
WYNIKI MINERALOGICZNYCH I GEOCHEMICZNYCH BADAŃ EWAPORATÓW ZE ZŁOŻA TAUDENNI-AGORGOTT (MALI, SAHARA ZACHODNIA)

Results of mineralogical and geochemical investigation of evaporates from the Taoudenni-Agorgott deposit (Mali, Western Sahara).

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Field as well as mineralogical and geochemical investigation of evaporates of Taoudenni-Agorgott deposit were performed. It was stated out that the profile is composed of halite, glauberite, gypsum, carbonates, quartz and clay minerals. The sequence of the presence of minerals at the profile suggests the deposit is the result of evaporation of salty lake during drying of climate at the Sahara Desert. Mineral composition of evaporates suggest that Na-Cl reach like evolved to Na-Ca-SO₄ phase and next was fully evaporated and coated with detrital sediments.

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Introduction

The Taoudenni-Agorgott salt deposit was visited during the field trip to the Malian desert in the year 2008. The salt deposits were studied in-situ and evaporates samples were collected in one of the existing open pit mine in that area. The aim of this paper is to review

previous works concerning studied area and to compare results of field and laboratory investigation with the earlier data.

Geographical settings

The Taoudenni-Agorgott salt deposit is located in the northern part of the Mali Republic, around 600 km deep into the Sahara Desert interior (fig. 1). Geographic coordinates of present-day working excavations called New

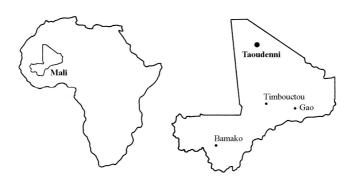


Fig. 1. Location of Taoudenni. Sahara Desert covers all areas of Mali Republic north of Timbouctou.

Agorgott are 22°36'N and 4°02'W. The local depression of Taoudenni (circa 130 m AMSL) is the lowest area of the West Africa within more than thousand kilometers. Salt mines are situated at almost plane surface of ancient lake covered with muddy-gypsum crust. From the south, Taoudenni-Agorgott depression is bounded by the rocky scarp with Djebel Fum el-Alous culmination. Djebel al-Gara (283 m AMSL) and Djebel al-Kudi mountains tower above the central part of the ancient lake, and in the north, Djebel Hammou-Salah mountain ascendant to 315 m AMSL. Depression zone with a fossil record of additional ancient lakes stretch dozens km from Taoudenni to the NW (Sbeita) and more than 120 km to the SE (Telig, Haijad) reaching the El Gettara ancient lake and the El Khnâchîch escarpment. The area between the Taoudenni depression and the El Khnâchîch escarpment and stony plateau to the south is covered mainly with eolian sands, while the area to the north of the depression zone is occupied by the stony desert Hamâda el Haricha (Harichat).

Moreover, whole region is cut by a dense, anisotropic system of dolerite dykes. They form elongated elevations that are clearly visible in topography.

Salt mines of Taoudenni (fig. 2) are historically interesting and have been functional since the end of 16th century. Exploitation was transfered there from nearby Teghaza mines (founded at least in 10th century) after captured them by Moroccan Empire in the end of 16th century (Dziubiński, 1983; Tymowski, 1979). Both of them were connected with the ancient transsaharan caravan route and till present-day Taoudenni is a destination of salt caravans beginning from Malian towns south of the Sahara. Distance from salt mines to the closest village – Araouane reaches more than 400 km to the south and to the nearest town – Timbouctou (Tombouctou, Timbuktu) around 700 km. The roundtrip for camel caravans, counting hundreds of animals, takes up to 5 weeks. The way of salt exploitation as well as output caravan transportation has not change during the span of centuries (Pająk, 2009; Pająk, 2010; Pająk, 2011).



Fig. 2. One of the salt pit at the Taoudenni-New Agorgott mines (phot. J. Pajak).

General geology

The studied site is located in the northern part of the Taoudenni syneclize, one of the largest sedimentary basins in the world. It covers over 2.000.000 sq. km of the West African Craton (Villeneuve, 2005) and the thickness of sedimentary strata reaches 4000 meters (Guiraud et al., 2005). Sedimentation began around 1000 Ma and continued until the end of Carboniferous (Villeneuve, 2005). Outcrops of these formations are exposed at the Taoudenni basin rims while the central part is covered with the Mesozoic-Cenozoic sedimentary rocks.

