Thermal Characterization and Mineral Composition of the Egyptian Alabaster "Carbonate Rocks"

M. Blasy

Department of Geology, Faculty of Science, Zagazig University, Wadi Sannur, South Cairo, Egypt

Abstract: ***Representative rock samples from the banded Egyptian alabaster collected from the Wadi Sannur quarry (53 km SE of Beni Suef, south Cairo). Two distinct bands with a transition zone inbetween. The early crystallized band is white, opaque, and fine-grained. The other band is mostly translucent, coarse–grained and pale-yellowish brown. The participation of the constituents in banded alabaster carbonate rock was determined combining three methods of analysis, microscopic examination, atomic absorption spectroscopy (AAS) and thermogravimetry (TG). The three methods are used in a complimentary way in order to specify the exact composition of each band in the Egyptian alabaster carbonate rock. Calcite represents the main mineral composition in the translucent band, calcite and brucite represnts the main composition of the white one. Calcite and hydromagnesite form the main components of the transition zone but are variable. The percentage of the minerals can be determined with accuracy, only through TG analysis by mass loss. The effect of CO_2 and $H2_O$ pressure on the temperature reactions has been discussed.***

Keywords: Calcite, brucite, hydromagnesite, TG-TGA, AAS,

1. Introduction

Alabaster is a term which is used to refer to tow forms of calcium, calcite alabaster and gypsum alabaster. They have been used in carving and ornaments for centuries. The ancients favored calcite alabaster, a very hard form of calcium carbonate. This stone was originally imported from Egypt, and is known in archeological literature as "Oriental Egyptian Alabaster ", consists of nearly pure calcium carbonate **(Hintze, 1930).** It is often found in caverns as deposited mineral in the form of stalagmites with layered structure.

Naturally occurring carbonate rocks are extremely important natural resources finding widespread applications **(Boynton, 1980)** and thus being placed among the important raw materials. The main constituents of the Egyptian alabaster are calcite and variable amounts of brucite and hydromagnesite. The geology, mineralogy and geochemistry of the Egyptian alabaster and their country rocks are the subject of the work of many researchers throughout the years.

From reactions occurring in minerals or other chemical substances during thermal treatment (heating or cooling) for example during dehydration, or loss of CO_2, H_2O, etc., the mass loss which can be determined with thermogravimetry(TG), can be clearly identified and accurately measured. The quantitative determination of the percentage of dolomite, calcite (or other carbonated salts with satisfying accuracy in carbonated rocks can be realized from the mass variations observed, when these can be attributed to specific compounds, through information from literature and XRD measurements **(Dagounaki et al.2004).**

In this work, the thermogravimetry (TG), microscopic examination and atomic absorption analysis (AAS), are used simultaneously to specify the exact composition of each band in the banded type of Egyptian alabaster carbonate rock. The aim is to detect which band is composed of nearly pure calcite, as raw material of CaO-based expansive agent. The results are contributing in the study of mode of formation of the banded Egyptian alabaster.

Today, mining and prevalent methods are developed and most of investigation centers related to mining try to produce non-explosive and non-environmental pollution. Expandable powders as (CaO) are suitable materials substituting for explosive materials in mining activities. It is produced after calcination of calcite. Non-explosive demolition agents are mixed with clean water and poured into pre-drilled holes on rock and concrete. This agent will expands and exerts significant thrust on the hole –wall. The induced pressure fractures the wall and splits the rock across the line of the drill holes without producing noise, vibration, toxic gases or flying debris **(Murray,et al.1994)**

2. Geology and Samples

Egyptian Alabaster calcite occurs mainly in Wadi Sannur, near Beni Suef and in Wadi Assiuty (both South of Cairo). The country rocks of alabaster from these localities are found as Low –lying hills East of Beni Suef (about 120 km South of Cairo) and consist mainly of Upper Eocene limestone intercalated with shale. In Wadi Sannur (53 km SE of Beni Suef), the hills consist of Middle Eocene nummulitic limestone **(Akaad and Naggar, 1965)**. Egyptian Alabaster exhibits a variety of structures, as banding, veins, botryoidal and cavity filling. Banding is a characteristic feature of Egyptian Alabaster calcite consisting of alternating bands of pale yellowish –brown ranslucent and milky –white opaque bands. Gradation of growth sometime has been observed between the white and the translucent bands. The bands vary greatly in thickness; a thin white band may be followed by a thick or a thin band of the translucent one which may be followed by a rather thick –white band, (Fig. 1)

