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The natural hydrous sodium silicates from the northern bank of Lake Chad: occurrence, petrology and genesis

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Abstract

Hydrous sodium silicates sometimes associated with zeolites, form in an alkaline environment, in which there is a high concentration of dissolved silica. Such an environment existed during the Holocene in N'Guigmi interdunal depressions (Lake Chad), which led to the precipitation of various types of hydrous sodium silicates, including magadiite, kenyaite, and zeolites. Scanning electron and optical microscope observations allow several microstructures to be distinguished. These microstructures result from either precipitation sequences or a transformation along a diagenetic gradient. New petrological, microstructural and geochemical data confirm the transformation of magadiite into kenyaite during its diagenetic evolution, of which the final stage is probably Magadi-type chert. The study of various deposits of these minerals (hardened beds, scattered isolated crystals, mineralized plant debris, irregular concretions) have been used for paleo-environmental reconstruction. The decrease in the abundance of magadiite concretions in the sedimentary sequence can probably be explained by the climatic evolution of the region.

Keywords: Arid environment; Diagenesis; Holocene; Lake Chad; Silicate minerals; Sodium

1. Introduction

Since their discovery (Eugster, 1967), naturally occurring hydrous sodium silicate minerals have been studied at various sites worldwide (Hay, 1968; Mac Atee et al., 1968; Rooney et al., 1969; Maglione, 1970; Sheppard et al., 1970; Johan and Maglione, 1972; Perinet et al., 1982; Icole et al., 1983). Their occurrence and mineralogy have been summarized in numerous papers (Eugster, 1969; O'Neil and Hay, 1973; Maglione and Servant, 1973; Tardy, 1981; Icole and Perinet, 1984). Neoformation of sodium silicate is related to specific conditions, such as those found in alkaline carbonate-rich hydrogeochemical environments, which are a source of silica. Nevertheless, there are difficulties in their use in paleo-environmental reconstructions, for example the variability in their precipitation (synsedimentary or diagenetic), the rarity of their occurrence, and the metastability of the mineral (they transform into chert). Despite numerous analyses and syntheses of these minerals in the laboratory, several aspects of

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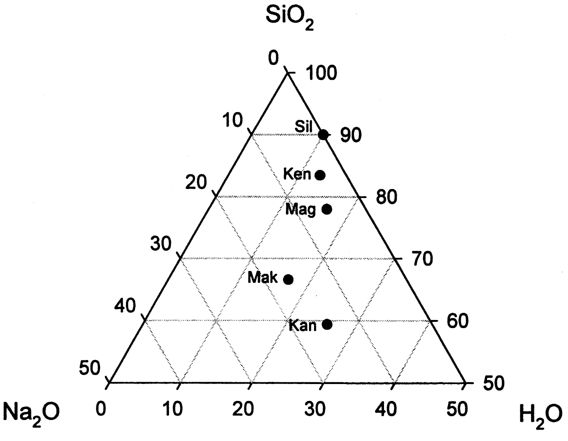


Fig. 1. Upper part of the ternary diagram Na_2O–SiO_2–H_2O showing the position of various hydrous sodium silicates (from Johan and Maglione, 1972). Ken, kenyaite; Kan, kanemite; Mag, magadiite; Mak, makatite; Sil, silhydrite.

their formation and transformation in natural environments remain unclear (Tardy, 1981).

The aim of this paper is to present new information regarding the occurrence, microstructure, weathering and diagenesis of samples from the northern bank of Lake Chad (N'Guigmi, Niger). In addition, scanning electron microscope (SEM) observations on different types of concretions allow a variety of microstructures to be identified.

2. Previous studies

Several types of hydrous sodium silicates have been recognized and described in the literature (Fig. 1). The two most common forms, magadiite and kenyaite, were discovered in Kenya in the sixties (Magadi Lake, Eugster, 1967). Since then, other minerals have been identified, such as: (i) makatite, an accessory mineral associated with magadiite (observed in Magadi Lake deposits by Hay, 1968, and studied by Sheppard et al., 1970), and (ii) kanemite, only associated with natron and described in interdunal evaporites of Kanem in Chad (Fig. 1; Johan and Maglione, 1972; Perinet et al., 1982).

2.1. The mineral nomenclature

2.1.1. Magadiite

Magadiite ($NaSi_7O_{13}(OH)_3$, $3H_2O$) was first described in Pleistocene sediments from Magadi Lake (Kenya) by Eugster (1967). Many occurrences were subsequently described (California, Mac Atee et al., 1968; Oregon, Rooney et al., 1969; East Africa, Hay 1968). The Chad basin constitutes one of the richest sites in hydrous sodium silicates. Many places in this region have been investigated such as the Ténéré (Maglione and Servant, 1973), and various interdunal depressions located in the Kanem (Maglione, 1970) and the southern Manga (Icole et al., 1983). Several types of magadiite occurrences have been reported: synsedimentary beds within lacustrine deposits (Eugster, 1967; Maglione, 1970), accumulations crosscutting sediment beds (Hay, 1968; Rooney et al., 1969), nodules and isolated concretions (Maglione, 1970; Icole et al., 1983), or crystals scattered in sediments (Sheppard et al., 1970; Maglione, 1976; Perinet et al., 1982).

Freshly precipitated, magadiite appears as a *plastic white paste* ("pâte blanche, très plastique", Maglione, 1970, p. 178). However, when exposed to drying and dehydration, it rapidly loses its plasticity and irreversibly hardens. It has a superficial crack network with small prisms separated by fissures, comparable to desiccation cracks (Icole and Perinet, 1984, p. 175). Most of the scanning electron microscope photos in the literature show very thin sheet-like crystals, belonging to the monoclinic system.

2.1.2. Kenyaite

Kenyaite ($NaSi_{11}O_{20.5}(OH)_4$, $3H_2O$) forms nodules inside layers of magadiite from the High Magadi Beds (Eugster, 1967) and the High Natron Beds (Hay, 1968). It has never been described in the form of beds, but could correspond to a weathering residue of magadiite (Eugster, 1967; Maglione and Servant, 1973). Nevertheless, kenyaite is also found at the center of magadiite concretions (Icole et al., 1983). In this case, it is closely related to magadiite and can result in either primary precipitation (Icole and Perinet, 1984) or spontaneous transformation of magadiite (Hay, 1968; O'Neil and Hay, 1973). This hypothesis has never been confirmed, although the transformation of makatite and kanemite into magadiite (Icole and Perinet, 1984) and the transformation of magadiite into kenyaite (Beneke and Lagaly, 1983) have been obtained in the laboratory.

2.2. Hypotheses of formation

The formation of hydrous sodium silicates is associated with a sodium carbonate-rich environment and the presence of a highly mobile source of silica in contact with brine (e.g. diatom frustules, volcanic glass). The overall process resulting in the precipitation of sodium silicates is generally agreed upon in the literature. The nature of brines is responsible for: (1) the alkalinity of the water ($\mathrm{pH} > 9$), (2) the high concentrations of dissolved silica (up to 2700 ppm), and (3) the incorporation of sodium ions into the silica lattice that precipitates when supersaturation takes place. Depending on concentrations in Na and Si, different sodium-rich silicate crystalline phases can form.

Two paths can explain the supersaturation of brines in regard to silica. The first is due to intense evaporation, concentrating ions in solutions and, in an advanced stage, silica precipitates (Al Droubi, 1976). In this case, the sodium silicates are closely associated with other sulfate and carbonate evaporite minerals. The second path is chemical: in these brines, a decrease of pH, even slight, can result in the supersaturation of the solution with regard to silica (Arbey, 1980). This process occurs when brines come into contact with water that is more diluted or more acidic (meteoric waters) or during mixing of masses of stratified waters (Icole and Perinet, 1984).

Two types of sodium-rich silicates can be distinguished, depending on the origin of the brine. If the parent solution is of lacustrine origin, the precipitation of sodic silicates is syngenetic, even if it occurred during an advanced stage of evaporation (Eugster, 1967). If the parent solutions are of phreatic origin, capillary action intervenes, favored by the grain size distribution and the texture of the silty-sand interdune deposits. The water moved by capillary action evaporates if in contact with a sub-aerial environment. This capillary flow is the result of the drying up of the lake and a lowering of the water table. The formation of sodium-rich silicates can be considered as an early diagenetic process (Maglione, 1976). Rooney et al. (1969) suggest that magadiite concretions can be formed from interstitial brines expelled from clay sediments during compaction and desiccation. Two additional paths are possible, one resulting from diagenetic evolution of organic matter (Eugster, 1969; Icole et al., 1983) and the other in relation to the location of hydrothermal springs (Eugster, 1967).

