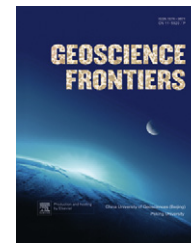


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ORIGINAL ARTICLE

## The geomicrobiology of bauxite deposits

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**Abstract** Bauxite deposits are studied because of their economic value and because they play an important role in the study of paleoclimate and paleogeography of continents. They provide a rare record of the weathering and evolution of continental surfaces. Geomicrobiological analysis makes it possible to verify that microorganisms have played a critical role during the formation of bauxite with the possibility already intimated in previous studies. Ambient temperature, abundance of water, organic carbon and bioavailable iron and other metal substrates provide a suitable environment for microbes to inhabit. *Thiobacillus*, *Leptospirillum*, *Thermophilic* bacteria and *Heterotrophs* have been shown to be able to oxidize ferrous iron and to reduce sulfate-generating sulfuric acid, which can accelerate the weathering of aluminosilicates and precipitation of iron oxyhydroxides. Microorganisms referred to the genus *Bacillus* can mediate the release of alkaline metals. Although the dissimilatory iron-reducing and sulfate-reducing bacteria in bauxites have not yet been identified, some recorded authigenic carbonates and “bacteriopyrites” that appear to be unique in morphology and grain size might record microbial activity. Typical bauxite minerals such as gibbsite, kaolinite, covellite, galena, pyrite, zircon, calcium plagioclase, orthoclase, and albite have been investigated as part of an analysis of microbial mediation. The paleoecology

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of such bauxitic microorganisms inhabiting continental (sub) surfaces, revealed through geomicrobiological analysis, will add a further dimension to paleoclimatic and paleoenvironmental studies.

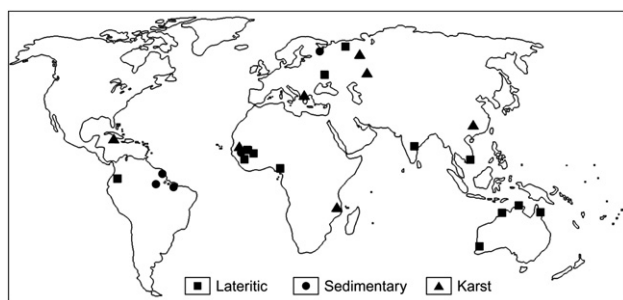
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## 1. Introduction

Continents, which possess much wider areas than limited marine basins, accumulate most sediment, but retain scarce geological records (Thiry et al., 1999). Bauxite, as the primary source of aluminum, represents a typical accumulation of weathered continental crust (Valeton, 1972) and has been one of the most important proxies for the reconstruction of paleoclimate (Price et al., 1997). According to Bogatyrev et al. (2009), lateritic bauxite, sedimentary bauxite and karst bauxite are the three major genetic groups of bauxite deposits (see Fig. 1). Each genetic group of bauxite has experienced separation of aluminum (Al) and silicon (Si) by the accumulation of Al, and the removal of Si, alkali metals, and rare earth elements from parent rock (sediment) during its weathering.

Bauxite is among the best rock paleoclimatic indicator for warm and wet paleoclimates (Fig. 2). It can be used to verify paleoclimatic maps and models (Bárdossy and Aleva, 1990; Price et al., 1997; Bárdossy and Combes, 1999) because it records various climatic, biological and pedogenic conditions of the prevailing paleoenvironments (Valeton, 1999). Generally, high temperature, humidity and precipitation are widely regarded as the main conditions (Akayemov et al., 1975; Tardy et al., 1991) for its formation. However, Taylor et al. (1990) and Bird and Chivas (1993) proposed that the early Tertiary bauxites of Australia might have formed in a relatively wet, and cool to cold climatic setting. This contradiction and more recent evidence implies that an alternative geological agent, the activity of microorganisms not necessarily related to typical climate factors, may also play a significant role in mobilizing elements during bauxitization (Bucher, 1921; Zajic, 1969; Natarajan et al., 1997; Ehrlich, 2002). If this is correct, the related biomineralization processes should have been recorded in the bauxite.

Bauxite has also been an important target for studies of paleoweathering, paleosurfaces and related continental deposits (Bárdossy and Combes, 1999). As the relict of colloidal precipitates resulting from deep chemical weathering of silicates, bauxite itself experienced an evolution from open, strongly oxidized conditions to gradually enclosed, reduced environments. The changes of color, and more equivocally the mineral assemblages, indicate the transformation of minerals and redox stage in bauxites. Moreover, as the most hydrated (~15%), supergene rock on