Large Taoudenni basin could be divided into 8 subbasins (Villeneuve, 2005) and the salt mines of Taoudenni-Agorgott are situated within the precincts of Hank subbasin. In the north, it borders with the Archaean to Palaeoproterozoic cratonic basement of the Reguibat Shield in the Eglab Massif (Fabre, 2005; Przybyłek, 1993; Villeneuve, 2005).

Lower and Upper Carboniferous detrical and carbonate sediments form the nearest surroundings of the Holocene Taoudenni-Agorgott salt deposit (fig. 3) (Mees, 1999; le Verati et al., 2005). The Lower Carboniferous rocks (Teraza Group) belong to the Safia Formation (Late Visean foraminifera) and the Haricha Formation (Serpukhovian foraminifera), while the Upper Carboniferous rocks (Jakania Group) belong to the Hammou Salah Formation (Namurian/Bashkirian? flora and fauna) and the Jakania Formation (Upper Westphalian?/Upper Moscovian-Kasimovian? flora and fauna) (Fabre, 2005; Villeneuve, 2005). Total thickness of the Taoudenni basin Carboniferous deposits reaches 200-400 meters.

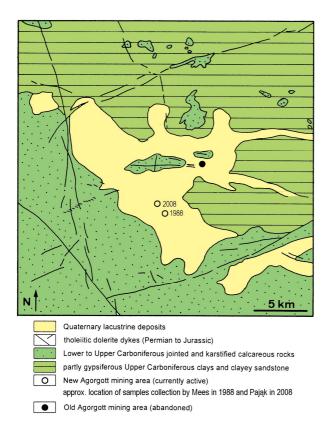


Fig. 3. Geological sketch map of Taoudenni area with approximate location of samples collection by Mees in 1998 and Pająk in 2008 (after Mees, 1999).

The Safia (20-35 m) and the Haricha Formations (25-50 m) mainly consist of organic-rich carbonates with coral fossils and *Gigantoproductus* (Fabre, 2005; Przybyłek, 1993). They form stony deserts covered with a limestone cap. Hamada Safia is located in a distance of 30-40 km north of Taoudenni, while Hamada Haricha (or Harichat) is situated in the close vicinity north and east of Taoudenni sebkha. The section of the Safia formation is composited of light-blue limestones with interbeddings of nodular limestones and red argiles. A few meters of marls and sandy-clayey deposits with gypsum separate this formation from the overlaying limestones of Haricha Formations (Fabre, 2005). These fine-clastic layers are impervious for groundwater and possibly could be the reason for lakes and swamps forming

in the wet period of the Holocene. This was also a preferential zone for the Early Jurassic doleritic sills intrusions that are groundwater impermeable too (Fabre, 2005). Doleritic dikes and sills were formed 197-198 Ma during the break-up of the Pangea supercontinent and development of the Central-Atlantic Magmatic Province (CAMP) (le Verati et al., 2005; Golonka et al., 2006). After Villemur (1967), strongly fractured Visean limestones contain a groundwater aquifer that determined occurrence of sebkhas in the Taoudenni area, however, recent foraminifera dating suggests the Serpukhovian Age of the carbonates belonging to the Haricha Formation (Fabre, 2005). Genesis and arrangements of these sebkhas could be linked to a regional draining system of this aquifer (Przybyłek, 1993 after Villemur, 1967). The Haricha Formation is composed of thick limestone and dolomite layers interbedded with marls or sandy marls. The last 20 m of the profile is a record of transition between marine, lagoonal and continental deposits (Fabre, 2005). Global regresion could be linked to a formation of the supercontinent Pangea and large southern polar ice cap (Golonka et al., 2006). The overlaying Upper Carboniferous sediments are typically continental sandy-clayey deposits (Fabre, 2005). Escarpments of the Hammou Salah Formation, up to 100 meters high, tower above the Taoudenni-Agorgott sebkha. Profile of this formation is made of thick layers of reddish mudstones, siltstones and sandstones interbedded with thin carbonate and gypsum strata. Fossil records of these deposits indicate lacustrine environment of sedimentation (Fabre, 2005). The overlaying Jakania Formation is formed mainly of sandstones and mudstones and could be observed at the El Khnâchîch escarpement (Fabre, 2005). The most characteristic feature of this formation is a large accumulation of silicified tree trunks at the El Khnâchîch Plateau, which are clearly visible along the caravan trail to the salt mines.