2.3. Early diagenesis

These minerals can undergo important structural changes, such as a loss of sodium, which can result in the formation of chert. Eugster (1967) suggested that leaching as a result of weathering can explain the transformation magadiite–kenyaite–chert in the High Magadi Beds. This hypothesis, also favored by Maglione and Servant (1973), is based on numerous field observations: the lateral transition from a magadiite zone to a chert zone within the same bed, the disappearance of magadiite and its replacement by kenyaite and microquartz in concretions exposed to weathering. Nevertheless, other data are difficult to explain using this hypothesis, i.e. cherts in unweathered zones present in cores, the predominance of magadiite in the outer surface layer of concretions, and of kenyaite and quartz in the core (Icole et al., 1983).

These observations suggest another type of formation and many hypotheses have been proposed. The first, suggested by Hay (1968) and supported by O'Neil and Hay (1973) on the basis of isotopic data, assume a spontaneous release of sodium, whatever the nature of the solutions and environments. The second necessitates a sequence of precipitations occurring in sediment pores: magadiite–kenyaite–amorphous silica (the latter crystallizing into quartz). The dehydration of magadiite could also lead to the development of quartz and the chert facies (Icole and Perinet, 1984). Therefore, magadiite precipitation can result in the final fixing of silicon (transformation into chert) and is potentially an important step in the biogeochemical cycle of this element in sub-arid environments.

3. Geological setting

Samples have been collected along an outcrop located near the north bank of Lake Chad (Fig. 2). The sediments are related to an interdune lacustrine

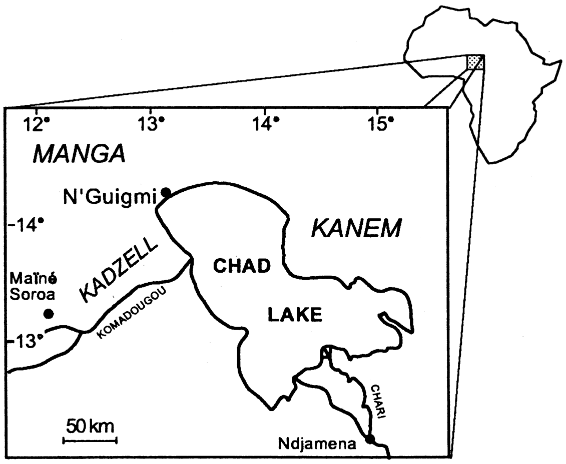


Fig. 2. Location map of N'Guigmi.

infilling that formed during the Holocene. During this period, climatic fluctuations and hydrologic conditions allowed the development of numerous interdunal lacustrine systems in the Chad Lake Basin (Servant and Servant, 1970; Durand et al., 1984, Durand, 1995).

Paleo-environmental analyses on deposits of the interdunal lake at N'Guigmi (Niger) indicate a climatic change from sub-arid (lacustrine sequence) to arid (palustrine sequence) conditions, followed by a final drying up of the lake (Gasse, 1987; Durand, 1995; Sebag, 1998). The oldest sedimentary sequences were deposited in a *lacustrine* system fed by a surficial water supply that episodically dried up. The youngest sedimentary sequences (3810 ± 100 years 14C BP to 1870 ± 100 years 14C BP) indicate a *palustrine* environment with a phreatic water supply, colonized by higher plants and micro-organisms. Diatoms and sedimentological data show a reducing environment characterized by high salinity and pH.

At N'Guigmi, the increase of aridity of the Chad basin after 5000 BP (Durand, 1995) is indicated by the transition between ombrotrophic to minerotrophic conditions, similar to the one observed in present-day Kanem ponds (Maglione, 1976). Phreatic input into the system could have been supplemented by infiltrations coming from Lake Chad, only 2 km away. The recent climatic evolution led to progressive drying up of interdunes. Today, they only exist as annual ponds.

The cut NGI 10 is 1.70 m thick and constituted by a clayey and calcareous diatomite deposited in a palustrine sedimentary environment, in a small gulf, at the edge of the interdunal system (Durand, 1995; Sebag, 1998). Cut NGI 10 contains numerous concretions that compose up to 38% of the sediments (Fig. 3). Three types can be distinguished: irregular concretions, hardened beds, and mineralized bullrush fragments. During a previous study at the N'Guigmi site, magadiite was only identified in the bullrush stems (Icole et al., 1983). This study provides new data showing that magadiite occurs in at least three other forms.

4. Methods

Various types of naturally occurring hydrous sodium silicates were observed in this study. Mineral identification was performed with a Siemens D500 X-ray diffractometer on crushed powder. Acquisition data were compared with ASTM mineral charts. Petrographical analysis was made on 30-μm-thick thin sections at various magnifications, under polarized and cross-polarized light. The Si, Na, Al, Ca, K, Mg, and Fe contents in magadiite concretions were measured using an atomic absorption spectrometer (AAS Perkin–Elmer). The microstructure of the magadiite concretions was observed using a field-effect scanning electron microscope (FE-SEM,

