

## SMECTITIZATION OF DIATOMS IN A LACUSTRINE ENVIRONMENT: THE DEBATE IS STILL OPEN

*La smectitisation des diatomées en milieu lacustre : le débat reste ouvert*

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### Abstract

The smectitization of diatoms is a phenomenon that occurred in the hyperalkaline, high-salinity lakes of the Altiplano in the Andes. Smectite is a clay mineral which is commonly used as a proxy to help reconstruct the paleo-climate of continents. Therefore, the possibility that smectite derives from diatom frustules rather than from weathered aluminosilicates on emerged land would challenge this paradigm. The present study aims to investigate diatom smectitization in Lake Pavin, a crater lake (maar) in the French Massif Central (Auvergne region), which appears to gather the suitable characteristics to promote smectitization. The study focuses on the examining the possible progressive degradation of diatom frustules and ornamentations in relation to sediment depth and elapsed time, and its connection to potential smectitization processes. Our SEM-based observations of the siliceous parts of diatom frustules show no evidence of chemical alteration or dissolution of bio-silica remnants, in samples of any age (younger than 6353 aBP). The XRD-based mineralogical exploration points to the absence of smectite in most of the samples examined. Consequently, if diatom smectitization has been well documented in other cases, Lake Pavin is not an ideal location for further research.

### Résumé

La smectitisation des diatomées est un phénomène observé dans les lacs de l'Altiplano andin, caractérisés par une salinité élevée et des conditions hyperalkalines. La smectite est un minéral argileux généralement considéré comme un indicateur paléoclimatique utile à la reconstitution des conditions régnant sur les continents. Dès lors, l'hypothèse selon laquelle la smectite proviendrait des frustules de diatomées plutôt que d'aluminosilicates altérés sur les terres émergées remet en question ce paradigme. L'objectif de cette étude est d'explorer la smectitisation des diatomées dans le lac Pavin, un lac de cratère (maar) situé dans le Massif Central français (région Auvergne-Rhône-Alpes), qui présente a priori les caractéristiques propices à ce phénomène. L'accent est mis sur l'examen de la dégradation progressive des frustules et de leurs ornements en fonction de la profondeur au sein des sédiments, c'est-à-dire, en fonction du temps écoulé, en lien avec les processus potentiels de smectitisation. Nos observations au microscope électronique à balayage des parties siliceuses des frustules de diatomées ne révèlent aucune altération chimique ni dissolution des résidus de biosilice, quel que soit l'âge des échantillons (plus récents que 6.353 ans BP). L'analyse minéralogique par DRX indique l'absence de smectite dans la plupart des échantillons examinés. Par conséquent, si la smectitisation des diatomées a été observée dans certains cas ailleurs dans le monde, le lac Pavin ne constitue pas un site approprié pour la mettre en évidence.

## 1. INTRODUCTION

This project addresses the question of whether diatom frustules (the siliceous skeletons of these unicellular photosynthetic eukaryotes) transform into smectite after death. In sedimentary contexts where detrital inputs are considered predominant, smectite (a phyllosilicate mineral) is classically used by geologists to reconstruct the evolution of the paleoclimate (Milot, 1967a, 1967b; Kübler, 1968; Chamley, 1989). Smectites are widely accepted to be formed on land masses at the expense of feldspars in highly hydrolyzing climatic conditions (i.e. hot and humid) in poorly drained, waterlogged environments (e.g. alluvial plains; Singer, 1984; Chamley, 1989; Thiry, 2000). These minerals are carried by erosion and land-to-sea transfers and are deposited in marine or oceanic environments. They are collected by marine sediments, which thus record the “ambient atmosphere”, which is strongly controlled by the hydrolysis conditions that prevailed on the land masses that provided the terrigenous sedimentary particles. Using smectites as a paleoclimatic tracer is a well-established concept that is still widely accepted today, as evidenced by a large body of international scientific literature (e.g., Abdullayev & Leroy, 2017; Dianto, 2019; Gosh *et al.*, 2019). However, some of our previous observations have revealed sedimentary deposits containing significant amounts of smectite, for which we cannot find a satisfactory explanation in terms of the paleoclimatic, geological or hydrodynamic context. Examples include the Cariaco Basin (Riboulleau *et al.*, 2014); the Southern Ocean (Beny *et al.*, 2020), the Atlantic Ocean (Skonieczny *et al.*, 2016) and a Corsican lake (Leblanc *et al.*, 2020). Additionally, relatively early work on an Andean lake (Badaut & Risacher, 1983) suggests that smectites may sometimes result from the rapid transformation of diatom skeletons (within a few weeks). More recently, several studies have highlighted the diagenetic transformation of biogenic siliceous particles into clay minerals in various sedimentary contexts, including soils, lakes and marine sediments at different depths (Yuretich *et al.*, 1998; Fagel *et al.*, 2003; Pace *et al.*, 2017; Steiner *et al.*, 2022; Pellegrino *et al.*, 2023; Müller *et al.*, 2023). In 2025, Zhao *et al.* conducted laboratory experiments in which the degradation of diatom frustules was carried out in artificially cations enriched seawater, in order to examine the transformation of “simple” silicon oxide into a more complex phyllosilicate. This chemical reaction is known as reverse weathering. The authors observed the formation of iron-bearing smectite and mica within 40 days (Zhao *et al.*, 2025). While the authors discussed the consequences that reverse weathering may have on marine alkalinity, they did not consider its implications for interpreting the origin of smectite. Here, we focus on smectite (a large family of phyllosilicates) because, mineralogical and chemically, this relatively complex mineral, is more susceptible to diagenetic evolution than other clay