3. Microscopic Examination

In thin section, the translucent band is pale yellowish-brown. This color may be after crystallization due to the penetration of iron–rich solution through the open spaces and interstices between the calcite crystals. It fades by heating on the Bunsen burner for a few minutes .This band is composed of calcite grains, 2-5 mm across in mosaic aggregate and exhibiting wavy extinction .The crystals have generally different optical orientations with rhombic cleavages and polysynthetic twinning .The white band on the other hand has lower Sp G (2.63) than that of translucent band (2.73) and sometimes show vesicular texture **(Fig. 2).** It is composed of fine crystals of calcite less than 0.05 mm with brownish and dark brownish dusty grains of brucite mineral. The latter is usually found in clusters and patches associated with calcite grains. The presence of brucite in the white band suggesting its later crystallization from the interstitial Mg –rich solution as Mg^{+2} ion is more soluble in water than Ca^{+2} ion.

The transition band is between the translucent and white bands with wavy and irregular boundary. It has relics of white band tapering and finishing out (Fig.1) suggesting replacement reaction and formation of hydromagnesite on the expense of brucite in the presence of CO_2. The transition band is composed of feather –like crystals of hydromagnesite with some grains of calcite. The feather –like crystals of hydromagnesite are standing at right angles to the boundary line, sometimes bended and curved, and reaching in size up to 0.3x4mm .The crystals not show any twinning . The crystallization history of the alabaster bands can be suggested as follow. At first, the calcium carbonate mineral was deposited rapidly from carbonated water as CO_2 given off. The precipitate has some interstitial Mg+2 –rich solution, giving later brucite mineral and some vesicles. This stage resulted in release of heat and building up of CO_2 pressure. The crystallization of calcite led to enrichment of magnesian ion in the solution; these conditions of high temperature and pressure and enrichment of magnesian ion slowed down the rate of crystallization giving coarse crystals of calcite (Pytkowicz, 1965), as well as some replacement reaction to the already crystallized white band giving a transition zone. The highly hydrated nature of the Mg^{+2} ion prevents the formation of anhydrous Mg CO_3 phases. The building up of CO_2 pressure within the cave may lead to fracturing and ⁄or jointing the walls of the cave and escaping of CO_2 gas. Such sudden release of pressure may lead to income of carbonated water. Calcium carbonate has incorporated in this water particularly when the circulating groundwater through limestone has CO_2. Another layer of fine –grained calcite and brucite will rapidly precipitated when the CO_2 is given off, followed by transition zone and translucent layers, giving the layered structure of Egyptian alabaster simulating oscillatory zoning (Fig.1).

4. Experimental

The studied banded Egyptian alabaster carbonate rock samples collected from Beni Suef Mine (south Cairo). The white, transition and pale- brown translucent bands were separated and each one was grounded with agate mortar and pestle and then sieved to less than 60 µm diameter and submitted to thermal analysis by means of Schimadzu TGA -50 H. Each powdered sample was heated by 10 ºC ⁄ min. under static air atmosphere, from ambient temperature to 1200 ºC at Central Laboratories Sector of the Egyptian Mineral Resources Authority in Egypt.

Atomic absorption analysis for the elements Ca, Mg, Fe, Na, K, Zn, Cu, Ba and Mn have been carried out for the three powdered bands by using the Atomic Absorption ⁄ 2⁄0 Spectrophotometer ⁄ VGP. The elements composition of the three bands is shown in table (1)

Table 1: chemical analysis of the three bands of Egyptian alabaster

Element %	*White band*	*Transition band*	*Translucent band*
Ca	31	39	44
Mg	17	7	0.1
Fe	0.04	0.001	0.02
Mn	0.01	0.005	0.007
Na	0.025	0.0012	0.007
K	0.031	0.001	0.015
Ba	0.05	0.012	0.06
Cu	0.032	0.011	0.003
Zn	0.028	0.013	0.08