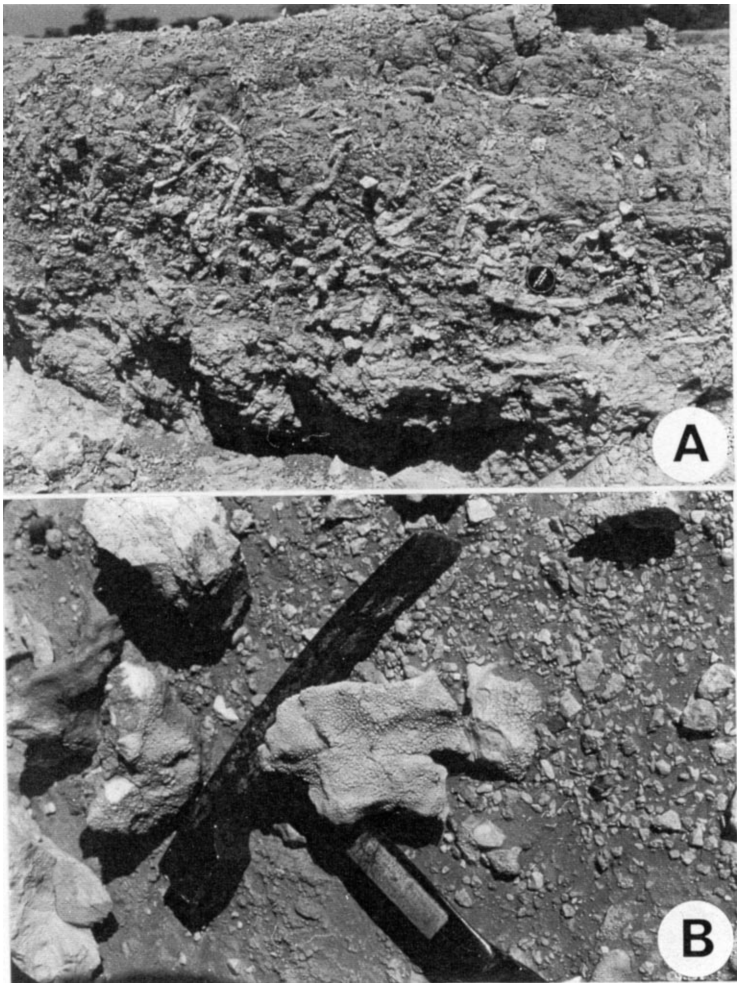


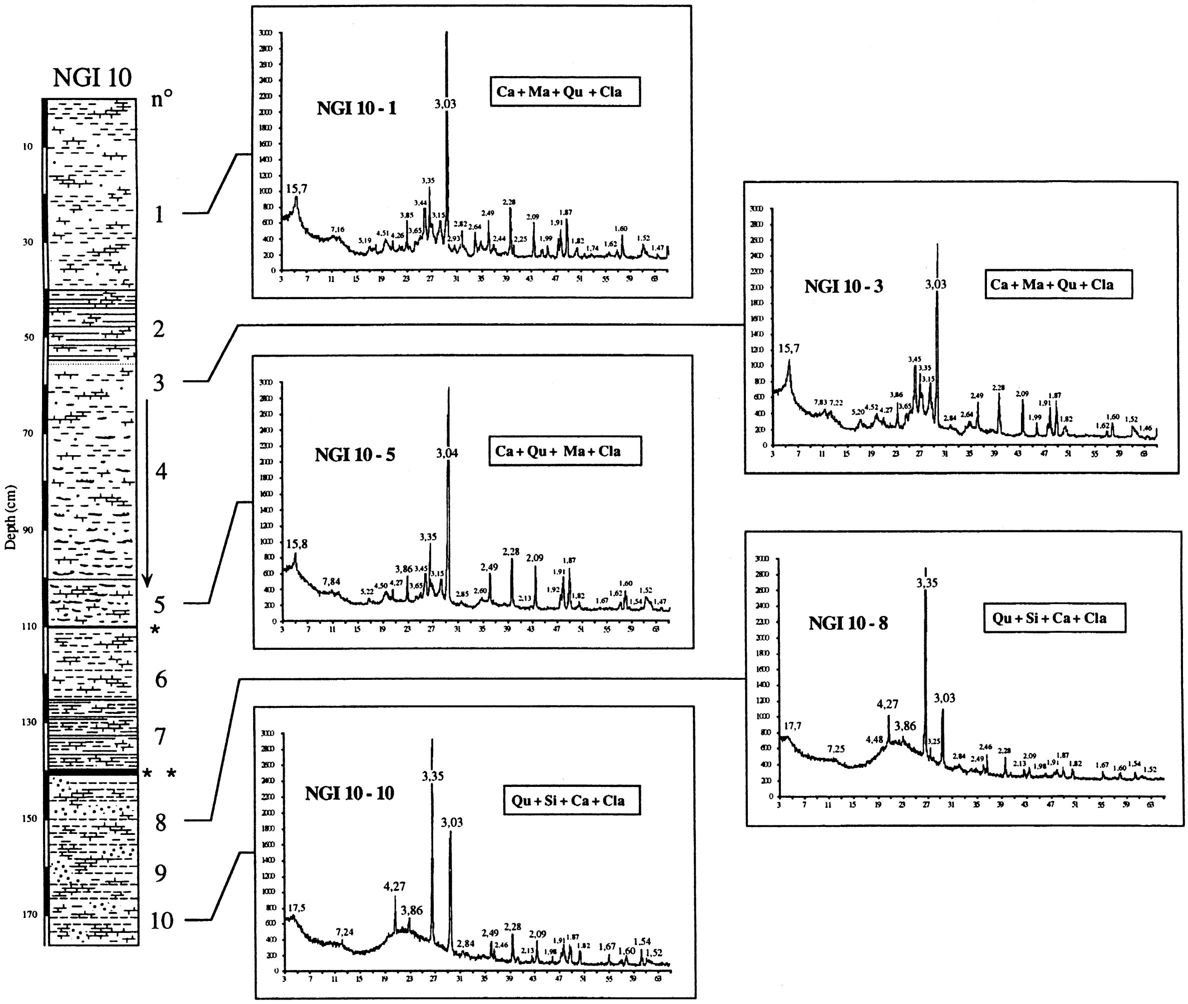
Fig. 3. Field photographs. (A) Cut in a limey–clayey diatomite showing distribution of plant stems and roots, which have mineralized into magadiite. The cut is 1.75 m thick. (B) Magadiite concretions showing a surficial desiccation network. They cover the whole pond area. These concretions are exposed by eolian deflation from the surrounding diatomite and undergo present-day weathering (hammer for scale).

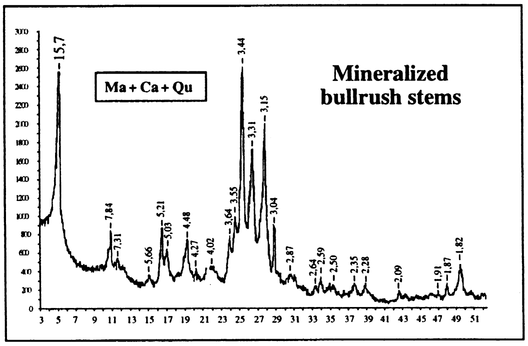
JEOL 5400) coupled with a Link Analytical microprobe analyzer. In order to characterize the crystallographic structure and mineralogical nature, the sample powder was observed with a transmission electron microscope (TEM JEOL 100C), coupled with a goniometric stage for microdiffractometry. The TEM beam was accelerated to 100 kV and its resolution was 1.4 Å on gold. Unfortunately, the crystallography could not be studied at high magnification. After a few seconds of a structured diffraction pattern, the pattern changed (probably due to excessive heating by the electron beam), leading to an amorphous structure. The diffraction pattern could not be photographed with the equipment available.

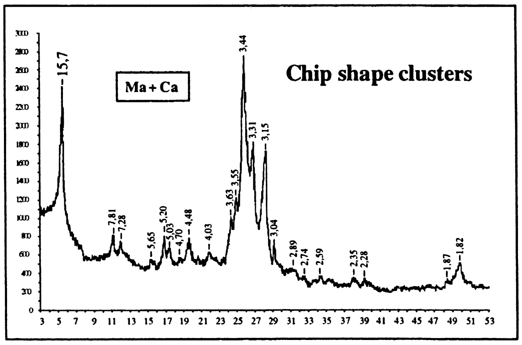
5. Results

5.1. Four occurrences of hydrous sodium silicates from N'Guigmi

Magadiite was identified as the principal constituent of: (1) mineralized bullrushes, (2) hardened beds, and (3) irregularly shaped concretions. It is also


NGI 10
n°
Depth (cm)
10
30
50
70
90
110
130
150
170
1
2
3
4
5
6
7
8
9
10
*
* *
NGI 10 - 1
Ca + Ma + Qu + Cla
3,03
15,7
NGI 10 - 3
Ca + Ma + Qu + Cla
3,03
15,7
NGI 10 - 5
Ca + Qu + Ma + Cla
3,04
15,8
NGI 10 - 8
Qu + Si + Ca + Cla
3,35
4,27
3,86
3,03
17,7
NGI 10 - 10
Qu + Si + Ca + Cla
3,35
3,03
4,27
3,86
17,5


Ma + Ca + Qu
Mineralized bullrush stems
15,7
7,84
7,31
5,66
5,21
5,03
4,48
4,27
4,02
3,64
3,55
3,44
3,31
3,15
3,04
2,87
2,64
2,59
2,50
2,35
2,28
2,09
1,91
1,87
1,82


Ma + Ca
Chip shape clusters
15,7
7,81
7,28
5,65
5,20
5,03
4,70
4,48
4,03
3,63
3,55
3,44
3,31
3,15
3,04
2,89
2,74
2,59
2,35
2,28
1,87
1,82

present as scattered crystals within clayey silt sediments (calcareous clay diatomite; Fig. 4), and has been identified using X-ray diffraction:

1. The plant stems are grouped in biocenosis or scattered in sediments (Fig. 3). This was the only form of hydrous sodium silicates studied by Icole et al. (1983). These concretions have a variety of shapes and sizes, including bullrush stems, roots and rootlets. Mineralized stalks have a hollow central section with irregular boundaries, which can be up to 10 mm in diameter. Certain stalks retain the surface imprints of the plant's ribs. Roots and rootlets show no organic structure and their cross-section is composed of massive crystic material.
2. Fragments of the hardened bed originate in the layer that overlies bed NGI 10-5 (Fig. 4). It is a massive hardpan about 5 mm thick. Its surface is irregular (bumps and hollows mold the sediment surfaces). Desiccation cracks are absent. It is composed of a massive gray porcelaneous material.
3. Irregularly shaped concretions (up to 10 cm long and 1 cm thick) have complex forms that are irregular and sometimes slightly digitated. Some of them can be described as clusters of chip-shaped concretions. They are rich in impurities (quartz grains, coal) and can have a cortex in which massive porcelaneous beds alternate with dark layers composed of thin beds of clays and organic matter. The concretion's surface has a network of small polyhedrons separated by thin cracks. In cross-section, the periphery of these concretions is slightly weathered and the center is commonly hollow.
4. Magadiite has also been identified in clayey calcareous sediments at the top of cut NGI 10. In this case, magadiite occurs as scattered crystals within clayey silt sediments. Only layers at the base of the cut (NGI 10-8 and NGI 10-10, where magadiite is absent) contain enough amorphous silica (diatom frustules) to produce the characteristic bump in the background signal recorded on the diffractogram (Fig. 4).

