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A Sulphate-rich Maar Lake in the Pliocene of Hungary

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Abstract: Sedimentation in maar lakes is driven mainly by climate and post-eruptive fluids. Organically rich sediments of the basaltic Pula maar (W Hungary), considered as soil remediative material, have been explored by numerous shallow core-wells. XRD and main element measurements have been done on core samples taken at every half meter and meter, respectively, of a 50 m thick well profile. Aragonite and algal organic matter are major components. Gypsum (up to 16%), glauberite (up to 5%), pyrite (up to 4%) and presence of elemental sulphur has been detected in a great number of samples. Sulphate dissolved by post-eruptive fluids from anhydrite content of the Triassic basement at about 3 km depth is suggested as main source of the sulphur. The upward moving water cooled and became oversaturated for sulphate, which precipitated in the anoxic bottom water or already in the pore space of the sediments.

Key words: gypsum, glauberite, post-eruptive fluids, meromictic lake

1. Introduction

The catastrophic CO_2 outbursts of the Monoun and Nyos maar lakes (Cameroon) in the mid-1980s focused attention to post-eruptive fluids and led to a 15 years monitoring of water chemistry of these lakes [1]. But a reconstruction of long-term post-eruptive fluid discharge to a maar lake is possible only by studying the lacustrine sediments filling the crater.

Maar lake sediments are valuable archives of evolution of climate. In the last three decades detailed geochemical and to a lesser extent mineralogical study of Late Pleistocene-Holocene sediments of several recent maar lakes, especially those produced by alkaline basaltic volcanism active in Europe (Eifel Mts, Germany, Massif Centrale, France, and Monte Vulture, Italy) have been carried out. These studies focused mainly on evolution of climate characterized by drastic changes accompanying the end of the last Glacial and to a lesser extent the Holocene.

The organically rich early Pliocene maar sediments of W-Hungary (Fig. 1a) formed in a period characterized by relatively quiet climate. These sediments, considered first as fossil energy source then as soil remediative material, have been explored by numereous shallow (mostly < 100 m) coreholes in the 1970-80s [2]. The core material of some of these wells has been extensively analysed for chemical and mineralogical composition but the interpretation of the data obtained, organic geochemical ones excepted [3], remained unfinished.

The aim of this work is to show that drastic stratigraphic changes of these maar sediments at least partly reflect changes in post-eruptional fluid discharge. Here first we describe the variations of chemical/mineralogical composition along the sediment column filling the Pula maar crater. In this exercise we use the abundant data deposited in the Open File Report 1811/30 of Archives of the Mining and Geological Survey of Hungary. The data set used consists of x-ray diffractograms of 104 samples and elementary composition of half of them obtained on the about 50 m thick lacustrine sequence penetrated by the Put 30 core well. Then we attempt to characterize evolution of post-eruptive fluid discharge into the lake with emphasis on the source of sulphate and on formation of the different sulphur-bearing minerals.

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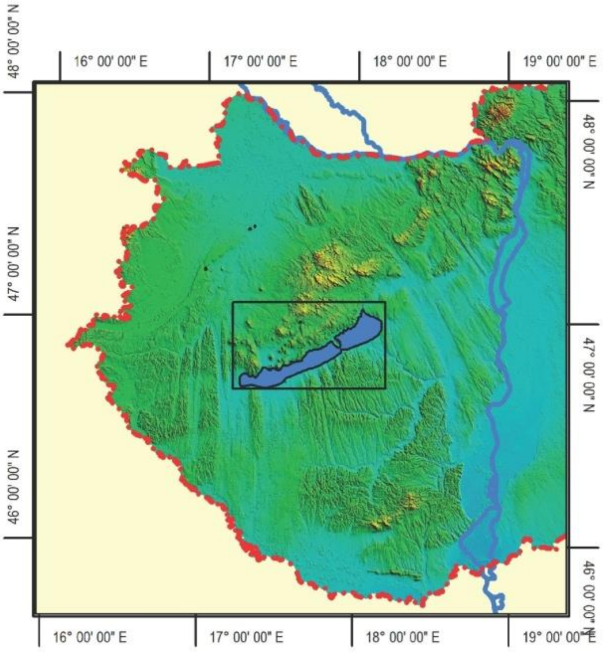

