40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France
e-mail: Alain.meunier@univ-poitiers.fr

C. S. Cockell
CEPSAR, Open University Milton Keynes, Milton Keynes MK7 6AA, United Kingdom

Introduction

Since the pioneering work of Bernal (1951), clay minerals have been considered as potential templates for the natural synthesis of pre-biotic molecules during the early stages of the Earth's geological history (Cairns-Smith 1982; Lahav 1994; Brack 2006 among others). Today, clay minerals are widespread over continental and oceanic crusts on Earth (see Meunier 2005 and references therein). Dioctahedral Al-rich smectites are particularly abundant in the weathered superficial mantle covering the continents. They are dominant in calc-alkaline volcanic areas where they form bentonite deposits (Huff 2006). These nearly monomineral layers result from the aqueous alteration of volcanic ashes which are formed of Si-rich volcanic glass (rhyolite-dacite). Depending on the composition of the solutions, the crystal-chemical properties of the Al-rich smectites vary between the beidellite and montmorillonite end-members (Ddani et al. 2005; Christidis and Huff 2009). Dioctahedral Fe-rich smectites (nontronite) are much less abundant in continental areas. They are typically formed either by alteration of mafic-ultramafic rocks in association with trioctahedral Mg-rich smectites or in the vicinity of submarine hydrothermal vents.

Montmorillonite has a high cation exchange capacity which favours the concentration of organics in the interlayer region. The concentration of monomers is a necessary preliminary step before polymerization (see Ferris 2005, 2006; Lambert 2008 and references therein). Nucleotides are bounded by van der Waals forces in the smectite interlayer region (Brack 1976). Then, polymerization occurs if the clays are "activated" that is to say if: (i) the interlayer regions are saturated by proper cations, (ii) pH conditions are favourable. For instance, the cyclization of nucleotides is higher in Zn^{2+} - rather than in Na^{+} -montmorillonites (Ferris et al. 1986). This is why, until now, most of the catalytic properties have been measured on homoionic Al-rich clays and particularly on Na^{+} saturated montmorillonite using the procedure recommended by Banin et al. (1985). However, the use of bentonite clays, i.e., Al-rich dioctahedral smectites (montmorillonite) which are artificially prepared should be re-examined from a geological point of view. Indeed, two questions have to be considered: 1- what kinds of clay minerals (specifically smectites) were present in the Earth's crust during the Hadean to early Archean period (4.5–3.5 Ga)? 2- Were these smectites appropriate for the synthesis of prebiotic molecules?

These questions are difficult to address because clay minerals are highly reactive either in surface conditions where they are constantly submitted to weathering or in buried sediments where diagenetic reactions constantly transform them. No remnants of the original smectites can be found in sediments or alteration profiles of the early Archean and *a fortiori*, in the very rare Hadean rocks. The low grade metamorphism reactions in the 3.5 Ga Pilbara and Barberton formations have erased their original crystal-chemical properties. Because these properties cannot be directly studied, we need to refer to present geological analogues in which similar clay minerals are formed today, to experimental synthesis in controlled redox-temperature conditions or to thermodynamical simulations.

The purpose of the present paper is to address the following questions with the aim of giving new insights on the possible importance of Fe-rich clay minerals:

- 1) Taking into account the geological characteristics of the Earth's crust during the Hadean period, what kinds of clay minerals are expected to be the most frequently encountered?
- 2) What specific crystal structures are expected to be commonly observed in these clays formed from the Hadean crust?

- 3) Could these clays have significant catalytic properties compared to montmorillonite?
- 4) Were the clay-rich sites statistically distributed in the Hadean rocks in a way favouring the catalysis of prebiotic molecules (large surfaces exposed to chemical exchange with the ocean water)?

Earth's Crust Composition and Surface Conditions During the Hadean

Rocks from the Hadean eon are extremely rare and their dating is still debated. They are mafic rocks (O'Neil et al. 2008). However, the oldest terrestrial remnant we know is not a rock but a mineral: zircons from the Jack Hills formation in Australia. These crystals are 4.4 to 4.0 Ga old (Wilde et al. 2001). In spite of the fact that zircons can be formed through the melting of trondjemites (Coogan and Hinton 2006; Rollinson 2008), the Jack Hills examples probably came from granitoids because of the presence of quartz and feldspar inclusions. The $^{18}\text{O}/^{16}\text{O}$ ratio of zircons indicates that they crystallized in presence of liquid water (Wilde et al. 2001; Amelin 2005). However, even if the formation of a terrestrial magma ocean during accretion remains an unanswered question, at least, the mantle was undoubtedly partly molten. Thus, the surface of the early Earth was probably formed of lava with chilled solid parts composed of peridotite derived rocks (komatiite to basalt). The geothermal gradient being significantly higher during the Hadean and early Archean period, the convection cells were small and rapid (Davies 1992). Thus, the komatiite-basalt crust was much more rapidly recycled than the ocean floor is today. Consequently, in spite of the probable existence of granitoids before 4 Ga, the Earth's crust at that time was mainly composed of komatiitic-basaltic forming ocean floor and emerged plateaus. The former continent embryos were dominantly composed of Na-rich rock series (Tonalite-Trondhjemite-Granodiorite or TTG) while K-rich ones (granitoids) are thought to form later. Granitoids became more abundant at the end of the Hadean period (Armstrong 1991) but were largely submerged by oceans.

The crust has been heavily bombarded by meteorites and comets up to about – 3.9 Ga (Late Heavy Bombardment or LHB). The LHB is the source of siderophile elements in the mantle. The oceans are considered to have been permanently formed after LHB; they were certainly temporarily vaporized several times before. The LHB enhanced the hydrothermal alteration reactions between ocean water and the komatiite-basalt crust because of fracturing and heating effects (Cockell 2006). Hydrothermal solutions and ocean water were enriched in dissolved transition metals and phosphate (Kakegawa et al. 2002). Particularly, the amount of dissolved Fe^{2+} and other transition metal ions was higher than today. Oxygen did not exist at this time. It appeared in the atmosphere as a by-product of biological activity, specifically photosynthesis (Canfield 1998; Pavlov and Kasting 2002).

It is obvious that the clays which are expected to be dominant during the Hadean-early Archean period should derive mostly from the alteration of mafic-ultramafic rocks and partly from TTG rather than from bentonites which are mostly related to calc-alkaline magmatism (Schoonen et al. 2004). Huff (2006) shows that montmorillonite is almost completely absent in bentonite deposits older than 300 Ma. Most often, old deposits are potassium-rich (K-bentonites) and are composed of illite-smectite mixed layer minerals. K-bentonites have not been observed after the Paleozoic. In other words, this excludes the possibility of considering Al-rich clay minerals formed in bentonites such as montmorillonite to be adequate candidates for the catalysis of prebiotic molecules during Hadean. The most

plausible clay species should be those formed from mafic-ultramafic rocks through different fluid-rock interaction processes. Three geological systems have to be considered for the formation of clay minerals from mafic-ultramafic rocks during Hadean:

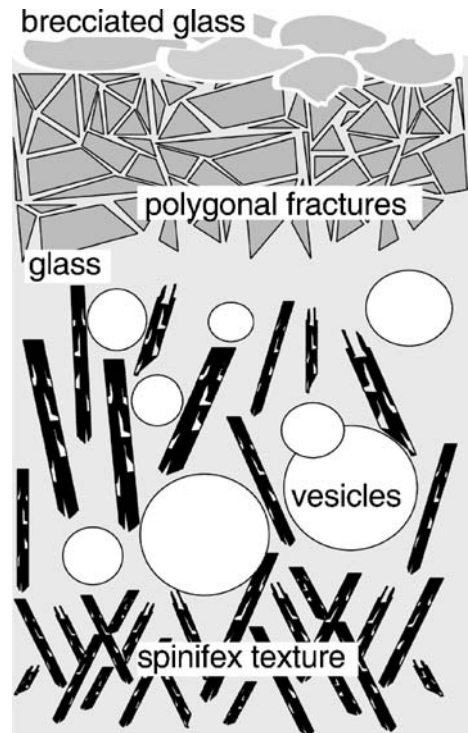
- 1 – post-magmatic crystallization at the end of the cooling stage.
- 2 – interaction of ocean water with the lava surface (sea weathering) or meteoritic water (atmospheric weathering);
- 3 – hydrothermal alteration (black smokers and brine pools at mid-ocean ridge spreading centres, white smokers far from mid ocean ridges).

