Characterization and Origin of Dolomite Associated with Hydrothermal Iron Ore in Paleozoic limestone, Kinta Valley

by

Farid Faliq Bin Shukri

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Approved by,

(Prof Dr Bernard Pierson)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(FARID FALIQ BIN SHUKRI)

ABSTRACT

Dolomite occurring in association with hematite in the Kinta Valley, particularly in Kek Lok Tong (KLT), Gunung Rapat and Gunung Panjang (GP), Tambun commonly displays a curved or "saddle" crystal shape. Based on preliminary observations, the dolomite is believed to be hydrothermal in origin. However, this assumption needs to be supported by chemical analyses. XRD analysis was conducted to verify the dolomite mineralogy. Samples were sent to the University of Miami for stable (carbon and oxygen) isotope analysis to determine the environment of the dolomite formation. XRF analysis was conducted to measure concentrations in major and trace elements in the dolomite.

The isotopic analysis shows that the $\partial^{18}O$ values for the dolomite are highly depleted, ranging from $-18.4^{0}/_{00}$ to $-16.37^{0}/_{00}$ and the $\partial^{13}C$ values are slightly positive, ranging from $0.63^{0}/_{00}$ and $1.15^{0}/_{00}$.Compared with other analyzed hydrothermal dolomite like dolomite in Western Canada, Guilin, and Southern Cantabrian Zone Spain , the $\partial^{18}O$ values ranging from $-13.9\ ^{0}/_{00}$ to $-3.5^{0}/_{00}$ and $\partial^{13}C$ values ranging from $-2.7^{0}/_{00}$ to $5.2^{0}/_{00}$.KLT, Gunung Rapat and GP, Tambun dolomite is relatively within above range except slightly depleted in the $\partial^{18}O$ values. In addition to that, according to Taury Smith (2004), hydrothermal dolomites typically have depleted δ18O values which are between -2 to –20‰ .From the XRF analysis, the dolomite shows the non stoichiometric ratio of $CaCO_3$ and $MgCO_3$ .The concentration for iron and manganese are quite high ranging from 1100ppm to 34400ppm for iron and 7200ppm to 13100ppm for manganese. The two metals most enriched in hydrothermal vent fluids are iron and manganese (Holland and Turekian, 2010). Other minerals also have been identified such as silicon, titanium, aluminum, sulfur, phosphorus, potassium, molybdenum, cerium, yttrium, antimony, rubidium, thorium, vanadium, nickel, arsenic, niobium, chromium, uranium, plumbum, zinc and copper. The concentration for the valuables metal like argentum, platinum and aurum is very low so much so that they can be considered negligible.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Background of the project

The limestone hills of the Kinta Valley are Paleozoic (Permian) in age and are about 260 million years old. They are the remnants of a thick carbonate layer that was part of a very large Paleozoic carbonate complex that covered large parts of South-East Asia and that was exposed and dissolved over the past 50 million years (Pierson et al., 2009) , forming the tower karst hills that we see today.

The Permian limestone of the Kinta Valley overlies extensive younger granite bodies which have affected the texture and composition of the limestone through contact metamorphism (Pierson et al, 2009). The granite is most likely the source of hydrothermal fluids that have deposited the minerals such as the hematite that we now find in the hills.

Hematite occurs as scattered vertical veins or “chimneys” several meters thick, in the limestone hills of the Kinta Valley, especially in Kek Lok Tong (KLT) in Gunung Rapat and Gunung Panjang (GP) in Tambun, where it has been exploited as iron ore. Occurrences of hematite in the limestone hills are most likely of hydrothermal origin. Dolomite ($CaMg (CO_3)_2$) is commonly associated with these occurrences of hematite and could also be of hydrothermal origin. Hydrothermal dolomite is generally interpreted to have formed as result of hot fluids related to hydrothermal activity and/or burial alteration of limestone (Al-Aasm, 2003).

We assume that the dolomite in that area is hydrothermal in origin based on reasons that the association of the dolomite with the hematite and saddle crystal shape of the dolomite. To support with the assumption, we conducted chemical analysis such as stable (carbon and oxygen) isotopes and XRF analysis.

1.2 Problem statement

The character and chemical composition of dolomite associated with hematite at the Kinta Valley, particularly in KLT in Gunung Rapat and GP in Tambun area have not been studied yet. It has been assumed that the dolomite in that area is hydrothermal in origin but it has never been proven. Analyzing the chemical composition of the dolomite will help us confirm its hydrothermal origin as it will reflect the chemical signature of the hydrothermal fluid.

1.3 Objective

1. Analyze the geochemical composition(isotopes, major and trace elements composition) of the dolomite, which we find associated with hematite deposits KLT in Gunung Rapat and GP in Tambun

2. Verify a hydrothermal origin of the dolomite, contemporaneous with the hematite.

1.4 Scope of study

Sample and analyze the chemical composition (carbon and oxygen isotopes, XRF analysis) of dolomite from two old iron mines/quarries at Gunung Rapat and Tambun, Kinta Valley, where dolomite occurs in association with hematite.

1.5 Relevancy and benefit of project

The purpose is to establish a reference or calibration data point for hydrothermal dolomite, especially with regards to the chemical and isotope composition of the dolomite.

CHAPTER 2

THEORY

2.1 Mineral formation

The passage of hydrothermal solutions through the Earth's crust is invariably accompanied by alteration (Robb, 2006). Alteration of a rock by the fluid passing through it is marked by the development of mineral assemblage that is different from the original one and reflects the rock composition as well as the properties and amount of fluid that has traversed the system(Robb, 2006) .The nature of hydrothermal alteration also provides an indication of fluid properties associated with ore formation and there is commonly close relationship between the chemical relations involved in alteration and those responsible for metal deposition(Robb, 2006).

The mineral assemblages that form as the result of hydrothermal alteration vary as a function of five factors (Reed, 1997) which are temperature, pressure, host rock composition, fluid composition and the ratio of fluid to rock in the alteration process.

2.2 Formation of dolomite

2 possible chemical reactions for the dolomite formation can be taken into the considerations which are direct precipitation and $CaCO_3$ replacement (Tucker et al., 1990)

Direct precipitation:

$Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \rightleftharpoons CaMg\,(CO)_3$

Replacing of the $CaCO_3$:

$2CaCO_3 + Mg^{2} \rightleftharpoons CaMg\,(CO)_3 + Ca^{2+}$

The formation of the dolomite at our studies areas are believed to follow the second reaction where the hot hydrothermal fluid that contains the magnesium sources cannibalized the limestone and form the dolomite.

2.3 Formation of hematite

Hematite is the mineral form of iron (III) oxide (Fe_2O_3). Hematite is a mineral, colored black to steel or silver-gray, brown to reddish brown, or red (Klein& Dutrow, 2007). Occurs in contact metamorphic deposits and as an accessory mineral in feldspathic igneous rocks such as granite(Klein and Dutrow, 2007).The principle concentration mechanism for iron ore deposits is related to the fact that the metal occurs in two valance states, namely Fe2+(the ferrous ion) which is generally soluble in surface waters and Fe3+(the ferric ion) which is insoluble in surface water and precipitates out of surface solution(Robb, 2006).Alteration that is associated with oxidizing fluids often results in the formation of minerals with high Fe3+/Fe2+ and in particularly hematite associated K-feldspar, sericite, chlorite and epidote (Robb, 2006).Below are the chemical reaction for the formation of hematite:

$4Fe^{2+} + O_2 + 4H2O \rightarrow 2Fe_2O_3 + 8H^+$ (Krauskopf and Bird, 1995)

2.4 Hydrothermal dolomite

The word "hydrothermal" was originally applied to hot waters and mineralization associated with magmatism (Gilbert 1875; Morey and Niggli 1913; Holmes 1928; Stearns et al. 1935; Machel and Lonee, 2002). As recommended by Machel and Lonnee (2002) the term "hydrothermal" should be used only for those dolomite, which formed by hydrothermal fluid at higher temperatures compared to the surrounding rocks. Commonly, hydrothermal dolomite is associated with metallic sulfide ores, barite, fluorite and/or hydrocarbon (Scholle & Ulmer-Scholle, 2006). According to Taury Smith (2004) hydrothermal type of dolomitization must involve some sort of episodic convection. In this model, fluids flow up faults when the faults move, enter and alter the formation and are then cycled back down through inactive faults and fractures. It may be that magnesium, iron and other elements are leached out of the basement rocks and transported upward during periods of active fault movement.