minerals. If it turns out that smectite sometimes originates from the transformation of diatom frustules in lacustrine or marine environments rather than feldspars on the continent, the value of smectites as a paleoclimatic marker of continental zones must be re-evaluated. It is not a question of denying the value of sedimentary smectites as paleoclimatic tracers, but rather of improving our understanding of the genesis of these minerals in order to avoid pitfalls when interpreting clay data, and make optimal use of these valuable “paleo” markers.

Lake Pavin, a crater lake in the Auvergne region of France, was chosen as the location for the study workshop because it is a diatom-rich environment. This is notable, given that other French lakes, such as Lake Geneva, Lake Bourget and Lake Annecy, tend to be carbonate-rich. Furthermore, while diatom blooms occur each year in these three alpine lakes, they are mainly oligospecific (comprising two or three taxa) and short-lived (Frossard *et al.*, 2022). In contrast, Lake Pavin hosts diverse diatom populations distributed throughout the year (Rimet & Druard, 2009; Jacquet *et al.*, 2020; Frossard *et al.*, 2022; Sereyissol *et al.*, 2024), enabling the collection of a wide variety of diatom taxa and morphologies. This makes it possible to study how taxonomy and the shape of siliceous objects influence the transformation of frustule silica into smectite minerals. Rapid mineralogical transformation of silica requires alkaline and basic water, as is the case for Lake Pavin (Olivier & Boulègue, 2004). A dating system is also required to assess the role of time in mineralogical transformation by dating the studied samples. Lake Pavin has been the subject of numerous studies since the beginning of the 20th century (Chassiot *et al.* 2016, 2018), and existing databases meet our requirements. Additionally, this lake has a very small catchment area and is surrounded by dense vegetation, which limits the input of particles from the air.

## 2. GENERAL FEATURES OF LAKE PAVIN

Lake Pavin is a 92-m-deep meromictic maar located in the Mont-Dore region of the Massif Central in France, at an altitude of 1,197 m above sea level (Fig. 1). It has a diameter of 750 m and the surface area of 0.44 km<sup>2</sup>. Its bowl-like shape results from a phreatomagmatic eruption that occurred around 7,000 years ago. The lake has a small watershed of 0.36 km<sup>2</sup> which is now densely covered by forest. Water input is principally due to precipitation and inputs from subaerial and underwater sources located around the crater rim and at the foot of the nearby Montchal stratovolcano. The outflow heads north through an outlet and reaches the Couze Pavin, a tributary of the Allier River and, in turn, the Loire watershed. Lake Pavin is a permanently stratified meromictic lake, with an upper, oxygenated, seasonally mixed water layer (mixolimnion) and a permanently anoxic, sulfidic layer below a depth of 60 m (monimolimnion) (Fig. 2; Busigny *et al.*, 2016; Havas *et al.*, 2023; Jézéquel *et al.*, 2016).