From the table, the translucent band is rich in calcium, while the white band is rich in magnesium element. The transition band has values of Ca and Mg suggesting a transition zone. Na, K, Cu, Mn, and Fe elements are high in the white band. The high content of Mg element in the white band can be interpreted to its high solubility in the interstices water which crystallized later as dusty grains. It must be taken into account that in carbonate rocks, the elements Ca and Mg are possibly present not only in the form of dolomite and calcite but also in the constituents of the impurities or as aggregates **(Dagounaki et al. 2004).** Therefore, the results obtained from the method of AAS do not discriminate the part participating in calcite or hydromagnesite. In the TG-TGA method this determination is direct and consequently the results are accurate. **El-Hinnawi and Loukina (1971)** found that, the magnesium contents of the limestone (country rock) and alabaster is low, although the translucent bands contains up to 5.6% Mg CO3. It is mainly located in the structure of calcite and the mineralogical composition of the translucent bands has been determined as magnesian calcite and that of the milky –white bands as normal calcite. It is important to remember that El-Hinnawi and Loukina (Op. cit.) not noticed the transition band.

5. Thermal Analysis

The chemically analyzed bands not represent pure mineral but has variable gradations between each other. In the literature, for pure calcite sample the expected mass decrease is 43.97 % in one step at 900 ºC. Various chemical components in calcite has shown that the TGA peak temperatures are varied **(Shahraki et al. 2011).**The quantitative determination of the percentage of calcite, brucite, hydromagnesite or other constituent with satisfying accuracy in the studied banded alabaster calcite can be realized from the mass loss which can be determined with the thermogravimetry (T G) **(Dagounaki et al. Op cit).**Here each band shows replacement texture and graded to the next band, and sometime show the appearance of oscillatory zoning **(Fig.1).**

TGA curves of the three bands of the Egyptian Alabaster calcite **(Figs.3, 4, 5)** indicate endothermic reactions.

Results of the thermal decomposition show that the sample from the white band is market by tow endothermic peaks of reactions **(Fig 3).** In the first peak, the reaction is started at 220 ºC, reaches a peak at 275 ºC and finished at 380ºC with mass loss equal to 17.36% .This is attributed to the removal of H_2O as a result of dehydroxilation of brucite, $Mg(OH)_2$ which accords **Suneetha et al. (2007), and Bruni et al. (1998).** The second peak has also endothermic reaction, started at 650 ºC, reached the maximum at 875 ºC and ended at 950 ºC with mass loss equal to 36.56 % as a result of the decarbonation of calcite.

The thermal behavior of the sample from the coarsely crystalline pale-yellowish brown translucent band (Fig.4) shows, two endothermic peaks; the first one is small at 325 ºC, with mass loss equal to 0.48% corresponding to the removal of physical water. The second endothermic reaction has the onset temperature of reaction at 675 ºC, reaches the maximum at 887 ºC and finished at 970 ºC with mass loss equal to 44.1% due to the decarbonation of calcite. Maitra et al. (2005) found that, pure calcite decomposed to Ca O and CO_2 between 900 and 960 ºC

The thermal behavior of the sample from the transition band has TG curve (Fig. 5), more or less differs than those of the above tow distinct bands. The reaction begins at 360 ºC and ended at 500 ºC with five small peaks at 360, 370, 425, 450 and 500 ºC with mass loss equal to 9.57 % for the dehydration and decarbonation processes of hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. (i.e. removal of hydroxile ion, water of crystallization and removing of CO_2, this accords Hollingbery and Hull (2012). Another endothermic reaction, starts at 620 ºC, reaching the maximum at 775 ºC and finished at 850 ºC, with mass loss equal to 37.3% as a result of decomposition of calcite to Ca O and CO_2.

6. Conclusion and utilization

The banded Egyptian alabaster is composed of three bands. The coarsely crystalline translucent band is more suitable as an expansive agent. It has large amounts of CaO, with negligible amounts of MgO. CaO-based expansive agent is suitable substitute for explosion materials in mining activities. The presence of large amount of MgO decreases its quality. The decomposition temperatures of calcite in the three bands are different. The peak temperature of calcite decomposition in the coarsely- crystalline translucent band (887 ºC) is higher than that of white (875 ºC) and transition band (775 ºC). The hydration degree of CaO was increased by increasing the calcination temperature **(Shahraki et al. 2011).**

The endothermic peak of the calcite in the transition zone is lower than that of calcite in the white and translucent bands. The liberation of CO_2 and H_2O during the decomposition of hydromagnesite and increasing their pressure causes a lowering of TGA peak temperatures **(Wilbum et al. 1991, and Paulik et al.1980).**