Fig. 1a **Location of the Pliocene maars in W-Hungary (grey dots outcrops of Pliocene maar sediments).**

2. Geological Setting

The Pula maar (Bakony Mts) is the product of alkaline basalt volcanism active during Latest Miocene and Pliocene times in W. Hungary [4]. The Pannon Lake, covering the area during the Late Miocene, retired already before the eruption of the Pula maar [5]. Geological map of the Southern Bakony Mts is shown on Fig. 1b.

The followings summarize the results obtained during the last 30 years, relevant for our work [1, 2, 6, 7].

The ring of the maar is lying on a 50-100 m thick succession of Middle to Upper Miocene siliciclastic sediments. The Miocene strata is underlayed by an about 3 km thick Triassic succession with anhydritic sandstones and dolomites of the Hidegkút Formation at its basis. Outcrops of the Hidegkút Formation have been mapped along the northern shore of the lake Balaton and its sediments have been penetrated by the Szi-1 corewell (Fig. 1b).

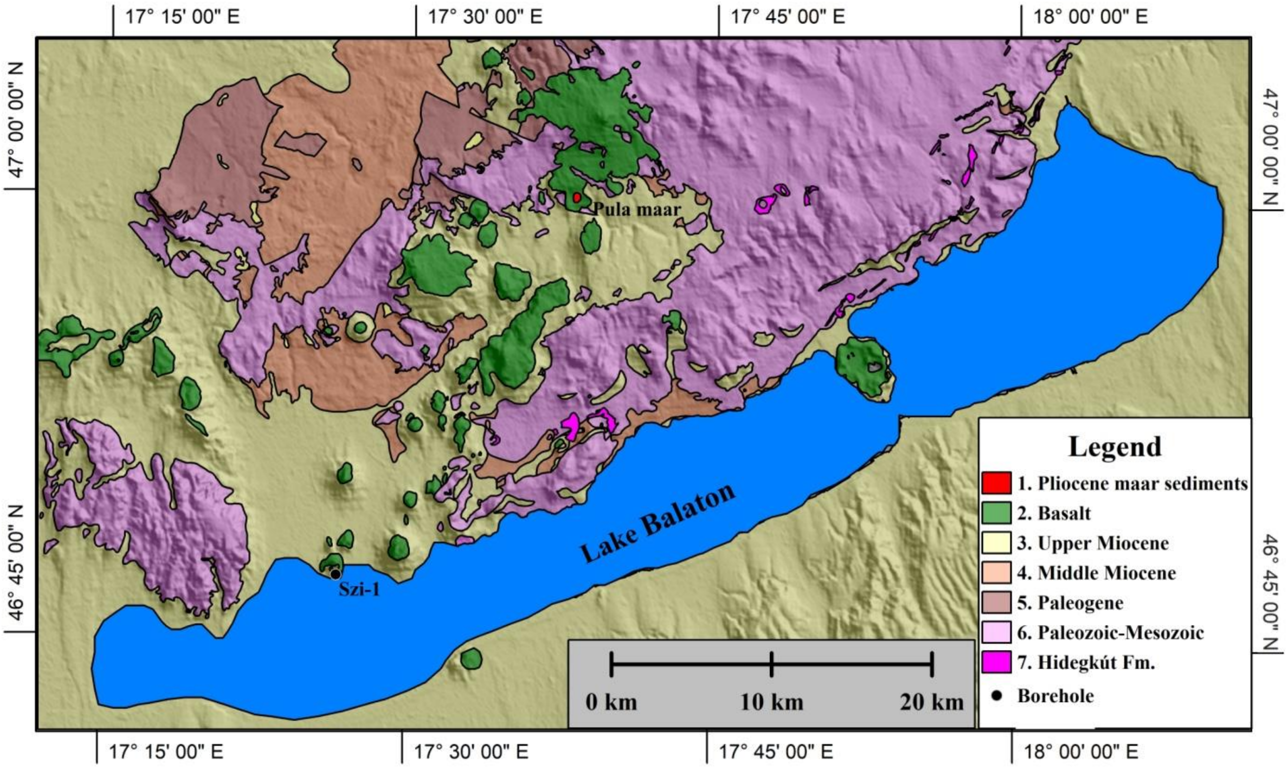

Fig. 1b **Geological map of the S-Bakony Mts. (courtesy of Gábor CSILLAG).**

The bulk of the partly eroded strata filling the central part of the Pula maar crater consists of frequently laminated alginite interbedded with few volcanoclastic layers, while the marginal part of the crater has been filled with primary and reworked pyroclastic materal. Botriococcus algae and freshwater diatoms are main precursors of the organic matter (OM). The basal part of the lacustrine strata is dominated by eroded ring material while its uppermost part consists of marls and bentonite, respectively. Plant remains dominant in these marls suggest swampy environment.

The lake formed within the crater was min. 100 m deep, its surface was about 1 km^2. It was stratified, the upper fresh water layer was underlain by anoxic water; the deep water anoxia was the result of high organic production in the upper waters, rich in nutrients liberated mainly from the basaltic material of the ring.

Fossil plant assemblage shows temperate, humid climate with mean annual temperature and precipitation ranging between 10°C to 16°C and 650 to 1200 mm, respectively [8].

3. Results

The followings are based mostly on the profile of the Put-30 core well, representing the sediments deposited in the central part of the lake.

The maar sediments — covered by terrestrial Quaternary and underlain by basalt — are developed between 52.3 to 2.8 m depth in this well [2]. 103 samples have been analysed by x-ray diffractometry (XRD) and 38 among them for amount of sulphur (S) by ICP-AES.

3.1 Variation of Mineralogical Composition Along Depth

Sediments are a mixture of eroded, partly weathered material of the maar ring (basalt glass, clay minerals, quartz, feldspar, dolomite), OM of mostly algal origin [3], biogenic opal, aragonite and other carbonates, apatite, HCl-soluble sulfate minerals and pyrite. The main mineralogical characteristics of the sediments are displayed on Fig. 2.