Evaporate deposits from Northern Mali including those from Taoudenni-Agorgott depression was a subject of sedimentological, mineralogical and petrological studies before. Works of many authors clearly indicated genesis of evaporates including salt deposits as a result of palaeolake evaporation processes during the Holocene (Delibrias et al., 1991; Fabre, 1983; Fabre, 1991a; Fabre, 1991b; Fabre et al., 1988; Oxnevad, 1991; Petit-Maire et al., 1987; Schulz, 1991a; Schulz, 1991b). Detailed results of sedimentological, mineralogical and petrological investigations of Taoudenni-Agorgott evaporates were published by Mees (1998, 1999). Salt lake deposits consist mainly sediments with a high glauberite (Na₂Ca(SO₄)₂) content and in a lesser degree salt beds containing bloedite (Na₂Mg(SO₄)₂·4H₂O), thenardite (Na₂SO₄) or halite (NaCl). They formed in a perennial lake that experienced a gradual decrease in water depth. Textural features in glauberite rich parts of the palaeolake profile are showing variations in glauberite content and crystal size, that is reflecting depth of the water

due to changes in water supply and to short-term variations in evaporation rates. Layering deposits were formed in shallow water, whereas unstratified deposits were produced during high lake level stages. Also halite textures indicate changes in water depth and short-term

variations in evaporation rates. The oldest halite beds are largely unaltered cumulate deposits,

whereas the youngest layers developed exclusively through bottom growth (Mees, 1999). A large majority of halite deposits (including layers with samples XI-VII from fig. 4) are placed between 6,500 years BP and 4,500 years BP. Beginning of halite deposition is interpreted as shifting from an early to middle Holocene humid period to more arid conditions, leading up to the hyperarid period that continues to the present (Mees, 1999). Salinity of the palaeolake is connected with geological nature of the catchment areas. water-rock interactions in the aquifer, as well as atmospheric inputs. with Increased rainfall leads to more intensive salt-crust dissolution and to rise of groundwater salinity. Radiocarbon ages suggests that recharge of groundwater aquifers took place between 13000-2000 years BP (Gasse, 2002)

Material and methods

- A. Sampling & profile
- B. Microscopic examination
- C. X-ray diffractometry

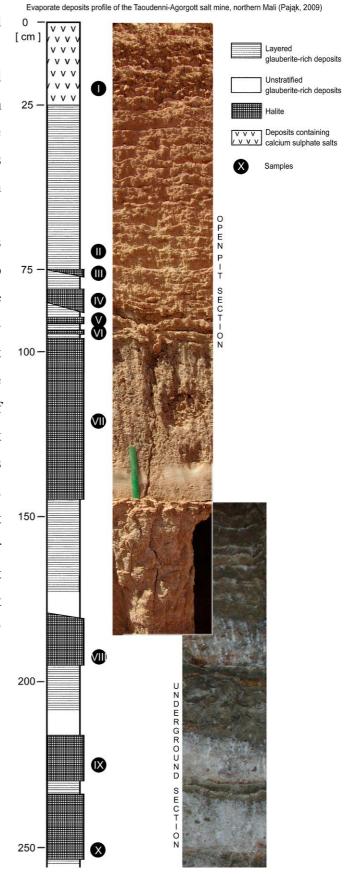


Fig. 4. Geological profile of the study deposits. Salt mine of Taoudenni-Agorgott, pit with coordinates 22°36'45"N and 4°02'24"W (Pajak, 2009).

D. Determination of chemical composition

A. Sampling

Samples were collected at the north-westernmost pit of the Taoudenni-New Agorgott salt mines that was exploited in the beginning of the year 2008. Geographic coordinates of this excavation are 22°36′45″N and 4°02′24″W. The investigated profile is shown as fig. 4. Surface and underground photographs of the outcrop correspond to entire geological profile., They represent evaporates as well as detrital material deposited between salt layers. Most of layers starting from the depth close to 3 meters up to Earth surface were collected, including all halite layers (fig. 5 & 6). Sampling points are marked at the right side of the profile with Roman numerals.

