International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Mineralogy of Aragonite Carbonate Veins, Dissecting Dokhan Volcanics, Northern Eastern Desert, Egypt

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Abstract: ***The aragonite carbonate veins are hard with bone-like appearance, associated with carbonate-rich basic dykes. All are hosted in andesitic and basaltic volcanic rocks of Dokhan type and. The carbonate rocks are composed of ultra fine grains of aragonite with minor phases of calcite, magnesite and cerussite as detected by x-ray diffraction (XRD) and differential thermal analysis (D.T.A). They are of calcite carbonate according to IUGS with CaO (56.1 Wt%), MgO %),L.O.I.(31Wt%) and poor in Sr, Ba,Y, REEs, Cr, V, Ni, Ti, Co, V but rich in Pb and Zn elements than those of magmatic carbonate rocks. This suggests hydrothermal crystallization of aragonite under low temperature and high C_2O gas pressure.***

Keywords: aragonite, hydrothermal, DTA, XRD, XRF, carbonate veins.

1. Introduction

World-wide carbonates appear to be associated with faulting and rifting related to doming **Le bas, (1977**) **and Woolley and Kempe,(1989**).**Cullers and Graf (1984)** pointed out that carbonates have higher rare –earth element (REE) contents and higher Lree ⁄ Hree (e.g. La ⁄ Lu) ratios than any other igneous rock. The study aims to identify the mineral and chemical compositions of the carbonate veins dissecting the basement rocks in an attempt for ascertain their origin. Different methods of study have been carried out (e.g. geochemical analysis of major, trace and REE; XRD and DTA analysis).In general the origin of carbonate rocks represents a baffling problem. Some petrologist thought 1- remobilized limestone, 2- replacement of silicate rock by carbonate-rich solution, 3- hydrothermal deposits. Others consider its origin due to: - 1- partial fusion of mantle rich in CO_2, Ba and Sr, 2-fractional crystallization and liquid immiscibility of CO_2-rich magma **(Barker, 1983).**

2. Geology and Petrography

The aragonite carbonate veins are dense, hard and yellowish white color with bone like appearance and composed of ultrafine grains of carbonate minerals. They are found as veinlets dissecting the brecciated andesitic and basaltic volcanic rocks (Fig.1) around Wadi Esh El Mallaha. The vein reaches in width up to 1 meter .The associated basic dykes are mainly of melilite basalt and lamprophyre. They are easily effervesces with HCl as aragonite carbonate vein. Lamprophyre is hard, reddish brown in color and composed of kaersutite, andesine, melilite (Ca-silicate), magnetite, antigorite, apatite and carbonate minerals. Melilite basalt is hard, dark grey in color and composed of labradorite, melilite, apatite, magnetite and batches of carbonates (Fig. 2). Most olivine and plagioclase minerals are partly to completely replaced by antigorite and carbonate minerals respectively and occur as pseudomorphs (Fig.3). The carbonate rocks are hard ,yellowish white in color with bone like appearance .they are composed mainly of very fine grains of carbonate minerals (Fig.4) , (they are difficult to identify by using the polarizing microscope).

Fig. 1

Figure 1: Aragonite carbonates veinlets in volcanic rocks

Fig. 2

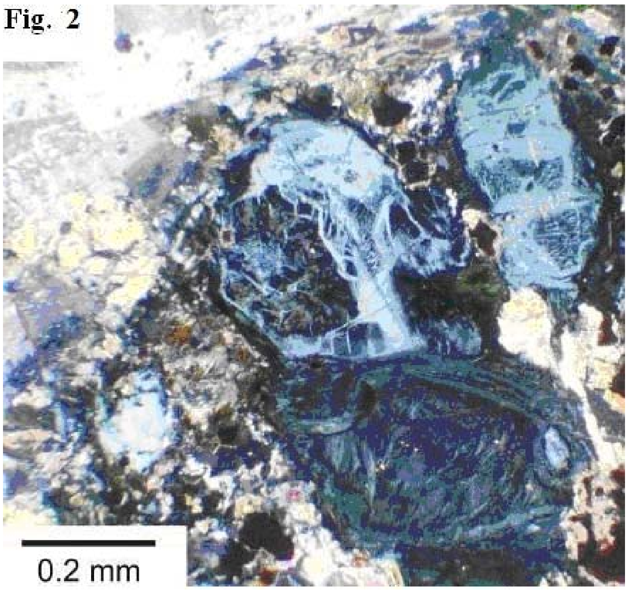

Figure 2: Oval grain of melilite (inky blue color) with carbonate batches in melilite basalt, C.N