5.2. Petrology of N'Guigmi concretions

5.2.1. Present and former voids

Petrographic observations have been made on thin sections of handpicked clusters of chip-shaped concretions and mineralized bullrush stems. All the samples observed contain two kinds of voids (desiccation cracks and fenestrae), some being partly infilled with various types of crystals. Fenestrae (septarian) are pores with irregular outlines showing a radiating crack pattern. These pores are partly infilled by palissadic crystals showing undulatory extinction. The desiccation cracks have various shapes: horizontal planes, skew, craze and curved planes. The horizontal planes are sparse in the groundmass narrow (30–70 μm), and short (300 μm–2 mm). Their edges are not coated by any crystals and they crosscut the septarian lateral cracks. Therefore, the horizontal planes constitute a second generation of cracks, posterior to the precipitation of hydrous sodium silicates. The skew, craze, and curved planes have various sizes and their edges are always irregular and coated or infilled by light-colored crystals.

5.2.2. Groundmass

The groundmass of concretions consists of micrite-sized grains and consists of aggregates of crystals characterized by undulatory extinction. Fine- and coarse-grained textures have been observed (Fig. 5a), the latter being enclosed in the former. On a larger scale, the coarse texture shows plate-like micro-crystals organized in small fan aggregates.

5.2.3. Void-filling phases

The centers of the two types of concretions (chips

Fig. 4. N'Guigmi NGI 10 cut description. The numbers given along the profile refer to the lithology: (1) brownish diatomaceous and calcareous shale in a prismatic structure including 5.0-wt% concretions, (2) brownish diatomaceous and calcareous shale constituted by thin laminae including 5.0-wt% concretions, (3) brownish diatomaceous and calcareous shale in a polyhedric structure, (4) increase of concretion proportion (from 14.8 to 36.3 wt%) in unit 3, (5) brownish diatomaceous and calcareous shale with concoidal cracks and 5.7 wt% of concretions, (6) brownish and rusty-colored diatomaceous and calcareous shale with only 0.5 wt% of concretions, (7) grey diatomaceous and calcareous shale constituted by thin laminae, (8–10) marly diatomaceous grey silt. (*) Hardened bed, ≈ 5 mm thick. (**) Organic matter rich bed. Results of X-ray diffraction performed on bulk samples, mineralized bullrush stems and chip-shaped clusters: Qz, quartz; Ca, calcite; Cla, clays; Si, crypto-crystalline silica; Ma, magadiite.

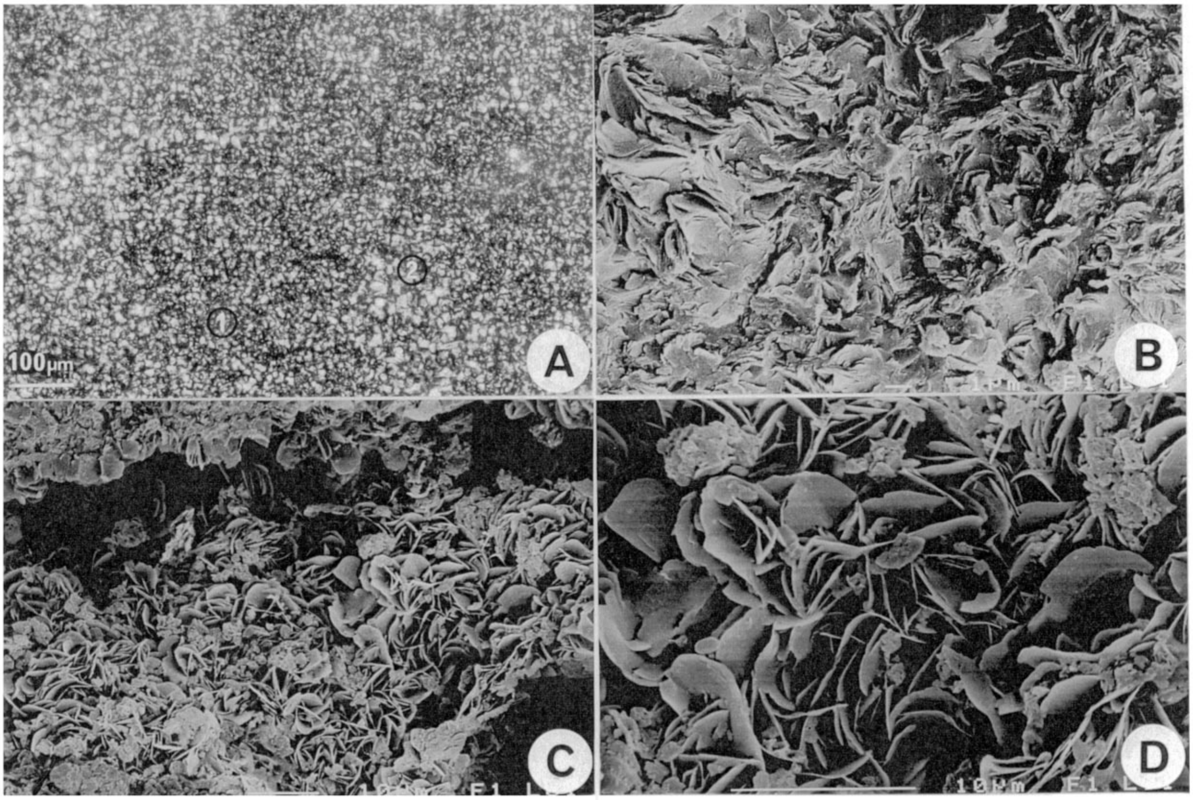


Fig. 5. Massive and plate-like structure. (A) Irregular concretion. Optical microscope photograph in cross-polarized light. Groundmass constituted by magadiite observed in concretions. Two kinds of fabrics have been observed: (1) fine-grained magadiite, and (2) coarse-grained magadiite. (B) Irregular concretion. Scanning electron microscope (SEM) view. Massive magadiite microstructure, locally showing a layered fabric. (C) Bullrush stem. SEM view. Plate-like microstructure of magadiite. This microstructure is mainly located close to cracks and pores. (D) Bullrush stem. Close-up of the randomly oriented plate-like microstructure showing platy crystals.

and bullrush stems) are infilled by a much greater proportion of micritic calcite than in the periphery. As observed by Schubel and Simonson (1990, p. 766) in cherts from Lake Magadi, “the groundmass in some samples also contains calcite crystals that are distinctly coarser than the carbonate which is finely disseminated in the groundmass”. The concretion’s outer layer is coated by micrite and microsparite calcitans, which are the components of the enclosing sediment. Inside the groundmass, eolian quartz grains are slightly corroded and embedded into one or two rims of palissadic light-colored crystals. The overgrowth of the rims sometimes gives a hexagonal shape to the initially rounded to sub-rounded quartz grain.

The pores are coated by a continuous layer of light-colored crystals (Fig. 6a). In cross-polarized light, these bands are composed of individual crystals side by side, with an undulatory extinction, forming a palissadic texture. This texture is associated with and can progressively lead to pseudo-spherulitic crystals (Fig. 7a), and eventually to spherulitic crystals. These textures have also been observed by Rooney et al. (1969) and were described as “spherulitic magadiite in massive fine-grained magadiite matrix” (p. 1038). Schubel and Simonson (1990) observed under the SEM “spherical aggregates of plate-like crystals” in cherts from Lake Magadi.

5.3. Hydrous sodium silicate microstructures

SEM observations have been made on fragments of beds, chips and bullrush stems. Using the SEM, six