2.5 Characteristics of the dolomite

The crystal shape of dolomite is rhombohedral. Its colour commonly displays some shade of pink, flesh colour, may be colourless, white, gray, green, and brown or black (Klein& Dutrow, 2007). Its theoretical composition is 21.86% MgO, 30.41 %CaO and 47.73% CO2 (Klein& Dutrow, 2007) Early-formed dolomites can be separated into two distinct groups. Type 1 dolomites host stratiform ore deposits, whereas type 2 dolomites host open space-filling ore body (Auajjar & Boulegue, 2002).

On the basis of crystal shape, two kinds of dolomite are recognized. Planar (or idiotopic) dolomite consists of rhombic, euhedral (well-formed) to anhedral (poorly formed) crystals. Non planar (or xenotopic) dolomite is made of non planar, commonly anhedral crystal (Sibley and Gregg, 1987). The xenotopic texture of the dolomite with no planar crystals, gives evidence that the temperatures of deposition should have been higher than 50-60°C (Gregg and Sibley, 1984).

2.6 Saddle dolomite

Saddle dolomite (curved crystal shape) in both replacive and void-filling modes is characteristic of HTD facies (Davies and Smith, 2006). A first estimate of the thermal conditions during dolomite formation is given by the dolomite texture .Saddle dolomite requires minimum temperatures of 60-80 Celsius to precipitate with most occurrences being formed between 90 and 160 Celsius (Gasparrini et al., 2003).High temperature dolomites are usually related to hydrothermal in origin. The host rocks at our study locations were undergoing the contact metamorphism process which cooked the limestone into the marble. Later, the dolomite that precipitated at hill is believed to be formed under the high temperature from the hydrothermal fluid.

2.7 Zebra dolomite

Hydrothermal zebra dolomite is typically composed of alternating horizontal layers (approx. 1-10 mm) of dark, fine-grained dolomite and white, coarse-grained, sparry, void-filling dolomite (Sharon, 2005).Light coloured dolomite sheets representing dolomite replacement of the host limestone or recrystallization of an earlier dolomite generation (Nielsen et al. ,1998). Dark coloured dolomite representing dolomite precipitated in extensional micro fractures or cavities (Nielsen et al., 1998). Hydrothermal dolomite reservoirs commonly have other features that may help identify them as hydrothermal in origin including: breccias, ***zebra fabrics***, leached limestone, leached dolomite, pore-, fracture-, and vug-filling calcite, anhydrite, barite, celestite, sulfide minerals, quartz, bitumen and microporous limestones (Taury Smith, 2004).

CHAPTER 3

METHODOLOGY

3.1 Field Observation

The studied outcrops are located in KLT, Gunung Rapat and GP in Tambun, Kinta Valley, where hematite has been exploited as iron ore. The first outcrop is located in the well-maintained garden of the KLT Chinese temple and the second outcrop is located near agated residential area. Both outcrops are in open space areas and are easily accessible on foot.

In KLT (Gunung Rapat), the hematite occurs as a vertical vein or "chimney" several meters thick, sandwiched between outcrops of laminated limestones (Fig. 1).The hematite vein was measured to be 27m in width and about 150m in height. The contact between hematite and limestone appears to shift to the right as it goes uphill. The dolomite forms mm-laminations with the hematite (Figures. 3-4) or occurs as broken fragment of dolomite (breccias) (Figures. 2,6,7).Hydrochloric acid was used to distinguish between dolomite and calcite as they have a similar physical appearance with the naked eyes. Calcite will show a rapid dissolution when it reacts with the acid, compared to dolomite, which does not react to HCl. Commonly, dolomite crystals display a curved shape (saddle shape) through the hand lenses.

In GP (Tambun), the dolomite associated with the hematite can be found in large blocks at the foot of the hill (Figure 7) and is not as abundant as in KLT. Compared to the first outcrop where dolomite occurs as sub-parallel bands similar to zebra dolomite, in the hematite, only scaltered bodies of dolomite crystal were found at the second outcrop (Figure 8). At this second outcrop, the actual contact between dolomite and the host limestone could not be measured due to difficulties in accessing the site for safety reasons.

The following pictures illustrate the observations during the field visits:

Figure 1: Outcrop at KLT, Gunung Rapat. The Hematite "Chimney", sandwiched between outcrops of laminated limestone, is 27 m wide and about 150mhigh.

Figure 2: Brecciated appearance of the carbonate minerals (light colour) within the hematite (dark colour).

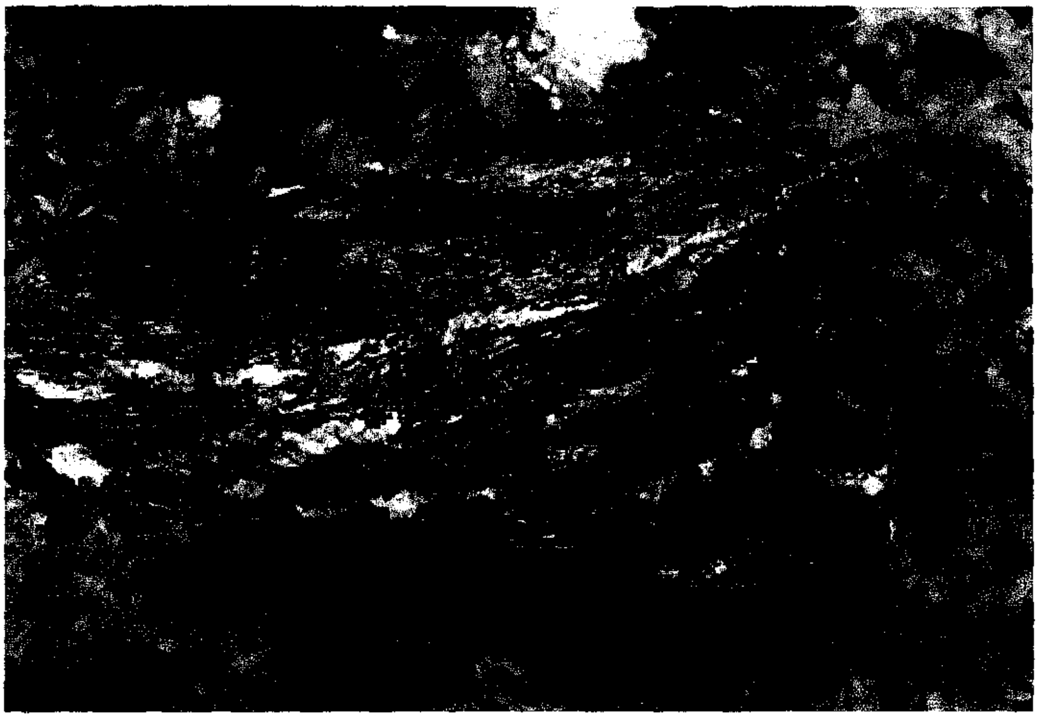


Figure 3: Banded hematite and dolomite at KLT, Gunung Rapat.

