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Analysis of the Carbonate in Limestone from Loikaw Area

Tha Zin[1], Than Than Myint[2], Ni Ni Sein[3]

Abstract

Chemical analysis has been made on carbonate rock samples obtained from the Lwetamu cave and Taunggwe Taung. In the determination of rock samples by titrimetric method, the major portion of the experimental work was concerned not only with the titration procedure but also with the methods of decomposing the samples and removing interfering elements which also form complexes with EDTA. Mineral contents in Limestone from Loikaw Area were determined by using EDXRF method. The EDXRF spectrum of calcite sample shows that 85.827 % and 98.994 % of Ca are present in the sample with small amount of impurities.

Key words: Carbonate rock samples, Titrimetric method, EDXRF method.

Introduction

The exterior of the earth is made up of solids, liquids and occluded gases. The solids are commonly called rocks. The term mineral is applied to these rock constituents. Minerals also occur in many other ways in nature and may be well crystallized, that is possessed definite external forms bounded by natural plane surfaces. Some of the most widely distributed minerals are carbonates. Several of them are of great importance commercially[6]. Limestone is a general term embracing carbonate rocks or fossils; it is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities,the most common of which are silica and alumina.

Limestone's abundance is evidenced by the fact that an estimated 3.5-4 % of the elements in the earth's crust contain calcium and 2% contain magnesium[2].

Calcium carbonate is dimorphous with modifications in the hexagonal and orthorhombic systems, known as calcite and aragonite, respectively. Calcite occurs very widely distributed. As limestone, marble, chalk and marl, it is found in large deposits, often of great thickness and extending over wide areas.It is also abundant as deposits around springs and

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in streams, and in cracks and cavities in igneous and sedimentary rocks. Often it is observed as an associate of metalliferous ore deposits[6].

Of course, as with most elements, there are strata of limestone laminated between layers of shale and sandstone that are so deep in the earth's crust as to be inaccessible. There are a great many different forms and types of limestone, varying in color, chemical composition, mineralogy, crystallinity, texture and hardness[2].

Types of Carbonate Rocks[3,4]

Calcite group

Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Magnesite	$MgCO_3$
Siderite	$FeCO_3$
Rhodochrosite	$MnCO_3$
Smithsonite	$ZnCO_3$

Aragonite group

Aragonite	$CaCO_3$
Witherite	$BaCO_3$
Strontianite	$SrCO_3$
Cerussite	$PbCO_3$
Malachite	$Cu_2CO_3(OH)_2$
Azurite	$Cu_2(CO_3)_2(OH)_2$

Mineralogy of Limestone[2]

All geological authorities are in agreement that limestone may be composed of four minerals, exclusive of impurities, having the following physical characteristics.

Calcite; $CaCO_3$

rhombohedral;molecular weight – 100.1;specific gravity-2.72; molecular volume-36.8,

hardness-3;may be colorless, but often variously tinted by impurities.

Aragonite; $CaCO_3$

orthorhombic; specific gravity-2.94; molecular volume- 34, hardness- 3.5 to 4; usually white but often tinted by impurities.

Dolomite; $CaMg(CO_3)_2$

rhombohedral,molecular weight 184.4;specific gravity-2.83;molecular volume-65.2, hardness 3.5-4;usually colorless, but often tinted pink or tan.

Magnesite; $Mg\ CO_3$

rhombohedral, molecular weight - 84.3; specific gravity-3; molecular volume-28.1, hardness-3.5-4.5; white, tan or brown.

Experimental Procedure

Gravimetric Method[5]

Principle

The solution of calcium free from interfering element is treated as follows. Calcium oxalate is precipitated from feebly ammoniacal solutions by means of ammonium oxalate. The presence of ammonium chloride hinders the precipitation of magnesium and does not interfere with magnesium. Magnesium is precipitated from the filtrate of calcium precipitate with phosphate in the presence of ammonium ions.

Reagents

1. Concentrated hydrochloric acid
2. 1:100 hydrochloric acid
3. Concentrated ammonium hydroxide solution
4. Saturated bromine water
5. 1% ammonium chloride solution
6. 1:1 hydrochloric acid

Procedure

(i) Loss on Ignition

About 0.5 gm of the sample was accurately weighed in a weighed covered crucible and dried at 110°C for an hour. The crucible was cooled and weighed. Then the crucible and the contents were ignited slowly for 30 minutes at the maximum temperature,cooled and weighed. The loss in weight represented hygroscopic and absorbed moisture and the amount of carbon dioxide in the sample.