Post-Magmatic Fe-Mg Clays

Mesostasis and Columnar Joints

There are no modern komatiite lavas, the most recent ones being 88 Ma old are found in Gorgona Island, Columbia (Echeverria 1980). Most of the well preserved komatiite lavas are found in Komati 3.5-Ga formation in the Barberton Greenstone Belt, South Africa. In spite of low grade metamorphism reactions, the structure and microstructure of the lava are conserved, particularly the olivine skeletal crystals forming the typical spinifex microstructure (Fig. 1). The komatiite bodies still exhibit a vesicular texture in their upper part (Dann

Fig. 1 Schematic representation of the upper part of a komatiite lava flow (simplified from Arndt et al. 2008). From top to bottom, the section shows four levels exhibiting different structures: brecciated pillow lava; massive glassy zone fragmented by polygonal fractures; vesicle-rich level; glass-skeletal olivine (spinifex texture) level. The glassy zones are represented using different grey colors



2000, 2001; Beresford et al. 2000, 2002) and columnar fractures (Arndt et al. 2008). The originally vitreous parts, i.e., the mesostasis, are now totally recrystallized into chlorite (Arndt et al. 1977). According to Dann (2001), the vesicles in the upper levels of komatiite bodies may represent up to 30% of the volume. Their size observed in thin sections varies from 0.5 up to 2.5 mm. Komatiites lava are expelled at higher temperature than basalts. The formation of skeletal crystals on one hand and of vesicles in the other hand, is due to a quenching stage. Similar features are observed in basaltic lavas. Can we infer that the mesostasis of komatiite is similar to that of basalts?

Even if the water content of komatiite magma is still debated, it is probable that the residual fluids were: (i) enriched in the same volatile components as present basalts are, i.e. H₂O, Cl, K, P, light rare earth elements (LREE) and (ii) concentrated in the open spaces, i.e., vesicles and inter-crystalline voids (vesicles result from the separation of a gas phase from the magma (ebullition); inter-crystalline voids or diktytaxitic voids, appear later during the last cooling stage of the basaltic lava before total solidification when crystals form a continuous solid framework). According to Peck et al. (1977) the solidus temperature for basalt lavas is 980°C. Thus, the mineralogical composition of komatiite mesostasis was certainly similar to that of basalts but the relative proportions of mineral phases could be different due to the higher Fe and Mg contents. Indeed, because the amounts of water is not known, the proportion of Fe,Mg-rich clays versus anhydrous silicates is undeterminable.

Modern analogues for the study of the komatiite mesostasis can be found in the Fe-rich sequence of basalt to hawaiiite lavas in the Mururoa seamount (French Polynesia). Mas et al. (2008) show that subaerial, submarine lava flows and dyke exhibit all chilled thin vitreous margins (Fig. 2a) contrasting with a thick inner part which is highly crystallized (Fig. 2b). The mesostasis fills the diktytaxitic voids of the massive crystallized inner parts. Before total solidification of the lava (post-magmatic crystallization stage), the residual fluids become oversaturated with respect to different mineral species which form an assemblage of tiny crystals of pyroxene, apatite, Fe,Mg-clay minerals (Table 1) and K-feldspars overgrowths on plagioclase surfaces (Fig. 2c). Pyroxene, apatite and K-feldspar micro-crystals form first, then, they are coated by clays exhibiting a palissadic structure (Fig. 3c). In some cases, the residual liquid can reach the boiling pressure-temperature conditions. Then, the separated gas phase concentrates in the centre of the diktytaxitic voids while the liquid phase is abruptly oversaturated with respect to apatite and Fe-rich clay minerals (Fig. 2d). It is to be noticed that these small-size mineral assemblages constituting the mesostasis are not formed through the alteration of a glassy precursor (Mas et al. 2008; Meunier et al. 2008). The proportion of mesostasis varies from 10 to 20 % (surface area % in thin sections) according to the type of volcanic body: dyke or submarine-subaerial lava flows respectively.

Polygonal columnar fractures have been observed in the internal architecture of komatiite lavas in spite of metamorphic transformations (Arndt et al. 2008). Columnar joints are opened after total solidification of basalt lava flows (<980°C). The opening of fractures triggers the ebullition of the residual solutions which are expelled to the atmosphere as gas. These solutions and gas are oxidizing and slightly acidic. Before boiling, the solutions interact with the columnar surfaces as the joint propagates inside the lava body. This “auto-alteration” process is marked by the formation of secondary mineral deposits sealing the joints. The basaltic flows of the Parana basin (Gonçalves et al. 1990) exhibit intercolumnar deposits formed of two Fe,Mg-rich clays (saponite, celadonite) + cristobalite + Ca-zeolites sequences sealed by portlandite. The presence of Ca-zeolites ± portlandite indicates that the pH conditions become alkaline during alteration (pH>9).

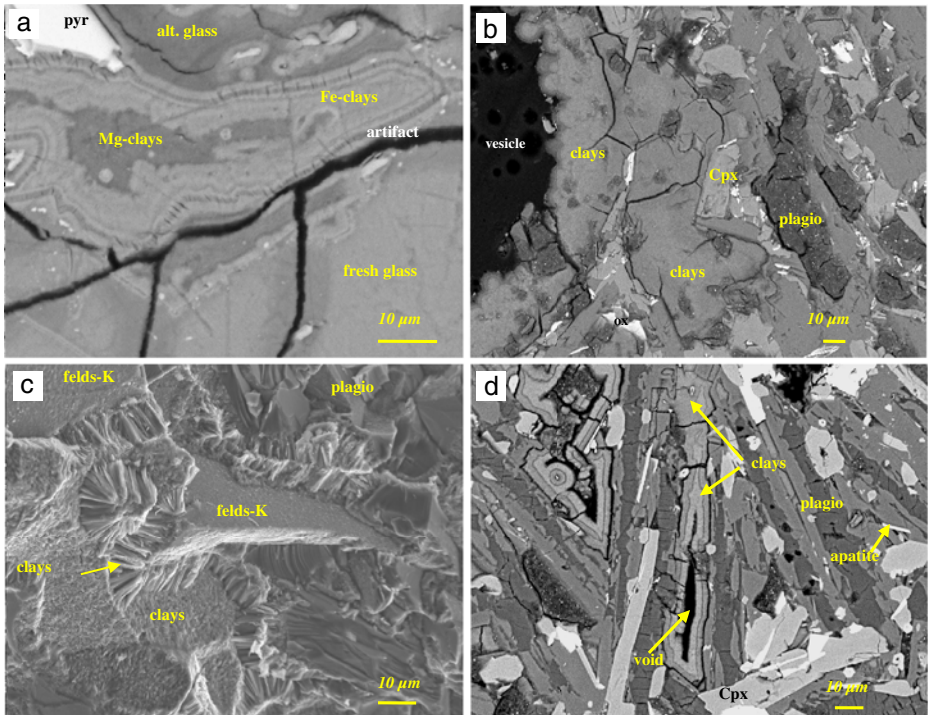


Fig. 2 SEM images (BS: backscattered electrons; SE: secondary electrons) of clay deposits in different volcanic bodies forming a basalt-hawaiite series from Mururoa sea mount, French Polynesia (Mas 2000). **a** Fe- and Mg-clay rims on the wallrocks of fractures in the glassy chilled margin of a submarine lava flow (BS). **b** Fe-Mg clays in vesicle and connected diktytaxitic voids in the inner crystallized body of a submarine lava flow (BS). **c** Palissadic texture of clay crystals in a diktytaxitic void from a subaerial lava flow (SE). **d** Clay rims deposited on the edges of diktytaxitic voids in a dyke during a post-magmatic stage (BS)

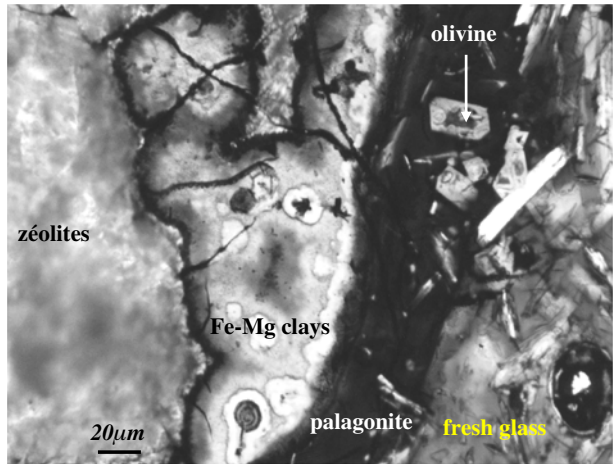
Properties of the Clay-Rich Surfaces Exposed to Solutions

Assuming that all sections of lava inner crystallized parts in the komatiite-basalt suite have a distribution of mesostasis micro-settings similar to that observed in the Mururoa seamount, one can roughly estimate a density of reactive sites per square meter. The average size of mesostasis micro-settings can be represented by a square of 50 µm side. According to Mas et al. (2008), there are about 50 to 100 sites observable on a single thin section of Mururoa basalt (30×40 mm). In other words, 8×10^4 to 16×10^4 clay micro-

Table 1 Clay mineral assemblages forming the mesostasis of the massive crystallized inner parts of Fe-rich basalt-hawaiite lavas in Mururoa atoll, French Polynesia (Mas et al. 2008). Sap/Chl, No/Chl, Cel/Chl, Cel/No: mixed layer minerals composed of saponite (Sap), nontronite (No), chlorite (Chl) or celadonite (Cel) layers

Volcanic body	Chilled margins	Massive parts
Sub-aerial hawaiite	Saponite + nontronite	Sap + Sap/Chl + Ce
Submarine basalt	Sap/Chl + No/Chl + Chl	Sap/Chl + No/Chl + Ce
Dyke hawaiite	Nontronite + Celadonite + Cel/Chl	Nontronite + Cel/No + Saponite

Fig. 3 Example of sea weathering of the chilled margins of a submarine flow from Mururoa Atoll (thin section observed in plane light; Mas 2000). The volcanic glass is altered (palagonite) along the solid surfaces in contact with sea water (fractures and open vesicles). The voids are sealed by zoned secondary mineral deposits. Fe,Mg-clays rim the altered surfaces; the centre of the void being sealed by zeolites



settings per square meter are outcropping on any surface crosscutting the crystallized inner parts of the basalt lava bodies. This means that any fault or fracture could expose myriads of clay micro-settings to ocean water during the Hadean.