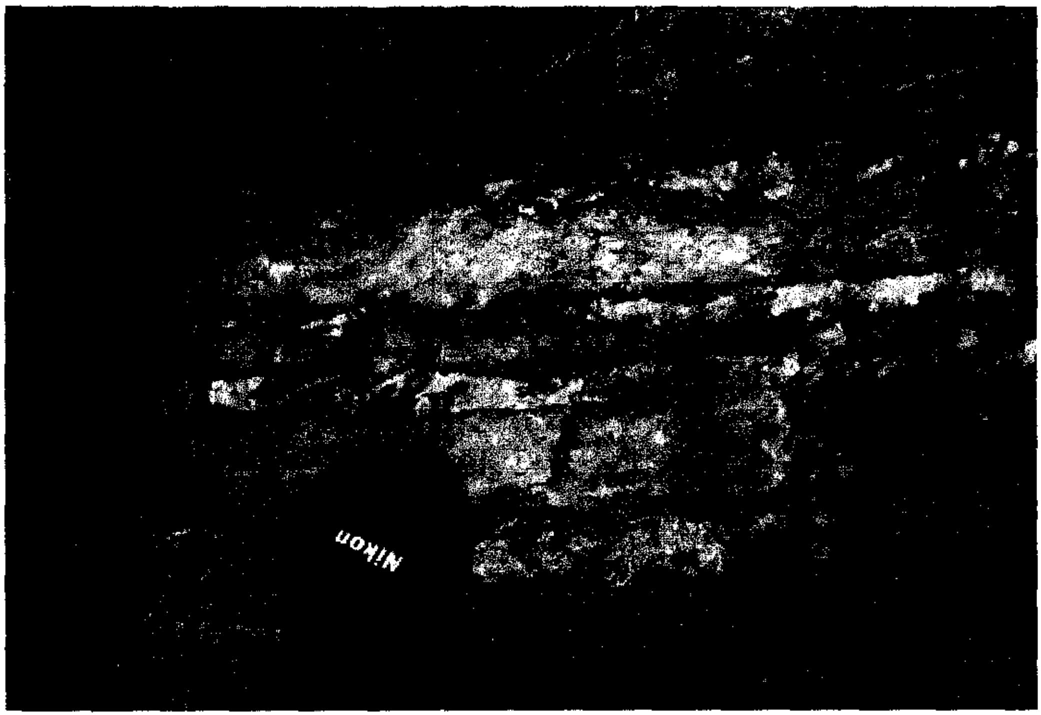


Figure 4: Laminated dolomite with hematite inclusions at KLT, Gunung Rapat

Figure 5: Light pink crystals of dolomite in a hematite deposit at KLT, Gunung Rapat

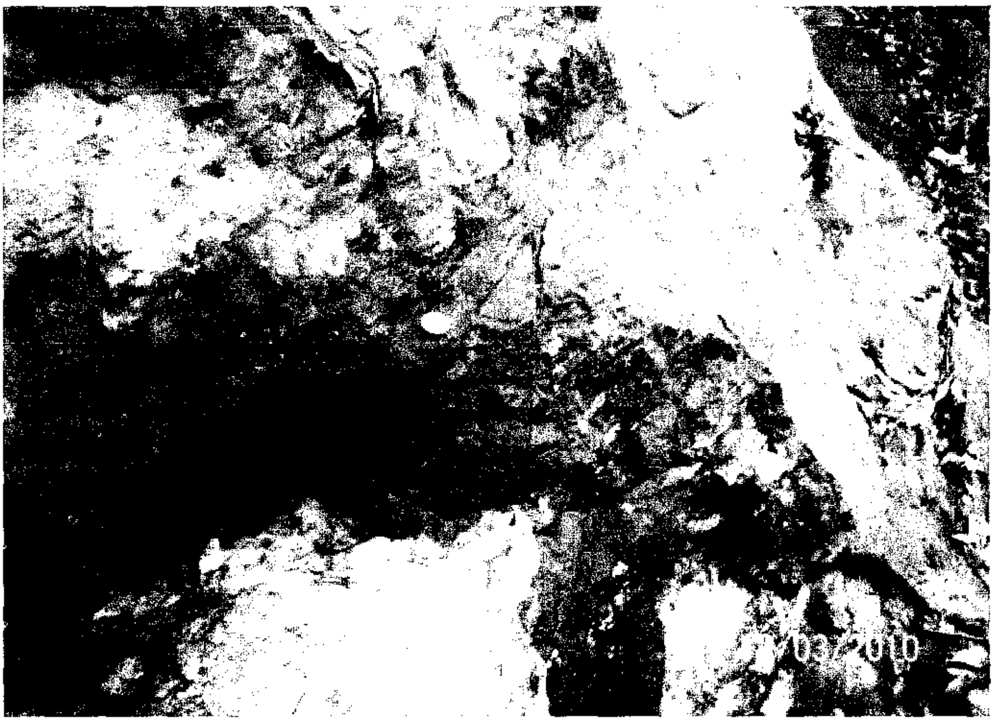


Figure 6: Massive hematite (dark) and dolomite crystals (light) at GP, Tambun

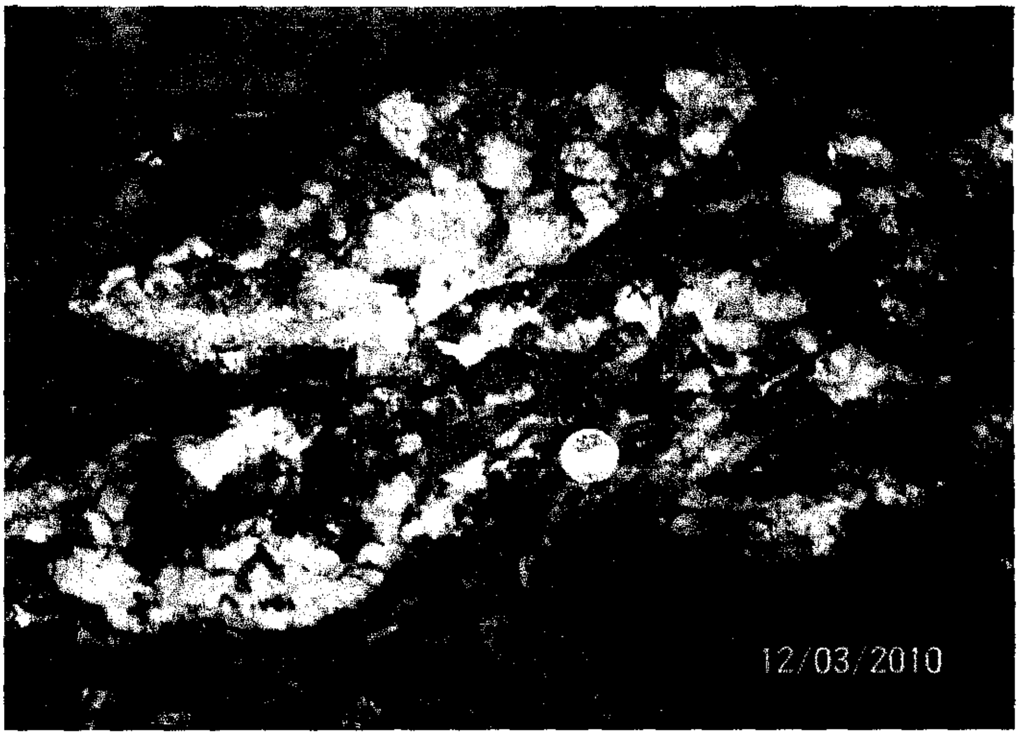


Figure 7: Hematite (dark) and dolomite (light) at GP, Tambun

3.1.1 Rock samples pictures

Figure 8: Inside surface of the rock. Dolomite crystals (light) and hematite (dark) in a hand specimen from KLT, Gunung Rapat (KLT 2.1)

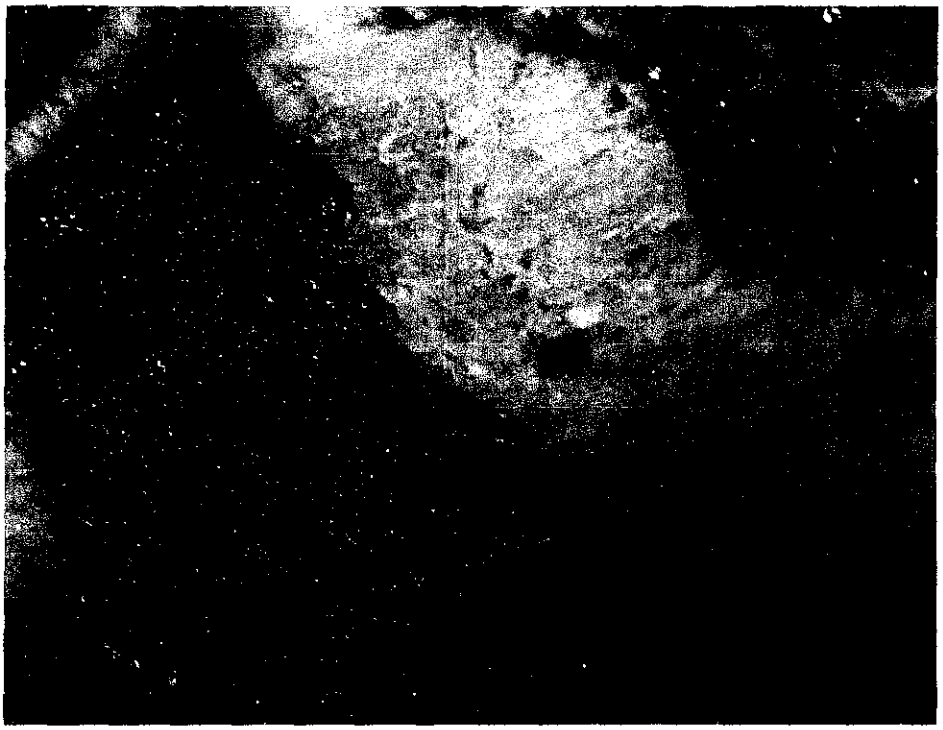


Figure 9: Contact between the hematite and the dolomite in a microscopic view (Top box from KLT 2.1)

Figure 10: Hematite fills in the fracture of the dolomite in microscopic view (Bottom box from KLT2.2)

Figure 11: Botryoidal hematite (dark) in a microscopic view (KLT 8)

3.2 XRD Analysis

XRD analysis was conducted to confirm the dolomite mineral composition. A total of 11 samples were analyzed. In order to obtain a diffraction pattern of a mineral, the samples were ground to <270 mesh. Parameter of 2θ of (3° to 60 °) was used.