(ii) Separation of Silica

The residue after ignition was transferred to a small covered crucible and 5 ml of distilled water was added. Then 5 ml of concentrated hydrochloric acid was added to it. This solution was evaporated to dryness on a steam bath and the residue was heated for one hour at 100°C. 5 ml of concentrated hydrochloric acid was added and the mixture was stood for 3 minutes. 25 ml of water was then added and heated on the steam bath for 10 minutes. It was filtered and the precipitate was washed thoroughly with 1:100 hydrochloric acid. The filtrate was evaporated to dryness in the original crucible, and the residue was heated to about 100°C, and then 5 ml of concentrated hydrochloric acid was added and digested as before. It was filtered and washings were reserved for the separation of combined oxides. The two silica precipitates were placed in a weighed crucible and ignited to SiO_2. The percentage of SiO_2 presented is reported.

Table 1. Percentage of SiO_2 in Calcitic Limestomes from Loikaw Area

No.	Sample	Percentage of SiO_2
1.	Calcitic Limestone 1	6.8
2.	Calcitic Limestone 2	0.24

(iii) Separation of Combined Oxides (Fe_2O_3,Al_2O_3,TiO_2,Mn_3O_4 and P_2O_5)

The filtrate from the silica precipitate was heated nearly to boiling; pure concentrated ammonium hydroxide was added slowly until a slight precipitate appeared. Then 5 ml of fresh saturated bromine water was added and ammonium hydroxide was added drop wise with stirring until a slight excess was presented. The liquid was stood for 10 minutes near the boiling

point, and then filtered. The precipitate was washed four times with hot 1 % ammonium chloride solution. The filtrate was tested with ammonium hydroxide for complete precipitation.

The precipitate was dissolved in 10 ml of hot 1:1 hydrochloric acid and the solution was placed in the original beaker and diluted to 75 ml with distilled water. The above procedure was repeated, using 5 ml of bromine water, filtered and the precipitate was washed thoroughly with 1 % ammonium chloride solution. The filtrates and washings were reserved for the determination of calcium. The residue were placed in a weighed crucible and ignited to "R_2O_3"(mixed oxides). The percentage of "R_2O_3" was calculated.

Table 2. Percentage of R_2O_3 in Calcitic Limestomes from Loikaw Area

No.	Sample	Percentage of R_2O_3
1.	Calcitic Limestone 1	2.12
2.	Calcitic Limestone 2	0.72

Complexometric Method[1,7]

Principle

Under suitable conditions of pH, calcium and magnesium can be titrated with the disodium salt of ethylenediaminetetra-acetic acid (EDTA) which forms chelate complex with calcium and magnesium ions. The titration of calcium is carried out at pH 12 by adjusting the final pH with sodium hydroxide using calcon as indicator. The sum of calcium and magnesium can be titrated on a separate solution buffered to about pH 10 with ammonium hydroxide and ammonium chloride. Eriochrome Black T being used as indicator. Potassium cyanide and ascorbic acid were always added to prevent interference from traces of certain metals, such as zinc, copper, manganese, etc.

Reagents

(a) Standard EDTA Solution (0.05 M)

25 g of EDTA was dried in an oven at 80°C for 2 hours and then allowed to cool in desiccator. About 18.16 g of the salt was then accurately weighed and dissolved in distilled water and made up to one litre in a volumetric flask.

(b) Buffer Solution (pH = 10)

142 ml of concentrated ammonia solution was added to 17.5 g of A.R ammonium chloride, diluted to 250ml with distilled water.

(c) Calcon Indicator

Calcon indicator is used in the complexometric titration of calcium in the presence of magnesium at a pH of about 12.3 in order to avoid the interference of magnesium. The indicator solution was prepared by dissolving 0.5 g of the dyestuff in 50 ml of ethanol.

(d) Eriochrome Black T

0.5g of the dyestuff was dissolved in 15ml of triethanolamine and 5ml of absolute ethanol.

Procedure

(i) Sample Preparation

About 0.5g of the sample was accurately weighed and 1ml of hydrofluoric acid and 3ml of 70 percent perchloric acid were added. It was heated gently for 5 minutes, cooled and 3ml of concentrated hydrochloric acid was added. 20ml of distilled water and 5 drops of saturated bromine water were then added and boiled gently for 5 minutes to expel excess bromine. It was then cooled and transferred to a 500 ml volumetric flask and made up to volume with distilled water.