Hellmuth et al. (1993) using ^{14}C -doped resin showed that basalts are impregnated a few millimetres depth from the surface of injection. This experiment demonstrates that the pores are 3D-connected and form a tortuous pathway network inside the massive rock. Because the pores are mostly concentrated in the clay micro-settings, one can deduce that the mesostasis micro-settings are 3D connected in basalts. In other words, each mesostasis microsite in contact with ocean water or solutions is a “door” opening the way of any solution to a complex network of clay-rich structures inside the basalt. This property enhances the chemical exchanges between solution and rocks. The effect is multiplied by the columnar joints which, when opened, expose a large surface of the lava bodies to solutions. Besides, they are themselves covered by Fe,Mg-clays similar to that forming the mesostasis.

Clay Minerals Formed from Weathering of Komatiite-Basalt Rocks

Atmospheric Weathering

Today, the weathering of mafic-ultramafic rocks is controlled by local chemical micro-systems in which kinetically controlled water-mineral interactions lead to the crystallization of a series of Mg- and Fe^{3+} -rich clay minerals (Velde and Meunier 2008 and references therein). The magmatic minerals (olivine, pyroxene) and their metamorphic products (serpentine) react with meteoritic water and are transformed first into trioctahedral species such as talc, kerolite or stevensite-saponite. With increasing weathering intensity, these secondary products are themselves destabilized giving dioctahedral Fe-rich clays (nontronite). Is this process comparable to Hadean atmospheric weathering? Because of the lack of oxygen in the atmosphere, the Fe ions should be mainly in the ferrous state. However, nontronite has been identified on Mars surface (Poulet et al. 2005) and was shown to form under non-oxidizing atmospheric conditions using thermodynamic simulations (Chevrier

et al. 2007). If we still ignore how the Hadean atmosphere interacted with the komatiite-basalt crust, we can infer that the global effect was limited by the small surfaces and the short persistence of newly emerged crust.

Sea Weathering

Presently, two types of basalt sea weathering are dominant: 1 – the formation of palagonite during quenching of lavas flowing under water; 2 – the formation of a black halo in low temperature conditions. Palagonite is a mixture of altered glass with embryos of clay minerals (Juteau et al. 1979; Staudigel and Hart 1983; Thorseth et al. 1991). In some cases, this weathering process has been shown to be linked to microbial activity (Furnes et al. 2004; Staudigel et al. 1995, 2006). The fresh glass to palagonite transformation leads first to the deposition of Fe- and Mg-rich clay rimming the dissolved fracture wallrocks (Fig. 3). The middlepart of the void is sealed by zeolites (Mas 2000). The weathering profile from surface to unaltered massive rock is schematically represented in Fig. 4.

During the Hadean, oceans were more voluminous than today and covered the major part of the Earth's surface (Arndt 1999). Thus, the sea weathering processes of the chilled and brecciated margins of basalt and komatiite pillow lavas or flows was probably one of

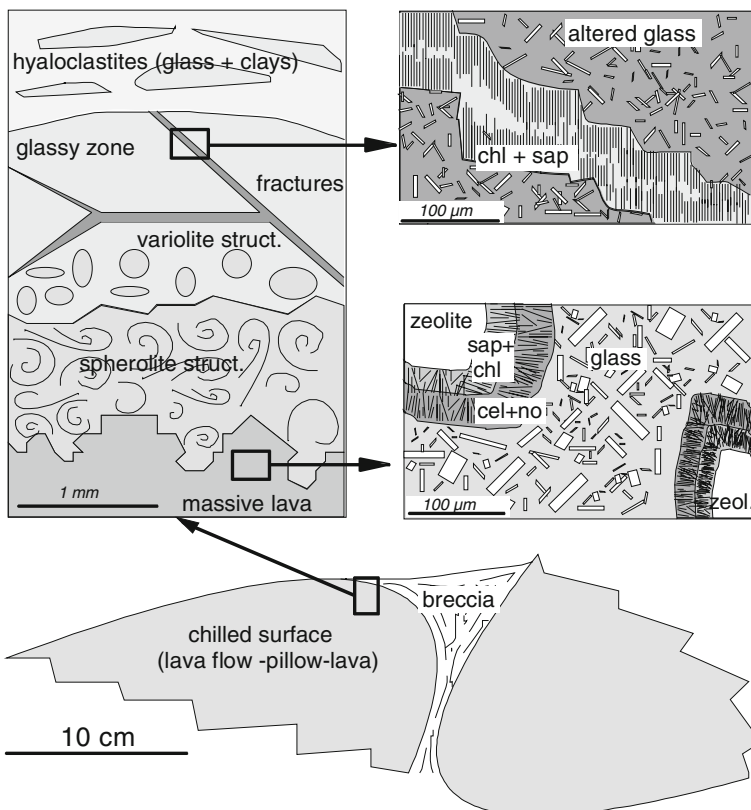


Fig. 4 Simplified representation of a sea weathering profile of pillow lavas (from Juteau et al. 1979 and Meunier 2005). The rock interfaces with sea water (surface and fractures of pillow lavas) are punctuated by innumerable clay-rich micro-settings

the major processes forming clay minerals. Even if seawater was probably different from today: higher temperature, slightly acidic (pH 5-6) and dissolved iron concentration approaching 100 ppm (Macleod et al. 1994), it is probable that mineral reactions accompanying palagonite formations were not different since they are buffered by the rock composition. According to Arndt et al. (1977, 2008), the surface of komatiite lavas is ordinarily vitreous and brecciated (Fig. 1). Interactions with ocean water during the quenching stage probably produced a palagonite-like crust in which Fe-Mg clay minerals were formed.

Low-temperature sea water weathering mostly refers today to interactions between totally cooled basalts and sea water (<4°C). It forms a black halo on the rock surfaces in contact with sea water, either on those surfaces not coated with sediments or on the walls of open fractures in the ocean floor (Andrews 1977; Alt and Honnorez 1984). The development of black halos is a function of the basalt age. Poorly crystalline clay minerals whose chemical composition varies between that of nontronite and celadonite are formed. The chemical balance of exchanges in the rock shows an enrichment of K and H₂O and a depletion of Si, Mg, and Ca (Thompson 1973). During the Hadean, such a low-temperature weathering process was not active for periods long enough to produce clay minerals in comparable quantities relative to the other alteration or post-magmatic processes. Indeed, the ocean water was frequently heated to boiling by large impacts and quickly heated when it was circulated in fracture networks induced by the shocks (Cockell 2006). Schoonen et al. (2004) showed through geochemical simulations of komatiite weathering ($P_{\text{CO}_2} = 5 \text{ atm}$, $T = 75^\circ\text{C}$, isolated system) that Mg-rich clay minerals form first and in dominating quantities. They form also from TTG weathering, but in lower quantities.

Clay Minerals Formed Through Hydrothermal Alteration of Komatiite-Basalt Rocks

No remains of Hadean – early Archean hydrothermal vents have been discovered. Consequently, their potential effects on the origin of life must be researched in modern analogues. The reaction of peridotite-serpentine rocks with sea water has been considered to be the best analogue of early Earth alteration processes (see Russell et al. 2005 and references therein). Even by the late Archean, hydrothermal activity is estimated to have been three times that of the present day (Isley and Abbott 1999). However, contrary to present conditions, the marine sulphate was negligible in the Hadean ocean (Farquhar et al. 2000) making impossible the formation of anhydrite protected chimneys (black smokers). This is why Russell and Arndt (2005) suggested that the alteration analogue of the peridotite-serpentine rocks should be researched in present-day low-temperature (85–115°C) alkaline hydrothermal vents. They suggested that the vents observed in the Lost City hydrothermal field (Kelley et al. 2001) and the Eyjafjördur region (Geptner et al. 2002) could be adequate candidates. Their opinion is reinforced by the fact that both sites are characterized by an intense microbial activity today (Kelley et al. 2001; Geptner et al. 2002).

