



Geochemical Characterization of the Miocene Evaporites in the Gulf of Suez Region, Egypt

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Abstract

Evaporite-dominant strata had deposited as a result of the tectonic isolation of the Red Sea. A welldeveloped sequence of Miocene evaporites were exposed at Ras-Malaab and Marwet El-Khoshera areas in the Gulf of Suez (GS) region. To examine the quality of gypsum deposits of Ras-Malaab area for industrial application, different analytical techniques were used including; X-ray diffraction and fluorescence, microprobe analysis, trace elements analysis and loss of ignition analysis. The Xray diffraction peaks reveal that the samples are gypsum, anhydrite and bassanite, the microprobe analysis confirm that the studied samples are pure gypsum. The chemical composition of the pure gypsum is CaO (40.99%) and SO₃ (av. 58.93%) with very low concentrations of Cu, Zr, Rb and Y. The results indicate that the Miocene gypsum deposits of the Ras- Malaab of high quality which is suitable for cement, plaster of Paris, solid wallboard, ceramic and ammonium sulphate fertilizers and other different industrial purposes.

Keywords: Gulf of Suez evaporietes, Ras-Malaab, Red Sea Rift.

Introduction

Gypsum's chemical composition varies from one geographic region to the next, however it is mostly made up of calcium sulphate and a variety of accessory minerals, primarily carbonate, silica, and metal oxides (Sing and Eksi 1987, Green, et.al., 2017). Gypsum is mostly used in the production of plasters, cement, sulfuric acid and many other industrial purposes because of its low coast and aesthetics (Strydom, et.al., 1997; Mahmoudi, et.al., 2016). Glassmaking and other specialised industrial uses utilise pure gypsum. Additionally. plasterboards are amongst the building materials used in buildings for thermal insulation and air purification, and the manufacturing of plasterboards prefers natural gypsum that is of a high purity as the existence of impurities affects the gypsum's qualities (Roszczynialski, et.al., 1996). The geochemical characterization of the gypsum is significant to know the grade of ore, thus to the suitable industrial applications. The Gulf of Suez (GS) represent one of the major ancient marines evaporites (Aref etal., 1997). Meanwhile, both

exposed and subsurface sections of variable thickness, reaches several thousands of meters exist in the GS region. The extensive gypsumanhydrite deposits exposed at Ras-Malaab and Marwet El-Khoshera areas, which represent the best developed outcrops of the Miocene evaporites in the (GS) region (Said 1962) (Figures. 1, 2.). In this work some analytical techniques are used to characterize the Ras-Malaab gypsum and its applicability to the suitable industrial uses.



Figure 1. Location map of the study area.



Figure 2. Geological map of Wadi Gharandal and Ras-Malaab after Moustafa and Khalil 2016.

Geology and stratigraphy of the Gulf of Suez

The Phanerozoic successions of the GS are inconsistently underlain by the Neoproterozoic Arabian-Nubian Shield (ANS) (Fig. 3). The stratigraphic sequence of the GS contains that separated sequences by multiple unconformities related to major tectonic events Said 1962, 1990; Saoudi and Khalil, 1986; Evans, 1988; Richardson and Arthur, 1988;

Patton et al. 1994; Purser and Bosence, 1998; Bosworth and McClay, 2001; Jackson et al., 2006. The ANS is composed of volcaosedimentary arc-related successions, ophioliterelated rocks, gneissose belts, and different types of granitoides, that are frequently pierced by dykes and sills of basic and acidic intrusive, (Schurman, 1966.).

Paleozoic sediments from the Pre-Rift Succession are found in a variety of locations on both sides of the GS and have been discovered in the offshore boreholes in (Al Far, 1966; Abdallah and Adindani, 1963; Issawi and Jux, 1982). The late Oligocene to early Miocene Abu Zenima Fm is the oldest syn-rift rock block in the GS (Patton et al., 1994; Jackson et al., 2006). The Ras-Malaab post-rift Group is composed mainly of evaporites and clastics. The Ras-Malaab Group is made up of the Zeit Fm., South Gharib Fm., and Middle Miocene Belavim Fm., respectively (Fig. 3). The Belayim Fm is composed of the Baba evaporite Member, fine clastics of the Sidri Member, carbonates of the evaporites of the Feiran Member, and fine clastics of Hammam Faraun Member. Anhydrite and salt make up the majority of the underlying Late Miocene South Gharib (Fawzy and Abdel Aal, 1984). Anhydrite and shale strata interbedded in salt of the Zeit Formation. The Warden and Zaafarana Formations overlie unconformably the Miocene sequence (Figure 3).