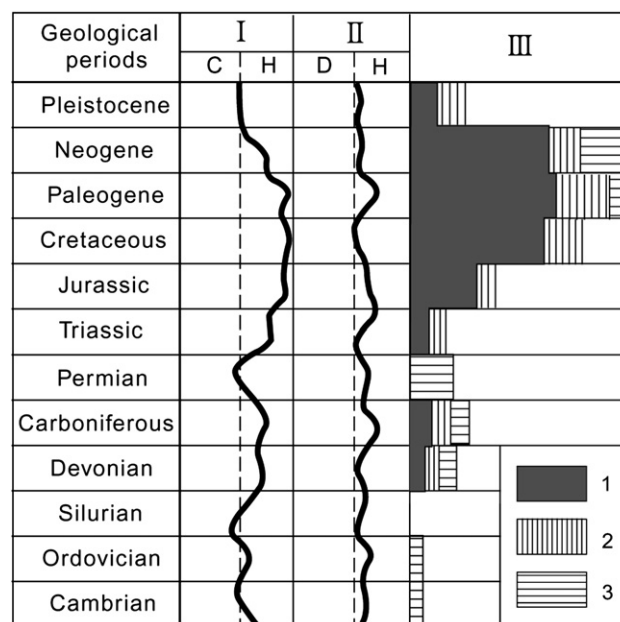


**Figure 1** Distribution of the superlarge bauxite deposits in the world (After Bogatyrev et al., 2009).

the Earth's surface (Bárdossy and Combes, 1999), bauxite contains enough water, organic carbon (~0.01–0.22%; Thompson and MacDonald, 1993), sulfur (sulfides and sulfates; Mora et al., 1996), and nano-iron (hydr)oxides, to be easily taken up by microbes. The above physical and chemical conditions in bauxite are suitable for most microorganisms to inhabit and, thus, the records of activity of these organisms preserved in the rock could provide a potential independent proxy for paleo-temperature/climate determinations (Boucot and Gray, 2001).

Because microorganisms have either a synergistic or an antagonistic effect on each other, the simultaneous presence of autotrophs and heterotrophs in ore deposits facilitates bauxite mineralization (Natarajan et al., 1997). Such microbial processes involved in bauxite have been studied mostly in order to improve the quality of lean grade ores (Groudeva and Groudev, 1983; Groudev et al., 1985; Natarajan et al., 1997). Although biogenic factors in forming bauxite deposits have been confirmed (Laskou and Economou-Eliopoulos, 2007), nevertheless the role of microorganisms in the formation and evolution of bauxite has long been overlooked.

The rapid development of geomicrobiology in the last several decades makes it possible to reexamine the role of microorganisms in bauxitization, with consequent formation of biosignatures and geochemical records. As a matter of fact, early studies did, to some



**Figure 2** Evolution of the scale of bauxite formation in the Phanerozoic depending on climate variation, modified after Bogatyrev et al. (2009). (I) Thermal regime: (C) cold periods, (H) hot periods; (II) humidity: (D) (low) dry periods, (H) (high) humid periods; (III) approximate distribution of the three major genetic types of bauxite reserves in the different geological epochs (shaded columns, see 1–3, bauxite groups: (1) lateritic, (2) sedimentary, (3) karstic).

extent, reveal the possible microbial activity in the geological history of bauxite, although perception was limited by techniques and research interests. This paper reviews those past studies that mentioned but did not stress the role of microorganisms toward the formation of bauxite. It tries to highlight their significance to a bauxite-related mineral ecophysiology on continental surfaces by discussing the following questions: (1) how do microorganisms participate in the formation of bauxite in geological history?; (2) are there any biosignatures preserved in bauxite that could be used to reveal the evolution of the paleomicroecology on a continental (sub) surface?; (3) how do we discriminate inorganic diagenetic minerals from the microbiogenic minerals in the bauxite?; and (4) what is the contribution of microbial activity to the formation of the stable isotopic composition of secondary aluminosilicates, carbonates and sulfides in the bauxite?

## 2. Geological characteristics of typical bauxites

Although the three genetic groups of bauxite deposits mentioned above (Fig. 1) undergo somewhat the same bauxitization process (Bogatyrev et al., 2009), they each have their own characteristics. Lateritic bauxites are generally formed by the strong chemical weathering of aluminosilicate rocks (Bogatyrev et al., 2009). For example, the lateritic deposit at Boke, Guinea, resulted from the long-term weathering and leaching of mafic volcanic rocks (basalts and gabbros; Xu and Zhang, 2009). The horizon in which the ore body is situated consists of three layers: an upper layer of laterite and massive bauxite; a middle layer of lateritic soil and earthy bauxite; and a lower bed of ferruginous clay rock and clay rock (see Fig. 3).

Sedimentary bauxites are primarily formed by the accumulation of lateritic bauxite deposits during mechanical transportation of surficial flows. In addition, the consequent weathering and transfer of Al and Fe play substantial roles in bauxitization, which not only foster the formation of bauxite from kaolin clays but also refine the primary clastic ores (Bogatyrev et al., 2009). As an example, bauxite in Henan Province of China of sedimentary genesis, is a single-layered ore body, but one of variable layered, lenticular, and funnel shapes (Sun and Wang, 2006). Lithologically, the stratum containing the ore body includes three different layers (see Fig. 4). The bottom layer is a variegated clay layer enriched in Fe. Bauxite is mainly deposited in the middle layer, which is composed of dark-gray and gray bauxite, and high-alumina, hard clay, and ferruginous clay rocks; carbonaceous clay. Ferruginous clay, and silty clay rocks and kaolin constitute the upper layer, which is characterized by terrigenous debris and carbonaceous precipitates.