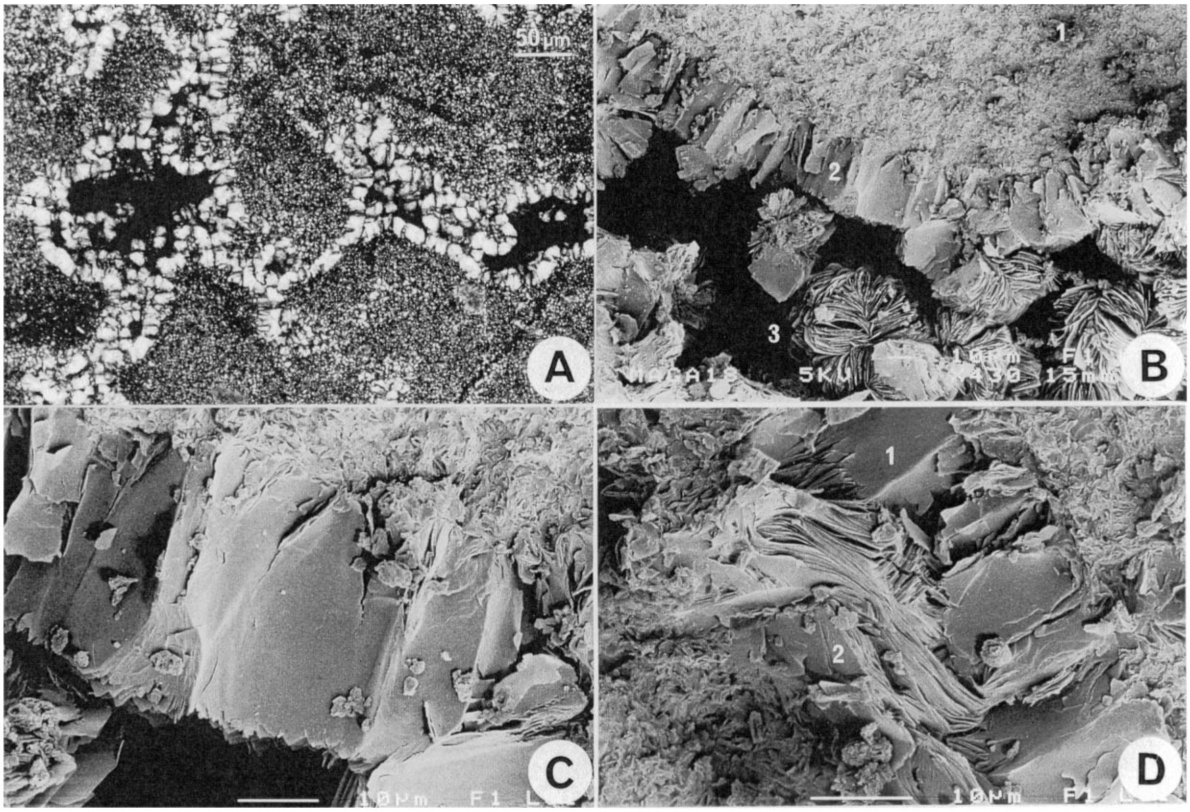


Fig. 6. Palissadic structure in irregular concretions. (A) Optical microscope photograph in cross-polarized light (XPL). Isopachous hydrous sodium silicate coat pore walls, showing a palissadic microstructure. Crystal extinction is undulatory. The transition between the magadiite groundmass and the palissadic coating is very sharp. (B) SEM view showing: (1) the magadiite groundmass in a massive microstructure, (2) the palissadic microstructure, and (3) hydrous sodium silicate spherulites. The last two fabrics are located inside cracks and pores. As observed in XPL, the transition between (1) and (2) is very sharp. (C) SEM view. Close-up of the palissadic microstructure. The crystals show a well-developed face that corresponds to the main crystal growth layer. (D) SEM view. Close-up showing palissadic structure enclosed in massive magadiite groundmass. Two stacks of sheet-like crystals are visible, parallel and perpendicular to the short axes (1) and (2), respectively.

crystal structures have been observed, sometimes associated with one another: massive and plate-like microstructures, palissadic and sheet-like microstructures, spherulitic bodies, isolated crystals. For each crystal type, the silicate and sodium-rich nature was confirmed by microprobe and/or X-rays. However, it was impossible to precisely determine both the chemical composition (structural formula) and the crystallographic characteristics. These groups can be distinguished according to their fabric and the crystal shape.

5.3.1. Massive and plate-like structures

The matrix mainly has a massive fine-grained texture (Fig. 5a and b) and sometimes contains aggregates of plate-like crystals. Most of the concretion texture is massive. It is present everywhere, except on the edges and inside the cracks, where microstructures are modified (Fig. 6b). The plate-like structure is only located close to cracks and pores (Fig. 5c). This structure is composed of randomly oriented flat plates (Fig. 5d). From their characteristics and their relative distribution, massive and platy microstructures correspond to the fine-grained matrix and coarse-grained matrix, respectively, observed under optical microscope.

5.3.2. Palissadic and sheet-like structures

The palissadic structure (Fig. 6a and b), which can

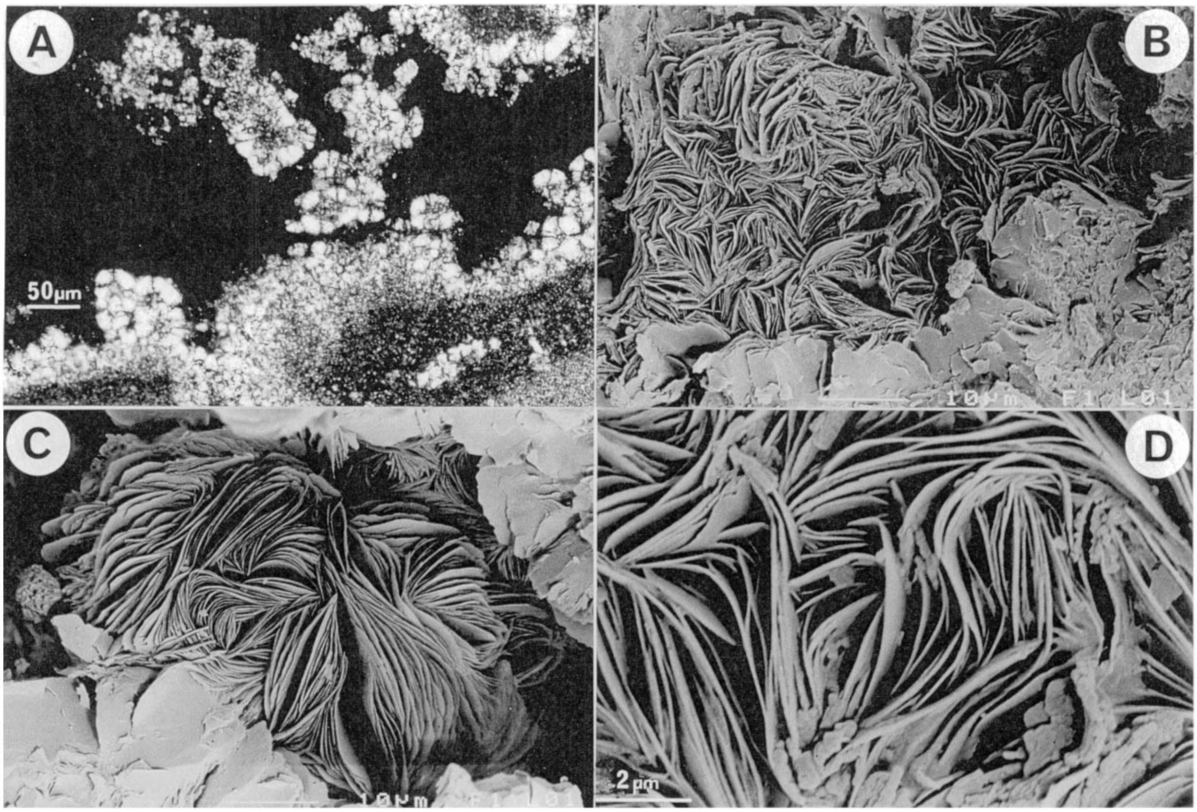


Fig. 7. Irregular concretions. (A) Optical microscope photograph in cross-polarized light (XPL). This photo illustrates the transformation of the magadiite groundmass into a spherule-like microstructure through a plate-like step. Contrary to the palissadic microstructure, the transition between the massive groundmass and the plate-like crystals is progressive and characterized by an increase in the crystal size. (B) SEM view of the sheet-like fabric. This microstructure is always associated with the palissadic fabric and characterized by partly randomly stacked thin bent crystals. (C, D) SEM views. Close-ups of the thin platy crystals composing the sheet-like microstructure.

be compact or platy, is always associated with crack planes within the concretions. Close-up observations, particularly in the transition from massive to palissadic structure (Fig. 6c and d), show that this structure is a stack of thin plates, all oriented in the same direction. This structure can evolve into a sheet-like structure formed by thin curved sheets (Fig. 7b–d). This structure is probably a result of the lack of any preferential direction of crystal stacking. In Fig. 6d, the plates tend to be organized in groups of crystals forming adjacent fans.

5.3.3. Spherulitic bodies

The isolated structures are always found in the middle of cracks (Fig. 8c). Two types of these spherulitic bodies have been observed: (1) the first is constituted by an agglomerate of smaller bodies composed of platy crystals (spherule-like microstructure, Fig. 8a and b), and (2) the second shows fine sheet-like crystals stacked together in a fan form (spherulitic microstructure, Fig. 8d). The first type is directly in contact with the massive or the plate-like fabric (Fig. 8a), whereas the second type is only related to the sheet-like structure (Fig. 8c).

