LATE QUATERNARY PALAEOCLIMATE RECONSTRUCTION BASED ON CLAY MINERALS ASSEMBLAGE FROM PRELUCA TIGANULUI (GUTÂI MOUNTAINS, ROMANIA)

LUCREȚIA GHERGARI[1], BOGDAN P. ONAC[1]

ABSTRACT. Several core samples were extracted from the overgrown crater lake of Preluca Tiganului, NW Romania. The overall lithology and the mineral assemblages (mostly clay) described from different levels within these cores, suggest three main periods having humid or dry conditions. Based on these findings, palaeoclimate conditions can be reconstructed the over the time period spanning 15,000 to 13,500 cal. years BP.

Key words: Late Quaternary, palaeoclimate, clay minerals, Preluca Tiganului crater, Gutâi Mountains, Romania.

Geography and geology of the studied area

The aim of this paper is to be present a tentatively reconstruction of the paleoclimate between 15,000 and 13,500 cal years BP based on clay minerals samples collected from Preluca Tiganului swamp.

The area investigated is situated in NW Romania at the border of Satu-Mare and Maramure¿ counties, southeast of the small town of Negreşti-Oaş, on the western flank of the Gutâi Mountains (Fig. 1a). This massif is part of the Eastern Carpathians, oriented in a NNW-SSE direction and averaging 600 meters in altitude. The highest peak in this region is Pietroasa, summit attaining an elevation of 1200 meters.

From a geological point of view this region occurs in a large range of intermediary and acidic rocks (andesites, dacites, and rhyolites) being generated by a Late Pliocene volcanic activity (Borcoş et al., 1979). Two subtypes of andesites occur. One subtype has as its main component pyroxenes (Săpânța andesite), while the other, is rich in quartz (Şuior andesite). The latter is highly weathered around the confluence of the Pietroasa and Tiganului creek (Fig. 1b). Weathering of these two subtypes supplied most of the material accumulated in the crater lake. In addition, quartz sandstone, clays and pyroclastic material also appear at lower altitudes.

The study site, Preluca Țiganului, is a small overgrowth crater lake with a surface of above 1 ha situated on the western slope of the Gutâi mountainous region at an altitude of 700 m a.s.l. (Fig. 1a). Gentle slopes surround the eastern and western side of the crater lake while the northern sloop is steep.

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Earlier investigations at Preluca Țiganului by Lupşa (1980) concentrated solely on the palynological analysis of a 710 cm long peat sequence. Recently, Wohlfarth et al. (2001) have undertaken a high-resolution study of pollen, plant macrofossil, charcoal, mineral magnetic and sedimentary analysis. The entire profile was dated by means of ^{14}C AMS.

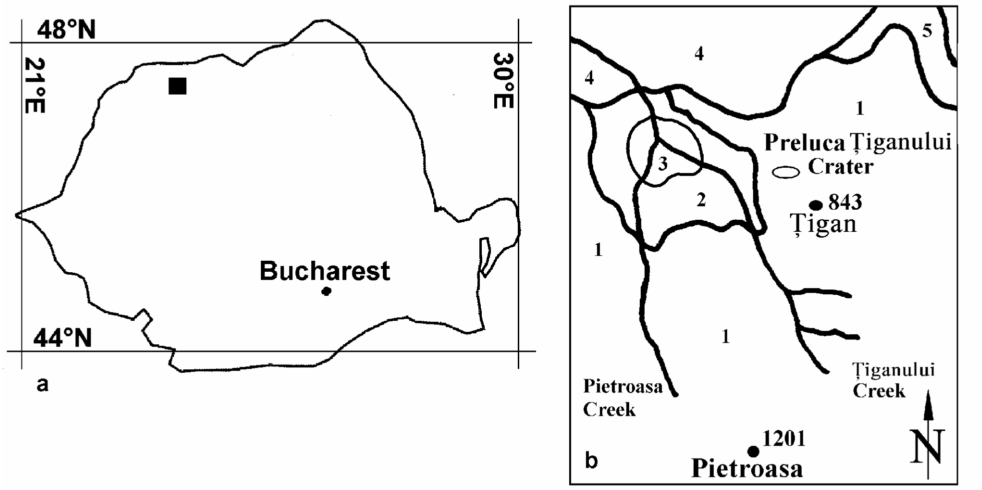

Fig. 1. *Map showing the location of Gutâi Mountains (a), and the geology around Preluca Țiganului Crater (b).*

Field and laboratory analysis

During fieldwork investigations, in June 1997, several cores were obtained along an E-W transect with a strengthened Russian corer having a diameter of 5 cm and a length of 1m. These cores were wrapped in plastic film, placed in half PVC tubes and transported to the Department of Quaternary Geology in Lund, Sweden. There, they were kept in storage at 4°C.