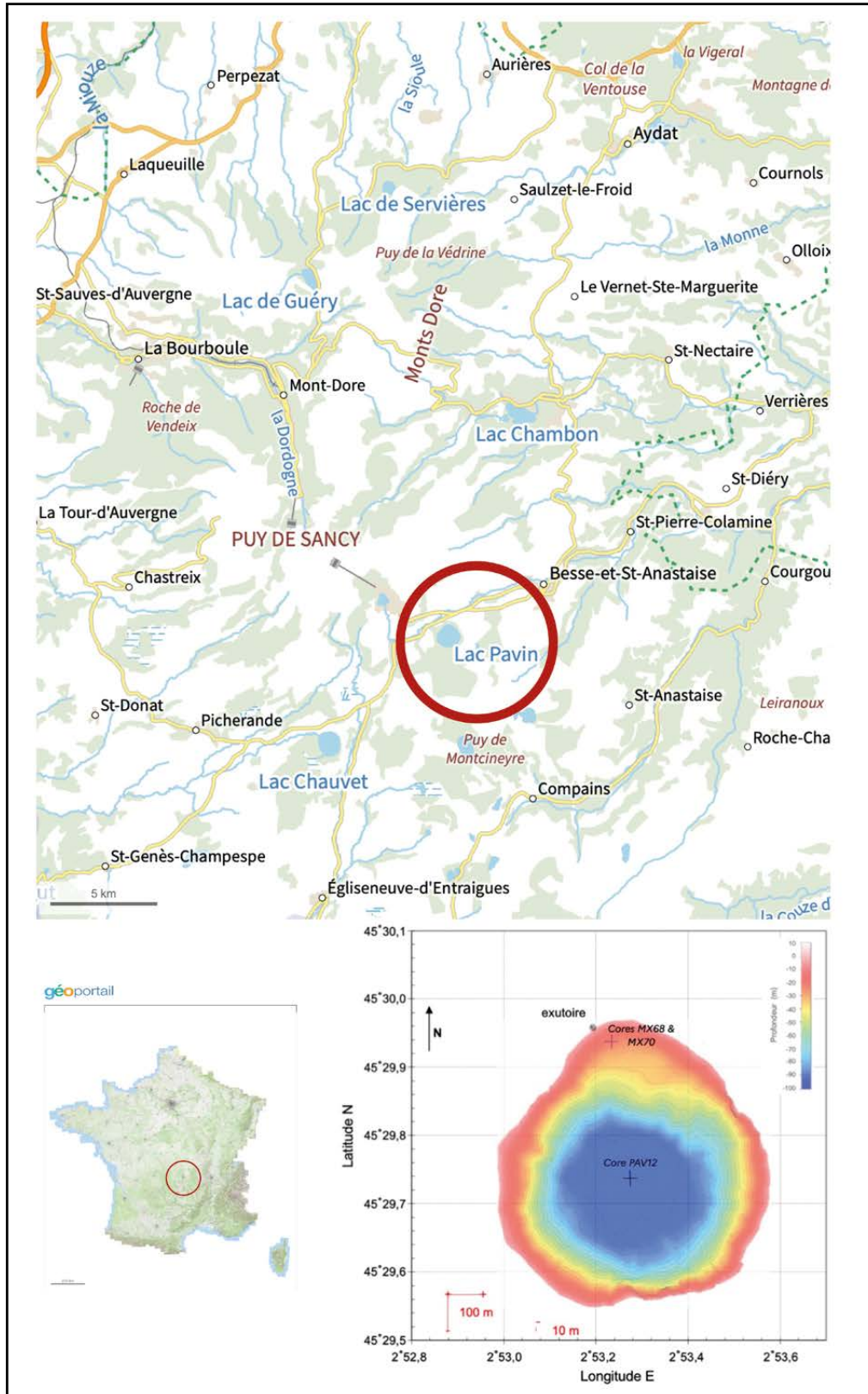


Figure 1. Location of Lake Pavin (A) in Auvergne (B), close to the Puy de Sancy volcano.(C) bathymetry of the lake and locations of the three cores studied. Panels A and B from the Géoportail website of the French Institut de l'information géographique et forestière (IGN), and panel C is adapted from Chapron *et al.* (2000).

Figure 1. Localisation du lac Pavin (A) en Auvergne (B), à proximité du Puy de Sancy, et (C) bathymétrie du lac, ainsi que la localisation des trois carottes étudiées. A et B proviennent du site web Géoportail de l'Institut de l'information géographique et forestière (IGN); C est adapté de Chapron *et al.* (2000a).