Karst bauxites are named for their confinement to karst zones with karstified or karstifying carbonate rocks (Bogatyrev et al., 2009). The chemical process in their formation is almost the same as that of lateritic bauxite. Moreover, the sedimentary process also

plays an essential role in the bauxitization. Karst bauxites gain Al through a variety of sources including the insoluble residue of limestones, other aluminosilicate material (volcanic ash and clay layers) within the limestones, or the erosion, transportation and weathering of aluminosilicate rocks located near the zone of karstifying limestones. Karstification can also enhance bauxitization. Bauxite deposits in the Zagros Mountain Belt, southern Iran are typical of the karst type (Zarasvandi et al., 2008). Here, the ore body is mainly situated stratigraphically between the Sarvak and Ilam Formations, occurring in karst cavities. Once again, the bauxitic horizons consist mainly of three layers: argillite-argillaceous bauxite (lower layer); bauxite zone (middle layer); and ferruginous limestone (upper layer). The bauxitic horizons vary in thickness from 1 m to 25 m depending on the topography of the area (Fig. 5).

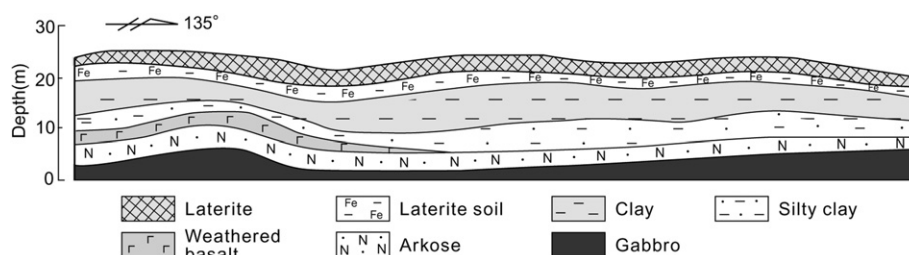
## 3. Mineralogy of bauxite

Bauxite is a type of aluminum ore consisting of several minerals. Generally, it is dominated by aluminum, oxygen and silicate in chemical composition with a mineral assemblage of gibbsite, boehmite and diaspor—often with subordinate amounts of goethite, hematite, kaolinite and quartz. Apart from the above, other minerals are also found in minor amounts, including galena, covellite, zircon, pyrite, calcium plagioclase, orthoclase and albite.

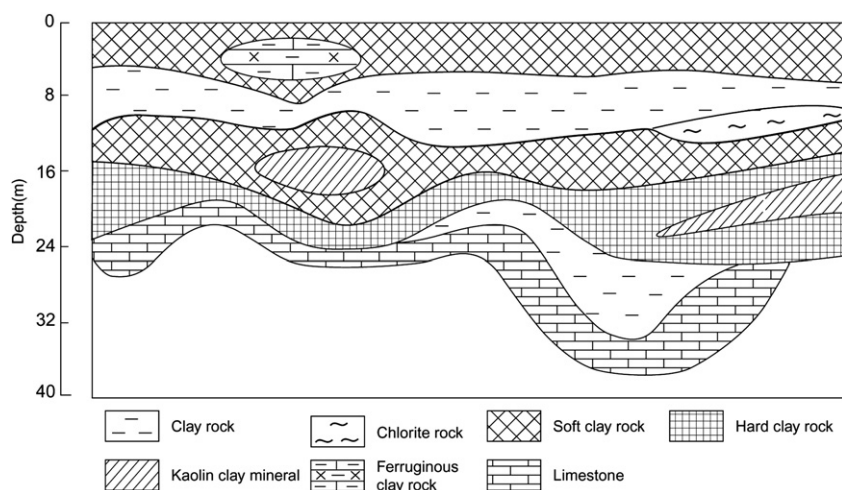
Because of the colloidal features of many bauxite minerals, scanning electron microscopy (SEM) is a good choice to study its mineralogy. The bauxite deposited at Maochang of Guizhou Province (Zhou, 2007) was examined using a field emission S4800 scanning electron microscope to yield its mineral assemblage: Super E × B technology was applied; pure secondary, compositional secondary and backscattered electrons could be collected and separated using one detector. Accelerating voltage is variable from 0.1 kV to 30 kV. In this study, 20 kV and 5 kV accelerating voltages were used to capture the SEM images with bulk and surface information, respectively. The SEM was also equipped with a Horiba EMAX Energy Dispersive Spectrometer (EDS) detector with EMAX energy software. To confirm the mineral assemblage of the sample, EDS measurements were carried out at 20 kV, and the distance between the gun and samples was set at 15 mm. The SEM images of typical minerals in the bauxite are shown in Fig. 6.

## 4. Biomineralization from oxidized to reduced environments

Ehrlich (2002) suggested that rock weathering resulting from the excretion of corrosive metabolic products, such as inorganic and organic acids, bases, and/or organic ligands by various microbes that facilitate enzymatic redox reactions, either oxidizes or reduces rock components so effectively that they might accelerate the



**Figure 3** Profile chart of bauxite in Boke, Guinea, where bauxitic horizons consist of the uppermost three layers (After Xu and Zhang, 2009).