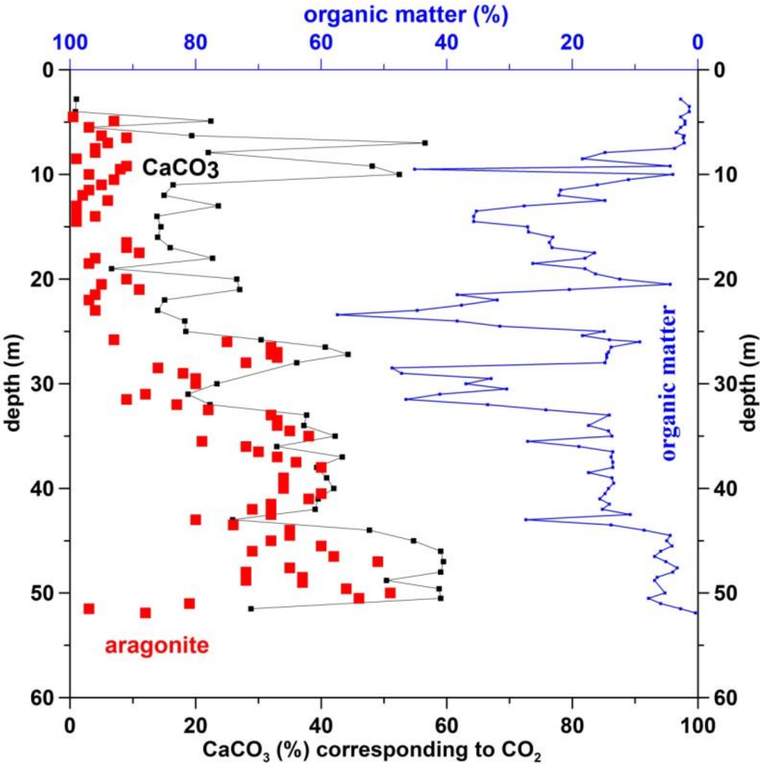

Fig. 2 Amounts of OM, carbonate and aragonite vs depth, Put-30 corehole (OM is calculated from TOC by multiplying with 1.4, carbonate calculated from CO$_2$ liberated by HCl and considered as pure CaCO$_3$).

In the lower part of the lacustrine strata, below 25 m aragonite is one of the major components, its amount can be as high as 50%; other carbonates are of secondary importance. In this depth interval aragonite shows a marked negative co-variance with OM.

Above 25 m amount of aragonite is < 15%, carbonates are dominated by calcite, its amount can be as high as 35%.

3.2 Sulphur and Its Forms

Results are shown on Fig. 3. We have to note that the limit of detection of individual minerals in case of the XRD technic used was 1%.

From the upper 10 metres of the lacustrine strata 18 samples have been analysed by XRD. In no ones pyrite has been detected and only one contains detectable amount of sulphate minerals (4% anhydrite). Three samples analysed for chemical composition contain no more than 0.5% sulphur (S). Hence the upper part of the lacustrine strata is relatively poor in S.

The distribution of S shows two broad maximums in the 14 to 19.5 and 25 to 31.5 m depth intervals where its amount ranges between 1.42 to 4.67% and 0.92 to 3.2%, respectively. These two intervals consist mostly of laminated alginite [2], very rich in OM (TOC varying between 11.8 to 25.8 and 6.7 to 35.2%, respectively (Fig. 3). Between these two intervals and below 31.5 m S is mostly below 1%.