Sub-samples for mineral magnetic analysis, loss on ignition, pollen, plant macrofossil analysis, and AMS ^{14}C measurements were taken from a majority of the cores. Mineralogic (clay minerals) and petrographic (fabric, geochemistry) studies were performed on terrigenous samples randomly selected from the coring point 2a (hereafter CP 2a) (7.6 - 8.6 m), and on a systematic set of samples collected from the coring point 2b (CP 2b) (7.5 – 8.5 m) and 3 (CP 3) (3.8 – 4.8 m) (for details see Wohlfarth et al., 2001).

The description of specific rock texture and structure relies on observations made with a polarizing microscope (Jenapol). Thin sections were prepared perpendicular to the rock stratification. Prior to our investigations the organic matter was removed with H_2O_2 (5%). The composition of the clay minerals was determined using the clay size fraction alone (<2 μm). A range of techniques were used to characterize these compositions including X-ray diffraction (XRD - DRON3) of natural and ethylen-glycol treated samples

(Fig. 2), infrared spectroscopy (SPECORD 75 IR) (Fig. 3), and transmission electron microscopy (TEM - B650). The arenite and silt grades were separated by means of 0.063 mm mesh.

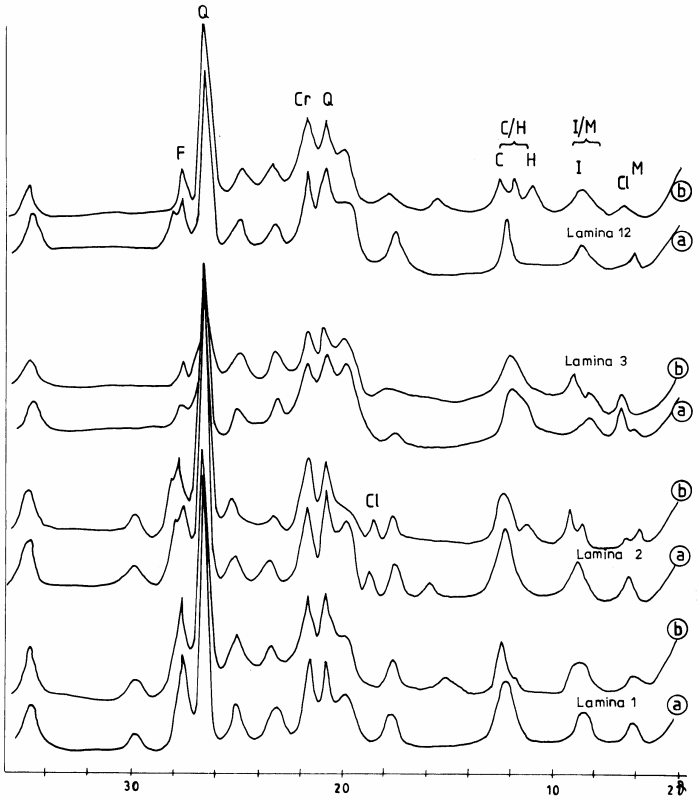

Fig. 2. *X-ray diffraction patterns of clay fraction for four laminae; (a) natural samples, (b) ethylene glycol-prepared samples. Kaolinite (C), kaolinite/halloysite (C/H), halloysite (H), cristobalite (Cr), illite (I), illite/montmorillonite (I/M), montmorillonite (M), chlorite (Cl), quartz (Q) and feldspar (F).*

Using a ***Spectroscan V*** instrument, a vacuum X-ray fluorescence spectrometer (XRF), the major and some minor elements (Na, Mg, Al, K, Ca, Cr, Mn, Fe, Cu, and Zn), from fifteen samples extracted at different levels from the reference core (CP 2b), were analyzed. The concentration of each element was calculated by a PC program through comparison with the results of twenty-five standard samples analysis. Plotted on the same diagram are both the major elements and the cumulative curves that show the percent frequency of the following three particle size classes (2.0 to 0.06, 0.06 to 0.004, and less than 0.004 mm) taken from each of the fifteen samples (Fig. 4).