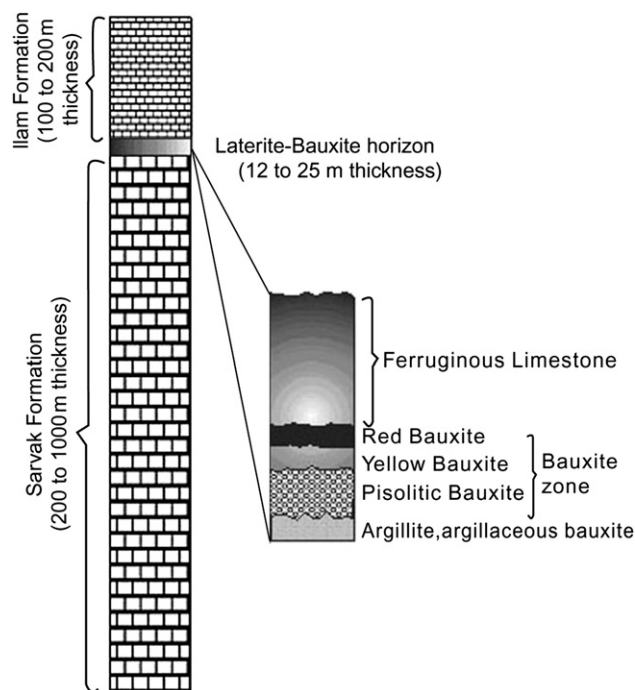
**Figure 4** Profile chart of sedimentary bauxite in Henan, China (After Sun and Wang, 2006).

bauxitization process. Natarajan et al. (1997) reported that *Thiobacillus ferrooxidans* can oxidize ferrous ions to ferric ions and cause intensive weathering of aluminosilicates by producing sulfuric acid during the oxidation process. Microorganisms belonging to genus *Bacillus* can mediate the release of alkaline metals. Bacteria belonging to the taxa *Bacillus coagulans* and *Bacillus polymyxa*, through the excretion of polysaccharides, can flocculate iron oxides, alumina and calcite. Pure culture experiments indicated that the microbial weathering of aluminosilicates can release iron as well as Si and Al directly from the silicates (Maurice et al., 2001a; Li et al., 2004), a process followed by precipitation of biogenic carbonates, sulfides and iron oxides. Coupled with chemical weathering processes, the long-term leaching of removable elements by microorganisms from silicates resulted in Al releasing from the lattices and enrichment in the relics,

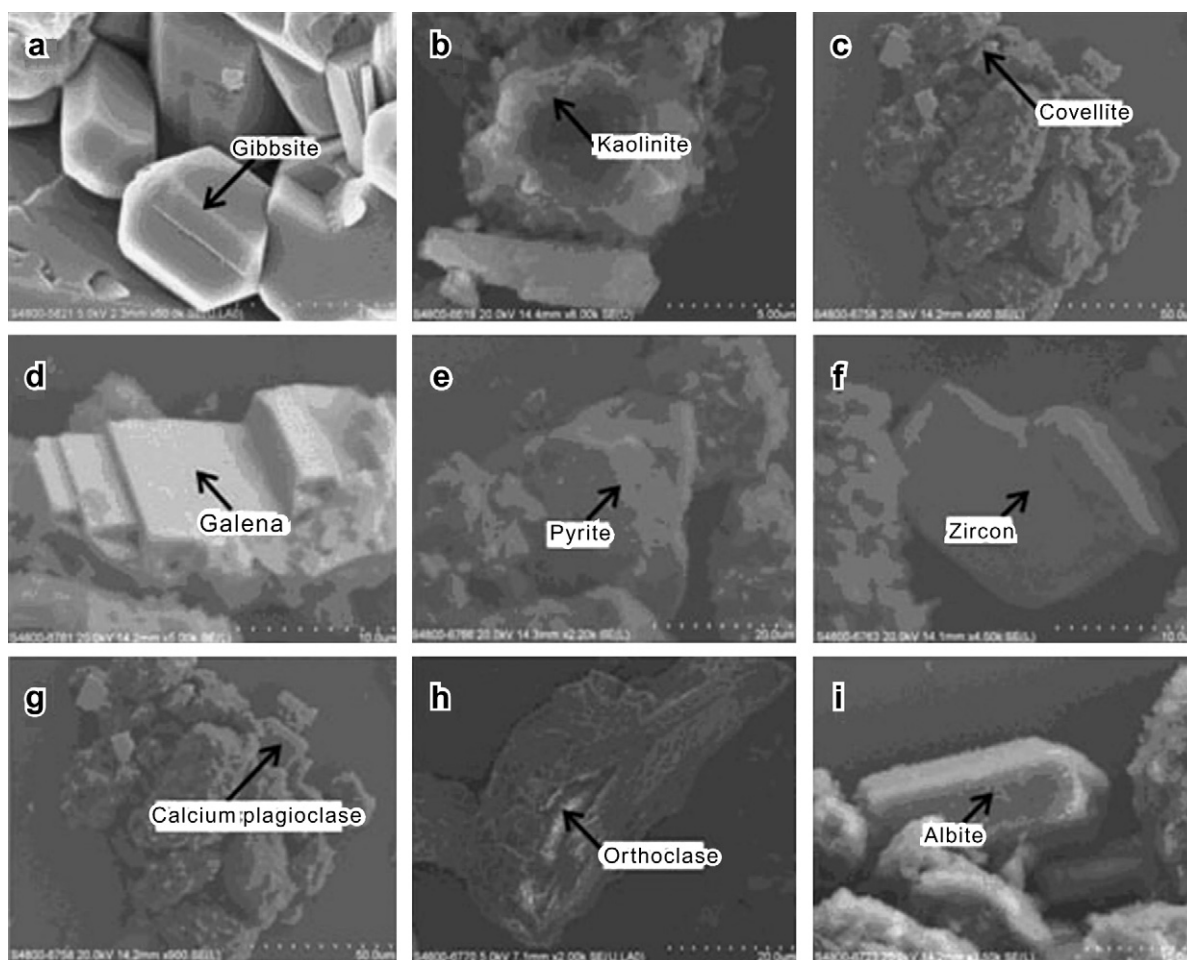
which promoted bauxitization (Bischoff, 1997b). Similar geological conditions in bauxite formation worldwide might result in similar microorganism consortia. Bauxite from the pisolitic deposit in Australia, deposits in the Amazon area of Brazil, and some on the island of Jamaica in the Caribbean have yielded similar bacterial cultures with similar physiology (Ehrlich and Wichert, 1997).