Samples collected in 2008 as well as described in this paper profile come from the pit lying much more to the west (or NWW) from the site investigated by Mees in 1988. Every year dozens of new pits are created to get access to halite layers, so the mine head is shifting

along surface of former palaeolake. Unfortunately it is hard to estimate the scale of the move during last 20 years of salt exploitation because detailed geographical position of the pit, where Mees collected samples is not indicated in the papers.

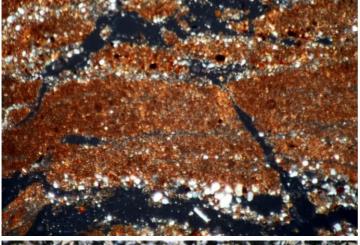




Fig. 5. A - Upper part of tested profile. One can see the transition of evaporates into upper detrital sediments.; B - Lower part of tested and explored evaporates. Thicker layers containing mainly halite. Intercalated with detrital material containing glauberite (phot. J. Pajak).



Fig. 6. A – Central part of profile. Layered halite and glauberite. B – Central part of profile –crystals of pure halite (phot. J. Pajak).





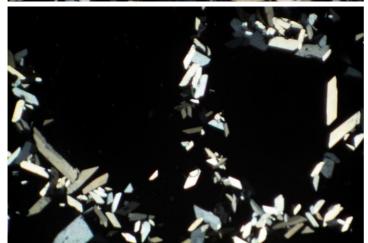




Fig. 7.

A - sample 1. Upper part of profile. Clay minerals mixed with small grains of quartz and clay minerals.

B – sample 3. Two generations of glauberite coarse and fine crystalline.

C – sample 7. Crystals of halite (black) with glauberite crystals at spaces between halite.

D –sample 9. Traces of glauberite horizon at pure halite layer.

All photos – Polarizing light microscopy, polaroides X, magnification 40 x.

B. Microscopic examination

Microscopic examinations were performed using POLMI A polarizing light microscope. Thin sections were obtained by cutting samples with the use of diamond cutter followed by polishing these thin plasters. Lastly, samples were fixed on glass.

Together with microscopic observations of structures and textures, the counting of mineral composition of samples was performed (fig. 7). Mineral composition of tested sediments was evaluated from the bottom sediments to the top. At the lower part of profile mostly coarse crystalline halite was determined. Higher up are present mixtures of medium or fine halite and fine crystallized glauberite. The amount of glauberite is higher up continuously growing to the top of evaporate sequence (tab. 1, fig. 8). Upper part of profile is composed first of all of gluberite mixed with detrital material represented by quartz and clay minerals. Sediments at this part contain traces of halite and gypsum. The top sediments of profile are composed only of detrital material i.e. clay minerals and quartz with traces of halite penetrating these sediments and crystallizing from liquids migrating, due to sun heating, up from deeper evaporates.

	Min	erals content of	of the investiga	ated profile	(vol. %)							
sample	mineral											
	halite	glauberite	carbonates	gypsum	clay minerals	quartz						
1	0,8	1,3	-	6,6	55,6	35,7						
2	15,4	45,4	5,4 -		25,1	14,1						
3	41,3	42,8	-	-	13,3	2,6						
4	22	44,7	6	-	12,1	6,3						
5	28,3	61,8	2,5	-	6,6	0,8						
6	36,7	55,8	1,6		3,2	2,7						
7	95,8	2	-	-	1,2	1						
8	14,9	71,5	-		11,4	2,2						
9	98,5		-	-	0,9	0,5						
10	93,6	3,8	-	-	2,2	0,4						
11	99	-	-	-	0,9	0,1						

Tab. 1. Mineral composition of the tested sediments (vol. %).

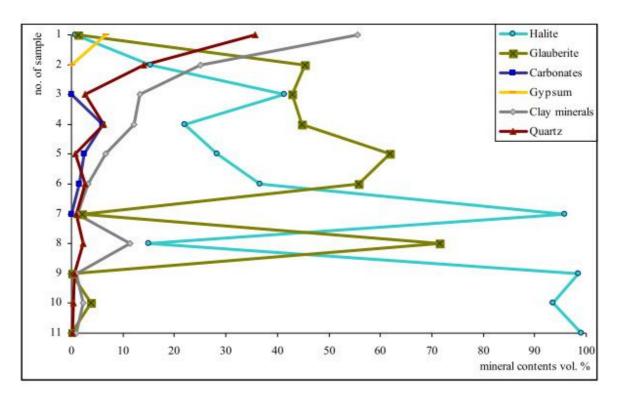


Fig. 8. Diagram illustrating mineral composition changes in the study profile.