5.3.4. Isolated crystals

Two types of isolated crystals have been observed under the SEM (Fig. 9a). Using the microprobe, they were found to contain sodium, aluminum and silica. These isolated crystals are tabular or styloidic (Fig. 9b and c) and are always associated with plate-like

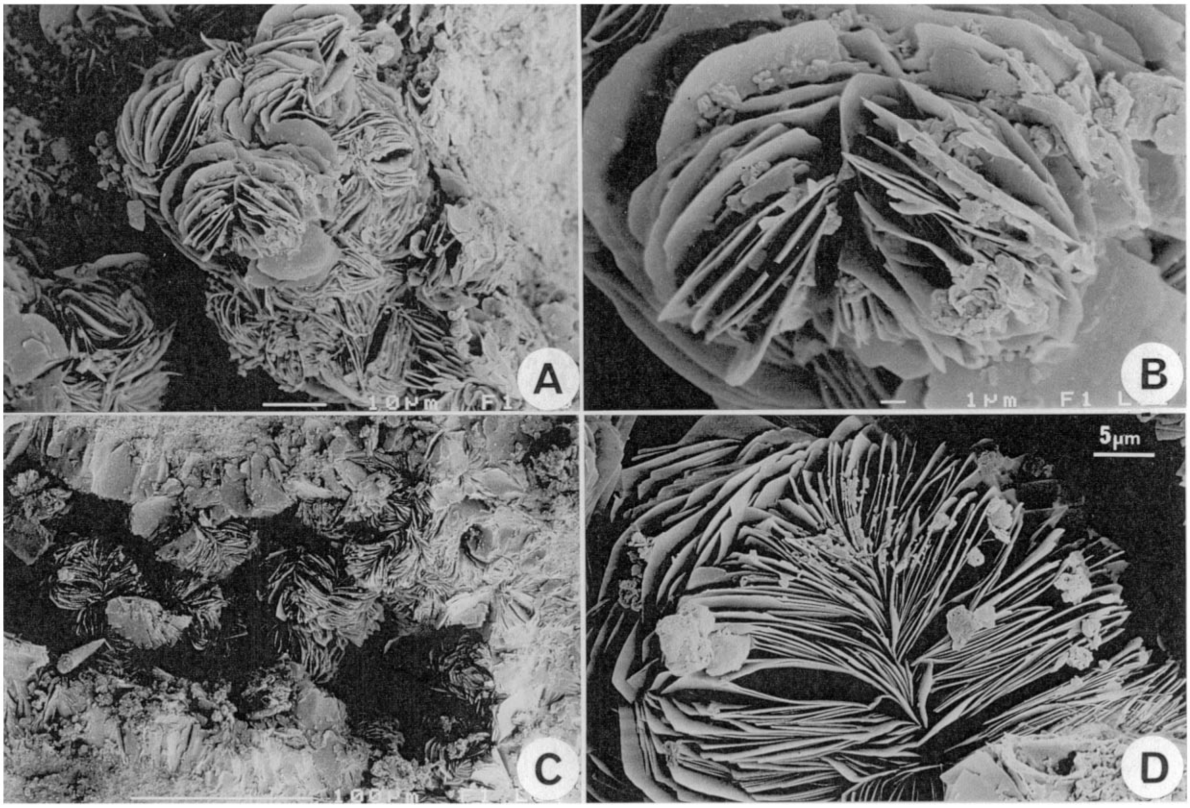


Fig. 8. SEM views of spherulitic bodies. (A) Bullrush stems. Spherule-like association of platy crystals directly in contact with the massive magadiite microstructure. (B) Bullrush stems. Close-up (A) showing the individual crystals composing the spherule-like bodies. (C) Irregular concretions. Spherulites made of hydrous sodium silicate crystal sheets associated with the palissadic and sheet-like microstructures. (D) Irregular concretions. Close-up of spherulite showing the fan-like assemblage of thin individual crystals.

crystals. They were only observed on fragments coming from mineralized bullrush stems.

5.3.5. Distribution of microstructures inside concretions

The microstructures are concentrically distributed. Some of them preferentially occupy the edges, whereas others are found in cracks situated in the central part of the concretions (Figs. 6a and 7a). Two distinct sequences of microstructures can be described, from the groundmass to the void. The first sequence starts with (1) the massive structure, grading into (2) plate-like crystals, ending in (3) spherule-like and/or parallelepipedic and styloidic crystals. The second sequence begins with (1) massive structure in sharp contact with (2) palissadic crystals, followed by (3) sheet-like crystals and (4) spherulites. The palissadic, spherule-like and spherulitic crystals are found in the same place and have the same habit as the calcedonite in the cherts, observed by Schubel and Simonson (1990).

5.4. Geochemistry of hydrous sodium silicates from N'Guigmi

Geochemical analyses have been performed on various samples of magadiite from N'Guigmi. Seven elements (Si, Na, Ca, Mg, Fe, Al and K) have been quantitatively measured by AAS. The data show that N'Guigmi magadiite has a similar composition to analyses in the literature (Fig. 10). In addition, three samples, plotted in the bottom right-hand corner, show an increase in Si and a concomitant decrease in Na content. These samples are composed of chip-shaped

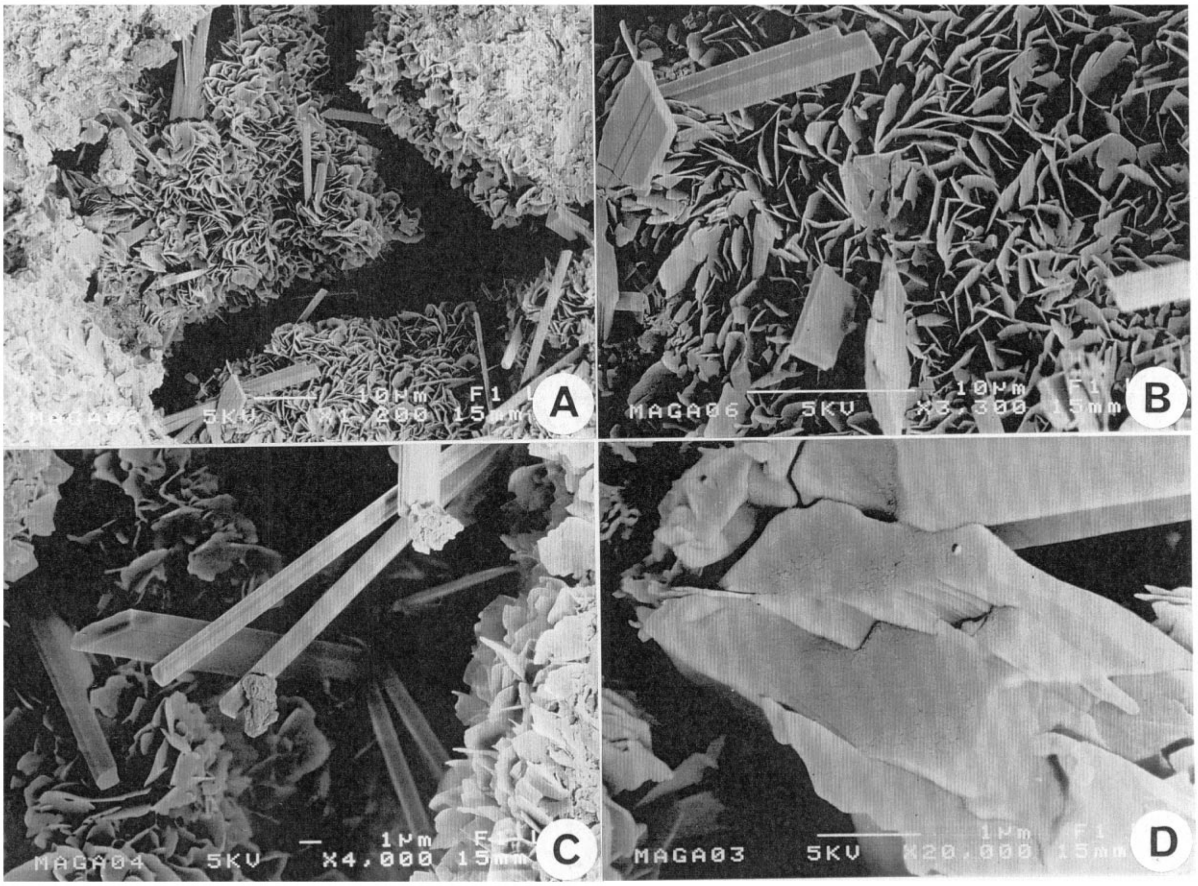


Fig. 9. SEM view of zeolites in bullrush stems. (A) General view of zeolite crystals associated with hydrous sodium silicates. These zeolite crystals are only found in pores, associated with the plate-like microstructure. (B) Close-up of parallelipedic zeolite crystals. (C) Close-up of needle and styloidic zeolite crystals. (D) Close-up of zeolite twinned crystals.

clusters with a desiccation crack network on their surface, indicating their sub-aerial exposure. This group can be interpreted as the result of Na leaching from initial magadiite during weathering, as suggested by Eugster (1969) and could constitute a precursor to diagenetic processes leading to chert.