3.3 Stable Isotopes

After the dolomite mineral composition had been confirmed, chemical analysis was conducted.4 samples of the dolomite were sent to the University of Miami for stable isotope (^{13}C and ^{18}O) analysis using a mass spectrometry. The results provide indications on the environment of dolomite formation and are conducted to support the argument that the dolomite is hydrothermal in origin by comparing them with world analyzed hydrothermal dolomite.

3.4 XRF Analysis

XRF is a technique that is used to determine the major elements and many trace elements in rocks and minerals, at concentrations from 1 or 2 ppm (parts per million) to 100 per cent. The results are based on a constant dry basis (%wt / %wt) of the sample after drying at 110°C.Traceability of the results was tested on the recovery of Certified Reference Material (CRM) NIST 88b with 95% of significant level. For calcium, EDTA titration method was also applied

Glass discs that contained the samples were usually prepared for major element analyses. Sample powder is fused with a known proportion of a commercially available flux, or as pressed powder pellets for trace-element analyses. It is made by mixing the sample powder with a binding agent. The mixture is pressed into a compact disc with a smooth upper surface.

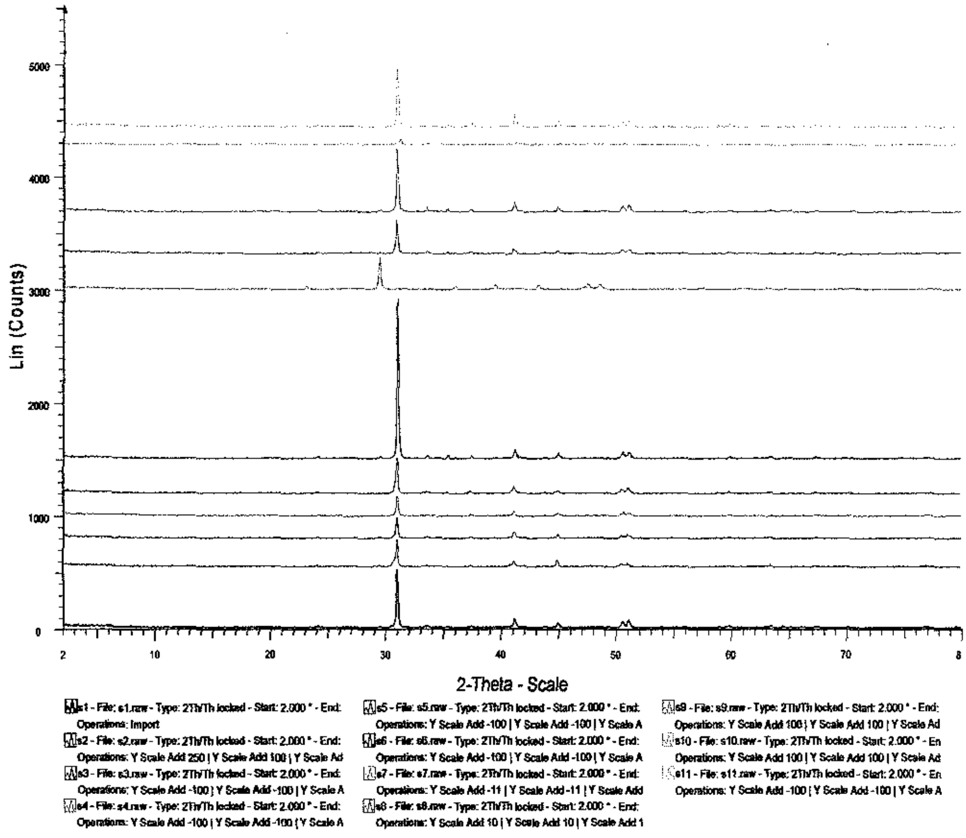
Major elements will be reported in the form of oxide as weight percent (e.g. calcium, CaO wt. percent) and trace elements in parts per million (ppm).

CHAPTER 4

RESULTS

4.1 XRD result

Figure 12: Diffraction pattern for the 11 samples from KLT and GP



10 out of 11 samples show a dolomite diffraction pattern and sample no.7 shows the calcite diffraction pattern (Figure 12). The mineral is determined by observing the highest peak, which is 31 degree for the dolomite and 29.5 degree for the calcite. KLT 1.1 is S1; KLT 1.2 is S2; KLT 2.1 is S3; KLT 2.2 is S3; KLT 3 is S4; KLT 5 is S5; KLT 6 is S6; KLT 7 is S7; KLT8 is S8; Tambun 2 is S9; Tambun 3 is S10; Tambun 4 is S11.

4.2 Carbon and Oxygen stables isotopes

Table 1: Values for $\partial^{18}O$ and $\partial^{13}C$ for dolomite at KLT , Gunung Rapat and GP, Tambun

Sample ID	$\partial^{13}C$	$\partial^{18}O$
TMBN-2	**1.15**	**-18.40**
KLT 2-1	**0.63**	**-17.30**
KLT 8	**0.92**	**-16.37**
TMBN 3	**1.07**	**-17.95**

Based on table 1, the values for $\partial^{18}O$ are highly depleted, ranging from $-18.4^{0}/_{00}$ to $-16.37^{0}/_{00}$ and the values for $\partial^{13}C$ are slightly positive, between $0.63^{0}/_{00}$ and $1.15^{0}/_{00}$. The values of $\partial^{18}O$ are slightly more depleted than other analyzed hydrothermal dolomite like those of western Canada, Guilin, and Southern Cantabrian Zone Spain (Figure 13), which show values of $\partial^{18}O$ ranging from $-13.9\ ^{0}/_{00}$ to $-3.5^{0}/_{00}$ .The values of $\partial^{13}C$ for KLT, Gunung Rapat and GP, Tambun dolomite are between $-2.7^{0}/_{00}$ to $5.2^{0}/_{00}$ and are similar to those of reference hydrothermal dolomites. Figure 13 shows the plotted values for the dolomite at KLT and GP, Kinta Valley compared to other analyzed hydrothermal dolomites. The comparison suggests that the dolomites of the Kinta Valley, associated with hematite deposits, are of hydrothermal origin.