Here, we review biomineralization processes that either happen in bauxite or could happen during bauxitization based on experiment. Interactions between microbes and earth materials through time produce altered mineral assemblages and the valence status of some elements (e.g., S, Fe, Mn). The early stage of bauxitization occurs during the formation and leaching of laterite minerals in tropical or subtropical monsoon climates (Bárdossy and Aleva, 1990). Bacteria-enhanced dissolution of silicates and iron oxides occurs either directly in order to access structural Fe (Maurice et al., 2001a), or indirectly as a byproduct of other microbial processes, such as Ca uptake (Anand et al., 1996) under oxic conditions. At the terrestrial surface, bioactivity produces second phase silicates (Aleksandrov and Zak, 1950; Zajic, 1969; Bischoff, 1997a; Kawano and Tomita, 2002) through direct or indirect pathways (Bosecker, 1997). The sulfide oxidizers (e.g., *Thiobacilli thiooxidans*) can directly oxidize sulfides to sulfuric acid (Karavaiko, 1962) or oxidize Fe(II)-containing silicates and oxides (e.g., acidophilic Fe oxidizers) to form magnetite, hematite and other iron compounds (Frankel, 1990; Chaudhuri et al., 2001). The reduction of Fe(III) to magnetic minerals also happens under this condition (Bazylinski and Frankel, 2003) by direct contact with the substrates and enzymatic catalyzing (Bosecker, 1997). Surfactants and organic compounds could probably prohibit microbial oxidation of reductive substrates during the leaching of metals (Bosecker, 1997), or to the contrary, help to extract oxidized substrates (e.g., sulfate or crystal Fe(III)) by dissimilatory metal/sulfate-reducing bacteria (Kalinowski et al., 2000). The (sub)surface of tropical soil as an environment enriched in meteoric water and a carbon source, precipitated second-order Ca- and Mg-carbonates (Whalen et al., 2002). In controlled experiments, Thompson and Ferris (1990) and Knorre and Krumbein (2000) showed that production of CO<sub>2</sub> by aerobic degradation of organic carbon increased alkalinity, and adoption of Ca<sup>2+</sup> and Mg<sup>2+</sup> on the surface of bacteria resulted in the precipitation of Ca–Mg-carbonates under aerobic conditions.

Along with the accumulation of relics of weathering products, bauxite is enclosed and gradually turned into a reductive



**Figure 5** Schematic stratigraphic section of the bauxitic horizon in the Zagros Mountain Belt (After Zarasvandi et al., 2008).



**Figure 6** SEM images of typical minerals in bauxite: (a) gibbsite as the major mineral; (b) kaolinite as the primary subordinate mineral, (c) covellite, (d) galena, (e) pyrite, (f) zircon, (g) calcium plagioclase, (h) orthoclase, and (i) albite as minor minerals.

environment due partly to the coupled interactions of microbes and the chemical environment. In this condition, anaerobic microbes dominate the biomineralization, as indicated below in controlled experiments: (1) dissimilatory metabolism of anaerobic metal-reducing bacteria precipitated magnetite and maghemite (Hanzlik et al., 1996), and ferro- and Mn(II)-carbonates (Frankel, 1990; Neelson and Saffarini, 1994) by producing metals and CO<sub>2</sub> simultaneously; and (2) strictly anaerobic sulfate-reducing bacteria produced iron sulfides by reducing sulfate (Donald and Southam, 1999; Matsuo et al., 2000; Paktunc and Dave, 2002; Bazylinski and Frankel, 2003; Li et al., 2004); or both sulfate and metals (Tebzo and Obratzsova, 1998). Alonso-Zarza et al. (2002) proved that microbial-related dolomitization during meteoric water-dominated diagenesis happened in a red mudstone bed in terrestrial deposits, which corroborated the formation of authigenic dolomite in bauxite, conjectured by the early studies of Bárdossy (1982).