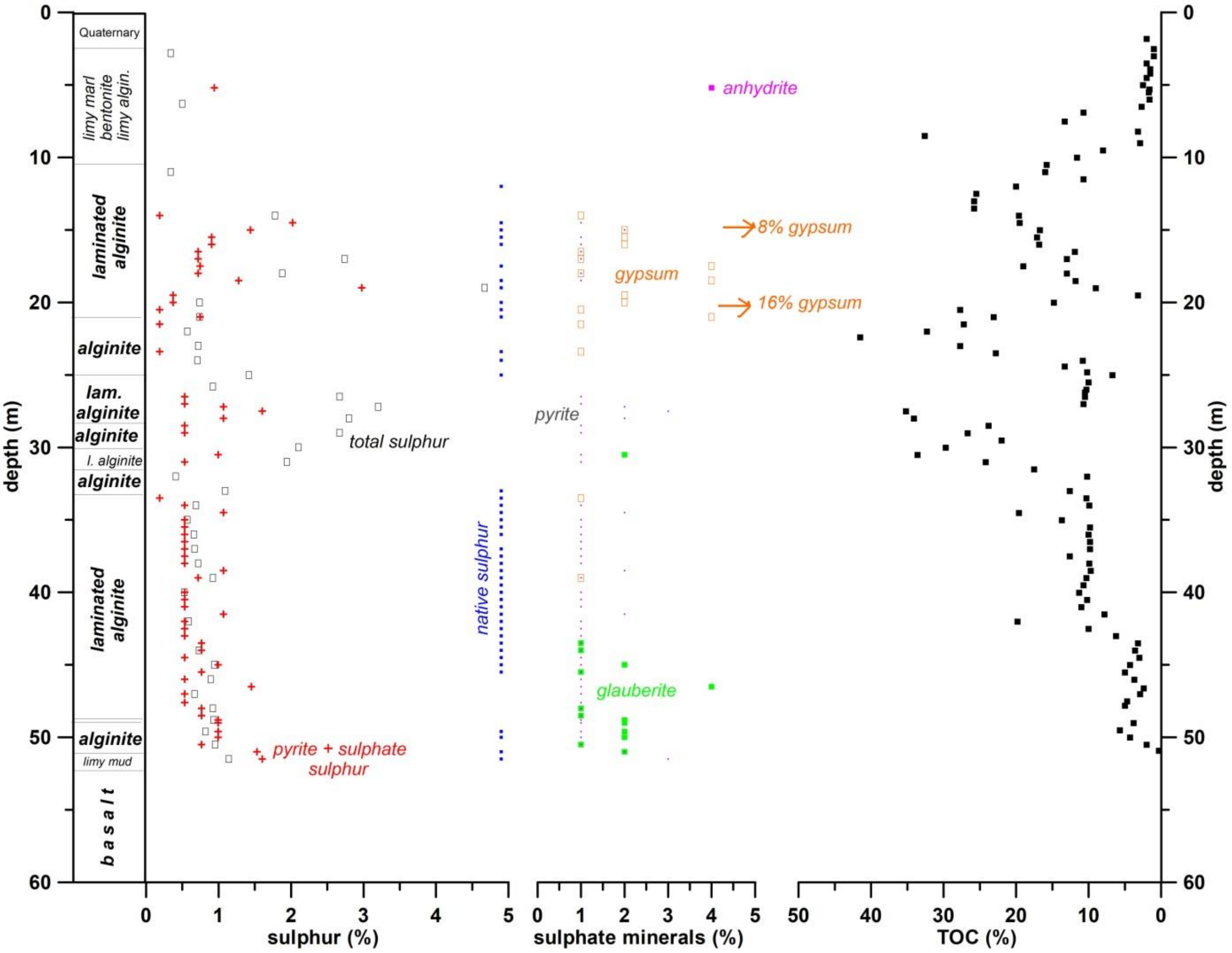

Fig. 3 Lithological column and variation of S, its forms and TOC vs depth (TOC is after (3)).

The presence of gypsum in detectable amount roughly coincides with the upper S maximum, its amount can be as high as 16 %. The bottom part of the lacustrine strata between 43 to 51 m is characterized by presence of glauberite up to 4%. In the 23.5 to 43 m depth interval sulphate minerals have been only seldom detected.

Pyrite has not been detected above 14.5 m and within the two S maximum and shows a small maximum between 27 to 29 m.

Each samples analysed by XRD were extracted by chloroform. Extraction revealed the presence of elemental sulphur in numerous samples, but its amount has not been measured. Sediments above 14.5 m and within the lower S maximum are free of elemental sulphur.

In the depth interval between 14 to 33 m the sum of sulphate-bound and pyrite-bound sulphur is markedly lower than S. The "lacking" sulphur is obviously present in organically bounded (S_{org}) and elemental forms. Since samples studied from between 25 to 33 m depth are free of elemental sulphur, here the "lacking" sulphur represents S_{org}.

4. Discussion

Before discussing our results an overview of the few data about amount and mineralogy of sulphur in Holocene-Late Pleistocene maar sediments seems to be useful.

4.1 Sulphur and Its Forms in Sediments of Recent Maar Lakes

In the sediments of the Lac du Bouchet (Massif Central, France) the S concentration is mostly below 0.5% but in some samples it can be as high as 1.8% [9].

Sediment samples taken from each 3 cm section of four and one shallow cores (50-70 cm), drilled in the Lago Grande di Monticchio (LGM) and Lago Piccolo di Monticchio (LPM) (S. Italy), respectively, have been analysed for chemical and mineralogical composition [10].

The amount of S varies mostly between 1.5 to 3% in the LGM but can be as high as 6% in the case of the anoxic LPM. Elemental sulphur represents mostly less than 10% of the S but its relative amount can be as high as 50% in the LPM sediments. The mineralogical composition has been determined after treatment with hot HCl (10%), hence there are no data for presence and amount of HCl-soluble sulphate and sulphide minerals.