(ii) Determination of Calcium

25ml of the sample solution and 25 ml of distilled water were introduced into a conical flask. 1g of ascorbic acid was added to it, stirred and stood for about 3 minutes. 20 drops of 50 percent sodium hydroxide was added to precipitate magnesium. 0.1g of potassium cyanide was added to prevent interference of metals like copper, nickel and iron.

This solution was heated to about 50°C and swirled occasionally for 3 minutes. It was then cooled and 1 drop of calcon indicator was added and titrated with 0.05 M standard EDTA solution. The end point was the disappearance of the last tinge of red, after which the indicator assumed its uncomplexed blue colour. The calcium content of the sample was then calculated and reported as percentage of calcium carbonate.

Table 3. Percentage of Calcium Carbonate in Calcitic Limestones from Loikaw Area

No.	Sample	Weight of Sample (g)	Volume of 0.05 M EDTA (ml)	Weight of $CaCO_3$ (g)	Percentage of $CaCO_3$
1.	Calcitic Limestone 1	0.5	9.5	0.4313	86.26%
2.	Calcitic Limestone 2	0.5	10.5	0.4767	95.34%

(iii) Determination of Magnesium

25ml of the sample solution was pipetted into the conical flask and 25ml of distilled water was added. 1g of ascorbic acid was added to it and stood for 3 minutes. 5 drops of sodium hydroxide and 0.1g of potassium cyanide were added and warmed to 60° C, swirled occasionally for 3 minutes.

This solution was cooled and 2ml of pH 10 buffer and 2 drops of Eriochrome Black T were added.It was then titrated with the 0.05M standard EDTA solution. The end point was the disappearance of the last tinge of red after which the indicator assumed its uncomplexed blue colour. The titration value was represented the total amount of calcium and magnesium. The value required for the calcium titration was subtracted and obtained the volume required for magnesium. The percentage of magnesium carbonate was calculated and reported.

Table 4. Percentage of Magnesium Carbonate in Calcitic Limestones from Loikaw Area

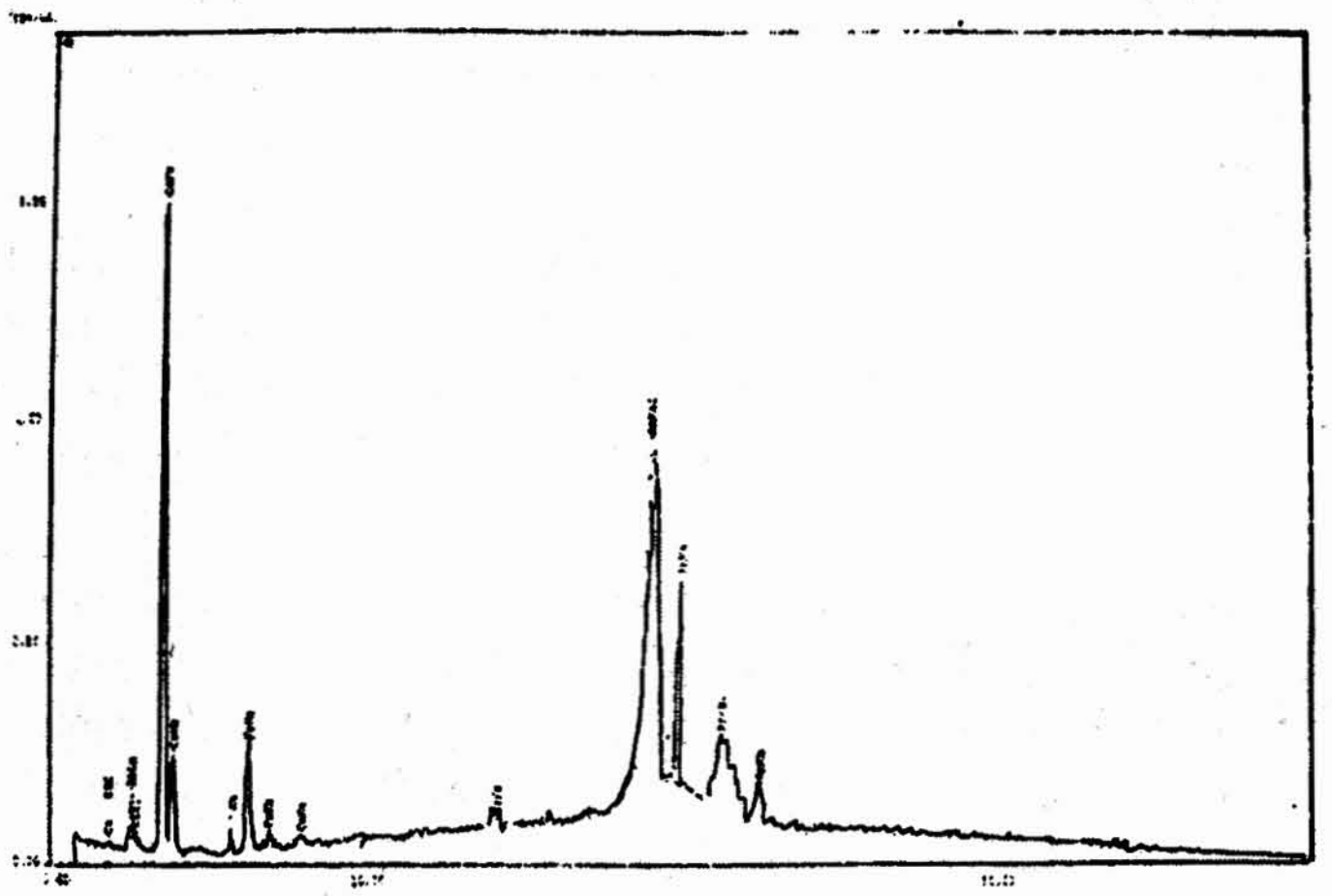
No.	Sample	Weight of Sample (g)	Volume of 0.05 M EDTA (ml)	Weight of $MgCO_3$ (g)	Percentage of $MgCO_3$
1.	Calcitic Limestone 1	0.5	0.2	0.0076	1.52
2.	Calcitic Limestone 2	0.5	0.2	0.0076	1.52