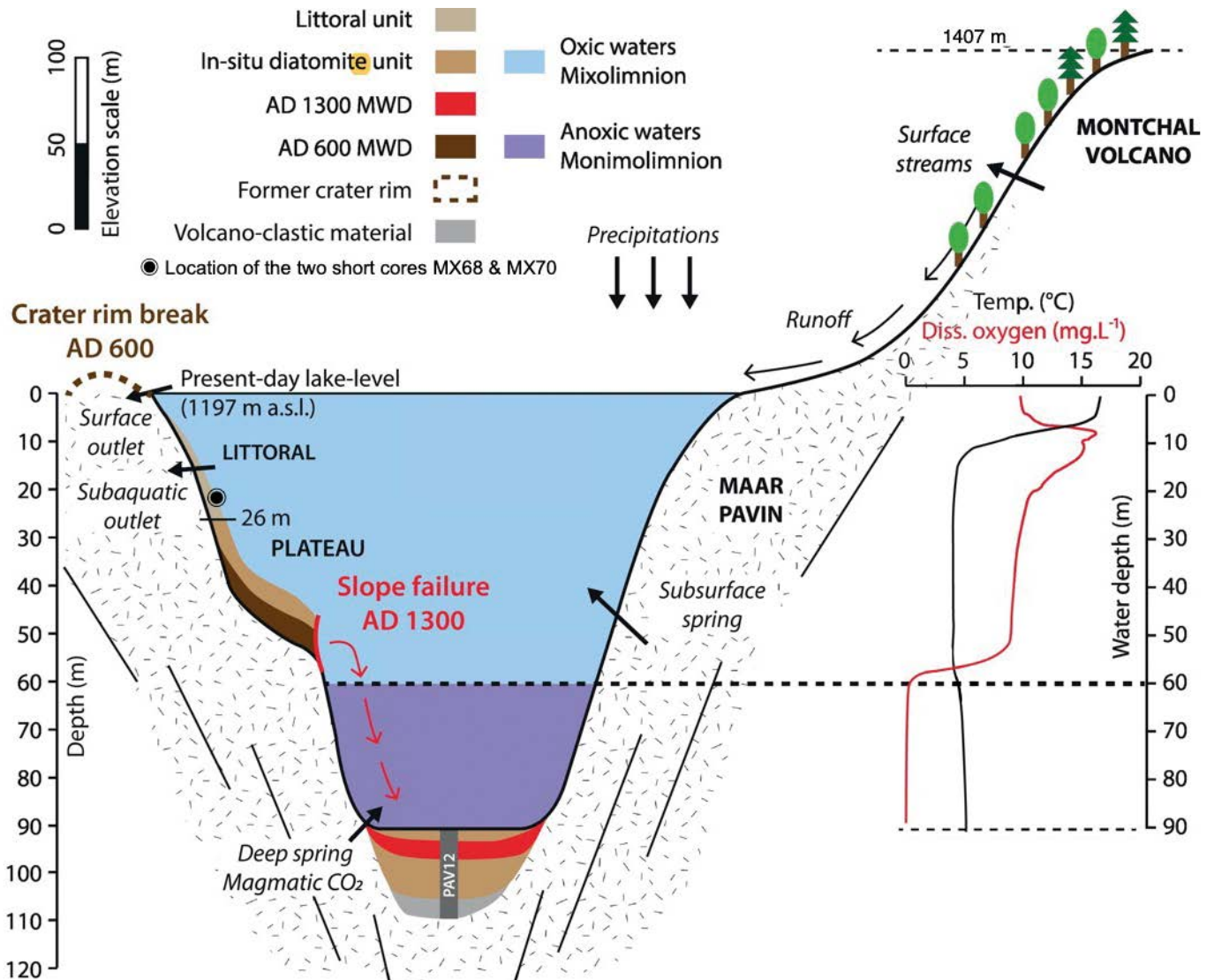


Figure 2. Cross section of Lake Pavin is showing the distinct layers of water layers, and the distribution of oxygen and temperature distribution with depth (modified from Serieyssol *et al.*, 2024).

Figure 2. Coupe transversale du lac Pavin illustrant la stratification marquée des couches d'eau, ainsi que la distribution de l'oxygénation et de la température en fonction de la profondeur (modifiée d'après Serieyssol *et al.*, 2024).

Lake Pavin has a relatively stable and protected environment allowing for sediment conservation. Detrital inputs are low, primarily from runoff. The lake is surrounded by a mixed deciduous and coniferous forest, which limits exposure to direct sunlight and protects the water from regional winds. This contributes to the lake thermal stability and the near absence of eolian dust inputs, as well as reducing the disturbances to the system. The lake yields sediments ranging from sands on shoreline banks to finer, typically lacustrine, sediments with dark brown homogeneous facies (Chapron *et al.*, 2010). Fine lacustrine sedimentation can be interspersed with sandy beds rich in leaf debris, reflecting sporadic, significant inputs of reworked sediments,

including a layer dated to 700 years ago (650 AD). The sedimentation rate is estimated to be between 1 and 3,4 mm per year (Chassiot *et al.*, 2016).