Figure 3. General stratigraphy of the eastern Gulf of Suez (modified after Darwish, 1993)

Moon and Sadek (1925) were the first describe and subdivide the Miocene to succession at Wadi Gharandal and Gabel Khoshera, and they introduced their

lithostratigraphic nomenclature of the Miocene succession of the GS that is still in use. Evaporites are assigned, tentatively, a late Middle Miocene age by Said (1962). The complete evaporite succession in the GS region has been classified by the Egyptian General Petroleum Corporation (E.G.P.C.) stratigraphic Committee (1964) into the Kareem, Belavim, South Gharib and Zeit Fms. constituting Ras-Malaab Group. The formations are of Langhian, Serravalian, Tortonian and Missinian as suggested by Garfunkel and Bartov (1977). Friedman (1972) and Wali and Abu-Khadrah (1987) assumed that the coastal Miocene evaporites of Western Sinai originated in an ancient sabakha environment. Youssef (1986) recognized both shallow subaqueous and superatidal sequences (sabkha) in the Miocene evaporites on Red Sea coast and also added that the former was incorporated into the prograding sabakha. The studied gypsum- anhydrite deposits are related to Gp. 1, Gp. 2 and Gp. 3 of Moon and Sadek's classification denoted as Markha. Shagar and Baba Members. respectively (E.G.P.C., 1964). The former two members belong to the Kareem Formation while the third one represents the lower part of the overlying Belayim Formation, the three members almost belong to the Upper Langhian. (Figure 3)

Material and Methods

All the geochemical analyses were carried out in the Mineralogical Institute labs at Karlsruhe University, Germany. X-ray diffraction analysis (XRD) was performed bv Siemens diffractometer 11, using a monochromatic incoming beam and Cu broad focus tube at 40 kV and 40 mA. The angle scanned was manually pulverised into powder form in the porcelain mortar and pestle at a scanning speed and data collecting interval of $0.01^{\circ} 2 \theta^{s-1}$. The diffraction patterns for each sample were compared to the Joint Committee of Powder Diffraction Data Service's (JCPDS) slandered patterns.

The Philips PSE was used to perform the microprobe analysis. Using an Ed-System Tracor 5502 and a 500 X scanning Microprobe, of 15 KV, 21 n A° -5 n A° SI (Li) Detector $640A^{\circ} \pm 40 A^{\circ}$ is the electron beam's diameter, with a magnification power of 5000X magnification. A computer software used the amended data as numbers of cations to create mineral formulations. Trace elements were determined by a Philips PW 1400 automatic Xray fluorescence spectrometer. The samples were pulverized in hardened steel and agate mortar then the powder was mixed in platinum crucibles with di-lithium tetraborate Spectro melt (Al2) in ratio of 1:4 (Wt.) and fused in a high frequency furnace at 1300°C for about 10 to 20 minutes to produce the fused discs. Pressed powder discs were used to determine the trace elements, including Ba, Cr, Ni, Zn, Rb, Sr, Y, Nb, V, Co, Cu, Ga, Pb, Zr and Ce. The analysis was calibrated using the USGS standard rocks, including G-2, GSP-1, AGV-1, JB-1 and BIR.

The sequential heating of the samples in a muffle furnace (as opposed to other procedures that entail gas collection and the measurement of amount either volumetrically or chromatically; Dean, 1974) is the foundation for quantitative assessments of sediment properties by income of loss-ofignition. After being oven dried to persistent weight (or dry matter) and cooled to room temperature, organic matter is burned in a first response at temperatures between 500 and 550 ^oC to produce ash and CO₂. According to Dean (1974), Maher (1998), and Heiri et al. (2001), the quantity of organic matter is the weight variance between the dry sediment and the 550°C ash, which is thought to have originated from organic material with the chemical formula (CH₂O)n.

Secondly, to determine how much CO₂ was released during the breakdown of the carbonate minerals, the same sample was torched at 925°C (Bengtsson & Enell, 1986; Heiri et al., 2001) or 1000°C (Dean, 1974; Maher, 1998) temperatures. According to Bengtsson and Enell (1986), the weight loss between loss-on-ignition at 550°C and loss-onignition at 925°C is multiplied by 1.36, which is the ratio between the molecular weights of CO₃ (60) and CO_2 (44), to determine the carbonate content in the original sample.