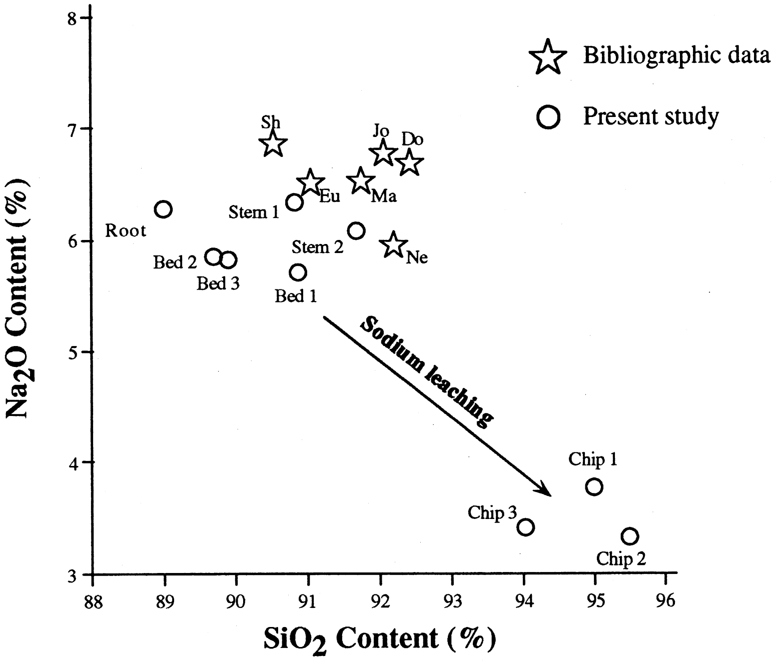
6. Discussion

6.1. The formation of magadiite

The N'Guigmi site constitutes an important deposit of natural hydrous sodium silicates because of its variety of facies: hardened beds, irregular concretions, mineralized plants and scattered crystals. Several types of formation are possible to explain these deposits.

6.1.1. Hardened beds

Different authors have described interstratified magadiite beds within ancient lacustrine sediments (Eugster, 1967) or present-day deposits (Maglione, 1970). The depositional mechanism proposed by Eugster (1969) can be applied to the hardened bed that overlies layer NGI 10-5. This magadiite bed is continuous, massive and molds the surface of the underlying sediments. It can be considered as synsedimentary. It may result from precipitation arising from late evaporitic brines that are highly alkaline



BIBLIOGRAPHIC DATA

	Collected by	Site location	Sample type	Reference
Eu	Eugster, H. P.	Magadi Lake (Kenya)	interstratified beds	Eugster, 1967
Do	Dohman, E. J.	Trinity County (California)	weathered volcanic glass	Mc Atee et al., 1968
Sh	Sheppard, R. A.	Trinity County (California)	weathered volcanic glass	Mc Atee et al., 1968
Ne	Neal, J. T	Alkali Lake (Oregon)	interstratified beds	Rooney et al., 1969
Jo	Jones, B. F.	Alkali Lake (Oregon)	interstratified beds	Rooney et al., 1969
Ma	Maglione, G.	Kanem (Chad)	beds and concretions	Maglione, 1970

Fig. 10. Plot of SiO_2 vs. Na_2O content (%) measured by atomic absorption spectrometry on magadiite beds, rootlets, stems, and chips. The data are compared with those from the literature (table). The plot shows that the composition of the chips may result from sodium leaching due to surficial weathering.

and enriched in dissolved silica. The supersaturation in regard to magadiite is due to a drop in pH caused by dilution of surficial water. The magadiite bed shows no trace of emergence or dehydration (cavities, surface desiccation crack network). Therefore, it was always in contact with solutions. The environment has undergone neither prolonged droughts nor lowering of the piezometric head before hardening of the magadiite bed.

6.1.2. Irregular concretions

Observations and analyses made on concretions from N'Guigmi support the following arguments regarding their genesis: (1) their exterior appearance indicates aerial desiccation (surface desiccation crack network); (2) elemental analyses (AAS) show relatively low sodium content and high silica content in comparison to other samples; and (3) the concretions have a layered appearance that is similar to beds described by Maglione (1970) in interdunal ponds at Kanem.

Based on these arguments, the following mode of formation is proposed. Magadiite, formed at the end of the sequence by evaporation, hardens and breaks up because of desiccation caused by interdunal droughts (Maglione, 1970; Icole and Perinet, 1984). The flakes, which have edges that curl up, show a polygonal crack network on their surface. Later, when water fills the small depressions, the magadiite “chips” are reworked and deposited within palustrine calcareous-clay sediments. Thus, the concretions represent the freshly reworked fragments of a magadiite layer, deposited at the end of the sequence during previous periods of evaporation. The presence of these concretions indicates episodes of drought that were long enough for the formation of magadiite chips. These episodes, responsible for a lowering of the water table, are also confirmed by the presence of outcrops containing polygonal desiccation mudcracks.

6.1.3. Mineralized plant fragments

Mineralization of plant fragments is interpreted by Icole et al. (1983) as being the result of precipitation from interstitial brine. The supersaturation of magadiite is related to a drop in pH, following CO_2 production by fermentation of organic matter after the end of the evaporative phase (Maglione, 1970). Our data do not contradict this process.

6.1.4. Scattered crystals

Magadiite scattered in the sediments can result from precipitation out of: (1) palustrine waters, or (2) phreatic waters by capillary suction in interdunal sediments (Maglione, 1976). In this latter process, the precipitation is associated with the microporosity and is early diagenetic. It implies a drying up of the lake and lowering of the piezometric head, either temporary and related to the lacustrine system or definitive and posterior to the lake’s existence.

6.2. Associated microstructures

From observations made under optical microscope and SEM, five groups of microstructures can be distinguished by their type of fabric and crystal habit. The transition between two microstructures can be either gradual (plate-like to spherulite-like, palissadic to sheet-like, sheet-like to spherulitic) or abrupt (massive to palissadic, plate-like to parallelepipedic or styloidic). Silicated concretions are constituted by at least three distinct crystal phases that correspond, respectively, to: (1) massive microstructures; (2) palissadic microstructures, plate-like and spherule-like, sheet-like and spherulitic, and (3) parallelepipedic and styloidic isolated crystals.

The massive microstructure is present almost everywhere in the thin sections. There is no doubt that magadiite composes most of the concretions (see X-ray diffraction results). Regarding kenyaite, Icole et al. (1983) have identified this mineral by X-ray diffraction in the center of similar concretions from the Manga. In addition, the laboratory-synthesized samples of Beneke and Lagaly (1983) are in the form of: (1) “spherical nodules of plate-like crystals … sometimes embedded in a matrix of amorphous silica”, or (2) “open aggregates of well-developed plates”. The “spherical nodules” are very similar to naturally occurring spherulitic bodies (spherule-like and spherulitic microstructures) observed in the concretions at N’Guigmi. As for “open aggregates”, they resemble the plate-like and sheet-like crystals previously described. Therefore, it is reasonable to think that the plate-like and spherule-like, sheet-like and spherulitic (and thus, palissadic) microstructures correspond to different types of kenyaite aggregates, resulting from various mechanisms. Because of its small proportion, this material has remained undetected using X-ray diffraction on bulk powder samples. Their crystalline characteristics along with aluminum detection by microprobe their distribution indicates that parallelipedic or styloidic crystals can be identified as zeolites, which have been found in similar environments by Maglione and Tardy (1971).

From the distribution of microstructures with regard to the porosity and their relative distribution, three transitions of microstructures can be distinguished: (1) massive to plate-like to spherulite-like, (2) massive to plate-like to zeolites, and (3) massive to palissadic to sheet-like to spherulitic. Certain associations have never been observed, such as massive to sheet-like or spherulitic, sheet-like to parallelepipedic or styloidic. These three sequences could have resulted from either: (1) a precipitation, or (2) an early diagenetic sequence.