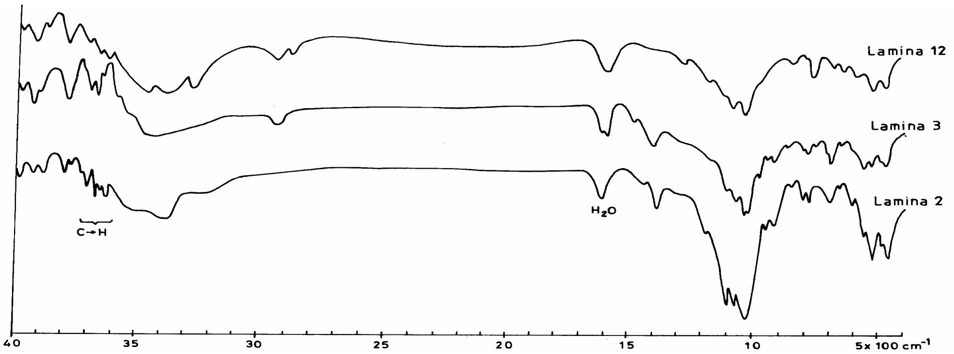

Fig. 3. *Infrared absorption spectra of clay fraction from three laminae.*

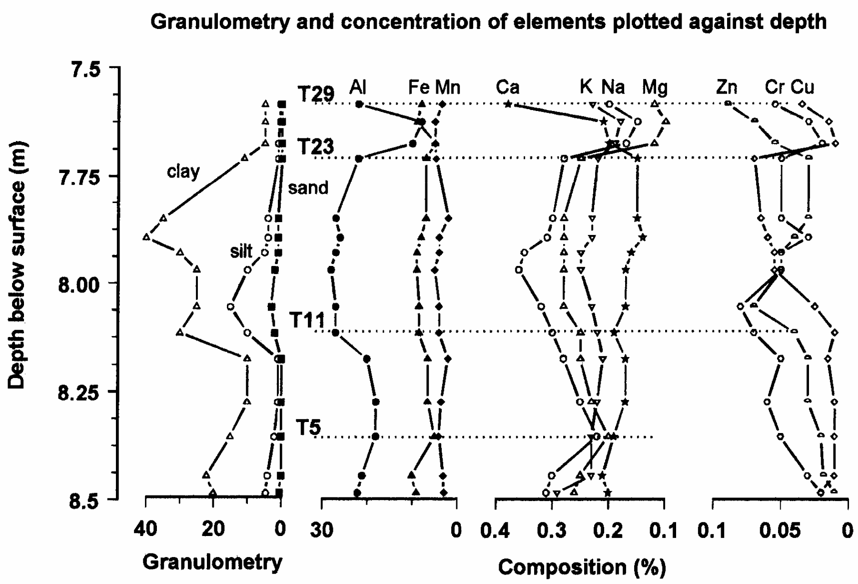

Fig. 4. *Plot of major and trace elements and the cumulative distribution curve for clay, sand and silt (samples were collected from the interval 7.5 to 8.5 m).*

Samples fabric

High contents of lutite and silt, and lesser amounts of arenite characterize the terrigenous rich laminae. Rudite particles were found only in the lower portion of the CP 2a core sample. Based on the particle size distribution of five samples from CP 2a, the following sediments were defined: siltic-arenitic clays, siltic clays, silty-clayey gyttja, and clayey gyttja.

Siltic-arenitic clay occurs in the lower part of the CP 2a (unit 1: 8.51-8.56 m; and 2: 8.465-8.51m) and contains 25-30% silt, 10-15% arenite and approximately 5% rudite (<10 mm in diameter). The rudite only appeared in unit 1. Thin section analysis revealed no structure and a rather poorly sorted material, characteristic of colluvial sediments (Pl. I, Fig 1, 2; Pl. II, Fig. 3).

Siltic clay appears as a thin oriented layer within the gyttja unit 12 (7.86 – 7.915 m). This layer exhibited a visible lamination due to alternating laminae made up of silt-size particles and clay minerals (Pl. II, Fig. 4). A special situation was noticed between 7,90-7,91 m in CP 2b where the rock is build up of soft pebbles consisting of reworked material (lutite-siltite) from the lower part of the sequence.

Clayey and silty-clayey gyttja (unit 3: 8.42-8.465 m) is a mixture of clay with relative amounts of silt and diatom frustules. The voids between diatom frustules are filled by clay, whereas when few occur, they are included within the clay (Pl. III, Figs. 5, 6).