The secondary mineral assemblages formed in the low-temperature alkaline hydrothermal vents are calcite-aragonite-brucite or saponite-calcite (Kelley et al. 2001). In both cases, the hydroxide and phyllosilicate phases are practically Mg-pure trioctahedral phases (Williams et al. 2005). The predominance of these magnesian phases in active hydrothermal systems is due to the fact that, when mixed with sea water, the solutions are iron depleted by the precipitation of sulphides or oxy-hydroxides. According to Macleod et al. (1994), this was not the case during the Hadean – early Archean period because the dissolved iron concentration in the ocean water was much higher than today (about 100 ppm versus

0.06 ppm). Besides, komatiites contain high amounts of FeO (10–12%) and other transition metals. Consequently, it is probable that the clay minerals formed in the low temperature hydrothermal vents were not Mg pure phases but exhibited a rather more variable composition between the Fe²⁺ and Mg end-members and included Ni²⁺, Co²⁺ and Cu²⁺ ions in their exchangeable interlayer sites.

Stratified hot brine basins have been discovered in the Red Sea (Hartmann 1980). These brines are alkaline and the temperature conditions vary from 40 to 60°C. The basaltic-ophiolitic floor is covered with metallic ore and clay deposits. Magnesian clays form from volcanic debris while Fe-rich ones are observed as overgrowth on detrital phyllosilicates. Ferric clays are associated with silicates (hisingerite) and more or less amorphous Fe-bearing oxy-hydroxides (ferrihydrite, ferroxlyite, hematite). Ferrous smectitic clays (Fe²⁺-stevensite) are associated with sulphides and contain small amounts of Cu and Zn (Badaut et al. 1985, 1992).

Crystal-Chemical Properties of the Fe-Rich Smectites

Metal Ion Sites in the Crystal-Chemical Structure of Smectites

The phyllosilicates are composed of two principal mineral families having distinct crystal structures: 1:1 minerals (octahedral sheet linked to one tetrahedral sheet); 2:1 minerals (octahedral sheet enclosed by two tetrahedral ones). The smectites belong to the 2:1 family. They exhibit an additional sheet (interlayer) formed of exchangeable cations whose positive charge compensates the negative one of the 2:1 layer. This particular structure gives smectites two fundamental properties enhancing the interactions with local environment: cation exchange capacity and hydration-dehydration. The chemical composition of smectites varies in large solid solutions either in the dioctahedral or trioctahedral species (see Appendix 1 for unit formulae). Ionic substitutions in the tetrahedral and octahedral sheets involve metallic tri- and divalent cations (Al³⁺, Fe³⁺, Fe²⁺, Mg²⁺, Cu²⁺, Ni²⁺, Co²⁺ ...). The substitutions generate local electric charge or crystal defects (clustering) which locally modify the energetic configuration of the 2:1 layer (Fig. 5). These sites contribute with the unsatisfied chemical bonds at the edges of the crystallite to the adsorption and polymerization of organic or inorganic compounds present in the solutions.

The adsorption capacity of metallic ions by clays is an important property for the catalysis of organic molecules. It is controlled by the amphoteric site density of the 2:1 layers including edges and exchangeable sites (Jaisi et al. 2008). The uptake of metal ions such as Ni, Co, Zn has been shown to form metal precipitates even in under-saturated conditions with respect to their pure oxy-hydroxides (Scheidegger et al. 1998; Thompson et al. 1999; Schlegel et al. 2001). Furthermore, Schlegel et al. (1999) and Dähn et al. (2003) reported the first direct structural evidence for the formation of monomeric inner-sphere surface metallic complexes on the layer edges of trioctahedral and dioctahedral smectitic clays, respectively. At higher metal loadings, Dähn et al. (2001, 2006) observed the neoformation of a Ni phyllosilicate. These experiments are to be compared with the formation of hydroxyl-interlayer minerals (HIMs) in soils evolving today in natural conditions (Meunier 2007). The polymerization of Al(OH)₃ and /or Fe(OH)₃ produces discontinuous “brucite-like” sheets in the interlayers of expandable clay minerals (Fig. 6a). Then, the thickness of HIM layers being identical to that of chlorites ($d_{001}=14.2$ Å), the adsorbed organic molecules such as ethylene-glycol, alkyl-ammonium or amino-acids form a single sheet in the interlayer space (Lagaly and Weiss 1970; Rausell-Colom and Salvador

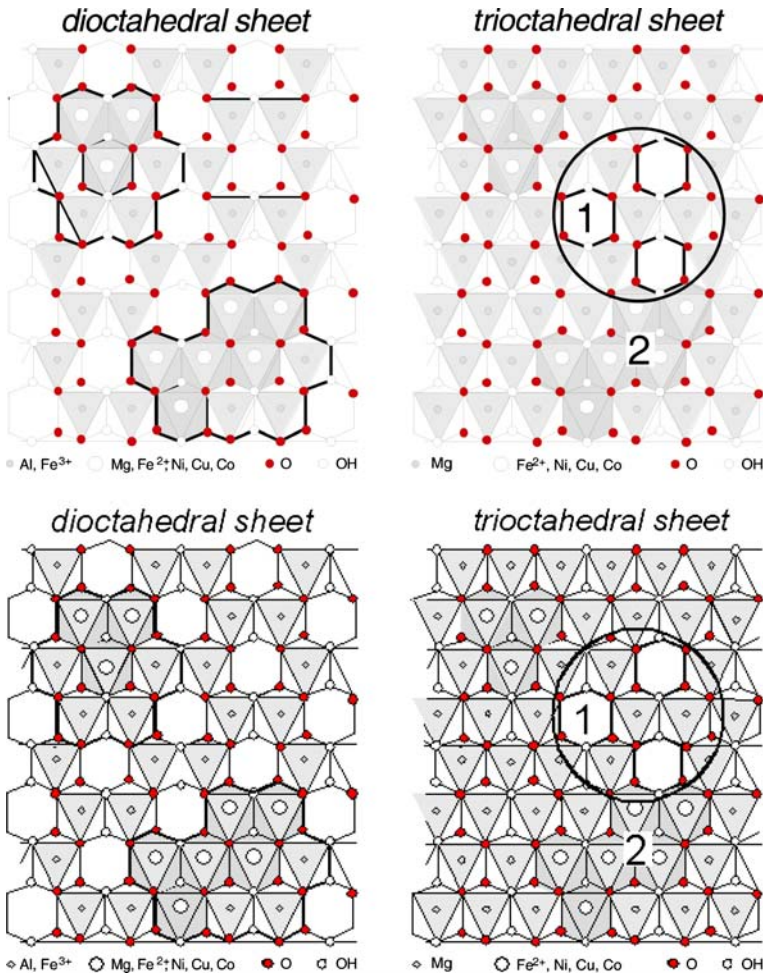


Fig. 5 Schematic representation of clusters and domains in the octahedral sheet of Mg-Fe clays. Dioctahedral sheet: trioctahedral domains are formed by replacement of the vacant site by bivalent cations (bold lines: clusters of bivalent cations); trioctahedral sheet: (1) dioctahedral domains are formed by replacement of divalent cations by a vacant site; (2) trioctahedral clusters of Fe, Ni, Cu, Co are formed by replacement of Mg cations

1971; Violante et al. 1995). The natural HIMs forming in soils are dioctahedral (Al, Fe³⁺) because of pH and oxygen fugacity conditions prevailing today. Because the “brucite-like” sheet is discontinuous, it creates tortuous pathways for the dissolved compounds to enter inside the interlayer zone (Fig. 6b). This increases the contact surfaces with the metal-hydroxide chains inside the interlayer zone whose electro-chemical properties are now explored using molecular dynamics (Cygan et al. 2009).