Sample : Sample1
Operator: SM
Comment : Solid sample (without cell) / Air
Group : solid_air
Date : 2007-11-20 11:36:28

Measurement Condition

Instrument: EDX-700	Atmosphere: Air	Collimator: 10(mm)	Spin: Off

Analyte	TG	kV	uA	Fl	Acq.(keV)	Anal.(keV)	Time(sec)	
Si-U	Rh	50	Auto	--	0 - 40	0.0 - 40.0	Real - 99	26



Quantitative Result

Analyte	Result	Std.Dev.	Proc.-Calc.	Line	Int.(cps/uA)
Ca	85.827 %	0.686	Quan-FP	CaKa	10.688
Fe	9.548 %	0.169	Quan-FP	FeKa	2.165
Mn	2.029 %	0.106	Quan-FP	MnKa	0.481
Cu	1.056 %	0.044	Quan-FP	CuKa	0.386
Sr	0.747 %	0.021	Quan-FP	SrKa	0.827

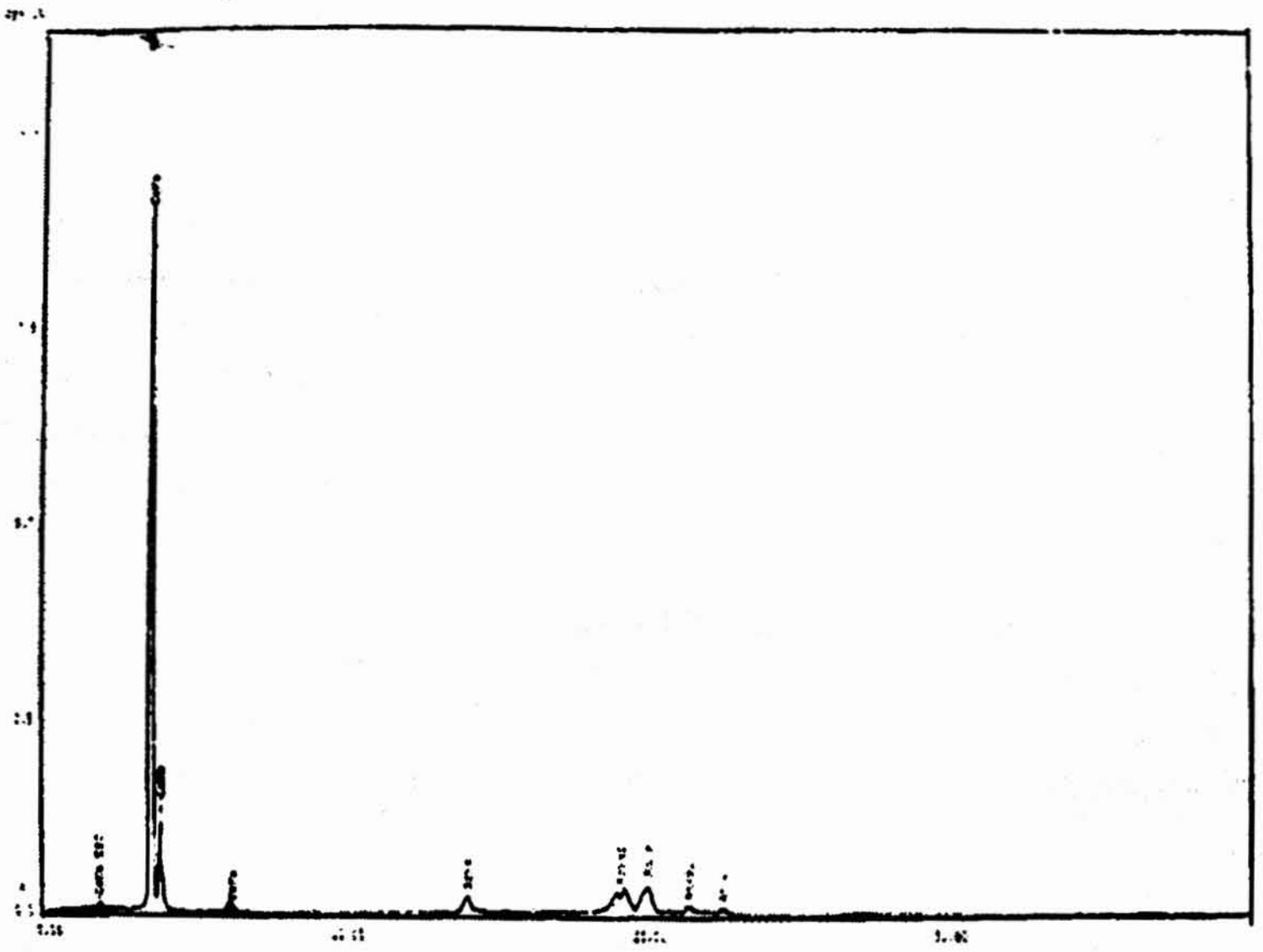
Fig. 1 (a) EDXRF Spectrum of Calcitic Sample 1

Sample : Sample3
Operator: GW
Comment : Solid sample (without cell) / Air
Group : solid_air
Date : 2007-11-20 11:41:02

Measurement Condition

Instrument: EDX-700 Atmosphere: Air Collimator: 10(mm) Spin: Off

Analyte	TG	kV	uA	FI	Acq.(keV)	Anal.(keV)	Time(sec)	D.T.(%)
Si-U	Rh	50	23-Auto	--	0 - 40	0.0 - 40.0	Real - 99	25



Quantitative Result

Analyte	Result	Std.Dev.	Proc.-Calc.	Line	Int.(cps/uA)
Ca	96.994 %	0.297	Quan-FP	CaKa	65.283
Fe	0.584 %	0.018	Quan-FP	FeKa	0.635
Sr	0.423 %	0.006	Quan-FP	SrKa	2.690

Fig.1(b) EDXRF Spectrum of Calcitic Sample 2

Results and Discussion