Figure 13: Comparison of the dolomite at KLT and GP, Kinta Valley with other analyzed hydrothermal dolomite (Gasparrini et al., 2006; Chen et al., 2004; Al-Aasm, 2003)

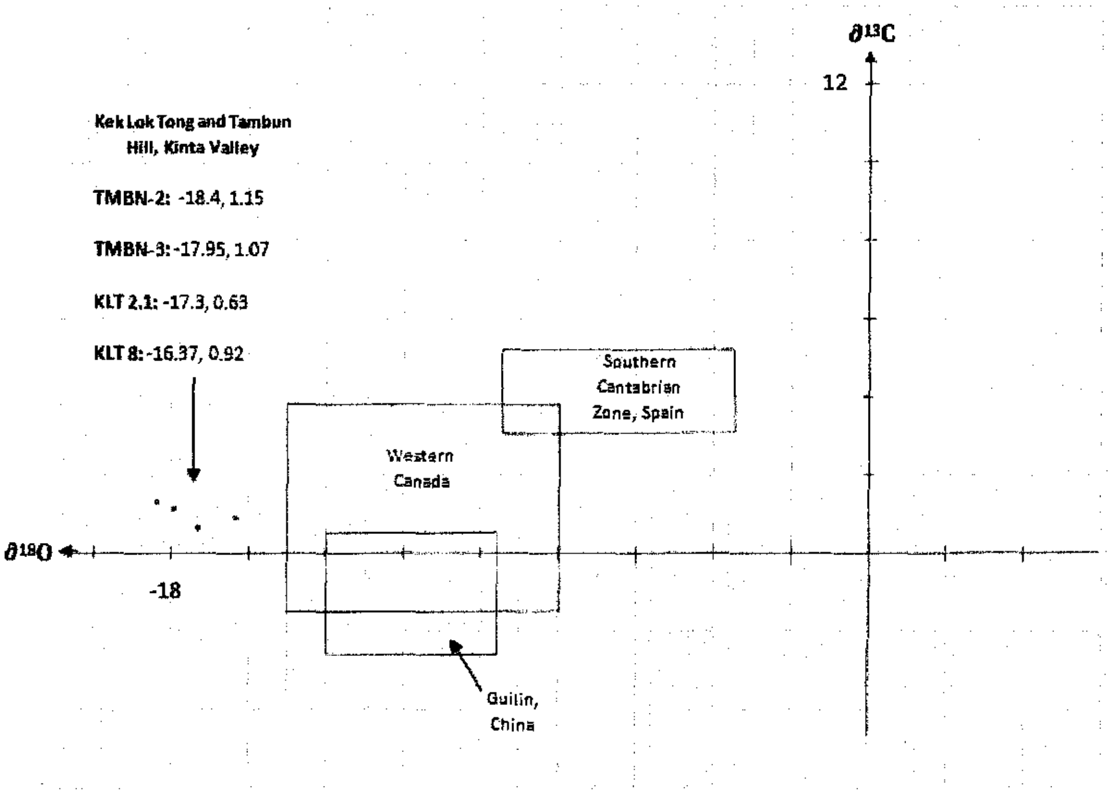
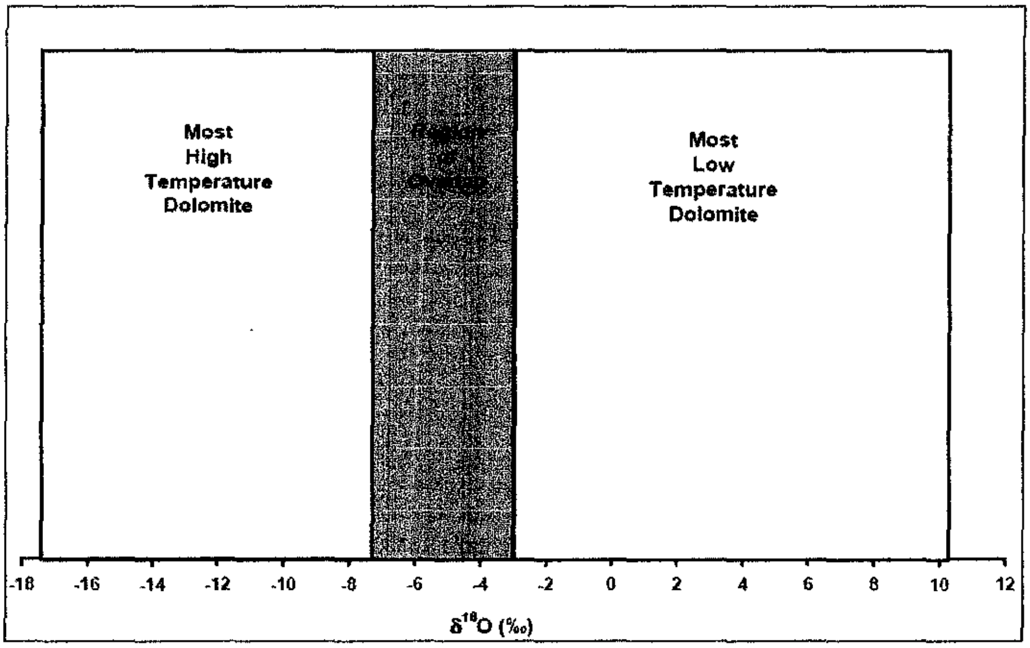


Figure 14: Dolomite categories based on their temperature with respect to $\partial^{18}O$ (Allan and Wiggin, 1993)



Allan and Wiggins (1993) categorized dolomites based on their temperature with respect to $\partial^{18}O$. Low temperature dolomites from sabkha, supratidal, reflux, marine-meteoric mixing zone environments, from formations of various ages that span most of the Phanerozoic,have$\partial^{18}O$ values that range from -6.5 to 9 $^{0}/_{00}$. High temperature dolomites from burial and gangue (hydrothermal) origin and associated dolomite cement from formations of various ages have$\partial^{18}O$ values that range from -16 to -2.5 $^{0}/_{00}$. KLT, Gunung Rapat and GP, Tambun dolomite $\partial^{18}O$ values fall within the high temperature range (Figure 14). High temperature dolomite is usually related with hydrothermal conditions.

Figure 15: Carbon–oxygen isotopic compositions of modern and ancient dolomites subdivided according to dominant pore water fluids where the dolomites are forming (Warren, 2000)

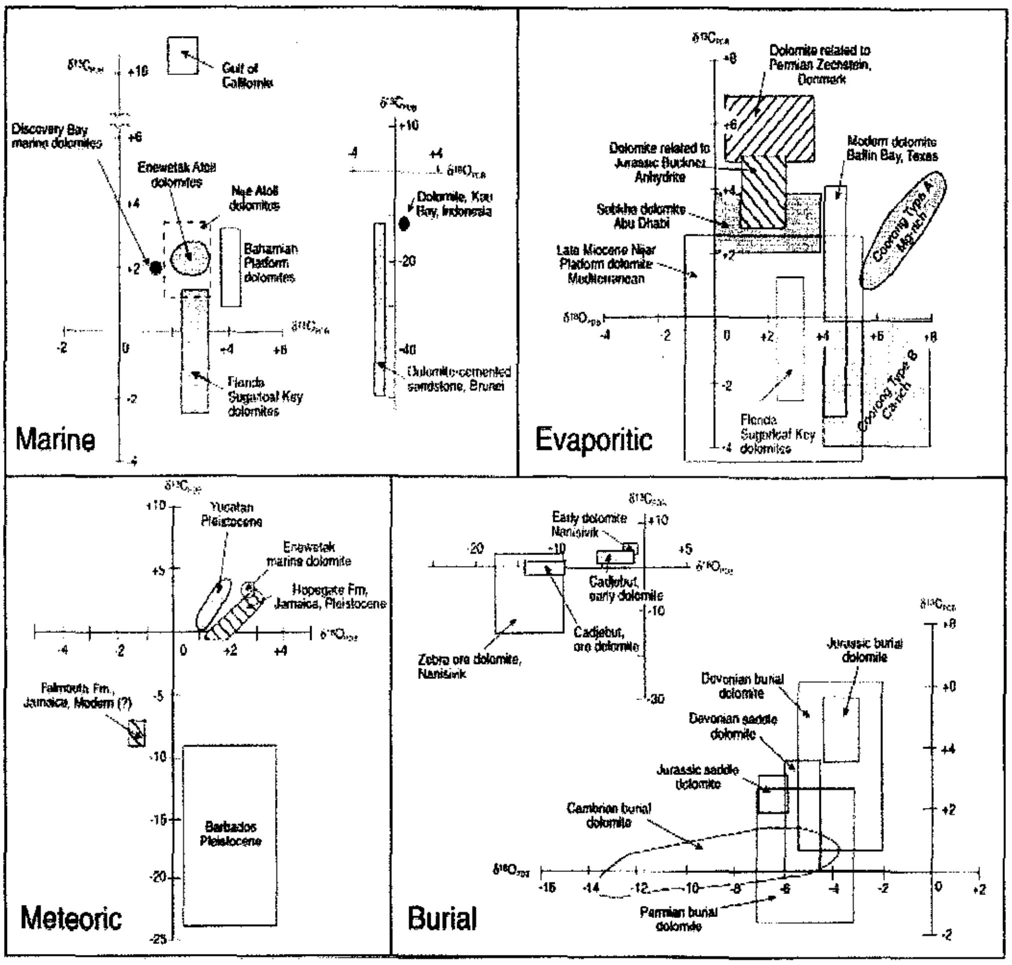


Figure 15 shows the four dominant fluids where dolomites form, i.e. marine, evaporitic, meteoric and burial. The burial dolomite isotope values show the closest similarity with KLT, Gunung Rapat and GP, Tambun dolomite. All of the $\partial^{18}O$ values are towards negative values (-2 to -18 $^{0}/_{00}$). $\partial^{13}C$ values are slightly positive (up to +6 $^{0}/_{00}$) and slightly negative (up to – 2$^{0}/_{00}$). Zebra ore dolomite from Nanisivik has the same range as the carbon-isotopic compositions of the Kinta Valley dolomite (Figure 15).