Taking into account the reducing and acidic conditions prevailing during Hadean, it is to be expected that equivalents of HIMs could also be formed but in the Mg-rich trioctahedral (saponite-stevensite) or the Fe-dioctahedral (nontronite-Fe montmorillonite) series rather than in the Al-rich one. The presence of divalent metal cations ($R^{2+} = \text{Mg, Fe}^{2+}, \text{Ni, Cu, Co}$) in basalt-komatiite rocks and ocean water favours their integration within the Mg- and

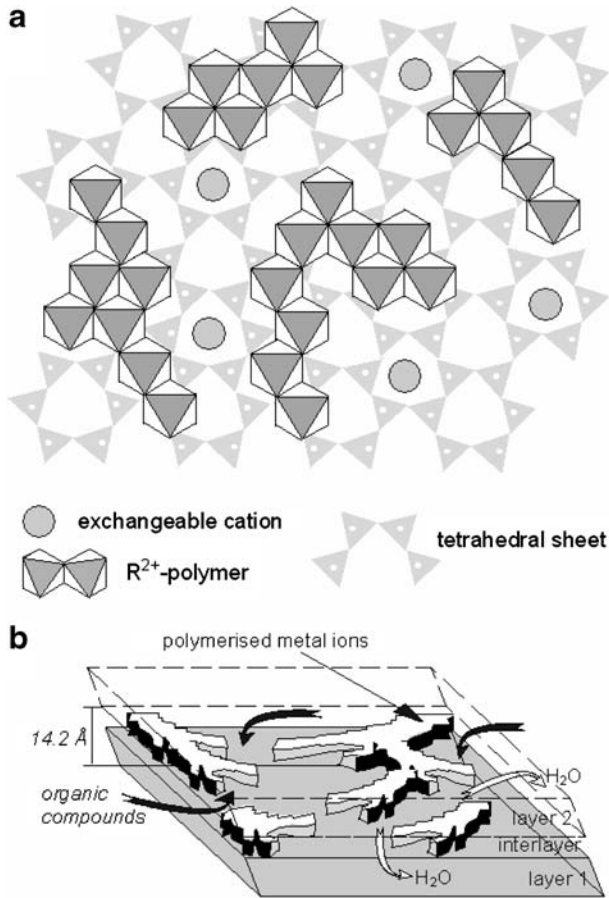


Fig. 6 Schematic representation of Hydroxy-Interlayer Minerals (HIMs). **a** Formation of polymerized “islands” or chains of metal cations in the interlayer of expandable clay minerals (from Meunier 2007). **b** Adsorption of organic compounds and expelling of water molecules

Fe-bearing clay minerals, either as adsorbed species or/and as structural elements. The adsorption of $R^{2+}(\text{OH})_2$ components partially saturates the exchangeable or edge sites. Then they polymerize, forming “islands” and chains of R^{2+} polymers whose structure is similar to that of HIMs formed in soils today.

The Crystal Structure of Fe-Rich Clay Minerals

The Fe-rich clay minerals and specifically the smectite species have an additional chemical property. Because the valency of iron can easily change in Earth’s surface conditions, these minerals are potential electron exchangers. Iron may be incorporated in both the octahedral, tetrahedral or interlayer sheets of smectites in the Fe^{2+} or Fe^{3+} oxidation states (Köster et al. 1999). Most often, Fe^{3+} is incorporated in dioctahedral smectites where it replaces Al^{3+} ones (homovalent substitution). However, this is not a rule since Fe^{2+} cations can be incorporated into the octahedral sheet of Al-rich smectites (Lajarige et al. 1998). Conversely, Fe^{3+} cations can be incorporated in trioctahedral smectites where they replace

bivalent ones (mostly Mg^{2+}). The heterovalent substitution generates the formation of vacancies in the octahedral sheet.

Experimental syntheses conducted under atmospheric conditions in the Si-Al-Fe-Mg-Na-H₂O system at pH 9-10 (200°C) show that an apparent continuous solid solution exists between the dioctahedral (beideillitic) and trioctahedral (saponitic) smectite end-members (Grauby et al. 1993, 1994). The runs having intermediate stoichiometric composition triggered the clustering of Mg^{2+} divalent ions and local dioctahedral (Al-Fe³⁺) or trioctahedral structures formed within single layers (Fig. 5). In natural systems, it seems that no solid solution between the di- and trioctahedral smectite end members exists. Table 2 summarizes the occurrences of the different Fe-Mg clay species in the principal geological sites offered by modern analogues. Segregation is commonly observed in trioctahedral Fe³⁺-Mg-Ni smectites where Fe³⁺-Al ions on one hand, and Mg^{2+} -Ni²⁺ ones on the other hand generally form di- and trioctahedral layers (Decarreau et al. 1987; Manceau 1990; Vieira Coelho et al. 2000; Gaudin et al. 2004).

The apparent contradiction between experimental results and observation of natural samples is due to the kinetics of the crystallization process. Indeed, experiments enhance the properties of nanoscale particles (formed quickly after hours, weeks or months) while in natural systems macroscopic crystals form after years or tens of years or more of slow crystal growth. Because energy minimization drives the number of crystal defects to decrease, the long-term process leads to a separation between di- and trioctahedral species. However, this separation is never perfect. Natural clay crystals exhibit lattice defects such as local clusters, vacant sites, interlayer composition heterogeneities, etc, which limit their growth (Meunier 2006).

The Catalytic Properties of Metal-Rich Clays

The polymerization reaction of prebiotic molecules was shown to be thermodynamically out of equilibrium in aqueous solution while it becomes possible when the organics are adsorbed on mineral surfaces (Lambert 2008). To be efficient templates, these minerals must have the following properties: (i) capacity for adsorption of organic molecules; (ii) capacity to concentrate the adsorbed molecules; (iii) ability to activate the polymerization process. From that point of view, the interlayers of expandable clay minerals are remarkably well adapted because of their cation exchange capacity, hydration properties and their local charge heterogeneities due to cation substitutions, crystal defects, clustering, etc (Cairns-Smith 1982; Brack 2006 and references therein). The dehydration of interlayer regions, *de facto*, concentrates the adsorbed species and favours their polymerization. Indeed, because at equilibrium, the polymerization reaction produces water, decreasing water activity automat-

Table 2 Natural occurrences of Mg-Fe clays in basaltic formations

Geological environment	Clay species	References
white smoker chimney	nontronite	Kohler et al. 1994
basalt – tuff	nontronite	Koster et al. 1999
Peridotite, Ferricrete	Fe-montmorillonite	
basalt – volcanic sediments	Fe-saponite	Desprairies et al. 1989 Parthasarathy et al. 2003
hydrothermal brines	Fe-stevensite	Badaut et al. 1985

ically increases polymer/monomer ratio. The dehydration of smectite interlayer zones can be triggered by three different phenomena: 1) temperature increase (drying); 2) migration of water molecules activated by chemical potential gradient between clay particles and solutions (Kozaki et al. 2008); 3) replacement of hydrated interlayer cations by non-hydrated ones (Ransom and Helgeson 1994).

The catalytic properties of clay minerals depend on the natural acid sites found in their crystal structure:

- tetrahedral substitutions form acid sites in the interlayer region by neutralisation of the resulting negative charge with protons or metallic cations,
- negative charges induced by unsatisfied chemical bonds at the edges of the octahedral sheet when neutralised by metal cations. A Brønsted acidity is due to the polarisation of the cation hydration shell,
- interlayer metal cations acting directly as Lewis acids.

Because organics are mainly adsorbed in the interlayer region of smectites compared to crystal edges and outer surfaces, they are considered to be responsible of their catalytic properties. Numerous experiments have been conducted on Cu-exchanged saponites (Fu et al. 1996; Szilagyi et al. 2005; Serefoglou et al. 2008 among others). They show that clay minerals adsorb more organic molecules when the interlayer region is saturated by metal cations (Franchi et al. 2003). The particular physical configuration of HIM interlayer increases the contact surfaces of adsorbed organics with metal hydroxides. This could have a positive kinetic effect on prebiotic reactions whose rate has been shown to increase with the contact surfaces (Schoonen et al. 2004).

The chemical reactions involving electron transfer are particularly efficient in the presence of Fe^{2+} -bearing clay minerals (Wang 1991; Parthasarathy et al. 2003). Iron-containing clay minerals are ubiquitously present in subsurface environments and structural Fe^{2+} can be formed from microbial Fe^{3+} reduction. Smectites (reduced nontronite and Fe-montmorillonite) have been largely studied for their degradation potential of organic contaminants (Stucki 2006). In contrast to ferric oxides and oxy-hydroxides, Fe^{3+} in clay minerals is less susceptible to reductive dissolution. Clays provides a renewable source of reduction equivalents. Under anoxic conditions, structural iron is reduced and Fe^{2+} can be incorporated in the interlayer region by ion exchange and as pH-dependent complexes on edge surface hydroxyl groups, as observed for other metallic elements. Hofstetter et al. (2003, 2006) showed that structural Fe^{2+} as well as Fe^{2+} complexed by surface hydroxyl groups contributed more significantly to contaminant transformation than interlayer Fe^{2+} ions do.

Conclusion

The idea we have of the date when life first emerged on the Earth varies with the process thought to be at the origin of the catalysis of prebiotic molecules. Since the Darwin's "warm little pond", numerous theories have been published. Among the recent ones, some have encountered some success. Parsons et al. (1998) considered that altered feldspar surfaces are the clue: life emerged when granites have been sufficiently abundant in the continent embryos, i.e., after 3.8 Ga. On the contrary, for Russell and Hall (1997), life emerged at redox and pH fronts between alkaline hydrothermal solutions and the Hadean sea water. Such hydrothermal systems may have been active on Earth much earlier (4.2 Ga). Because asteroid and comet bombardment was intense during Hadean, Cockell (2006) relates the emergence of life to impact craters. Nisbet and Sleep (2001) summarized the quest of the origins through one

question: “Where was Eden?” In spite of their elegance, the theories commonly accepted lead to a conflict with irreducible conditions for the emergence of life on Earth:

- compatibility with the Hadean geological conditions: granitoids were very rare. The young Earth was almost completely covered by komatiite-basalt lavas.
- numerous geological micro-settings scattered on the most part of the Earth’s crust rather than exceptional ones (the warm little pond) are required to statistically increase the probability of success of the catalytic reactions at temperatures lower than 40°C.