C. X-ray diffractometry

X-ray examination confirmed results of microscopic analyses. Solid samples were grinded to powder and put to diffractometer tests. X-ray patterns obtained using Freiberger Prazisionsmechanik URD6 diffractometer (fig. 9) confirmed evolution of evaporates during crystallization and sedimentation from chlorite to mixed phases chlorite-sulphate and next to sulphate. The sedimentation at the basin is finished by filling up detrital sediments.

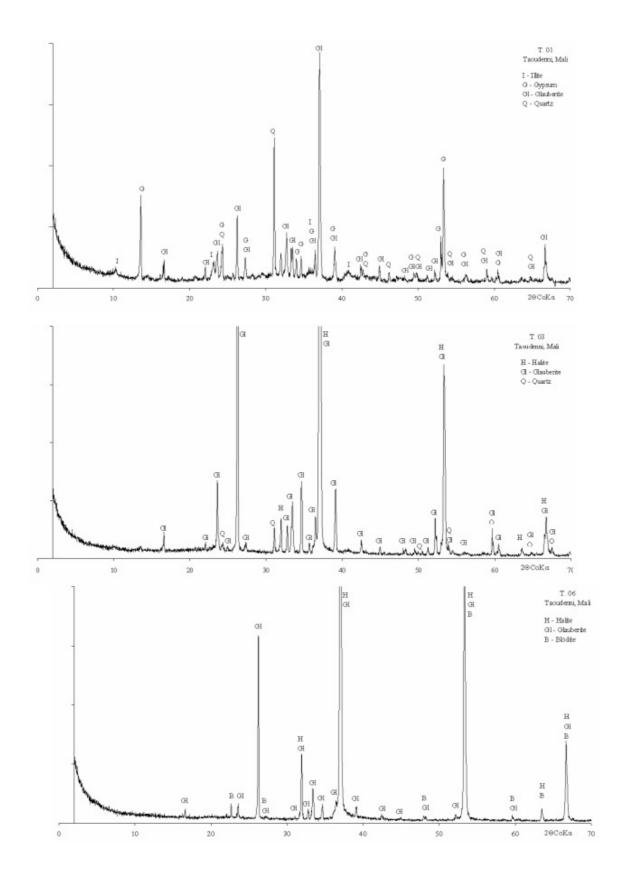


Fig. 9A. The X-ray powder diffraction patterns of examined samples: 1, 3, and 6.

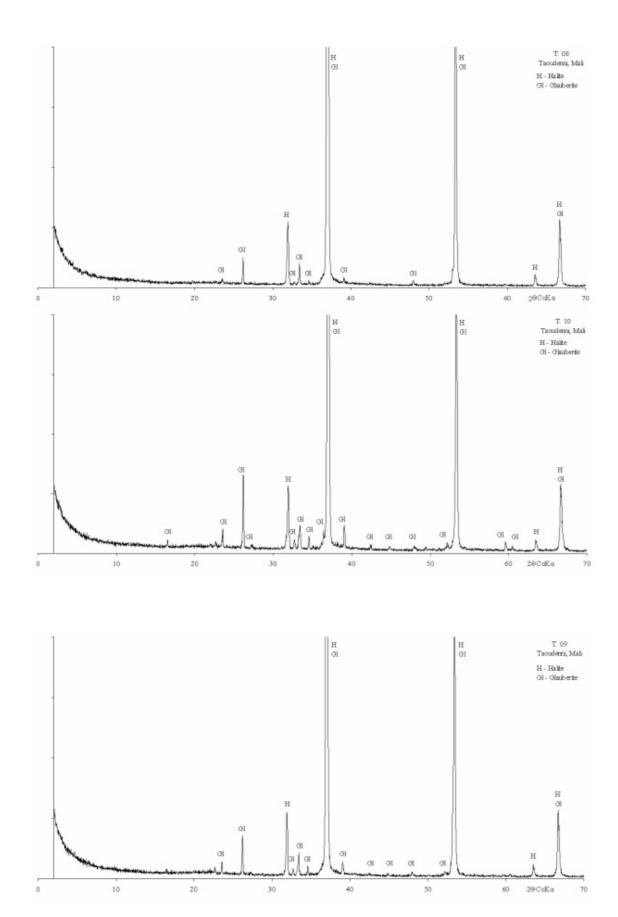


Fig. 9A. The X-ray powder diffraction patterns of examined samples: 8, 9 and 10.