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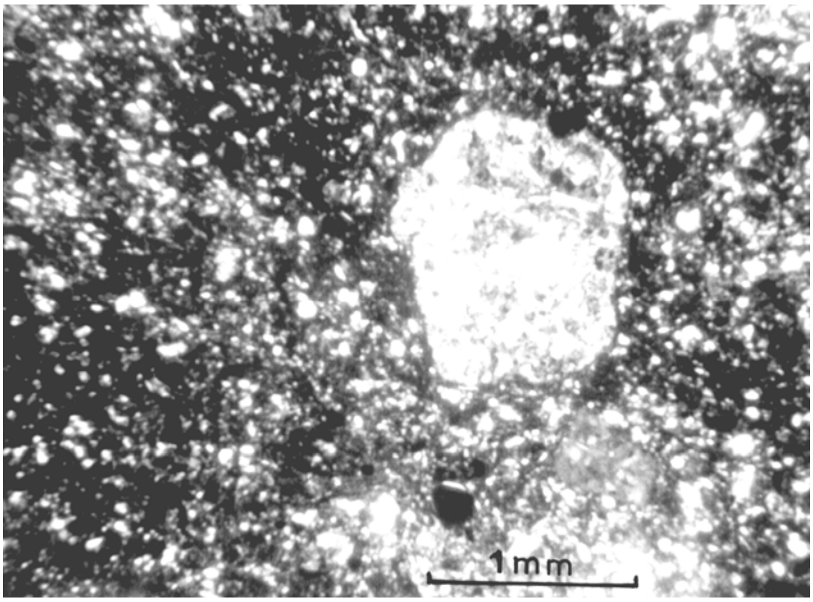
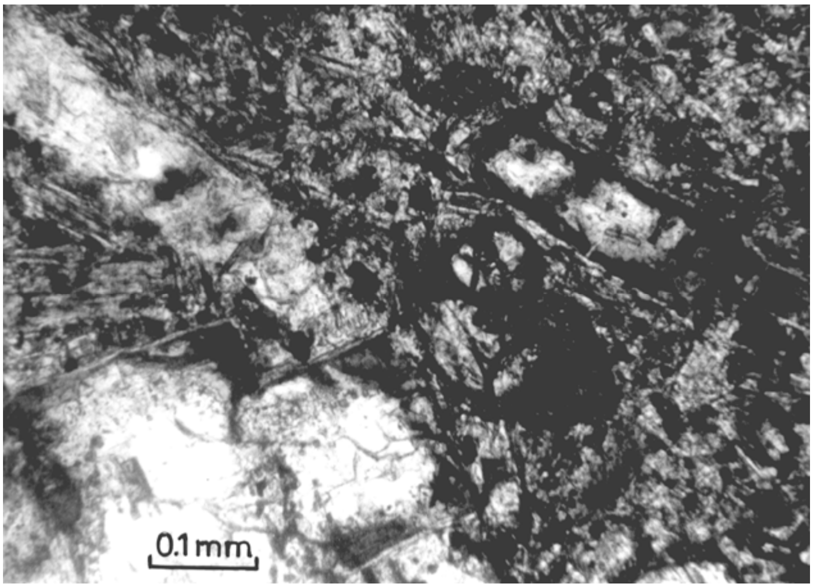
Petrography and mineralogy of rocks

Lithoclasts observed within rudite and arenite grades are made of pyroxene andesites having pilotaxitic or intersertal mass, porphyry-gabbros and volcanic glass.

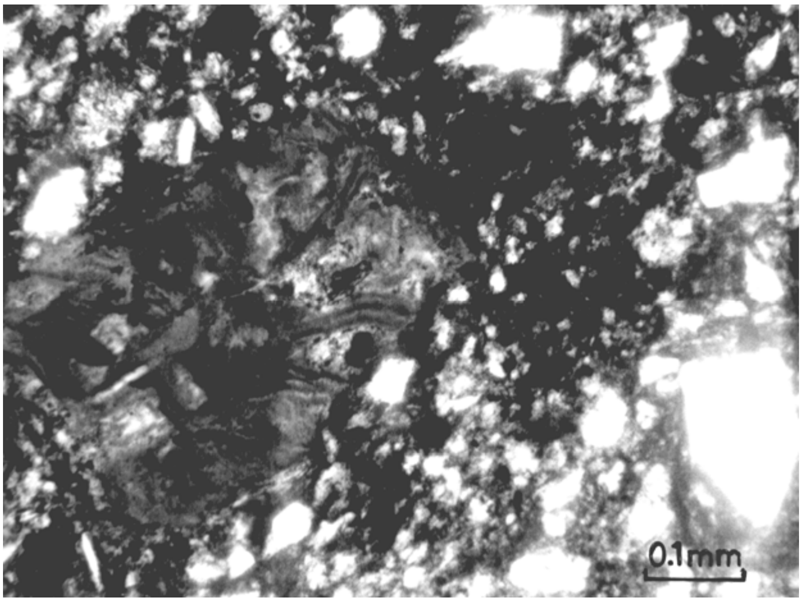
Crystoclasts are common in the arenite and silt grades. They are usually subangular, rarely angular, suggesting a short distance of transport. The presence of weathering sensitive minerals such as olivine, pyroxenes and amphiboles indicate quick burial processes. The crystoclasts may have the following mineral composition: quartz (both magmatic and metamorphic), plagioclase, pyroxenes (hypersthen and augite), green hornblende (rare), muscovite and biotite lamellae. Olivine, zircon, titanite, garnets, epidote, tourmaline and apatite also appear, but only subordinately (Table 1).