The question is not “Where was Eden?” but rather “Was Eden necessary”? Contrarily to the opinion of Nisbet and Sleep (2001), to have a chance to survive a hostile Earth, prebiotic molecules would have to be formed in great quantities and continuously from reactive areas as large as possible. The efficiency of chemical reactions leading to the synthesis of prebiotic molecules is statistically low because a great number of conditions have to be satisfied simultaneously (Shapiro 2007). To be successful, these reactions have to be repeated in a huge number of reactive sites for long periods of time. This is offered by the specific geology of the Earth crust during the Hadean to early Archean period. Indeed, the crust was almost exclusively composed of komatiite-basalt lavas and the major part of the surface of the young Earth was submerged by the first oceans (Fig. 7). Thus, myriads of reactive clay micro-settings (tens of micrometers wide) offered the conditions for chemical exchange, adsorption and concentration for organics dissolved in the ocean water. Because the clays forming in komatiite-basalt rocks were Fe-rich and included other transition metals, their catalytic properties were enhanced by their ability to transfer electrons. When formed during a post-magmatic stage, these clays are associated with phosphates. Phosphorus is a fundamental element for biological molecules and specifically RNA. This leads us to consider the surface of the early Earth as a giant chemical reactor. If

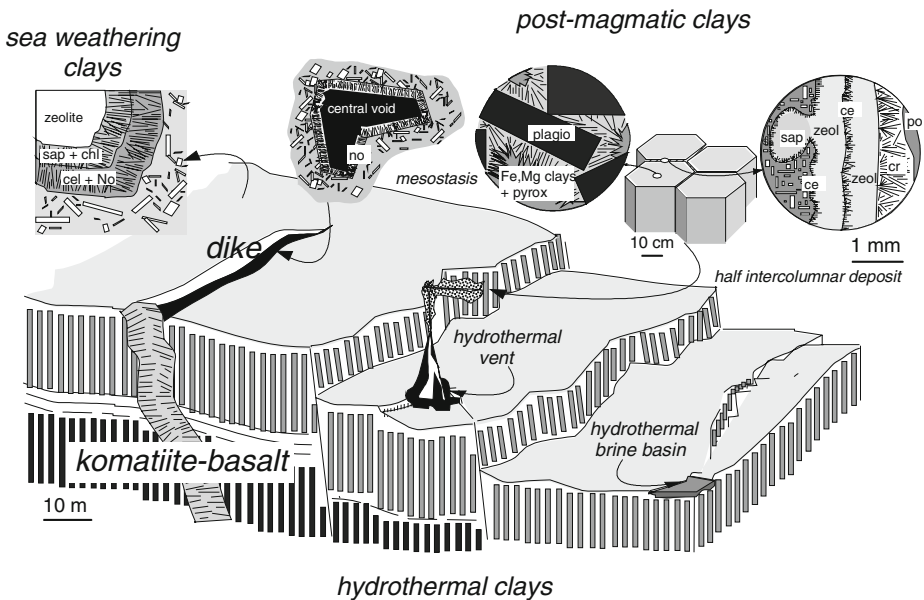


Fig. 7 Schematic representation of the distribution of Fe, Mg clay-rich micro-settings in the basalt-komatiite crust in contact with the Hadean ocean

true, then, the synthesis of prebiotic molecules was highly probable and did not result from a “miracle”. From that point of view, the Earth should not be considered as an exceptional planet. Similar conditions may have existed or still exist in other planets or satellites in our solar system or in others. The way to check this hypothesis could be to explore in detail the nontronite-rich areas discovered on several regions of the Mars southern hemisphere (Poulet et al. 2005). Because they were detected on the basaltic formations, these sites could be the best analogues we could have of the Hadean terrestrial crust.

As far as the authors are aware, the reactivity of Fe-rich clays and particularly Fe²⁺ bearing smectites has not been deeply studied up to now with the aim of synthesizing prebiotic molecules. Most of the experimental works devoted to the synthesis of complex organic molecules such as DNA or RNA, were undertaken using iron poor smectites. It is clear that the effort devoted to the experimental synthesis of prebiotic molecules should be now focused on the catalytic potentiality of the Fe-rich clays rather than on Al-montmorillonite. Because Hadean terrestrial conditions were so different from the present ones, the study should be based on Fe-rich clays experimentally synthesized in controlled chemical and physical environments. It is obvious that the effort should be sustained by chemists and geologists since the catalytic efficiency does not depend only on the crystal chemical properties of these smectites but also on their texture and petrophysical properties which rule their accessibility to solutions.

Acknowledgements This study was supported by the University of Poitiers and the Institut des Sciences de la Terre et de l’Univers du Centre National de la Recherche Scientifique (INSU-CNRS).

Appendix 1

Clay species	Unit formula	Electrical charge
Kaolinite	Si ₂ O ₅ Al ₂ (OH) ₄	x=0 ; y=0
Serpentine	Si ₂ O ₅ (Fe ²⁺ , Mg) ₃ (OH) ₄	x=0 ; y=0
Talc	Si ₄ O ₁₀ Mg ₃ (OH) ₂	x=0 ; y=0
Celadonite	Si ₄ O ₁₀ [(Al, Fe ³⁺) (Fe ²⁺ , Mg)] (OH) ₂ K	x+y=−1.0; IC=+1.0
Beidellite	[Si _{4-x} Al _x] O ₁₀ (Al, Fe ³⁺) ₂ (OH) ₂ K _x	−0.3<x<−0.6; y=0; +0.3<IC<+0.6
Montmorillonite	Si ₄ O ₁₀ [(Al, Fe _{2-y} ³⁺) Mg _y] (OH) ₂ K _y	x=0; −0.3<y<−0.6; +0.3<IC<+0.6
Saponite	[Si _{4-x} Al _x] O ₁₀ [(Fe ²⁺ , Mg) _{3-y-z} , (Al, Fe ³⁺) _y , □ _z] (OH) ₂ K _{x+y-2z}	−0.3<x<−0.6; y+2z=0; +0.3<IC<+0.6
Stevensite	Si ₄ O ₁₀ [(Fe ²⁺ , Mg) _{3-y-z} , (Al, Fe ³⁺) _y , □ _z] (OH) ₂ K _{x+y-2z}	x=0; 0.3<y+2z<−0.6; +0.3<IC<+0.6
Chlorite	[Si _{4-x} Al _x] O ₁₀ [(Fe ²⁺ , Mg) _{3-y-z} , (Al, Fe ³⁺) _y , □ _z] (OH) ₂ AlMg ₂ (OH) ₆	−0.3<x<−1.0; 0<y+2z<−0.7; IC≅+1.0

Chemical composition of the half unit cell of some phyllosilicates. x : Si for R³⁺ substitution in the tetrahedral sheet ; y : R²⁺ for R³⁺ substitutions in the octahedral sheet ; z : number of octahedral vacancies (□) : IC : electrical charge of the interlayer cations.