These sequences could be organized in the following way (Fig. 11):

1. Magadiite precipitates in its massive fabric (massive microstructure) because of a supersaturation in late evaporative brine. The decrease in available dissolved elements in solution (mainly Na) results in a change in geochemical equilibria and leads to the precipitation of kenyaite, due to an

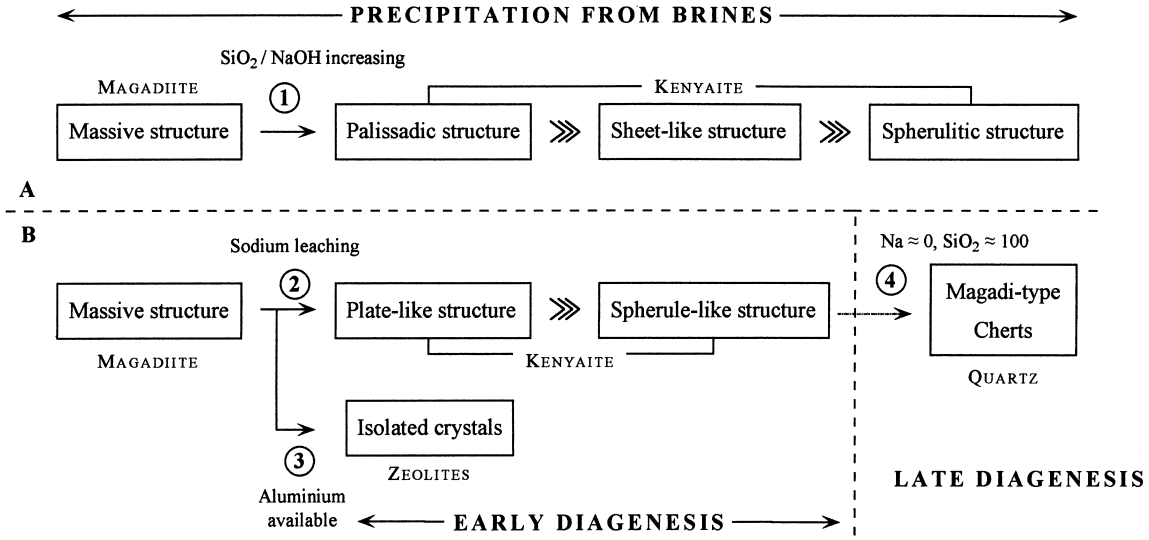


Fig. 11. Microstructural and mineralogical pathways. Three pathways can be proposed to interpret the succession of the various microstructures observed. (A) precipitation from brines: magadiite precipitates from solution. An increase in the SiO_2/NaOH ratio leads to kenyaite precipitation. Different types of microstructures are directly related to this ratio. (B) Early and late diagenesis. Leaching of sodium leads to precipitation of kenyaite. Zeolites can form if any aluminum is available in the environment. During late diagenesis, the magadiite concretions can transform into Magadi-type cherts.

increase in the ratio of SiO_2/NaOH. The palissadic fabric of crystalline plates changes in relation to the evolution of ionic concentrations (Fig. 11a). The transition between the palissadic and sheet-like microstructure is characterized by the formation of well-developed individual crystals, which gradually aggregate into fans (Fig. 12). Finally, the spherulitic structure corresponds to the coalescence of fans.

2. Massive magadiite forms during early diagenesis (Fig. 11b). The final drying up of the depression leads to the hardening of silicated sodic concretions that crack. This early diagenesis is accompanied by the rearrangement of crystals, leading to kenyaite crystals in plate-like and/or spherulite-like shapes. The transition between the phases of magadiite and kenyaite is not as sharp as in the case of syngenetic precipitations. The presence of mobile aluminum (alterations of clays and diatom frustules) leads to the formation of sodic aluminosilicates, i.e. zeolites (Fig. 9). The final phase in the evolution of magadiite concretions leads to Na depletion and chert formation (late diagenesis).

6.3. Paleo-environmental implications

The genetic mechanisms proposed improve paleoenvironmental reconstructions based on diatom studies (Gasse, 1987; Durand, 1995) and on recent sedimentologic analyses (Sebag, 1998). These studies indicate that the depositional environment was palustrine with occasional stratified waters. This environment was fed by a phreatic water table in a sub-arid context (evaporitic sedimentation, high salinity). Both the diatoms and the sediments indicate a shallow-water environment, colonized by plants and microorganisms (Cyanobacteria) and susceptible to important short-term fluctuations (drought, high water levels, evaporative phases). The study of hydrous sodium silicates emphasizes certain aspects of the evolution of the lake system, as it has been described in the literature.

Before the deposition of the hardened bed (base of bed NGI 10-5), ionic concentrations do not allow the precipitation of magadiite, despite high evaporation. Therefore, this bed is related to an important modification in the lacustrine interdunal system (lacustrine alkaline carbonate-rich waters). After deposition of the bed, repeated fluctuations of wet/dry periods are

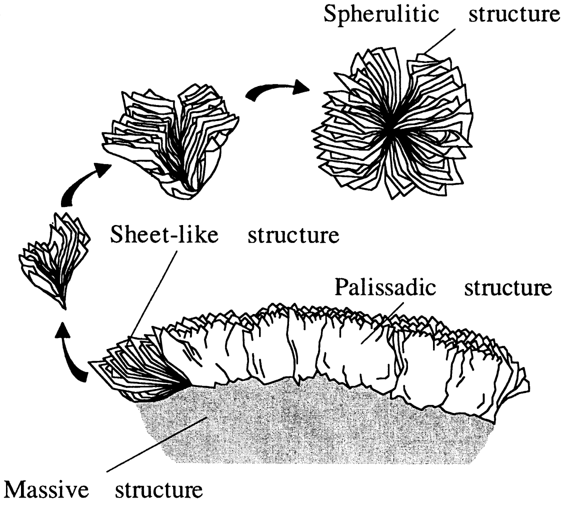


Fig. 12. Sketch showing the transition from palissadic to spherulitic microstructure, passing through the sheet-like fabric step. The palissadic microstructure is directly in contact with the massive magadiite.

favorable to the formation of magadiite (evaporitic episodes followed by water dilution). The evaporation episodes last various lengths of time and are responsible for the desiccation cracks that lead to chip (flake) concretions. During these episodes, the plant debris buried in these sediments mineralize.

The decrease in the abundance of concretions above bed NGI 10-5 can probably be explained by the climatic evolution. Increasing aridity, confirmed on a regional scale (Durand, 1995), leads to a decrease in the frequency of dilution phases by meteoric water, and proportionally, a decrease of beds within the sediments. In addition, this climate change led to interdunal systems that, in several millenia, experienced more and more frequent droughts (centennial, decennial, pluriannual, annual). This favors the formation of magadiite scattered throughout the sediment by evaporation, either syngenetically or early diagenetically. Higher and higher evaporation rates imply: (1) stronger concentrations of waters (syngenetic precipitation), and (2) capillary suction (diagenetic precipitation) during periods of lowering of the piezometric head, which become longer and more frequent.

The diagenetic transformation of naturally occurring sodic silicates into cherts is the main limitation of their use as paleographic indicators. This transformation results in Na depletion and seems to be spontaneous or at least favored by weathering. In the N'Guigmi basin, the transformation of magadiite into chert appears to have been stopped by aridification. Kenyaite is not transformed into quartz and exists in various forms.

7. Conclusions

This study gives new information about hydrous sodium silicates that are neither transformed into cherts nor the result of direct precipitation from present-day brines. These minerals correspond to an intermediate stage of diagenesis. For the first time, these minerals have been used as paleo-environmental indicators, because they occurred at the end of hydro-sedimentary sequences in an interdunal palustrine environment.

The main conclusions are:

1. The chemical analyses on material that has undergone weathering reinforces the hypothesis of leaching of Na and minor ions. If spontaneous transformation of magadiite into cherts is possible (Hay 1968; O'Neil and Hay, 1973), the contribution of weathering (leaching of Na) to the magadiite–chert transformation should not be ignored.
2. SEM observations reveal the existence of different crystalline structures, identified under optical microscope, and other sodic silicate phases, probably

kenyaite and zeolites. These microstructures are found concentrically around internal cracks within concretions and could correspond to either: (1) a precipitation sequence, or (2) an early diagenetic sequence (Fig. 11). Nevertheless, at N'Guigmi, this diagenetic evolution seems to have been stopped and the transformation of magadiite–kenyaite into chert as an early or late diagenetic process has not been observed.

3. This study shows that hydrous sodium silicates should not be underestimated as tools for paleoenvironmental reconstruction during the Holocene.

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