### 3. MATERIAL AND METHODS

#### 3.1. Sediment cores

Three sediment cores were studied. The two short sediment cores analyzed in this study (cores MX68 and MX70) were collected at a depth of 20 ms in the northern part of the lake, near its outlet (Figure 2; N 45°29.93724, E 2°53.23428), using a 90 mm-diameter UWITEC corer. These both 30 cm-long cores were retrieved from the upper plateau, a

relatively shallow area of the lake characterized by well-oxygenated conditions. Samples were collected at 2 cm intervals, then dried and stored in plastic boxes prior to analysis. Each sample was associated with a precise core depth, enabling the monitoring of possible frustule degradation from the surface layer (1 cm below the lake bottom) to a depth of 29 cm. According to Chassiot *et al.* (2016), Figure 23.4 of their paper allows for an estimation of the sedimentation rate based on the PAVO8 sediment core. Using the conventional radiocarbon reference date of 1950, an age of 400 years cal BP corresponds to 475 years before 2025. Over this period, 30 cm of sediment accumulated, yielding an average sedimentation rate of 6 mm per year.

A longer core (PAV12; Chassiot *et al.*, 2018; Serieyssol *et al.*, 2024) has been sampled. This core was collected in the deepest part of the central lake (Fig. 2). Two diatomite layers (the upper and lower diatomite units, respectively) are separated by a reworked mass of sediment linked to regional earthquakes at ca. 600 and ca. 1300 CE (Chapron *et al.*, 2010, 2016; Chassiot *et al.*, 2016a, 2016b). From base to top, the stratigraphy of PAV12 can be summarized as follows: (1) a basal unit (1045–1400 cm) consisting of laminated volcanoclastic materials interbedded with turbidites, (2) the lower diatomite unit (628–1045 cm), (3) the reworked mass (228–628 cm), and (4) the upper diatomite unit (0–228 cm). Eight samples have been picked along the core (Table 1). As PAV12 is much longer than the MX68 and MX70 cores, the ages of the samples studied here are much higher, spanning an interval of 3297–6353 years cal BP.

Table 1. Age distribution with depth for core PAV12 (after Serieyssol *et al.*, 2024).

Tableau 1. Distribution des âges en fonction de la profondeur pour la carotte PAV12 (d'après Serieyssol *et al.*, 2024).

| Sample ID | Core number | Depth range (cm) | Cal BP (a) |
|-----------|-------------|------------------|------------|
| DICo68    | PAV12-1C    | 545-550          | x          |
| DIC103    | PAV12-1E    | 830-840          | 3297       |
| DIC102    | PAV12-1E    | 840-850          | 3433       |
| DICo90    | PAV12-1E    | 950-960          | 5021       |
| DIC122    | PAV12-1F    | 1010-1030        | 6051       |
| DIC121    | PAV12-1F    | 1031-1036        | 6231       |
| DIC120    | PAV12-1F    | 1040-1045        | 6353       |
| DIC110    | PAV12-1F    | 1115-1120        | x          |

### 3.2. Analyses

The diatoms were imaged using a scanning electron microscope (SEM) with two modes: secondary electrons (SE) and backscattered electrons (BSE). The microscope

was equipped with a EDS-probe. An aliquot of sediment was dispersed in a drop of distilled water, placed directly on the stub until it was air-dried. The stubs were coated with a carbon conductive layer of 20 nm thick to enhance electron conduction during SEM observation.

Clay-size fraction extraction was processed following the protocols described in Bout-Roumazeilles *et al.* (1999). X-ray diffraction (XRD) was performed using a Bruker D8 Endeavor (Cu, 40kV and 40 mA) coupled with a Lynxeye XE-T, with a scan range of 2,5°2theta and 60°2theta for the bulk rock and 32,5°2theta for the clay fraction. Identification and quantification were performed using Macdiff software and X-PERT Highscore+. We searched within database products using both the Powder Diffraction File (PDF2®), which is linked to the International Center for Diffraction Data (ICDD), and the RRUFF project.

## 4. RESULTS

### 4.1. Diatoms

SEM observations allow us to examine diverse populations of frustules with varied morphologies as well as forms related to the different stages of the reproductive cycle of lake diatoms, such as very fine filaments and auxospores (Figs. 3 and 4). While the frustules encountered are very similar to those previously identified in studies of Lake Pavin, we will refrain from making any taxonomic identification (as we are not specialists) and instead focus our observations on the various types of bio-silica objects we have observed. The objective is to establish whether the frustules or, more broadly, the siliceous objects associated with diatom skeletons, such as filaments, exhibit signs of dissolution. Thus, it appears from our observations that no trace of chemical degradation of the diatoms is visible. This applies to all samples observed, regardless of core sample, depth (and therefore age), taxon, fineness, size, or degree of ornamentation of the objects and structures. Figures 3 and 4 shows that even the most delicate structures, which would be expected to be the most fragile chemically, are well preserved.