Results

X-ray diffraction analysis

To control the kind and quantity of the minerals in gypsum samples, both qualitative and quantitative analyses were carried out. Gypsum samples were heated for 48 hours to respective T of 130, 200, and 300°C. They were cooled in a range of T and comparative humidityconditions. The main peaks of the studied gypsum samples are gypsum, anhydrite and bassanite where the minor peaks show the different elements like clay minerals The XRD traces of gypsum samples did not lose weight above 250°C, where almost all the analyzed samples are the same minerals (Figure 4. a, b and c.)



Figure 4. a, b and c are the X-ray diffraction of the examined Ras-Malaab gypsum.

The purity of the studied samples of Ras-Malaab has been confirmed by microprobe analyses. Microprobe analysis were done for nine gypsum samples and the results listed in Table 1. Where CaO ranges from 39.57% to 41.67%, which show very limited difference with an average of 40.99% and SO₃ ranges from 56.33% to 60.43% with average of 58.93%.

Table 1:	Microprobe	analysis	in	Ras-Malaab
Gypsum.				

Sample No.	CaO	SO ₃	Total
1	41.17	58.83	100.00%
2	40.87	59.13	100.00%
3	41.65	58.35	100.00%
4	41.13	58.87	100.00%
5	41.22	58.78	100.00%
6	41.35	58.65	100.00%
7	40.91	56.33	100.00%
8	39.57	60.43	100.00%
9	41.02	58.98	100.00%

Trace element analysis for Ras-Malaab gypsum

Nine samples of Ras-Malaab gypsum were analyzed for trace elements (Ba, Cr, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr and Nb). All analysis is listed in Table 2. From the obtained analysis, Ba, Cr, Ni, Ga, Pb, Zr and Nb under the detection limit, while Cu, Zr, Rb and Y show very low concentrations. Sr represent some low value rather than the first one. The results of the X-ray fluorescence analyses show the high purity of the studied samples from the trace elements.

 Table 2: Trace element analysis for Ras-Malaab
gypsum

Sample No.	Cu	Zn	Rb	Sr	Y
1	0.0004	0.0025	0.0005	0.0839	0.0002
2	0.0005	0.0026	0.0004	0.1354	0.0003
3	0.0003	0.0025	0.0004	0.0851	-
4	0.0004	0.0024	0.0004	0.0986	0.0003
5	0.0005	0.0026	0.0004	0.0835	0.0003
6	0.0005	-	0.0005	0.0781	0.0003
7	0.0003	0.0024	0.0006	0.0818	0.0003
8	0.0004	0.0026	0.0004	0.1041	0.0003
9	0.0003	0.0024	0.0004	0.0817	0.0003

Loss of ignition calculation for Ras-Malaab gypsum

The loss-of-ignition is an extensively used method to evaluate sediment qualities, such as organic matter, water content, inorganic carbon, and minerogenic deposit. (Maher, 1998 and Dean, 1974). Nine samples were analyzed to calculate the loss of ignition, the ignition loss of gypsum is listed below in Table 3, CO₂% ranges from 0.1112 to 0.6268 and H₂O% in the range of 15.235 to 19.979 with a total ignition loss between 15.363 and 20.193. The concentration of water in the gypsum is 17.34, with a small value of CO_2 (less than 1%) which reflect the purity of the studied samples.

Sample No.	1	2	3	4	5	6	7	8	9
CO ₂ %	0.6268	0.1112	0.8554	0.1845	0.2475	0.6215	0.1281	0.1357	0.2138
H ₂ O%	15.858	17.807	17.739	17.115	18.861	16.520	15.235	17.213	19.979
Ignition loss	16.484	17.918	18.594	17.300	19.109	17.142	15.363	17.349	20.193

Discussion

Pure calcium sulphate is never found in gypsum or anhydrite. There are other ions in the liquids from which they precipitate that may, to varying degrees, find their way into these sulphate minerals. According to Holser (1979) and Dronkert (1985), there are several ways whereby minor and trace elements might be incorporated into gypsum, including occlusion, fluid inclusions, surface adsorption, and solid solution.