The dehydroxilation of brucite to MgO and H_2O in the white band resulted in the release of H_2O vapor. The latter has small effect on lowering the TGA peak temperature of calcite. The utilization of brucite is in two ways, as fire retardant and as sequestration of CO_2 from the atmosphere. **Sonia et al. (2001)** found that the Magnesium hydroxide become attractive owing to its higher temperature of decomposition, about (380 ºC).than aluminum hydroxide (180 ºC) as fire retardant in many materials including thermosets, elastomers and thermoplastics. The reaction of magnesian minerals such as brucite with CO_2 is important in sequestration of CO_2 **(Veronik et al . 2008).** So the formation of hydromagnesite in the Egyptian alabaster may be a key to the sequestration of carbon dioxide from the atmosphere.

Figure 1: A photograph of a hand spacemen, showing the banding in the Egyptian alabaster

Figure 2: A photograph of a hand spacemen, showing vesicular texture in the white band

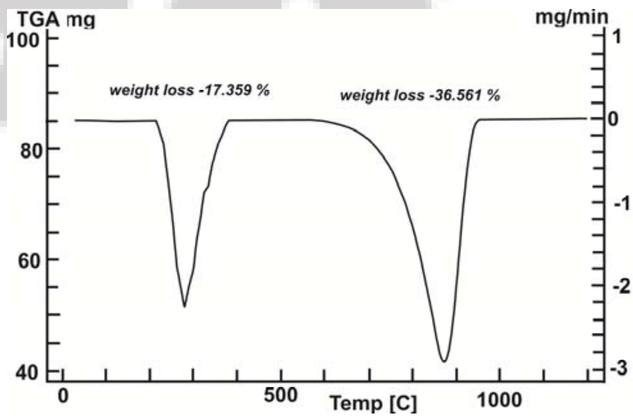

Figure 3: TG curve of the white band of Egyptian alabaster

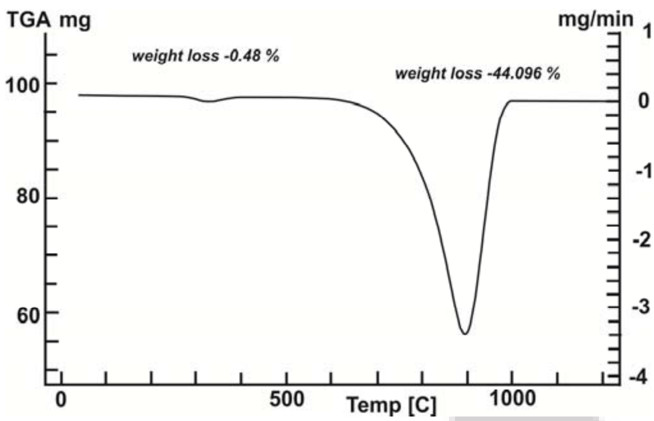

Figure 4: TG curve of the translucent band

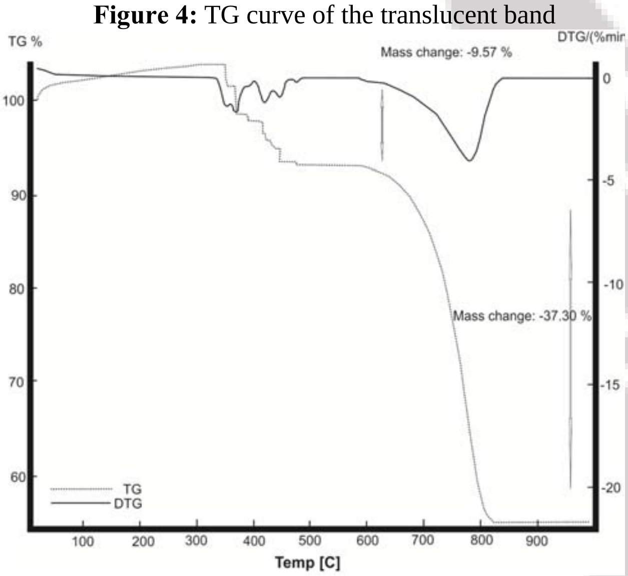

Figure 5: TG curve of the transition band of Egyptian alabaster

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