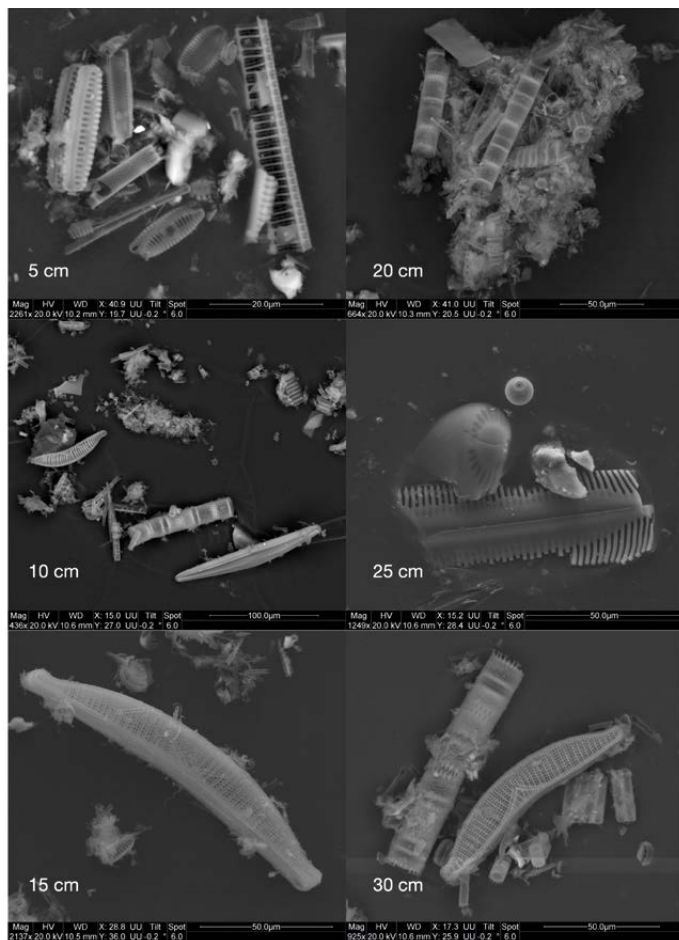


Figure 3. Scanning electron microscope (SEM) images of samples spanning the entire length of the short cores (here, MX68; every 5 cm). The frustules and related biosilica parts may be broken but there is no vertical evolution showing any dissolution trend. This can be compared with the absence of smectite, except in a one sample (core PAV 12, DIC 110; Table 2).

Figure 3. Images MEB d'échantillons prélevés sur toute la longueur des carottes courtes (ici, MX68; tous les 5 cm). Les frustules et les fragments de biosilice associés peuvent être fragmentés, mais aucune évolution verticale ne montre de tendance à la dissolution. Ceci est cohérent avec l'absence de smectite, à l'exception d'un échantillon (provenant de la carotte MX68, tableau 2).