References

- Alt JC, Honnorez J (1984) Alteration of the upper oceanic crust DSDP Site 417: mineralogy and chemistry. *Contrib Mineral Petrol* 87:149–169
- Amelin Y (2005) A tale of early Earth told by zircons. *Science* 310:1914–1915
- Andrews AJ (1977) Low temperature fluid alteration of oceanic Layer 2 basalts. *Can J Earth Sci* 14:911–926
- Armstrong RL (1991) The persistent myth of crustal growth. *Aust J Earth Sci* 38:613–630
- Arndt NT (1999) Why was flood volcanism on submerged continental platforms so common in the Precambrian? *Precambrian Res* 97:155–164
- Arndt NT, Naldrett AJ, Pyke DR (1977) Komatiitic and Iron-rich tholeiitic lavas of Munro Township, Northeast Ontario. *J Petrol* 18:319–369
- Arndt NT, Leshner CM, Barnes SJ (2008) Komatiite. Cambridge Univ. Press
- Badaut D, Besson G, Decarreau A, Rautureau R (1985) Occurrence of a ferrous trioctahedral smectite in recent sediments of Atlantis II Deep Red Sea. *Clay Miner* 20:389–404
- Badaut D, Decarreau A, Besson G (1992) Ferripyrophyllite and related Fe³⁺ - rich 2:1 clays in recent deposits of Atlantis II Deep, Red Sea. *Clay Miner* 27:227–244
- Banin A, Lawless JG, Mazzurco J, Church FM, Margulies L, Orenberg JB (1985) pH profile of the adsorption of nucleotides onto montmorillonite. *Orig Life Evol Biosph* 15:89–101
- Beresford SW, Cas RAF, Lambert DD, Stone WE (2000) Vesicles in thick komatiite lava flows, Kambalda, Western Australia. *J Geol Soc London* 157:11–14
- Beresford SW, Cas R, Lahaye Y, Jane M (2002) Facies architecture of an Archean komatiite-hosted Ni-sulphide ore deposit, Victor, Kambalda, Western Australia: implication for komatiite lava emplacement. *J Volc Geoth Res* 118:57–75
- Bernal JD (1951) *The physical basis of life*. Routledge and Kegan Paul, London
- Brack A (1976) Polymérisation en phase aqueuse d'acides aminés sur des argiles. *Clay Miner* 11:117–120
- Brack A (2006) Clay minerals and the origin of life. In: Bergaya F, Theng BKG, Lagaly G (eds) *Handbook of Clay Science*. Elsevier, Developments in Clay Science
- Cairns-Smith AG (1982) Genetic takeover and the origin of life. Cambridge Univ. Press
- Canfield DE (1998) A new model for Proterozoic ocean chemistry. *Nature* 396:450–453
- Chevrier V, Poulet F, Bibring JP (2007) Early geochemical environment of Mars as determined from thermodynamics of phyllosilicates. *Nature* 448:60–63
- Christidis GE, Huff WD (2009) Geological aspects and genesis of bentonites. *Elements* 5:93–98
- Cockell CS (2006) The origin and emergence of life under impact bombardment. *Phi Trans Royal Soc B* 361:1845–1856
- Coogan LA, Hinton RW (2006) Do the trace element compositions of detrital zircons require Hadean continental crust? *Geology* 34:633–636
- Cygan RT, Greathouse JA, Heinz H, Kalinichev AG (2009) Molecular models and simulations of layered materials. *J Mater Chem* 19:2470–2481
- Dähn R, Scheidegger A, Manceau A, Schlegel M, Baeyens B, Bradbury MH (2001) Ni clay neoformation on montmorillonite surface. *J Synchr Rad* 8:533–535
- Dähn R, Scheidegger AM, Manceau A, Schlegel ML, Baeyens B, Bradbury MH, Chateigner D (2003) Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite clay minerals: a polarized X-ray absorption fine structure study. *Geochim Cosmochim Acta* 67:1–15
- Dähn R, Jullien M, Scheidegger AM, Poinssot C, Baeyens B, Bradbury MH (2006) Identification of neoformed Ni-phyllosilicates upon Ni uptake in montmorillonite: a transmission electron microscopy and extended X-ray absorption fine structure study. *Clays Clay Miner* 54:209–219
- Dann JC (2000) The 3.5 Ga Komati Formation, Barberton Greenstone Belt, South Africa, Part I: new maps and magmatic architecture. *J South Afr Geol* 103:47–68
- Dann JC (2001) Vesicular komatiites, 3.5 Ga Komati Formation, Barberton Greenstone Belt, South Africa: inflation of submarine lavas and origin of spinifex zones. *Bull Volc* 63:462–481
- Davies GF (1992) On the emergence of plate tectonics. *Geology* 20:963–966
- Ddani M, Meunier A, Zahraoui M, Beaufort D, El Wartiti M, Fontaine C, Boukili B, El Mahi M (2005) Clay mineralogy and chemical composition of bentonites from the Gourougou volcanic massif (northeast Morocco). *Clays Clay Miner* 53:250–267
- Decarreau A, Colin F, Herbillon A, Manceau A, Nahon D, Paquet H, Trauth-Badaud D, Trescases JJ (1987) Domain segregation in Ni-Fe-Mg-smectites. *Clays Clay Miner* 35:1–10
- Desprairies A, Tremblay P, Laloy C (1989) Secondary mineral assemblages in a volcanic sequence drilled during ODP Leg 104 in the Norwegian sea. In: Eldholm O, Thiede J, Taylor E, et al. (eds) *Proc ODP Sci Results, College Station TX (Ocean Drilling Program) 104:307–409*

- Echeverria LM (1980) Tertiary or Mesozoic komatiites from Gorgona Island, field relations and geochemistry. *Contrib Mineral Petrol* 73:253–266
- Farquhar J, Bao H, Thiemens MH (2000) Atmospheric influence of Earth's earliest sulphur cycle. *Science* 289:756–758
- Ferris JP (2005) Mineral catalysis and prebiotic synthesis: montmorillonite-catalyzed formation of RNA. *Elements* 1:145–149
- Ferris JP (2006) Montmorillonite-catalysed formation of RNA oligomers: the possible role of catalysis in the origin of life. *Phil Trans Royal Soc B* 361:1777–1786
- Ferris JP, Huang CH, Hagan WJ Jr (1986) Clays as prototypical enzymes for prebiological formation of phosphate esters. *Orig Life Evol Biosph* 17:173–174
- Franchi M, Ferris JP, Gallori E (2003) Cations as mediators of the adsorption of nucleic acids on clay surfaces in prebiotic environments. *Orig Life Evol Biosph* 33:1–16
- Fu L, Weckhuysen BM, Verbeekmoes AA, Schoonheydt RA (1996) Clay intercalated Cu(II) amino acid complexes: synthesis, spectroscopy and catalysis. *Clay Miner* 31:491–500
- Furnes H, Banerjee NR, Muelhenbachs K, Staudigel H, de Wit M (2004) Early life recorded in Archean pillow lavas. *Science* 204:578–581
- Gaudin A, Petit S, Rose J, Martin F, Decarreau A, Noack Y, Borschneck D (2004) The accurate crystal chemistry of ferric smectites from the laterite nickel ore of Murrin Murrin (Western Australia). II. Spectroscopic (IR and EXAFS) approaches. *Clay Miner* 39:453–467
- Geptner A, Kristmannsdottir H, Kristiansson J, Marteinsson V (2002) Biogenic saponite from an active submarine hot spring, Iceland. *Clays Clay Miner* 50:174–185
- Gonçalves NMM, Dudoignon P, Meunier A (1990) The hydrothermal alteration of continental basaltic flows in Northern Parana Basin (Ribeirao Preto, Sao Paulo, Brazil). *Proc. 9th Int. Clay Conf.*, (eds Tardy Y. & Farmer V. C.). Strasbourg, 153–162
- Grauby O, Petit S, Decarreau A, Baronnet A (1993) The beidellite-saponite series: an experimental approach. *Eur J Miner* 5:623–635
- Grauby O, Petit S, Decarreau A, Baronnet A (1994) The nontronite-saponite series: an experimental approach. *Eur J Miner* 6:99–112
- Hartmann M (1980) Atlantis II Deep geothermal brine system. Hydrographic situation in 1977 and changes since 1965. *Deep-Sea Res* 27A:161–171
- Hellmuth KH, Siitari-Kauppi M, Lindberg A (1993) Study of the porosity and migration pathways in crystalline rock by impregnation with ^{14}C -polyméthylmethacrylate. *J Cont Hydr* 13:403–418
- Hofstetter TB, Schwarzenbach RP, Haderlein SB (2003) Reactivity of Fe(II) species associated with clay minerals. *Envir Sci Tech* 37:519–528
- Hofstetter TB, Neumann A, Schwarzenbach RP (2006) Reduction of Nitroaromatic compounds by Fe(II) species associated with iron-rich smectites. *Envir Sci Tech* 40:235–242
- Huff WD (2006) Volcanism and its contribution to mudrock genesis. *Turk J Earth Sci* 15:111–122
- Isley AE, Abbott DH (1999) Plume-related mafic volcanism and the deposition of banded iron formation. *J Geophys Res* 104:15461–15477
- Jaisi DP, Liu C, Dong H, Blake RE, Fein JB (2008) Fe²⁺ sorption onto nontronite (NAU-2). *Geochim Cosmochim Acta* 72:5361–5371
- Juteau T, Noack Y, Whitechurch H (1979) Mineralogy and geochemistry of alteration products in holes 417A and 417D basement samples (Deep Sea Drilling Project LEG 51). In: Donnelly T, Francheteau J, Bryan W, Robinson P, Flower M, Salisbury M (eds) *Initial Reports of the Deep Sea Drilling Project* LI, LII, LIII: 1273–1297
- Kakegawa T, Noda M, Nannri H (2002) Geochemical cycles of bio-essential elements on the early Earth and their relationships to the origin of life. *Res Geol* 52:83–89
- Kelley DS, Karson JA, Blackman DK, Frü-Green GL, Butterfield DA, Lilley MD, Olson EJ, Schrenk MO, Roe KK, Lebonk GT, Rivizzigno P, the AT3-60 Shipboard Party (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30° N. *Nature* 412:145–149
- Kohler B, Singer A, Stoffers P (1994) Biogenic nontronite from marine white smoker chimneys. *Clays Clay Miner* 42:689–701
- Köster HM, Ehrlicher U, Gilg HA, Jordan R, Murad E, Onnich K (1999) Mineralogical and chemical characteristics of five nontronites and Fe-rich smectites. *Clay Miner* 34:579–599
- Kozaki T, Jinhong L, Sato S (2008) Diffusion mechanism of sodium ions in compacted montmorillonite under different NaCl concentrations. *Phys Chem Earth* 33:957–961
- Lagaly G, Weiss A (1970) Inhomogeneous charge distribution in mica-type layer silicates. *Proceed Reunion Hispano-Belga Minerales de la Arcilla, Madrid*, pp 179–187
- Lahav N (1994) Minerals and the origin of life – hypotheses and experiments in heterogeneous chemistry. *Heter Chem Rev* 1:159–179