4.3 XRF result

Table 2: Major and trace elements concentration for the dolomite

No	Samples ID	CaO (%)	CaO* (%)	MgO (%)	MnO (ppm)	Fe_2O_3 (ppm)	SiO_2 (ppm)	Al_2O_3 (ppm)
1	KLT 2.1	32.1	31.6	20.3	4200	1100	200	70
2	KLT 2.2	31.1	30.5	20.7	4400	5500	400	110
3	KLT 5.0	30.3	31.2	19.6	4100	34400	4800	110
4	Tambun 3	30.0	30.1	19.7	11000	21900	200	50

No	Marking	TiO_2 (ppm)	P_2O_5 (ppm)	K2O (ppm)	Na2O (ppm)	S (ppm)	Sr (ppm)	Mo (ppm)
1	KLT 2.1	100	200	20	30	70	32	32
2	KLT 2.2	100	50	40	30	80	23	23
3	KLT 5.0	100	20	50	30	130	24	24
4	Tambun 3	40	10	70	50	50	35	22

No	Marking	Ce (ppm)	Y (ppm)	Sb (ppm)	Rb (ppm)	Th (ppm)	V (ppm)	Ni (ppm)
1	KLT 2.1	16	13	2.2	4.4	6	6.3	4.7
2	KLT 2.2	17	12	2.1	4.5	7	2.7	6.1
3	KLT 5.0	13	11	25	5.4	6	4.2	5.9
4	Tambun 3	12	10	1.9	9.9	3	3.3	1.5

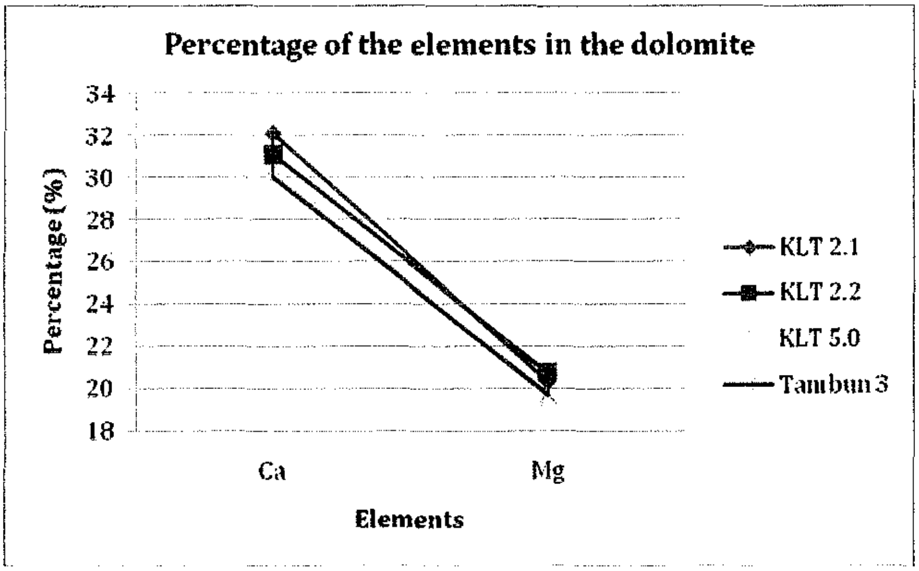
No	Marking	As (ppm)	Nb (ppm)	Cr (ppm)	U (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)
1	KLT 2.1	1.1	3.3	1.0	2	1	0.98	1.1
2	KLT 2.2	2.9	1.9	1.1	2	2	1.0	1.2
3	KLT 5.0	5.3	2.0	2.1	2	1	1.1	3.6
4	Tambun 3	6.1	2.1	4.5	ND	0.9	2.6	2.9

No	Marking	Ga (ppm)	Sn (ppm)	Ag (ppm)	Au (ppm)	Pt (ppm)	Hg (ppm)	LOI (%)
1	KLT 2.1	0.8	0.9	0.13	0.05	0.04	ND	45.9
2	KLT 2.2	0.7	0.8	0.15	0.04	0.03	ND	46.1
3	KLT 5.0	2.4	0.9	0.12	0.05	0.04	2	45.2
4	Tambun 3	0.3	0.8	0.09	0.03	0.02	ND	46.4

CaO* : EDTA Titration Method
LOI : Loss of ignition

4.3.1. Major elements

Figure 16: Percentage of calcium and magnesium in the dolomite at KLT, Gunung Rapat (KLT 2.1, KLT 2.2, KLT 5) and GP, Tambun (Tambun 3)



The percentage of calcium oxide and magnesium oxide indicates a typical dolomite composition. To determine the stoichiometric ratio of the dolomite, it needs to be converted into carbonate.

KLT2.1:

$CaCO_3$; 321 000 X 1.786 = 57 3214.3 ppm = 57.3%

$MgCO_3$; 203 000 X 2.1 = 426 300 ppm = 42.6 %

KLT 2.2

$CaCO_3$; 311 000 X 1.786 = 555 446 ppm = 55.5%

$MgCO_3$; 207 000 X 2.1 =434 700 ppm = 43.5 %

KLT 5

$CaCO_3$; 303 000 X 1.786 = 541 158 ppm = 54.1 %

$MgCO_3$; 196 000 X 2.1 = 411 600 ppm =41.1 %

Tambun 3

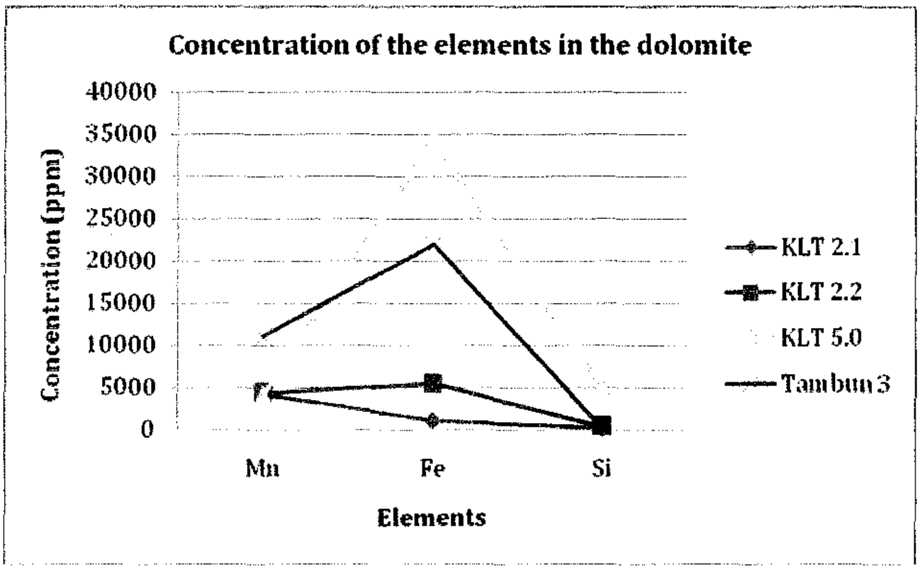
$CaCO_3$; 300 000 X 1.786 = 535 800 ppm = 53.6%

$MgCO_3$; 197 000 X 2.1 = 413 700 ppm = 41.4%

The result show that the dolomite at KLT, Gunung Rapat and GP, Tambun is non stoichiometric.

4.3.2. Trace elements

Figure 17: Concentration of manganese, iron and silica in the dolomite at KLT, Gunung Rapat (KLT 2.1, KLT 2.2, and KLT 5) and GP, Tambun (Tambun 3)



Manganese

Manganese concentrations are high for all samples. Tambun 3 records the highest concentration with almost 2 times as much as the samples from KLT.