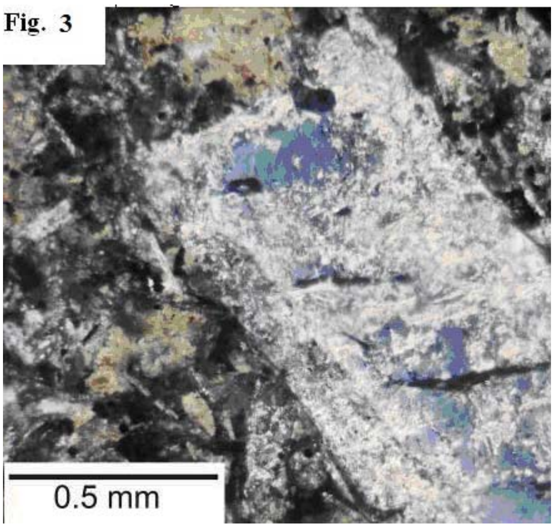

Figure 3: Euhedral plagioclase partially altered to carbonates and surrounded with brownish batches of carbonates in melilite basalt, C.N.

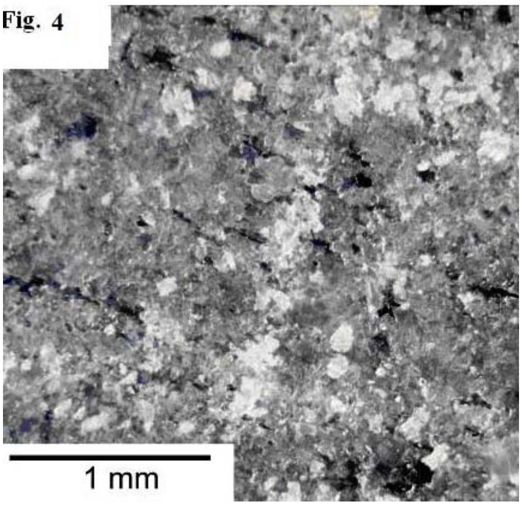

Figure 4: Finally crystalline carbonate minerals of aragonite vein, C.N.

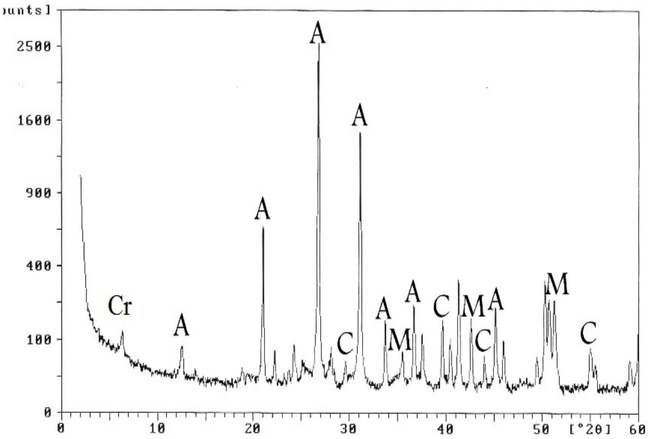

Figure 5: XRD pattern of aragonite carbonate vein rocks.(A=aragonite),M(magnesite),C(calcite), Cr (cerussite)