When subsurface bauxite is gradually exposed to the air again, ferrous iron minerals, such as siderite and pyrite, would be reoxidized by iron- (e.g., *T. ferrooxidans*) and sulfur-oxidizing (e.g., *T. thiooxidans*) chemolithoautotrophs, which grow autotrophically by fixing CO<sub>2</sub> from the atmosphere. These microorganisms and their oxidizing mechanisms have been widely used for biobeneficiation studies (Bosecker, 1997; Natarajan et al., 1997; Vasan et al., 2001). Different niches of microorganisms occupied the bauxite in different spaces and times; either enhancing the bauxitization or

increasing the bauxite quality by cycling the valent-variable elements. For example, the combined metabolism of sulfide-oxidizing, ferro-oxidizing and the sulfate-reducing bacteria can enhance the removal of iron and silicic substances. The formation of hallosite beds in Indiana, USA, is typical of microbial-accelerated cycling of elements in which the oxidation of sulfides by ferro- and sulfide-oxidizing bacteria produces sulfuric acid that removes part of the iron and silica. This is followed by reduction of sulfate by sulfate-reducing bacteria, which in turn provides sulfides and Fe(II) for the ferro- and sulfide-oxidizing bacteria (Bucher, 1921). The recycling of sulfur effectively promotes the removal of Fe, Ca, Mg and Si from the immature bauxite.

## 5. Evidence for microorganism activity in bauxites

Microbial-controlled mineralization produces materials with well-defined characteristics including morphology, grain size, stable isotope composition and particular physicochemical criteria. Most biogenic minerals reported recently (Moskowitz, 1995; Vasconcelos et al., 1995; Hanzlik et al., 1996; Donald and Southam, 1999; Knorre and Krumbein, 2000) might find their counterparts in bauxite. In fact, early studies as mentioned below have revealed that bauxite is a window for the study of (sub)surface microbial ecology of intra-continental environments.

Most bauxites contain 0.01–0.22% organic matter (Bárdossy, 1982; Thompson and MacDonald, 1993; Mora et al., 1996), which serves as the carbon source for microorganisms. The cooperative activity of the microbial food chain provides enough carbon for a variety of organisms. Laskou and Economou-Eliopoulos (2007) suggested that organic matter could also help to control the ‘redox conditions and facilitating the nucleation and growth of sulfides and oxides’.

Natarajan et al. (1997) inferred that the presence of members of the bacterial genera *Thiobacillus*, *Bacillus* and *Pseudomonas*, which were separated from the bauxite of the Jamnagar mines in Gujarat, India, were involved in bauxite formation based on the known ability of these organisms to weather aluminosilicates, to precipitate oxyhydroxides of iron, to dissolve and transform alkaline metal species, and to form alumina, silica and calcite. On the same basis, they also implicated fungi of the genus *Cladosporium* as reducing ferric iron and dissolving aluminosilicates.

Anaerobic microbes were assumed to play essential roles in the chain reactions resulting in the formation of Indiana “Kaolin” (Bucher, 1921); the contact between halloysite and the shale indicated a supply of carbon for microorganisms. Sulfate-reducing bacteria played a role in removing metals from the precursor of the kaolin. Oxidation of pyrite to sulfate in the shale was the first step in mobilizing elements; reduction of sulfate to hydrogen sulfide by sulfate-reducing bacteria was the second step, which combined with simultaneous chemical reactions produced an integrated cycle in mobilizing elements to exclude Al (Bucher, 1921). Sulfides, elemental sulfur and sulfates produced by different microbial activities and chemical reactions should have coexisted in this environment.

Caillère and Pobeguín (1963) identified native sulfur in a gray, pyritic, clayey bauxite from the Durban deposit, Ariège, France. The “sulfur-separating” bacteria presumably played an important role in the bauxite formation (Bárdossy, 1982). When compared to diagenetic pyrite, spherical pyrite of 2–50 µm in diameter, which has been called bacteriopyrites (Burić, 1966), is rare in bauxite. However, it is very probably one of the products of bacterial activity. In fact, this kind of framboidal pyrite has been proved to be the product of sulfate-reducing bacterial activities (Altschuler et al., 1983; Garcia-Guinea et al., 1997). Taylor and Hughes (1975) proposed a biogenic formation for the Rennell Island bauxite in the South Solomon Sea near Guadalcanal. The bauxite deposited in pockets of karstic limestone in Plio-Pleistocene lagoons on Rennell Island, was hypothesized to be the result of biodegradation of volcanic ash. Taylor and Hughes (1975) speculated that sulfate-reducers generated CO<sub>2</sub>, which caused weathering of aluminosilicates and ferromagnesian minerals in the volcanic ash, thus giving rise to transient kaolin that would dissolve at low pH to yield Al (III) and silicic acid. Such bacterial pyrite formation by sulfate-reducers would create the pH and Eh conditions that would in turn enhance the weathering of silicates in the volcanic ash.

Iron-reducing bacteria are possibly the most efficient microbial agent that can reduce ferric iron and mobilize it. Papiu et al. (1970) found rare “authigenic, automorphic” magnetite particles of very small grain size besides the clastic magnetite in bauxite. Benelavsky (1963) found some fine grain, “syngenetic” siderite in the Devonian bauxite of the North Urals. In fact, only iron-reducing bacteria can precipitate siderite in bauxite at neutral pH under anaerobic conditions, because bauxite represents the crust surface of strongly weathered tropical soil. Bárdossy et al. (1977) found that most of the siderite and its Mn-containing modification occurred in the lower part of the Campo Felice deposit associated with green clay and its transition into red bauxite. The green color clearly represents

a relatively reduced condition and indicates a lower Eh level than that of the red bauxite. The iron-rich grains of µm size from the green clay showed no traces of reworking (Bárdossy et al., 1977).