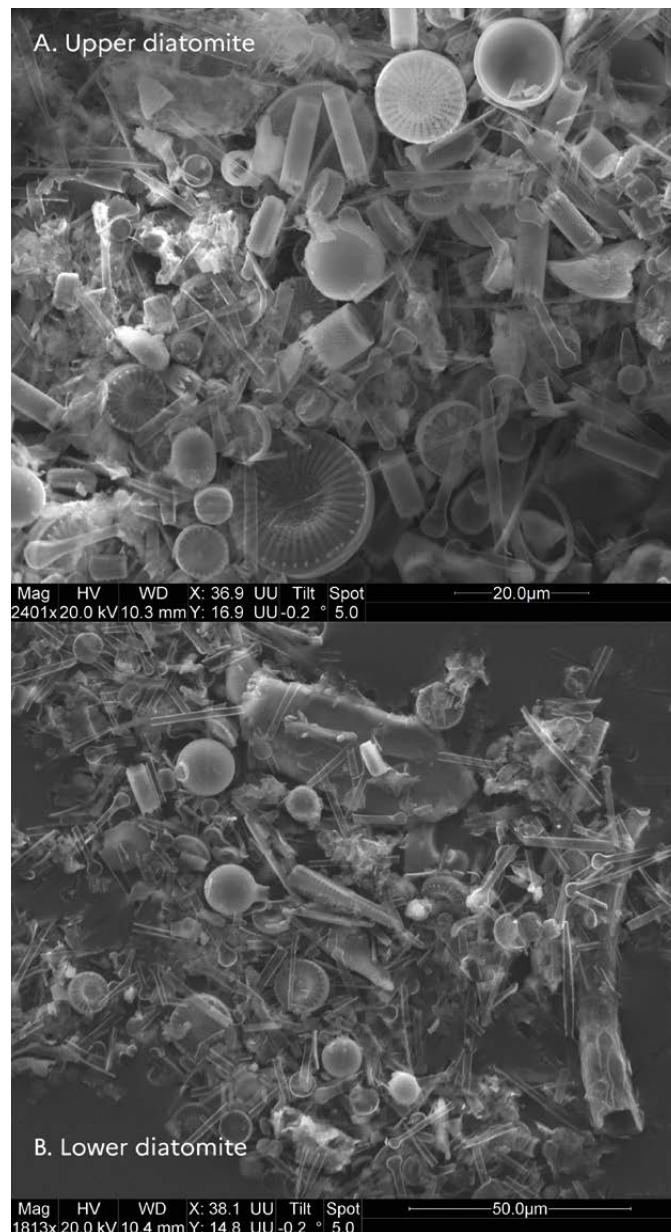


Figure 4. Scanning electron microscope (SEM) images of samples from the two diatomite layers : A for the upper layer and B for the lower layer. In both cases, the finest ornements are well preserved, showing no signs of dissolution.

Figure 4. Images MEB d'échantillons provenant des deux couches de diatomite : A pour la couche supérieure et B pour la couche inférieure. Dans les deux cas, les ornements les plus fines sont bien conservées, sans trace de dissolution.

## 4.2. Mineralogy

**Table 2** summarizes the minerals identified in the sediments. The presence of these minerals is logical, given the type of volcanism and magnetism of the volcanic context of Lake Pavin. Consistent with the purpose of this work, the

observation focused on the presence of smectitic minerals. No sample from the short cores revealed the presence of smectite as trace amounts. One sample of the long core (corePAV 12, sample DIC 110) contains smectite.

Table 2. Mineralogical composition of the bulk sediment and of selected clay-mineral assemblages for cores MX68 and MX70. The symbols + and ++ indicate that traces of pyroxene were detected but could not be quantified.

Tableau 2. Composition minéralogique du sédiment total et d'assemblages de minéraux argileux sélectionnés pour les carottes MX68 et MX70. Les symboles + et ++ indiquent la présence de traces de pyroxène non quantifiées.

| Core 68 bulk rock | quartz % | plagioclase % | k-feldspar % | pyroxene |
|-------------------|----------|---------------|--------------|----------|
| A (core top)      | 6        | 50            | 44           | ++       |
| B                 | 4        | 54            | 42           |          |
| C                 | 6        | 44            | 50           | ++       |
| D                 | 5        | 37            | 58           |          |
| E                 | 7        | 48            | 45           | +        |
| F                 | 9        | 47            | 44           |          |
| G                 | 8        | 48            | 44           | ++       |
| H                 | 6        | 30            | 64           |          |
| I                 | 7        | 38            | 55           | +        |
| J                 | 6        | 38            | 56           |          |
| K                 | 7        | 34            | 59           |          |
| L                 | 13       | 46            | 41           |          |
| M                 | 7        | 36            | 57           |          |
| N                 | 9        | 34            | 57           |          |
| O (core base)     | 12       | 36            | 52           |          |
| Average value     | 7,5      | 41,3          | 51,2         |          |
| Std deviation     | 2,4      | 7,2           | 7,4          |          |

| Core 68 Clay Minerals | Smectite % | illite % | kaolinite % |
|-----------------------|------------|----------|-------------|
| A (core top)          | 0          | 78       | 22          |
| B                     | 0          | 86       | 14          |
| C                     | 0          | 81       | 19          |
| D                     | 0          | 70       | 30          |
| E                     | 0          | 86       | 14          |
| F                     | 0          | 78       | 22          |
| G                     | 0          | 68       | 32          |
| H                     | 0          | 58       | 42          |
| I                     | 0          | 79       | 21          |
| J                     | 0          | 80       | 20          |
| K                     | 0          | 68       | 32          |
| L                     | 0          | 55       | 45          |
| M                     | 0          | 67       | 33          |
| N                     | 0          | 75       | 25          |
|                       |            |          |             |
| Average value         | 0,0        | 73,5     | 26,5        |
| Std deviation         | 0,0        | 9,5      | 9,5         |

| Core 70 bulk rock | quartz % | plagioclase % | k-feldspar % | pyroxene |
|-------------------|----------|---------------|--------------|----------|
| H (core top)      | 5,1      | 52,5          | 42,4         |          |
| I                 | 4        | 55            | 41           |          |
| J                 | 4        | 52            | 44           |          |
| K                 | 4        | 42            | 54           | +        |
| L                 | 3        | <b>54</b>     | 43           | ++       |
| M                 | 3        | 45            | 52           | +        |
| N                 | 3        | 49            | 48           | +        |
| O                 | 1        | 35,6          | 63,4         | +        |
| P                 | 7        | 43            | 50           |          |
| Q                 | 10       | 39            | 39           | +        |
| R                 | 9        | 51            | 40           |          |
| S                 | 8        | 43            | 49           |          |
| T                 | 6,9      | 44,6          | 48,5         |          |
| U                 | 7        | 42            | 51           |          |
| V (core base)     | 5        | 46            | 49           |          |
| Average value     | 5,3      | 46,2          | 47,6         |          |
| Std deviation     | 2,5      | 5,8           | 6,4          |          |