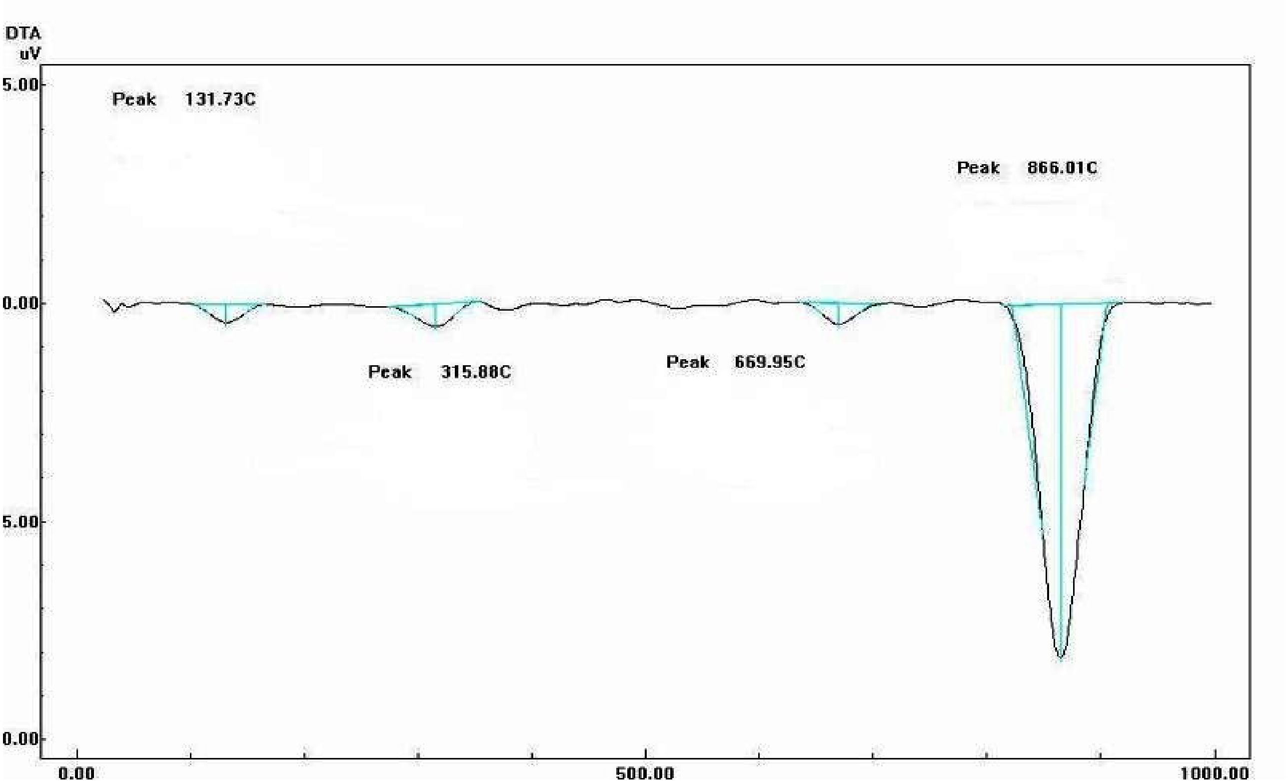

Figure 6: DTA (thermal curve) of aragonite carbonate vein rock.