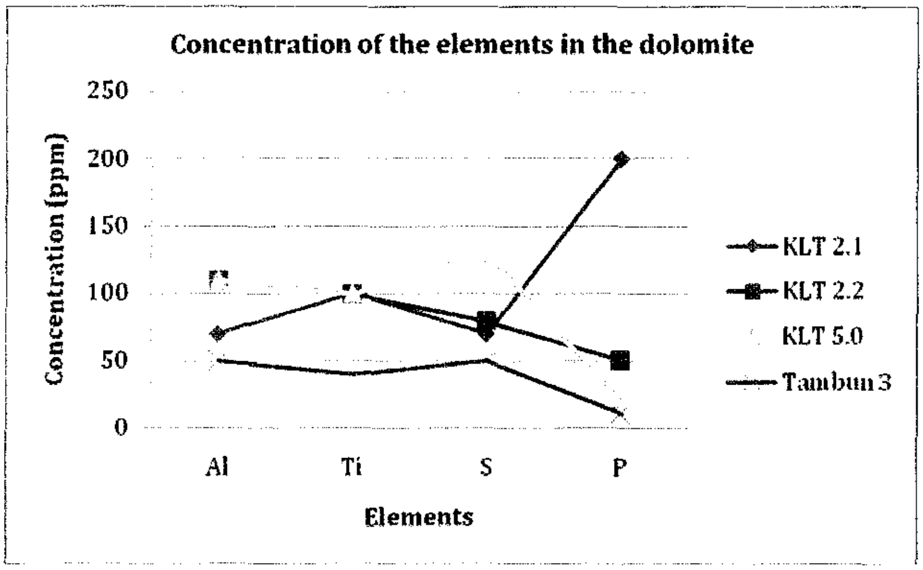
Iron

Iron is also present in high concentration .The concentration increases from KLT2.1, KLT2.2 to KLT5. Tambun 3 records a lower concentration than KLT5 but higher than other 2 KLT samples.

Silica

KLT 5 shows a very large difference (around ten times higher) compared to other samples concentration.

Figure 18: Concentration of aluminum, titanium, sulfur and phosphorus in the dolomite at KLT, Gunung Rapat (KLT 2.1, KLT 2.2, and KLT 5) and GP, Tambun (Tambun 3)



Aluminum

Tambun 3 has the lowest concentration while KLT2.2. and KLT 5 share the same concentration

Titanium

All KLT samples show a similar concentration, while Tambun 3 has less than 50% of the KLT concentrations.

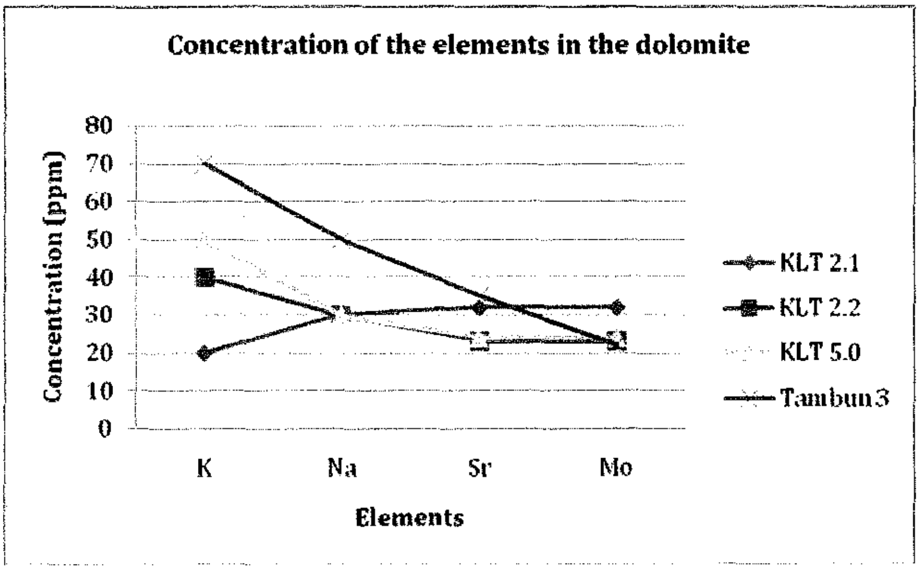
Sulfur

The concentration increases from KLT2.1, KLT2.2 to KLT5. Tambun 3 records the lowest.

Phosphorus

KLT 2.1 shows a big difference (around ten times higher) compared to other samples concentration.

Figure 19: Concentration of potassium, sodium, strontium and molybdenum in the dolomite at KLT, Gunung Rapat (KLT 2.1, KLT 2.2, KLT 5) and GP, Tambun (Tambun 3)



Potassium

The concentration increases from KLT2.1, KLT2.2 to KLT5 and Tambun 3 records highest concentration

Sodium

All KLT samples show the same concentration

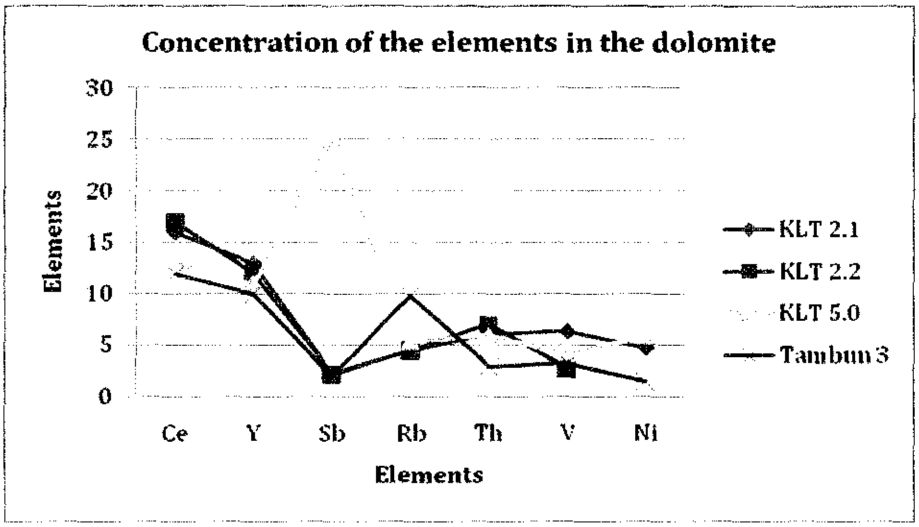
Strontium

The concentration decreases from KLT 2.1, KLT 2.2 and KLT 5 . Tambun 3 has the highest concentration.

Molybdenum

KLT 2.1 shows the highest concentration. KLT 2.2, KLT 5 and Tambun 3 values are quite similar.

Figure 20: Concentration of cerium, yttrium, antimony, rubidium, thorium and vanadium in the dolomite at KLT, Gunung Rapat (KLT 2.1, KLT 2.2, KLT 5) and GP, Tambun (Tambun 3)



Cerium

All the values are quite similar.

Yttrium

All the values are quite similar.

Antimony

KLT 5 shows the highest concentration which is about ten times with other samples.

Rubidium

Tambun 3 shows the highest concentration which is about two times with other samples.

Thorium

Tambun 3 shows the lowest concentration. All KLT samples show almost same values.

Vanadium

KLT 2.1 shows the highest concentration.

Nickel

Tambun 3 shows the lowest concentration. All samples show almost same values.

CHAPTER 5

INTERPRETATION

5.1 Initial assumption: the dolomite is hydrothermal in origin

The dolomite in KLT, Gunung Rapat and GP, Tambun in the Kinta Valley is assumed to be hydrothermal in origin. The assumption is being made based on

1. The dolomite is associated with hematite that is hydrothermal in origin
2. Dolomite crystals commonly are saddle type
3. Dolomite and hematite form a banding similar to a zebra structure

5.2 Chemical analysis

Chemical analysis such as stable isotopes (carbon and oxygen) analysis and XRF analysis were performed to verify that the dolomite in KLT, Gunung Rapat and GP, Tambun at Kinta Valley is hydrothermal in origin.