D. Determination of the chemical composition

The chemical analyses of selected samples were performed to determine the trace elements accompanying evaporates. They were done using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) method and analyzed with Perkin Elmer model Plasma-40 spectometer. Solid samples were decomposed with concentrated nitric acid (65%) at a pressure of 30 atm. and a temperature of 230°C with the use of Perkin Elmer microwave mineralizer. Methodology is useful for elements that could be coupled with argon plasma. Obtained data documents the presence of the trace elements, presented in table 2 and figure 10.

Content of chemical elements at tested profile (mg/kg)

element	Li	Ba	Sr	Mn	Zn	Cu	Со	Pb	Cr	Mo	v	Zr	As	PO4	В	Y
1	33,07	143,97	432,54	110,98	15,64	5,38	2,65	5,49	14,06	1,00	16,75	5,30	1,86	331,27	42,59	2,20
3	8,01	50,38	606,66	18,05	5,29	33,97	0,69	1,18	3,66	0,53	4,52	1,33	0,69	63,51	14,15	0,50
6	0,95	1,86	68,89	371,59	2,21	72,24	1,13	0,37	0,69	1,34	0,47	0,14	0,27	22,64	7,34	0,04
8	1,13	3,85	107,65	3,23	2,11	81,78	0,06	0,17	0,69	0,32	0,51	0,15	0,22	22,83	6,67	0,04
9	0,45	3,03	432,25	1,36	2,95	79,59	0,04	0,21	0,91	0,64	0,33	0,08	0,33	25,21	5,96	0,02
10	1,05	9,52	1170,50	2,12	2,85	66,45	0,07	14,69	0,65	0,87	0,42	0,09	0,36	16,87	5,00	0,04
11	0,32	0,58	62,32	0,70	2,15	68,91	0,02	0,13	0,46	0,08	0,15	0,04	0,16	17,03	3,02	0,01

Tab. 2. Results of chemical investigation of selected samples from the tested profile (ICP-AES method).

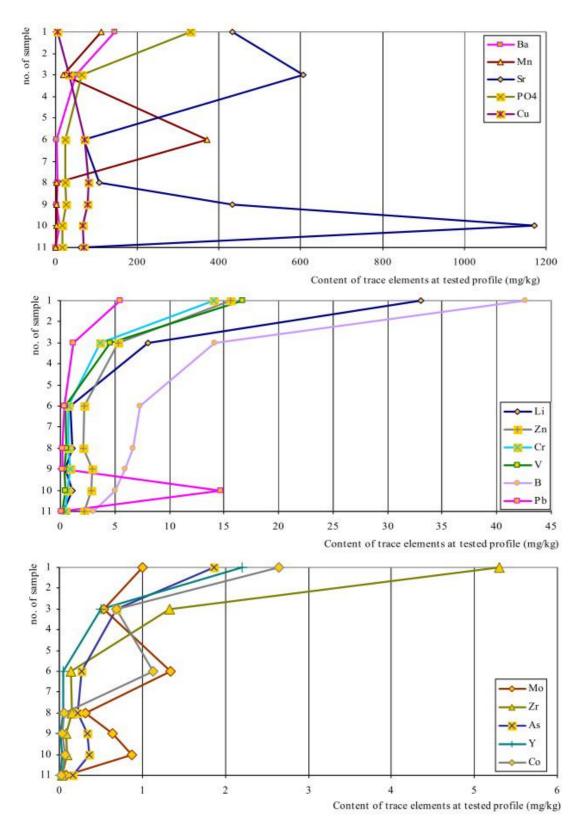


Fig. 10. Diagrams illustrating trace elements content in the study profile.