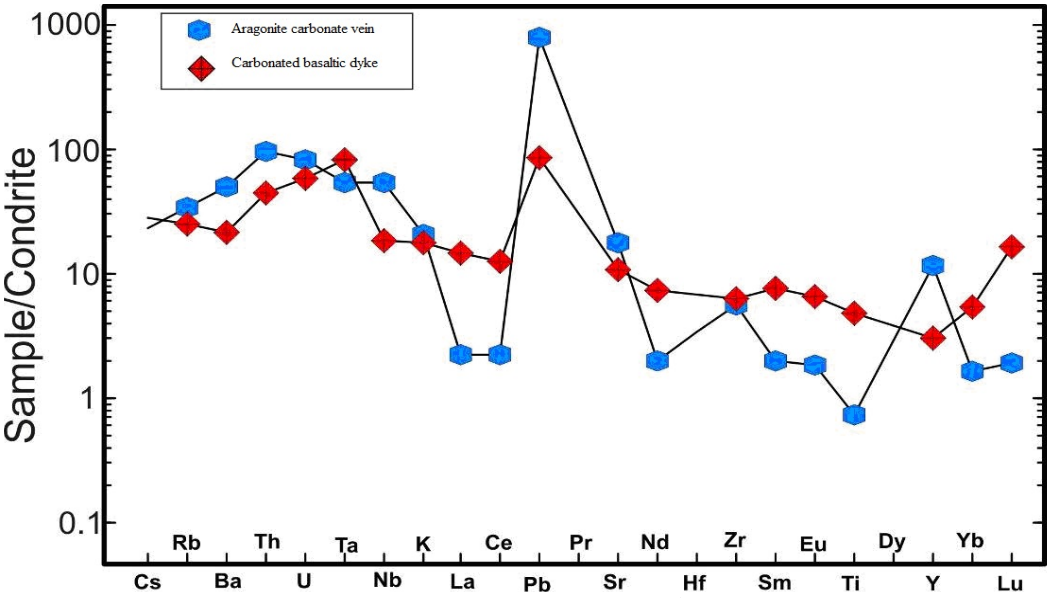

Figure 7: The condrite-normalized trace and REE pattern (after McDonough and Sun, 1995)

3. X-Ray Diffraction (XRD)

Carbonate rocks have been grinded to 200 meshes and subjected to x- ray diffraction at the Central Laboratories Sector of the Egyptian Resources Authorities, Cairo. The XRD patterns are shown (Fig.5). The 2Ø, d- spacing in Angstrom (Å) are shown in Table (1) and compared with ICDD files. The analysis indicates that, the carbonate rocks are composed mainly of aragonite with minor phases of calcite, magnesite and cerussite.

Table 1: 2Ø and d- spacing in Angstrom (Å) of carbonate vein at Esh area.

	2Ø	d-spacing (Å)
Aragonite	12.58	7.02
	21.01	4.22
	26.8	3.32
	31.1	2.87
	41.3	2.18
	45.1	2.0
	49.4	1.84
	50.26	1.8
Magnesite	35.5	2.52
	42.35	2.12
	45.72	1.97
	51.25	1.78
Calcite	29.6	3.01
	39.6	2.27
	43.9	2.06
	55.4	1.65
Cerussite	2.66	33.7

4. D.T.A. of Carbonate Rocks

The powder of carbonate is subjected to thermal decomposition at atmosphere (nitrogen) and heating rate 15° per minute. The thermal curves (Fig.6) shows the endothermic peaks of the corresponding mineral phases of carbonates which can be interpreted as follow:

The peak at 130° C corresponds to dehydration of some hydrous minerals.The peak at 315° C is attributed to dissociation of cerussite **(Warne and Bayliss, 1962**) while the endotheraml peaks at 669° C and 866° C represent the decarbonation of magnesite and calcite respectively **(Montaye et. al., 2002).** There are littile variations for the observed peaks than in the literatures due to heating rate, impurities and particular size of powder.Aragonite not show endothermal peak as it changes spontaneously to calcite above 450 ° C. The higher difference in the heat of dissociation of calcite and magnesite are used commercially to separate MgO from CaO **(Cuthbert and Rowland, 1947)**.

5. Geochemistry

Two representative samples from the carbonate veins and one from the associated carbonate-rich melilite basalt dissecting the basement rocks at Esh area are analyzed for major, trace and REEs elements at the laboratories of Nuclear Materials Authority, Egypt. The data is shown in Table (2)

Table 2: Geochemical analysis of aragonite carbonate vein and carbonate rich basaltic dyke

Rock type	Carbonate rich basaltic dyke	Aragonite carbonate vein	
Major oxides (Wt%)			
S. No.	9	11D	11
SiO_2	48.76	2.74	2.55
TiO_2	0.98	0.16	0.13
Al_2O_3	15.06	0.52	0.47
Fe_2O_3	5.1	1	0.89
FeO	3.01	0.05	0.04
MnO	0.17	0.02	0.02
MgO	6.02	10.58	6.57
CaO	9.81	52.13	56.1
Na_2O	4.73	0.52	0.54
K_2O	0.52	0.63	0.6
P_2O_5	0.1	0.45	0.43
L.O.I	5.67	30.98	31
Trace elements ppm and REEs			
Sr	211	356	211
Rb	15	8	33
Ba	144	360	306