Routine analysis of carbonate rocks include the determination of SiO_2, combined oxides R_2O_3(Al_2O_3, Fe_2O_3, TiO_2, Mn_3O_4 and P_2O_5), $CaCO_3$ and $MgCO_3$. The percentages of the principal constituents of limestone may vary over a wide range.Calcium carbonate, the main constituent of limestones, may vary over a wide range. Calcium carbonate, the main constituent of limestones,always occurs in large amounts. The calcitic limestone sample 1 and 2 were collected from Lwetamu Cave and Taunggwe Taung. Method used for present investigation includes the gravimetric method and complexometric method.

Conclusion

In this research project, two calcitic limestones were collected and analysed by gravimetric titration method and complexometric titration method. The percent weight of calcium carbonate in calcitic limestone samples 1 and 2 are found to be 86.26% and 95.34%. In each calcitic limestone samples 1 and 2, the magnesium carbonate content occurs 1.52%. The percent weight of SiO_2 in calcitic limestone samples 1 and 2 are found to be 6.8 and 0.24. The combined oxides R_2O_3 content in calcitic limestone samples 1 and 2 are observed 2.12 and 0.72.

The aim of the present determination is to analyse carbonate rocks by gravimetric method and complexometric method. It is found that under favourable condition titrimetric method afford quick and accurate results for the determination of calcium and magnesium in the rock analysis.

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