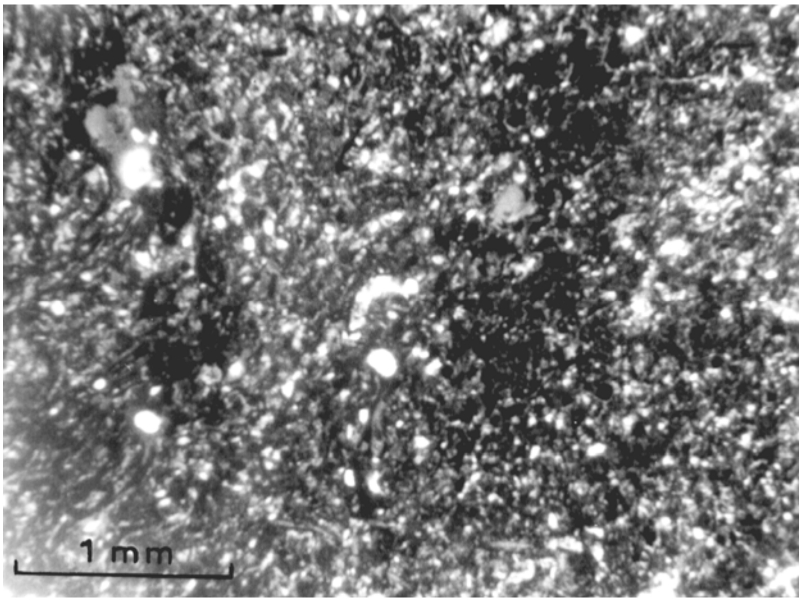
Plansa I. Fig. 1. *Siltic-arenitic clay with a lithoclast of pyroxene andesite (8.51-8.56 m) (plane polarized light).*



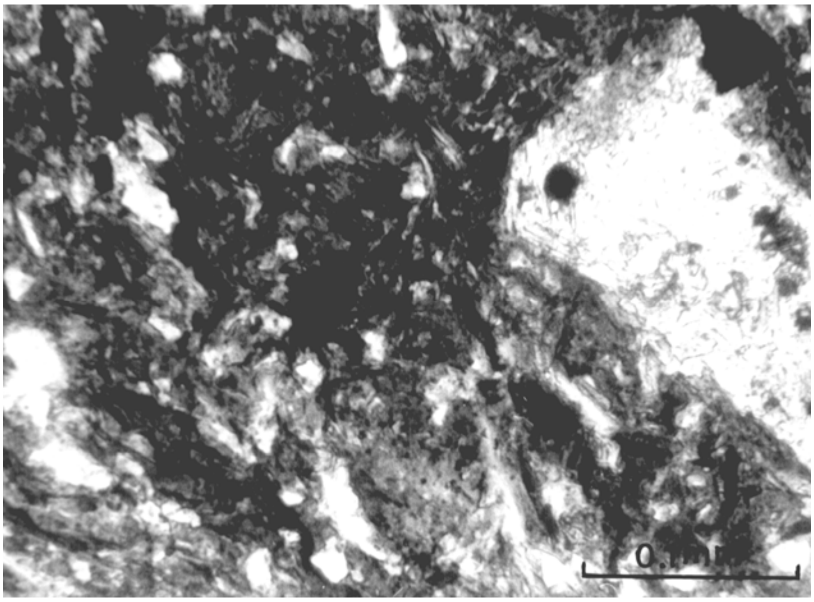
Plansa I. Fig. 2. *Basaltic andesite with pyroxenes and olivine lithoclasts in siltic arenitic clay (8.46-8.51 m) (plane polarized light).*



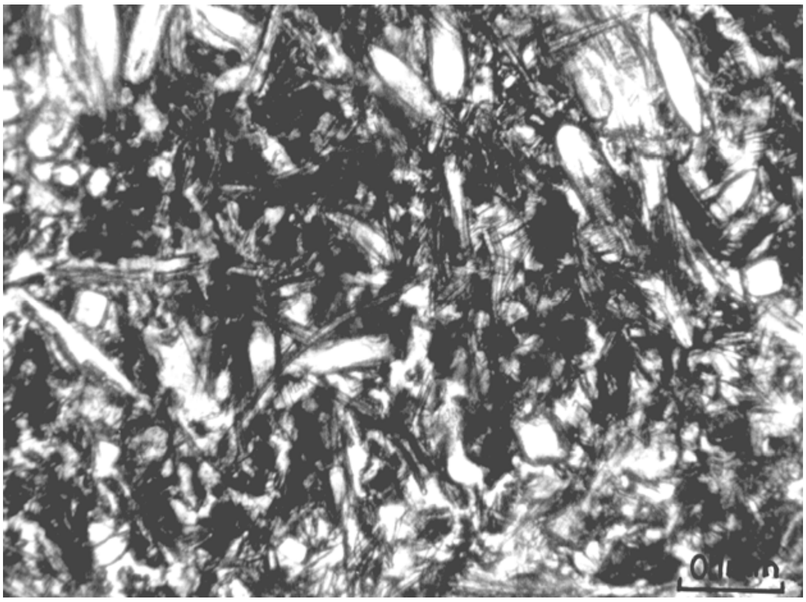
Plansa II. Fig. 3. *Fragment of volcanic glass and crystalloclasts of quartz in siltic arenitic clay (8.46-8.51 m) (plane polarized light).*



Plansa II. Fig. 4. *Siltic clay (7.86-7.91 m) (plane polarized light).*



Plansa III. Fig. 5. *Lithoclasts in clayey gyttja (8.42-8.465 m) (plane polarized light).*



Plansa III. Fig. 6. *Frustules of diatoms in clayey gyttja (8.42-8.465 m) (plane polarized light).*

Table 1.