Ni	123	6	14
Cr	417	15	13
Y	13	52	50
Zr	65	36	80
Ta	3	2	2
Nb	12	35	35
Co	48	8	8
V	87	6	15
Zn	53	198	133
Cu	25	54	32
Pb	13	97	141
U	1.2	1.5	1.8
Th	3.5	7.3	8
La	9.5	1.46	
Ce	20.8	3.73	
Nd	9.3	2.48	
Sm	3.1	0.81	
Eu	1	0.28	
Gd	3.2	0.82	
Tb	1.1	0.15	
Er	2.2	0.6	
Yb	2.4	0.73	
Lu	1.1	0.13	
Nd/Sm	3	3.06	
La/Ce	0.46	0.39	

6. Nomenclature

The chemical composition of the study carbonate is of $CaCO_3$. It has CaO, MgO and L.O.I equal 56.1 Wt%, 10.58 Wt% and 31 Wt% respectively suggesting calcite carbonate according to IUGS and **Barth and Ramberg (1966)**

7. Spiderdiagram

The condrite-normalized trace and REE pattern (after **McDonough and Sun, 1995**) of both carbonate and carbonate- rich melilite basalt shows the same pattern (Fig.7). The carbonate is lower in Cr, Ni, Co, V and Ti than melilite basalt due to absence of mafic silicate minerals in the carbonate. The lower contents of REEs , Ba, Sr and Y in both rocks rejecting magmatic origin. On the other hand the carbonate rocks show high contents of Pb, and Zn suggesting hydrothermal origin

It should to be noting that, the world REE bearing carbonate is > 100 times than that of condrite **(Wendland and Harrison, 1979).** The study carbonate is very poor in REEs.

The Nd/Sm and Ce/La ratios of both carbonate and carbonate-rich melilite basalt are similar suggesting clearly their intimate relation (i.e. the same source of solutions).The carbonate is mushily lower in REE as well as Cr, Ni, Co, V, Ti, Ba, Sr and Y but higher in Pb, and Zn suggesting hydrothermal origin. As the penetration of C_2O rich solution through the highly fractured carbonate- rich host rocks leach Ca ions. These carbonated solutions have been bonded in fracture planes and precipitated the carbonate minerals filling the fracture planes under high C_2O gas pressure.

The abundances of REEs of Uganda carbonatite rocks (Africa) can be written for comparison (La is ranged from 200 to 900, Ce from 370 to 2400, Nd from 116 to 1900, Sm from 20 to 270, Eu from 8 to 90, Gd from 8 to 140, Dy from 4 to 74, Er from 2 to 30, Yb from 1 to 8 and Lu from 0.2 to 0.8. Also REEs abundance of Angola carbonatite is La= 1500, Ce =1170, Nd =500, Sm=65 Eu =15, Gd =40, Dy19, Er= 11 Yb =6 and Lu =0.9 **(Loubet, et. al. 1972**). These means that the REEs abundances of magmatic carbonatite are enriched by a factor of 100 to 500. The LREE: HREE ratios of the study carbonate rocks are very small as compared with the magmatic carbonatites (ex. La :Yb ratio is ranged from 100 to 1000 for Uganda magmatic carbonatites but that of the study carbonate is about 2. Also the Nd : Sm of Uganda carbonatite is about 6 higher than that of study carbonate veins.

8. Conclusions

The aragonite carbonate veins are composed mainly of aragonite with minor phases of calcite, magnesite and cerussite The rocks are hard, dense with bone like appearance found as veins through brecciated volcanic rocks of Dokhan type.The associated basic dykes show some degrees of replacement to carbonate minerals. The REE abundances of the study carbonate vein and the associated carbonated basic dykes are more or less similar but much lower than those of magmatic carbonatite rocks. As well as, the LREE: HREE ratios of the study carbonate rocks are very small as compared with the magmatic carbonatites

9. Origin

The writers suggest that the aragonite most probably crystallized from carbonate rich -solutions under low temperature and high C_2O pressure. The presence of Mg ions led to crystallization of the aragonite (a dense form of carbonate). The carbonate –rich solutions filling the fractures, firstly precipitating carbonates, with release of C2O gas .The building up of gas pressure led to crystallization of aragonite instead of calcite. The aragonite is known as a high pressure metamorphic minerals associated with dense minerals as omphacite and lawsonite **(Coleman and Lee, 1962**)

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