Results

As one could see at the studied profile (fig. 4) layers containing mainly halite are intercalated with detrital material containing glauberite. It is also visible that generally upper part of the profile is more glauberite rich than a bottom part. Microscopic examinations of collected samples show also that glauberite content is higher in thinner halite layers (fig. 4, samples III-VI). Thick halite layers (fig. 4, samples VII and IX-XI) consist of almost pure NaCl with no glauberite impurity or with a very low glauberite presence (Tab. 1, fig. 8). The exception is sample no. VIII, thick layer of halit with the highest glauberite presence, as well as clay minerals. The middle part of the profile (Tab. 1 & fig. 8, samples no. IV-VI) contains also some carbonates. In the upper part of the profile (Tab. 1 & fig. 8, samples no. I-II) we can see the transition into sulphate deposition and detrical sedimentation. Especially clay minerals content is growing in the upper part of the profile, beginning from the sample no. VI (Fig. 8). Sediments in the upper part of the profile (samples no. I-II) contain traces of halite and gypsum. The top sediments of profile are composed only of detrital material i.e. clay minerals and quartz with traces of halite penetrating these sediments and crystallizing from liquids migrating, due to sun heating, up from deeper evaporates.

Glauberite as sulphate is grystallizing elaier than halite. It is mostly present at lake evaporites and rare as primary at sea deposits.

The X-ray examination confirmed results of microscopic analyses. The upper part of the profile shows transition from chlorite to mixed phases chlorite-sulphate and next to sulphate. The sedimentation at the basin is finished by filling up detrital sediments.

The trace elements that accompanying evaporates could also tell us about environmental changes during crystallization and sedimentation in the basin. Sample no. X is rich in strontium, molybdenium and lead. Strontium is also present in sample no. IX. Moreover sample no. VI is interesting and contain trace elements as follow: copper, manganese, cobalt and molybdenium. Copper is present in the lower part of the profile, below the sample no. VI. In the upper part of the profile (samles I-III) we can observe upward increase of some trace element content like: Sr, Pb, Cr, Zn, Zr, Y, As V, B, Li, Co, Mo, PO4, Ba and Mn.

The amount and kind of elements present at tested evaporites confirm strong influence of rocks surounding lake on evaporite chemistry. Most of typical sea evaporites das not contains elements determined at examined salts.

Disscusion

Detailed results of sedimentological, mineralogical and petrological investigations of Taoudenni-Agorgott evaporates were published by Mees (1998, 1999). Salt lake deposits consist mainly sediments with a high glauberite (Na₂Ca(SO₄)₂) content and in a lesser degree salt beds containing bloedite (Na₂Mg(SO₄)₂·4H₂O), thenardite (Na₂SO₄) or halite (NaCl). They formed in a perennial lake that experienced a gradual decrease in water depth. Textural features in glauberite rich parts of the palaeolake profile are showing variations in glauberite content and crystal size, that is reflecting depth of the water due to changes in water supply and to short-term variations in evaporation rates. Layering deposits were formed in shallow water, whereas unstratified deposits were produced during high lake level stages. Also halite textures indicate changes in water depth and short-term variations in evaporation rates. The oldest halite beds are largely unaltered cumulate deposits, whereas the youngest layers developed exclusively through bottom growth (Mees, 1999). Results of our examinations generally confirm results of the previous works published by Mees (1998, 1999). The studied profile is almost identical to that one from the Mees works, although there is a distance of at least few hundred meters between both tested sites. The minerals textures, as well as mineral and chemical composition of correlated samples are also very similar.

Conclusions

The mineral sequences of the tested profile suggest that the deposit is a result of repeated evaporation cycles, probably connected with the climatic fluctuation. Mineral composition of the upper part of the profile confirmed that Na-Cl reach like waters evolved to Na-Ca-SO₄ (D'Ans, 1933, Birchert & Muir, 1964). At the final phase of the lake existence water totally evaporated and the area was coated with detrital sediments.

Described sequence of sedimentation reflects climate changes (Pawlikowski, 1976, 1983) i.e. drying - desertation of the Sahara with some moister intervals. Precise determination of phases of mentioned process is impossible at this stage of investigation and needs more examination. Determination of the origin of lake is difficult as well. Chemical composition of sediments showed the lake was not connected with the sea. On the other hand, surrounding rocks are only subordinate built of minerals containing Na, Ca, Cl and SO₄. They represent mainly various detrital sediments, in lesser degree limestone or others rocks. Because of this one can suppose the origin and salinity of the lake as the result of migration and evaporation of deep, mineralized groundwaters (Kucha & Pawlikowski, 1986).

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