Ca-sulphate beds ranging in thickness from 1 to 20 metres make up the outcropping evaporitic sequence in the Gebel Zeit and Gemsa regions. Usually, variable proportions of gypsum and anhydrite combine to form these beds. Together with carbonates, biosilica-rich siltstones and marlstones that are interbedded also include calcium sulphates as solitary nodules, thin laminae, and dispersed crystals. X-ray analyses show variable levels of halite. As previously mentioned, these marginal successions (central Gebel Zeit and Ras El Ush area) most likely contained some halite layers that were intercalated and later disintegrated (Rouchy etal., 1995). Wadi Gasus, Wadi Wizr, and Wadi Teaban, three Red Sea locations, have secondary gypsum deposits with comparatively greater amounts of FeO, MnO, K2O, MgO, TiO2, Sr, and Zr. The values of Al-Bargan's principal gypsum differ from this signature (Aref, etal., 2003).

The gypsum at Ras-Malaab display grades around 100% suggesting a very high-grade gypsum. The standard values of American specification (2000) for gypsum utilization in the cement industries established an acceptable value at a maximum of 85% CaSO₄.2H₂O and MgO< 5%, while that of Lorenz and Gwodsz (2003) ranged between 70 – 80% CaSO₄.2H₂O. Considering this it was suggested that the gypsum deposits at Gashua, Garin Ari, Turmi and Jakaterre have satisfied these specifications because their CaSO₄.2H₂O values ranged from 87.59 - 89.59%, hence they can be suitable for cement production. Acceptable standard specification for the application of gypsum in the ceramic industries on the basis of the American standards ranged from 85% - 96%. Manufactures fertilizer production requires 85% - 90%, while for solid wall paper the value must greater than 85%. furthermore, according to the Indian standard specification for gypsum applications (Indian Mineral Yearbook 2014) for surgical plaster (96% min. CaSO₄.2H₂O), ammonium sulphate fertilizer (85-90%) CaSO₄.2H₂O), pottery (85%) min. CaSO₄.2H₂O), cement (70-75% and 80-85% CaSO₄.2H₂O for export quality cement), reclamation of soil (70% min. CaSO₄.2H₂O) and for extender in paints 75% min. CaSO₄.2H₂O. From the geochemical analysis of the gypsum from Ras-Malaab area, the CaSO₄.2H₂O of the studied samples are of high quality with 99%. Therefore, the gypsum deposits in the studied area are highly suitable for the manufacture of surgical plaster, cement, ceramics, fertilizer, reclamation of soil, solid wall paper and in paints.

Conclusions

In conclusion, the gypsum of the Ras-Malaab evaporates, which is fall within the Miocene sequence and on the bases of all the previously mentioned analytical techniques, indicate that the studied gypsum is a very high quality for cement, plaster of Paris, solid wallboard, ceramic, ammonium sulphate fertilizers, cement and paints and any other industrial purposes.

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Author statement

All the authors have equally contributed.

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الملخص العربي

عنوان البحث: التوصيف الجيوكيميائي لمتبخرات الميوسين في منطقة خليج السويس، مصر

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ترسبت الطبقات التى يهيمن عليها التبخر نتيجة للعزلة التكتونية للبحر الأحمر. تتبخر رواسب الجبس والأنهيدريت المكشوفة في منطقتي رأس الملعب ومروة الخشيرة، والتي تمثل أفضل النتوءات المتطورة للميوسين في منطقة خليج السويس. لدراسة جودة رواسب الجبس في منطقة رأس الملعب وانعكاساتها على التطبيقات الصناعية، تم استخدام تقنّيات تحليلية مختلفة مثل؛ حيود وفلورة الأشعة السينية، تحليل المسبار الدقيق، تحليل العناصر النزرة، وتحليل فقدان الأشتعال. يكشف حيود الأشعة السينية وقمم التألق أن العينات هي الجبس والأنهيدريت والباسانيت، ويتأكد تحليل المسبار المجهري أن العينات المدروسة عبارة عن جبس نقي بتركيبة محدودة من CaO بحوالي ٤٠,٩٩ ٪ و SO3 بمتوسط ٥٨,٩٣٪ بنسبة عالية جدًا. كميات منخفضة من Cu و Z و Rb و Y بالقرب من الصفر. تشير النتائج إلى أن رواسب الجبس في رأس الملعب من العصر الميوسيني تم تقييمها على أنها نقية جدًا وذات جودة عالية ومناسبة للأسمنت والجص الباريسي وألواح الجدران الصلبة والسيراميك وأسمدة كبريتات الأمونيوم وغيرها من الأغراض الصناعية المختلفة