S content of the < 0.185 mm fraction of sediments of the Schalkenmehrerer Maar (Eifel Mts, Germany) varies mostly between 1 to 4% in the 340 to 620 cm depth interval (what covers 2700 to 13000 years time interval) but it is as high as 8-10% between 510 to 560 cm, gypsum cristals are common between 340 to 620 m depth, they are abundant in the 512-538 cm interval and are lacking in the 395-405 cm interval [11].

4.2 Sources of the Sulphur in the Pula maar Sediments

The presence of anhydrite, gypsum and glauberite indicates that the deep water (or the porewater) was oversaturated for sulphate during several stages of the lake history. In absence of petrographic sudies the syngenetic or diagenetic nature of the sulphate minerals can not be clarified.

The crater has been filled with karstic water quickly after the phreatomagmatic explosion [7]. Karstic water and groundwater likely feeded the lake during its whole life, furnishing some sulphate to the lake.

Weathering and erosion of ring material, especially of basaltic glass obviously delivered sulphur into the lake.

Some sulphur entered the lake also with rain and from time to time with tephra of volcanoes active in the area.

But in view of the moderately humid and warm climate [8] neither of these sources can explain (i) oversaturation of the deep water (or the porewater) for sulphate during long stages of the lake evolution and (ii) the varying nature of the water-soluble sulphate minerals.

It is highly probable that underwater springs delivered an important part of the sulphur, likely in form of sulphate. I note that underwater springs are widely known in several recent maar lakes (e.g., 1).

4.3 Speculations About Post-Eruptional Sulphate Flux

Upward flux of post-eruptional fluids – water, SO_2 and CO_2 – is a general phenomena accompanying active volcanism. CO_2 outburst of maar lakes [1] is the most spectacular form of this flux.

Reaction of upward moving SO_2 with water results in sulphuric acid and very low pH. The high amount of aragonite (Fig. 2) strongly argues again acidic lake or pore water. I suggest that anhydrite content of dolomites and sandstones of the Hidegkút Formation cropping out along the northern shore of the lake Balaton and penetrated in the Szi-1 corehole (Fig. 1b) was the main source of sulphate precipitated in the lake and/or in its sediments.

Connate porewater of anhydrite containing marine sediments is obviously rich in Na and Cl. The post-eruptional water flowing through Triassic basement mixed with porewater, flushed it continously and started to dissolve its anhydrite content. During its upward movement water cooled and became oversaturated for sulphate which precipitated from the relatively sodium rich solution in form of glauberite. While after certain times the connate water of the anhydritic sediments has been flushed entirely, the dissolution of anhydrite continued. When this water inpoverished in sodium cooled, gypsum has been precipitated from it. This hypothetical mechanism would explains why in the lower part of the lacustrine strata glauberite while in its upper part gypsum is the dominant sulphate mineral (Fig. 3). Sulphur stable isotope measurements could help to answer this question.

The abundance of highly reactive algal OM made possible bacterial reduction of a significant part of the sulphate within the sediment or already in the bottom water. The H_2S produced has been fixed as pyrite or incorporated in the algal OM. It can not be exclude that some H_2S diffusing upward entered the upper, normally oxigenated water and was reoxidised to sulphate.

In the 33 to 25 m depth interval, one sample excepted, no sulphate mineral has been detected. It is likely that during deposition of the corresponding sediments the post-eruptive flux decreased and bacteria were able to reduce the bulk of the sulphate entering the maar.

5. Conclusions and a Hypothesis

Main part of the sulphur content of the maar sediments has been transported as sulphate dissolved in upward moving post-eruptive fluids.

The bottom water and the porewater were oversaturated for sulphate during long periods of the lake’s life.

Anhydrite content of the dolomites and sandstones developed at the basis of the Triassic is the source of sulphate of the post-eruptive fluids.

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