Mineralogic composition of the clay units in CP 2a

Mineral	Unit 1 (%)	Unit 2 (%)	Unit 3 (%)	Unit 12 (%)
Quartz	26	27	23	24
Plagioclase	20	18	20	22
Mica	11	11	10	10
Pyroxene	8	8	8	8
Clay minerals	26	28	34	27
Cristobalite	8	7	4	7
Other minerals	*	**	***	****

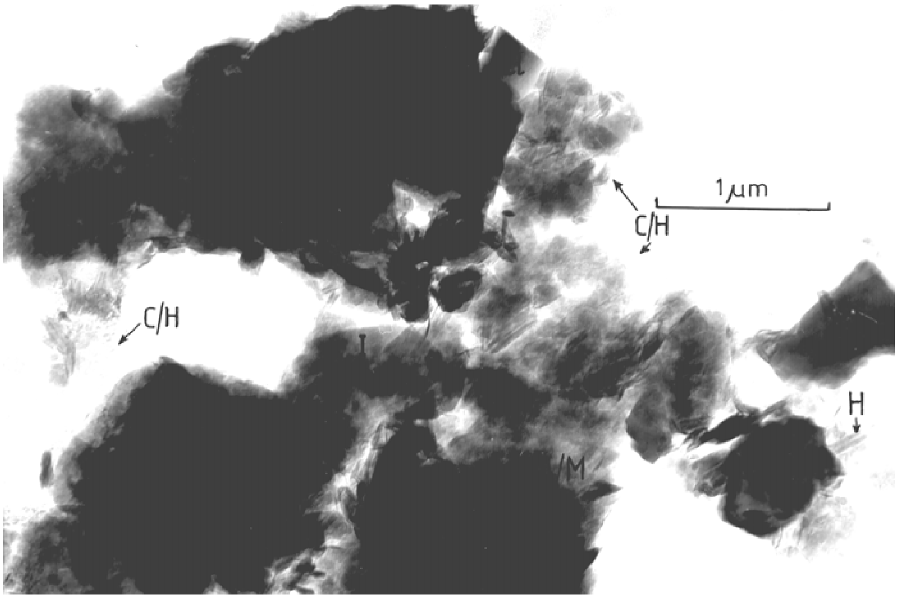
Table 2.

Mineralogic composition of clay fraction (without quartz and feldspars).

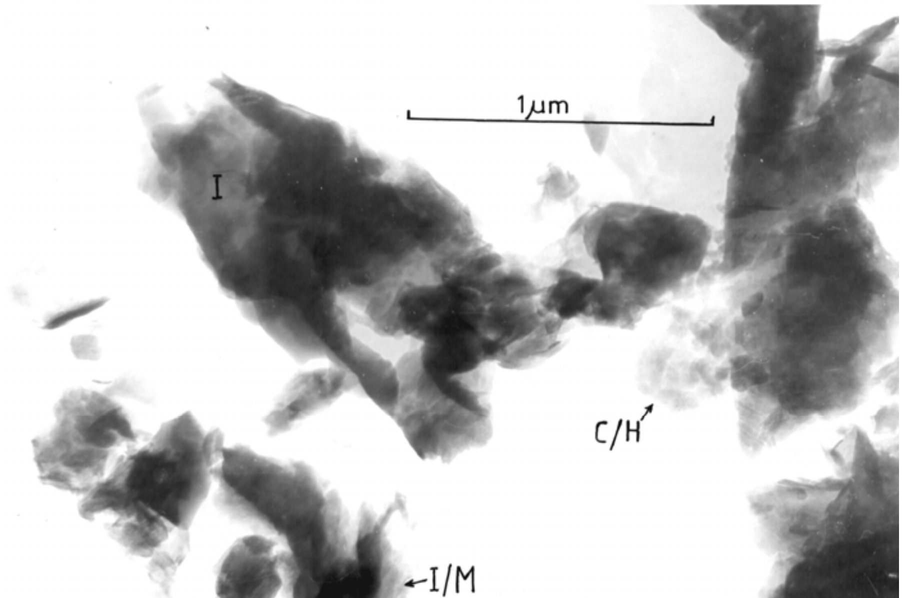
Mineral	Unit 1 (%)	Unit 2 (%)	Unit 3 (%)	Unit 12 (%)
Kaolinite, halloysite	35	38	43	34
Illite, illite/montmorillonite	29	26	25	32
chlorite/illite, chlorite, chlorite/smectite	13	17	21	13
Cristobalite	23	19	11	21