Additional evidence of microbial activity in bauxite is provided by the existence of finely dispersed authigenic dolomite/ankerite grains of 2–80 µm (Alliquander et al., 1974; Orbán et al., 1976). This peculiar, freshwater form of dolomite is obviously different from dolostone pebbles and debris because no secondary, metasomatic dolomitization of calcite crystals of primary precipitation could be found (Bárdossy, 1982). Such dolomite also shows framboidal morphology (Orbán et al., 1976), just like dolomite formed in sulfate-reducing environments in ancient (Wright, 1999) and modern (Vasconcelos and McKenzie, 1997) environments. Ankerite, a ferroan dolomite, has also been found in a similar situation (Benelavsky, 1963). The existence of dolomite/ankerite strongly implies that bacterial activity mediated the precipitation of [Ca, Mg, Fe](CO<sub>3</sub>)<sub>2</sub>, because of the kinetic obstacles met in abiotic formation under lower temperature (Warren, 2000). Though being regarded as of “syngenetic or early diagenetic origin”, research in the 1960s had already construed that dolomite cannot be formed at lower temperatures on the Earth’s surface by pure geochemical processes (Krauskopf, 1967). Vasconcelos et al. (1995) demonstrated that the mediation of bacteria (including sulfate-reducing taxa) is able to precipitate dolomite at lower temperatures in the laboratory.

## 6. Authigenic vs. microbial modified clay minerals

Most of the clays occurring in continental environments are of detrital origin and are supplied to the basins in periods of flooding or episodic discharges; their two main sources are pre-existing mudstones or soils developed on rocks by weathering. Although no distinctive signature has yet been found to discriminate authigenic clay minerals from microbially modified ones, clay minerals can be deeply modified by microbes and can even serve as a substrate for some microbes (Kostka et al., 1996; Li et al., 2004; Dong et al., 2009; Dong, 2010). Li et al. (2004) verified that sulfate-reducing bacteria (SRB) can significantly modify the composition of the surface of nontronite and its structure in weeks. The electron diffraction spectra of the surface of nontronite after 20 days incubation with or without the amended sulfate showed fast removal of Fe, Mg and Ca from the lattice, whereas Si and Al content on the surface of the relict nontronite were higher than on the fresh one. This implies that microorganism leaching of clays towards bauxite formation is a significant mechanism (Maurice et al., 2001b). Maurice et al. (2001b) have also demonstrated that aerobic *Pseudomonas mendocina* bacteria enhance the release of Al, Fe and Si from kaolinite. In the Indiana “Kaolin” noted above, microscopic grains found within the cells of the bacteria were similar to the kaolin grains, and some biomats made large structures like spherulites and radial shapes (Bucher, 1921). The surfaces of spherical to rod-shaped bacteria in weathered pyroclastic deposits of volcanic ash have also been found to be covered by poorly ordered silicate minerals, part of which was smectite-like (Kawano and Tomita, 2002), which also indicates an early stage of microbial-mediated bauxite formation.

## 7. Mineralization related to microbial-growing kinetics

The much faster removal of Ca and Mg from bauxite (Modak et al., 1999) and silicate minerals (Maurice et al., 2001a) by

microorganisms provides a significant sink for atmospheric CO<sub>2</sub> (Barker et al., 1997). Additionally, it has been assumed that microbial activity is partly responsible for the precipitation of fine particles of silica and alumina (Zajic, 1969). However, the ways that Al is released from the silicates to Al-oxides and/or oxyhydroxides remains unclear. A long controversial question about bauxite formation rests on the supposition that bauxite experienced metamorphism because enclosed boehmite ( $\gamma$ -AlOOH) and diaspore ( $\alpha$ -AlOOH) cannot be formed under surface  $P$ – $T$  conditions, although no other metamorphic minerals can be found in bauxite (Bárdossy, 1982). Yet, classically these two minerals were thought to form under surface  $P$ – $T$  conditions because they are mostly observed coexisting with iron oxyhydroxides with superegene genesis. An important geomicrobiological concept is that direct mediation by microbes can overcome the kinetic barrier of some types of mineralization under surface  $P$ – $T$  conditions (Vasconcelos et al., 1995; Donald and Southam, 1999). A hypothesis waiting to be tested is that boehmite and diaspore could be formed by microbial-mediated processes under ambient  $P$ – $T$  conditions. For example, elements such as Si, Mg, Ca, Fe, etc., can be detected by ICP analysis in sulfate-reducing bacteria-mediated dissociation of clay minerals, such as the nontronite (Li et al., 2004); undetected Al, with unknown mineralogy, was assumed to be adsorbed on the surface of the nontronite. Further study on the forms of microbe-released Al by X-ray absorption spectroscopy, which is insensitive to chemical and crystallographic environments except in the short-range of the targeted element, is strongly suggested.