| Core 70 Clay Minerals | Smectite % | illite % | kaolinite % |
|-----------------------|------------|----------|-------------|
| H (core top)          |            |          |             |
| I                     | 0          | 74       | 26          |
| J                     | 0          | 79       | 21          |
| K                     | 0          | 86       | 14          |
| L                     |            |          |             |
| M                     | 0          | 61       | 39          |
| N                     | 0          | 69       | 31          |
| O                     | 0          | 86       | 14          |
| P                     | 0          | 77       | 23          |
| Q                     | 0          | 80       | 20          |
| R                     | 0          | 78       | 22          |
| S                     | 0          | 77       | 23          |
| T                     | 0          | 71       | 29          |
| U                     | 0          | 79       | 21          |
| V (core base)         | 0          | 62       | 38          |
| Average value         | 0,0        | 75,3     | 24,7        |
| Std deviation         | 0,0        | 7,9      | 7,9         |

| Core PAV12 Clay Minerals | Smectite % | illite % | kaolinite % |
|--------------------------|------------|----------|-------------|
| DIC-68                   | 0          | 57       | 43          |
| DIC-90                   |            |          |             |
| DIC-102                  | 0          | 43       | 57          |
| DIC-103                  | 0          | 61       | 39          |
| DIC-110                  | 22         | 47       | 31          |
| DIC-120                  | 0          | 52       | 48          |
| DIC-121                  | 0          | 48       | 52          |
| DIC-122                  | 0          | 44       | 56          |
| Average value            | 3,2        | 50,2     | 46,6        |
| Std deviation            | 8,4        | 6,8      | 9,5         |

## 5. INTERPRETATION

The objective of this study is to search for evidence of the transformation of diatom frustule biosiliceous material of into smectite. Our observations reveal that the frustules show no signs of chemical degradation or dissolution: taxonomy, size, fineness, and depth in the maps are all irrelevant. In other words, no dissolution process can be observed over a depositional time frame of thousands of years (<6353 years). This does not mean that there was no dissolution at all, but no bio-silica object bears visible marks. Similarly, smectite is almost absent from the sedimentary record. The presence of this mineral in the cored sediments is not expected because the local-scale petrography of the watershed and the current and past climatic context over several millennia indicate that it should not be present in the lake unless authigenetic processes are involved.

No traces of the dissolution of the biosiliceous material were observed, no visible clay aggregate formations were detected by SEM. X-ray diffraction only detected smectite in a one sample. While the presence of smectite may be attributed to a diagenetic phenomenon, the transformation of bio-silica that is not necessarily involved. The origin of this smectite remains uncertain: is it due to wind-borne mineral inputs from local/regional soils, or is it authigenic? Even if the smectite is authigenic, this does not mean that it resulted from the transformation of diatoms; it could indeed come from the transformation of volcanic ash, for example. In other words, the arguments developed in this section invalidate the smectitization hypothesis of diatom frustules

in this lake over this timescale. The next question to ask is this: given that smectitization of diatoms has been proposed elsewhere, what factors could oppose it in the case of Lake Pavin? Is the pH level too close to neutral to promote the destabilization of bio-silica over periods of several millennia? Is the lake water too close to saturation in dissolved silica for frustule dissolution to occur? Is the cation content of the water column and interstitial waters too low for authigenic growth to be observed? One way to address these questions would be to examine the sediments of other lakes or paleolakes in Auvergne. In this region, lakes essentially have two origins linked to regional volcanism: maars and dam lakes formed against a volcanic flow (Boivin *et al.*, 2017). Finally, it may be possible to study sediments from French carbonate lakes (Léman, Bourget, Annecy) that contain less dissolved silica, where physicochemical conditions could more easily induce the chemical destabilization of diatom frustules.

## 6. CONCLUSION

The research conducted on Lake Pavin and presented here does not substantiate the hypothesis of smectitization of diatoms in this Auvergne lake within the timeframe considered. However, this finding does not invalidate the hypothesis in relation to other natural environments or longer time periods. This phenomenon has been observed or suspected in several instances, as reported above. Given the importance of understanding and interpreting 'paleo signals', this research will continue.

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