The *clay fraction* (<2 μm) has the following mineral composition: kaolinite, rolled kaolinite, halloysite, illite, illite/montmorillonite, chlorite/illite, chlorite/smectite, cristobalite (formed by kaolinisations processes), feldspars relicts and quartz crystoclasts (Table 2). The clay mineral fraction is dominated by the two-layer clays (1:1) kaolinite–halloysite (43-60%). The three-layer clays, illite and illite/montmorillonite represent only 30 to 40% of the mineral fraction. Three-layer (2:1), trioctahedral minerals correspond to an intermediary weathering phase, and are represented by interstratified chlorite/illite and chlorite/smectite, never exceeding more than 15%. The quantity of cristobalite has a constant weight within the terrigenous laminae (cca 20%) when related only to the clay minerals. In the clayey-gyttja and siltic clay layers diatoms use has significantly decreased the quantity of cristobalite.

All investigated clay minerals vary greatly in their degrees of crystallinity. Kaolinite forms pseudohexagonal fine plates, less than 0.4 μm in size (mean size 0.2 μm). Part of the kaolinite plates exhibit different degrees of rolling, sometimes achieving a tubular morphology that is specific to halloysite. Most of the halloysite is secondary in origin been derived from kaolinite, however, primary halloysite was also recognized (based on length and shape of the capillaries). The genesis of kaolinite is related to the weathering of feldspars from andesitic rocks. Weathering of micas resulted in formation of illite and illite/montmorillonite. Partially hydrated mica and illite usually appear as anhedral flakes. Euhedral illite crystals seldom appear. Illite/montmorillonite develop on the edge of large anhedral flakes of mica forming sheaf-like aggregates. The appearance of chlorite, chlorite/illite and subordinately chlorite/smectite interstratified phases, is due to the weathering of iron-magnesium minerals (Pl. IV, Figs. 7, 8).



***Plansa IV**. **Fig. 7.** TEM image of the clayey gyttja fraction extracted from siltic arenitic clay (8.51-8.56 m); kaolinite and rolled kaolinite (C/H), halloysite (H), illite/montmorillonite (I/M), illite (I), chlorite (Cl).*



***Plansa IV. Fig. 8.** TEM image of the clayey fraction extracted from clayey gyttja (8.42-8.465 m); illite (I), illite/montmorillonite (I/M), kaolinite/halloysite (C/H).*

The siltic clay layers within the peat unit originated in the weathering crust developed on the andesitic rocks that occur around the crater lake. The upper portion of this weathering crust was periodically washed into the basin. Herein, the clay minerals continued to transform. The end products of these transformations are pH and Eh-dependent. The high quantity of kaolinite and halloysite in the clay mineral association suggests cool temperate climate with rainfall up to at least 700 mm/year.

Palaeoclimatic significance of minerals assemblage from Preluca

Clay minerals in sediments can be useful indicators of paleoclimatic conditions, particularly when the sedimentary basins are small. Our paleoclimatic reconstruction mainly uses the systematic data obtained from CP 2b clay mineral association. The following analyses were considered when interpreting the climatic changes around Preluca site: the particle sizes distribution, the mineralogy of silt and arenite, and the main clay minerals ratio (underlying those minerals that reflect the pH/Eh of the environment, Fig. 5). In addition to the above data, the minor and major element concentrations were considered (Fig. 4). According to Churchman (2000), the two-layer/three-layer clay mineral ratio is mainly controlled by climate. Therefore, it is easy to recognize between warm and humid conditions typical for kaolinite or halloysite formation, or dry seasons, specific for illite or smectite formation. Furthermore, the formation of kaolinite and halloysite is favored by an acidic (pH ~3) conditions, and high leaching environments. Conversely, relatively low or no leaching environment, and conditions under neutral to low alkaline pH favor the formation of montmorillonite and three-layer clay minerals.

Interpreting both terrigenous and clay sediments from our cores in terms of quantitative variations, one can depict several rainy periods, several of them accompanied by flooding events. During the 1,500 years covered by our profile three distinct climatic periods were recognized (Fig. 5).

The digenesis conditions differ under which the weathering crust formed during the three main periods defined earlier. The clay minerals ratio depends on the subsurface weathering conditions, but also on the transformation they undergo after being deposited in the lake.

Within the first period, the two-layer clay minerals prevail over the three-layer ones. Low quantities of illite/smectite are present in the sediment. According to this situation, we believe the weathering crust formed under very humid and good drainage conditions. The transformation of kaolinite into halloysite has also continued within the lake sediment due to the acidic environment generated by the presence of organic matter. The highest quantity of halloysite and kaolinite/halloysite was recorded in the lower portion of the profile.