## 8. Stable isotopic geochemistry of biogenic minerals in bauxite

Variation of stable isotopes (H, C, S, O) has been used as an indirect method for dating regoliths, based upon changing composition of the atmosphere, either globally or in response to climatic variation of paleosurfaces (Bird and Chivas, 1989). The development of the laser-ablation stable isotopic analysis system and ion probes during recent decades has helped to analyze H, C, O and S isotopes of small grain size as well as for *in situ* analysis (Valley, 2001). This makes it possible to analyze “authigenic” dolomite, ankerite, rhodochrosite (Bárdossy, 1982) and siderite spherulites (Papiu et al., 1970) of very small grain size with possible microbial-induced genesis. C and O isotopic studies of microbial-precipitated dolomite (Vasconcelos et al., 2005) and siderite (Zhang et al., 2001) indicated possible temperature-dependent isotopic fractionations that could be used to indicate some ecophysiological conditions such as the source of carbon, the temperature and the precipitation conditions. The *in situ* measurement of H and O isotopes of aluminum oxides and hydroxides coexisting with those of possible biogenic magnetite, carbonates and sulfides helps to estimate the impact of microbial activity on hydrogen isotope composition, which might be significant in determining the temperature of bauxite formation and the concurrent climate (Vitali et al., 2001). A major proportion of reduced sulfur contained in deposits of elemental sulfur, pyrite, and base metal sulfides should have been derived from biological reduction of sulfate. On the basis of thermodynamic and kinetic arguments, Anisimov (1978) predicted that 150 °C would be the lower limit for geochemically significant abiological sulfate reduction. Keep in mind that bauxite always forms on the top of the continental surface, thus the authigenic sulfides in bauxite should be biogenic because sulfate is the only stable sulfur compound formed at the soil surface. The sulfides produced by sulfate-reducing

bacteria should be 15–65‰ lighter than their parent sulfate ( $\text{SO}_4^{2-} \rightarrow \text{S}^{2-}$ ) in open system (Machel et al., 1995; Machel, 2001). Ozturk et al. (2002) found lower sulfur isotope compositions of Fe-sulfides in bauxite ranging from 5.6‰ to –44.4‰, and pointed out that the most negative sulfur isotope values were ‘typical sulfides formed by bacterial-sulfate reduction at temperatures <50 °C’. The combination of O, C and S isotopic ratios can give criteria for the activity of sulfate-reducing bacteria in the precipitation of carbonates (i.e., ankerite, siderite and dolomite) by uptake of the metabolic residues of aerobic biodegraders. The H isotope composition of aluminum hydroxides has the potential to provide information about temperature and precipitation conditions that prevailed during formation of soils and bauxites (Bird and Chivas, 1989). Nevertheless, the calibration of H and O isotope fractionation between the most common Al-oxides/hydroxides (gibbsite) and water has met with some problems, for example, the so-called polymorph effect (Vitali et al., 2000) and the possibility of isotopic inheritance from precursor kaolinite in bauxite (Vitali et al., 2001). The stable isotopic compositions of these minerals might have been modified by intense activity of microorganisms when considering their potential to change the composition and even the mineralogy of bauxite (Natarajan et al., 1997; Modak et al., 1999).

## 9. Concluding remarks

Bauxite deposits have been studied in detail because of their economic value. They play an important role in the study of paleoclimate and paleogeography of continents because they constitute rare records of the weathering and evolution of continental surfaces. The recent rapid development of the subdiscipline of geomicrobiology makes it possible to verify the role of microorganisms in the formation of bauxite. Scrupulous examination of previous studies indicates that microorganisms did play a critical role in forming bauxites. Ambient temperature, abundance of water, organic carbon and bioavailable iron and other metal substrates provide a suitable environment for microbes to inhabit. *Heterotrophs* and Bacteria like *Thiobacillus*, *Leptospirillum*, *Thermophilic* have been proven to be able to oxidize ferrous irons and reduce sulfur to generate sulfuric acid, which can accelerate the weathering of aluminosilicates and precipitation of iron oxyhydroxides; microorganisms that belong to the genus *Bacillus* can mediate the release of alkaline metals. Although the dissimilatory iron-reducing and sulfate-reducing bacteria in bauxites have not yet been identified, some authigenic carbonates and “bacteriopyrites”, which appear to be unique in morphology and grain size, have been reported and are thought to be records of microbial activity.

Bauxite deposits mainly form at ambient pressure and temperature on the (sub)surface of continents. Abundant bioavailable irons, nutrient elements, sulfurs, and organic carbons make bauxite suitable for microorganisms to inhabit so that they become rare geological sites that can preserve records of microbiological activity on the surface of continents under strong weathering effects. Microorganism activities can produce a series of minerals with special morphologies and stable isotope compositions. A synthesized study of the mineralogy and stable isotope geochemistry of authigenic carbonates, sulfides and iron oxides and the geomicrobiology can determine the right  $P$ – $T$  conditions, and discern the diversity of metabolism and microbial ecology in the bauxites during their formation and evolution. Study of the geomicrobiology of bauxite thus adds a new dimension to determine the paleoclimate and paleosurface of continental (sub)surfaces.

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