- Lajarige C, Petit S, Augas C, Decarreau A (1998) Stabilisation d'ions Fe²⁺ dans le réseau de smectites ferrifères de synthèse. *C R Acad Sci Paris* 327:789–794
- Lambert JF (2008) Adsorption and polymerization of amino acids on mineral surfaces: a review. *Orig Life Evol Biosph* 38:211–242
- Macleod G, McKeown C, Hall AJ, Russell MJ (1994) Hydrothermal and oceanic pH conditions of possible relevance to the origin of life. *Orig Life Evol Biosph* 24:19–41
- Manceau A (1990) Distribution of cations among the octahedral of phyllosilicates: insight from EXAFS. *Can Miner* 28:321–328
- Mas A (2000) Etude pétrographique et minéralogique des mésostases d'unités basaltiques et hawaïiennes de l'Atoll de Mururoa (Polynésie Française). Origine des phyllosilicates en présence. Ph. D. thesis, Poitiers univ
- Mas A, Meunier A, Beaufort D, Patrier P, Dudoignon P (2008) Clay Minerals in basalt-hawaïite rocks from Mururoa atoll (French Polynesia). I. Mineralogy. *Clays Clay Miner* 56:711–729
- Meunier A (2005) *Clays*. Springer-Verlag, Berlin
- Meunier A (2006) Why are clay minerals small? *Clay Miner* 41:551–566
- Meunier A (2007) Soil hydroxyl-interlayered minerals: a re-interpretation of their crystallochemical properties. *Clays Clay Miner* 55:380–388
- Meunier A, Mas A, Beaufort D, Patrier P, Dudoignon P (2008) Clay Minerals in basalt-hawaïite rocks from Mururoa atoll (French Polynesia). II. Petrography and geochemistry. *Clays Clay Miner* 56:730–750
- Nisbet EG, Sleep NH (2001) The habitat and nature of early life. *Nature* 409:1083–1091
- O'Neil J, Carlson RW, Francis D, Stevenson RK (2008) Neodymium-142 evidence for Hadean mafic crust. *Science* 321:1828–1831
- Parsons I, Lee MR, Smith JV (1998) Biochemical evolution II: origin of life in tubular microstructures on weathered feldspar surfaces. *Proc Nat Acad Sci USA* 95:15173–15176
- Parthasarathy G, Choudary BM, Sreedhar B, Kunwar AC, Srinivasan R (2003) Ferrous saponite from the Deccan trap, India, and its application in adsorption and reduction of hexavalent chromium. *Amer Miner* 88:1983–1988
- Pavlov AA, Kasting JF (2002) Mass-independent fractionation of sulphur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* 2:27–41
- Peck DL, Hamilton MS, Shaw HB (1977) Numerical analyses of lava lake cooling models. Part II. Application to Alar lava lake, Hawaii. *Am J Sci* 277:415–437
- Poulet F, Bibring JP, Mustard JF, Gendrin A, Mangold N, Langevin Y, Arvidson RE, Gondet B, Gomez C, the Omega Team (2005) Phyllosilicates on Mars and implications for early martian climate. *Nature* 438:623–627
- Ransom B, Helgeson HC (1994) A chemical and thermodynamic model of aluminous dioctahedral-2/1 layer clay minerals in diagenetic processes - regular solution representation of interlayer dehydration in smectite. *Amer J Sci* 294:449–484
- Rausell-Colom JA, Salvador PS (1971) Complexes vermiculite-aminoacides. *Clay Miner* 9:139–149
- Rollinson H (2008) Ophiolitic trondhjemites: a possible analogue for Hadean felsic "crust". *Terra Nova* 20:364–369
- Russell MJ, Arndt NT (2005) Geodynamic and metabolic cycles in Hadean. *Biogeosciences* 2:97–111
- Russell MJ, Hall AJ (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *J Geol Soc London* 154:377–402
- Russell MJ, Hall AJ, Noyce AJ, Fallick AE (2005) On hydrothermal convection systems and the emergence of life. *Econ Geol*, 100th Anniv Sp. Paper 100:419–438
- Scheidegger AM, Strawn DG, Lamble G, Sparks DL (1998) The kinetics of mixed Ni-Al hydroxide formation on clay and aluminium oxide minerals: a time-resolved XAFS study. *Geochim Cosmochim Acta* 62:2233–2245
- Schlegel ML, Manceau A, Chateigner D, Charlet L (1999) Sorption of metal ions on clay minerals I. Polarized EXAFS evidence for the adsorption of Co on the edges of hectorite particles. *J Coll Inter Sci* 215:140–158
- Schlegel ML, Manceau A, Charlet L, Chateigner D, Hazemann JL (2001) Sorption of metal ions on clay minerals. 3. Nucleation and epitaxial growth of Zn phyllosilicates on the edge of hectorite. *Geochim Cosmochim Acta* 65:4155–4170
- Schoonen M, Smirnov A, Cohn C (2004) A perspective on the role of minerals in prebiotic synthesis. *Ambio* 33:539–551
- Serefoglou E, Kiriaki L, Gournis D, Kalogeris E, Tziaila AA, Pavlidis HS, Maccallini E, Lubomska M, Rudolf P (2008) Smectite clays as solid supports for immobilization of b-glucosidase: synthesis, characterization, and biochemical properties. *Chem Mat* 20:4106–4115
- Shapiro R (2007) A simpler origin for life. *Sci Am* 296:46–53

- Staudigel H, Hart SR (1983) Alteration of basaltic glass: mechanisms and significance for the oceanic-seawater budget. *Geochim Cosmochim Acta* 47:337–350
- Staudigel H, Chastain RA, Yayanos A, Boucier W (1995) Biologically mediated dissolution of glass. *Chem Geol* 126:147–154
- Staudigel H, Furnes H, Banerjee NR, Dilek Y, Muehlenbachs K (2006) Microbes and volcanoes: a tale from the oceans, ophiolites, and greenstone belts. *GSA Today* 16:4–102
- Stucki JW (2006) Iron redox processes in clay minerals. In: Bergaya F, Lagaly G, Theng BGK (eds) *Handbook of clay science*. Elsevier, Amsterdam
- Szilagyi I, Labadi I, Hernadi K, Kiss TIP (2005) Montmorillonite intercalated Cu(II)-histidine complex synthesis, characterisation and superoxide dismutase activity. *Stud Surf Sci Cat* 158:1011–1018
- Thompson G (1973) A geochemical study of low-temperature interaction of sea water and oceanic igneous rocks. *Am Geophys Union Trans* 54:1015–1019
- Thompson HA, Parks GA, Brown GE Jr (1999) Dynamic interactions of dissolution, surface adsorption, and precipitation in an aging cobalt(II)-clay water system. *Geochim Cosmochim Acta* 63:1767–1779
- Thorseth IH, Furnes H, Tumyr O (1991) A textural and chemical study of Icelandic palagonite of varied composition and its bearing on the mechanism of the glass-palagonite transformation. *Geochim Cosmochim Acta* 55:731–749
- Velde B, Meunier A (2008) *The origin of clay minerals in soils and weathered rocks*. Springer-Verlag, Berlin
- Vieira Coelho AC, Ladrière J, Poncelet G (2000) Nickel, iron-containing clay minerals from Niquelandia deposit, Brazil. 2. Behaviour under reducing conditions. *Appl Clay Sci* 17:183–204
- Violante A, de Cristofaro A, Rao MA, Gianfreda L (1995) Physicochemical properties of protein-smectite and protein-Al(OH)_x-smectite complexes. *Clay Miner* 30:325–336
- Wang MC (1991) Catalysis of nontronite in phenols and glycine transformations. *Clays and Clay Miner* 39:202–210
- Wilde SA, Valley JW, Peck WH, Graham CM (2001) Evidence from detrital zircons for the existence of continental crust and ocean on the Earth 4.4 Gyr ago. *Nature* 409:175–178
- Williams LB, Canfield B, Voglesonger KM, Holloway JR (2005) Organic molecules formed in “primordial womb”. *Geology* 33:913–916