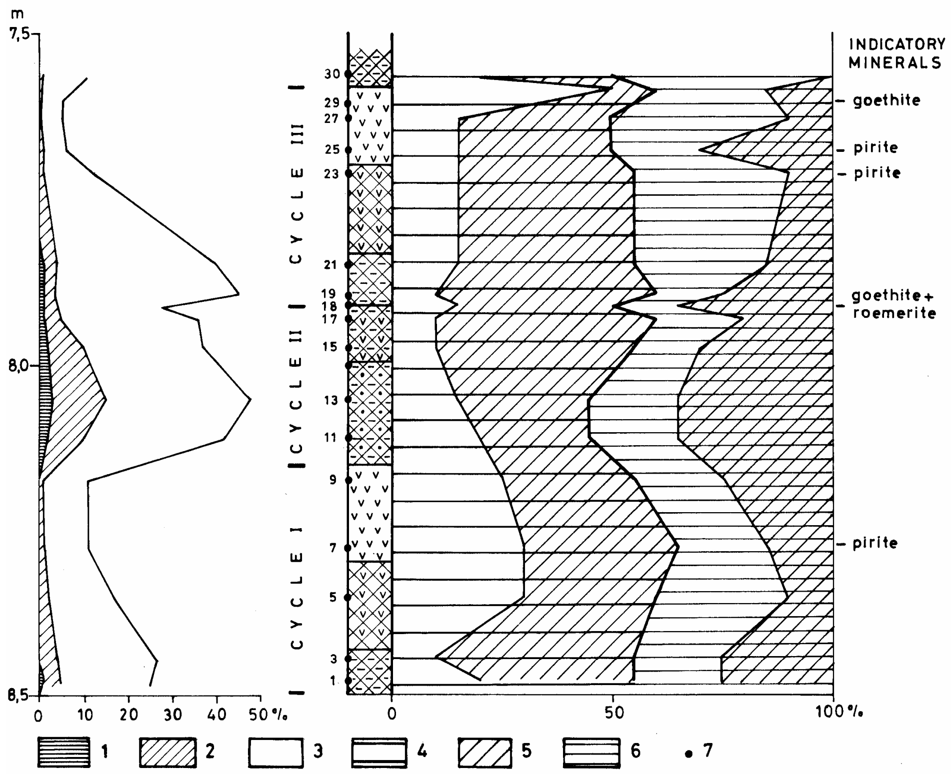


Fig. 5. *Granulometry of the siltic arenitic clay material and the content in clay minerals of the 7.5-8.5 m profile. The clay minerals are of 1:1 type (kaolinite and kaolinite/ halloysite + halloysite) and of 2:1 type (illite and illite/montomorillonite).*

Characteristic for the second period is the three-layer clay minerals and the abundance of expandable minerals. They formed (before being washed into the lake) under a warm climate. The increase of expandable minerals towards the upper part of this period suggests an oxidizing environment.

The third period was climatically similar to the first one, the only difference being the ratio between nonexpandable (more frequent) and expandable two-layer clay minerals. A flush flood at the end of this period seemed to be responsible for the presence of hydrothermal clay minerals (e.g., nacrite) within the sediment.

Based on these periods we did not quantitatively interpret the palaeoclimate regime, but only attempted to estimate the changes from humid to dry climate that occurred during the transfer (and residence) of the weathered crust into the lake. To estimate these changes, we interpreted the lithological sequence and its mineral assemblage. The main episodes depicted are outlined in the presentation below.

The first sediments to be deposited at the bottom of the former crater lake consist of siltic-arenitic clays (including up to 5% rudites). The presence of this lithologic unit suggests a period with a humid climate and active erosional processes in the nearby surroundings.

After this period, we suspect a less humid interval, when the lake experienced poor drainage conditions. The type of sediments accumulated during this period (clayey gyttja and peaty gyttja) emphasizes the evolution of the lake, and furthermore, suggests a reducing environment characterized by the presence of pyrite grains in the sediments.

Following was a period with humid conditions. Within this time interval at least two flush floods have been traced. These events are obvious when analyzing Fig. 5 where one can see sudden increases of arenite and silt (only one peak). The chemical composition of the sediments also commonly reflects this situation.

It has to be born in our mind that the mineral assemblages washed into the basin mostly reflect the climatic conditions under which those minerals were weathered. Therefore, the first period that was colder and less humid produced the minerals we found in the second period, whereas the warm and humid period that followed, was responsible for the rich kaolinite association described on the third period.

Lack of arenites, low contents of silt (< 1%) and lutite (generally below 10%) characterize the peat and peaty gyttja layers that accumulated under fairly stable climate conditions (very little or no precipitation at all) with very little allogenic input. A short period of total dryness was recorded at 7.88 m where the presence of goethite and pseudomorphs of roemerit (morphologically identified) after pyrite indicated an oxidizing environment. The prevalence of organic matter in the upper part of the profile is emphasized by the low content of detrital sediments and by the decrease of all major elements (Fig. 4).

Since the investigated sediments formed on land under different pedogenic, climate-related modifications, their palaeoclimatic significance were only tentatively interpreted.

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