5.2.1 Carbon and Oxygen Isotope

The isotopic composition of carbon and oxygen in any carbonate precipitated in isotopic equilibrium with a fluid depends on the isotopic composition of carbon and oxygen in the fluid, the temperature of the formation, and the relative proportions of dissolved carbon species such as CO_2,H_2CO_3,HCO_3- and CO_3^{2-} (Hoefs, 2004).

KLT, Gunung Rapat and GP, Tambun dolomites $\delta^{18}O$ values are highly depleted, ranging from $-18.4^0/_{00}$ to $-16.37^0/_{00}$ while $\partial^{13}C$ values are slightly positive, between $0.63^0/_{00}$ and $1.15^0/_0$.

KLT and GP dolomites have a similar range of $\partial^{18}O$ and $\partial^{13}C$ values. This similarity suggests that both dolomites formed from the same source. The effect of high temperature that were coming from the contact metamorphism, dolomitizing fluid and hydrothermal fluid, which precipitated the hematite depleted the $\partial^{18}O$ values

Before the precipitation of dolomite by the hydrothermal fluid, the limestone had undergone contact metamorphism. Hot magma intruded, coming in contact with the limestone and cooking the limestone into marble. This would cause the $\partial^{18}O$ values of the host rock to become depleted due to the high temperature of the magma.

During the dolomitizing process, the hot hydrothermal fluid cannibalized the limestone and formed the dolomite .The high temperature from the dolomitizing fluid is believed to deplete the $\partial^{18}O$ values.

Hematite occurs as scattered vertical veins or "chimneys" several meters thick within this limestone and is associated with dolomite crystals or veins. The effect of high temperature that depleted $\partial^{18}O$ values of the dolomite also comes from the hydrothermal fluid, which precipitated the hematite. According to Langhorne (2006), the increase in temperatures can drive $\partial^{18}O$ values towards more negative values.

The oxygen isotope composition of a rock depends on the ^{18}O contents of the constituent minerals and the mineral proportions. Garlick (1996) and Taylor (1967) listed hematite as having the lowest tendency to concentrate ^{18}O. As our dolomite is associated with hematite, it possibly affected dolomite in concentrating the ^{18}O which will lead to the depletion of $\partial^{18}O$.Apart from that, during the process of dissolution and reprecipitate of the carbonate minerals, some of the ^{18}O in the carbonate minerals could exchange with some of the ^{16}O in the formation of water. This would lead to a depletion of ^{18}O in the mineral.

Most oxygen isotopic analyses of saddle dolomite on a global scale and from Cambrian to Cretaceous hosts lie in the range of -2.5 to -18 $\partial^{18}O$ PDB (Allan and Wiggins, 1993; Lavoie and Chi, 2001) with the most common range between -5 and -12 $\partial^{18}O$. Depletion of the heavier ^{18}O isotope in saddle dolomite is attributed mainly to thermal fractionation (Qing and Mountjoy, 1994). Hydrothermal dolomites typically have depleted $\delta^{18}O$ values, which are between -2 to –20‰ (Smith, 2004).

$\partial^{13}C$ values are usually interpreted in terms of presence or absence of the organic carbon. Carbon isotopic ratios for our dolomite mainly reflect the contributions of inorganic carbon derived from the host limestone. The dolomites have $\partial^{13}C$ values buffered by the host limestones due to the dominance of HCO^{3-} derived from dissolution of the limestone calcite in the dolomitizing fluids (Land, 1985).

The dolomite from the two studied sites in the Kinta Valley have stable isotope values that fall within the range of the other global analyzed hydrothermal dolomite (Figure 5.2).This supports the initial assumption that the dolomite at Kinta Valley particularly in KLT, Gunung Rapat and GP, Tambun is hydrothermal in origin.

5.2.2 Major and trace elements analysis

According to John Warren (2000), their concentrations in ancient dolomites are determined by their concentrations in the parent fluids, the level of water rock interaction and the effective distribution coefficient between the dolomite and its parent water. A part from that, the mineralogy of the precursor carbonate also has an influence in determining the trace element signature.

Strontium, Sodium, Iron and Manganese are the elements that are usually used to describe the environment of dolomite formation. From table 2, Iron & Manganese show high concentration while Strontium & Sodium show low concentration. Manganese concentration is quite stable for all KLT, Gunung Rapat samples while iron concentration is not. When the concentration in iron decreases from one sample to another sample, the concentration in strontium is opposite to that (KLT 5 to KLT 2.1)

KLT and GP dolomites are believed to be hydrothermal in origin. The two metals most enriched in hydrothermal vent fluids are iron and manganese (Holland and Turekian, 2010). The high and not stable concentration of iron in our samples especially in KLT may be due to the contamination by iron from the hematite

The concentrations in manganese and iron resemble each other very closely. If the concentration in iron is high, the concentration in manganese will also be high. Exposure of such solutions to air and rapid increase in pH results in both minerals to precipitate resulting in the formation of iron minerals will small admixture of manganese (Holland and Turekian, 2010). If on other hand, the pH increases very slowly, iron compounds reach their limit of solubility before manganese compounds and so can precipitate while manganese is left in the solution (Holland and Turekian, 2010). This is the same with our case where we can see veins of hematite and no manganese precipitation. Above statement may explain the observation.

The low concentrations in sodium and strontium but high concentrations in iron and manganese indicate that our dolomite is not derived from marine fluids. Dolomites directly precipitated from seawater typically have strontium contents of several hundred ppm (Carballo et al., 1987; Gasparrini et al., 2006); higher contents are typical for dolomites precipitated in evaporitic environments (Butler and Burns, 1969; Gasparrini et al., 2006). As with strontium, the concentration of sodium can also be used to differentiate the dolomite types but all values are relative and not absolute indicators. The sodium concentration can be used as the indicator for the salinity of the dolomitizing fluids (Budd, 1997; Kirmaci, 2007).

KLT 5 might be the nearest sample with the hydrothermal source as the concentration of iron is the highest but the concentration of strontium is low (based on distribution coefficient).However, because the concentration differences are very close to each other for strontium and not consistent for the iron, we cannot determine exactly which sample is the nearest to the hydrothermal activities.

The Distribution Coefficient of a minor or trace element within carbonate mineral will approach 1.0 as its radius approaches that of the major element for which it substitutes, in this case, calcium (Allan and Wiggins, 1993). Iron has Distribution Coefficient larger than 1 while strontium has Distribution Coefficient lower than 1 (Allan and Wiggins, 1993). Those with a distribution coefficient that is larger than 1 will be decreased along the fluid flow and those with smaller than 1 will be increased.

CHAPTER 6

CONCLUSIONS & RECOMMENDATION

6.1 Conclusions

Based on the stable isotopes results, the dolomite of the Kinta Valley is within the range of the analyzed hydrothermal dolomites. The highly depleted $\partial^{18}O$ values are due to the effect of high temperatures from the contact metamorphism and the hot hydrothermal fluids. The association with hematite possibly affected the tendency of the dolomite to concentrate ^{18}O . Besides that, during the process of dissolution and reprecipitation of the carbonate minerals some of the ^{18}O in the carbonate minerals exchanged with some of the ^{16}O in the formation of water, leading to a depletion in$\partial^{18}O$. Apart from that, saddle dolomite also has depleted values of $\partial^{18}O$.

Commonly, hydrothermal dolomite has very high concentrations in iron and manganese but low concentrations in sodium and strontium. Major elements for the KLT, Gunung Rapat and GP, Tambun dolomite are Ca & Mg with other trace elements like Si, Al, Fe, K, Na, Mn, P, S, Sr, V, Ni, Cr, As, Rb, Y, Mo, Ce, Th. These trace elements are usually not present in low-temperature dolomites but may be common in hydrothermal dolomites.

In conclusion, the dolomite of the Kinta Valley, particularly from KLT in Gunung Rapat and GP in Tambun is hydrothermal in origin

6.2 Recommendation

6.2.1 Fluid inclusion homogenization temperature

Fluid inclusions are fluid-filled cavaties, usually 1-10 micrometre in diameter, in carbonate mineral (Roedder 1981; Allan and Wiggins, 1993). Homogenization temperature is a temperature where two- phase inclusion (liquid and its vapor) becomes one phase when they are being heated. It provides an estimate of the minimum temperature for the dolomitization process to occur. From that, we can use as the supporting evidence for the hydrothermal dolomite. Hydrothermal dolomites typically have fluid inclusion homogenization temperatures greater than 75°C (Smith, 2004)

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