CHAPTER V

GEOCHEMISTRY

Under the present investigation, additional attempt has been made to determine the geochemical characteristics of the lithostratigraphic sequences of the Nam Maholan Formation, and its subdivisions, namely, the Tham Suae Mop Member, the Ban Nong Hin Member, and the Phu Pha Khao Member, respectively in an ascending order. Altogether 41 representative samples have been employed for the geochemical analyses and the calcite/dolomite ratio throughout the approximately 500 metre-thick sequences. Besides, 59 representative samples have been used in the stable oxygen and carbon isotopes study.

For the chemical characteristic determination, the carbonate rock samples have been analyzed for CaO, MgO, SiO_2, Fe_2O_3, Na_2O, MnO, Al_2O_3, P_2O_5, and loss on ignition (LOI) using the atomic absorption spectrophotometry techniques at Analysis Division, Department of Mineral Resources, Thailand. The calcite/dolomite ratio has been determined using the X-ray diffractrometry techniques (Tennant and Berger, 1957). The stable oxygen and carbon isotopes study has been carried out at the central laboratory of Chengdu Institute of Geology and Mineral Resources, Sichuan Province, People Republic of China.

Geochemical characteristics

Calcium contents

Analytical results of totally 41 carbonate rock samples from a certain degree of variation in CaO content ranging from 27.11 to 55.23 wt. %, with an average of 45.85 wt. % (Table 5.1). The Tham Suae Mop Member of approximately 50 metres thick is lithologically characterized as a mixed carbonate-siliciclastic sequence. Analytical results of 3 representative limestone samples reveal that CaO content varies

Table 5.1 Chemical composition of carbonate rocks (wt. %)

of the Nam Maholan Formation (total analyses 41 samples).

Sample no	Cao	MgO	SiO2	Fe2O3	Na2O	K2O	MnO	Al2O3	P2O5	LOI	Ca/Mg
1	52.91	1.16	1.42	0.17	0.005	0.056	0.021	0.16	0.01	43.22	45.61
4	54.17	0.53	1.84	0.12	0.004	0.037	0.016	0.12	0.01	42.96	102.21
6	54.68	0.81	0.22	0.09	0.006	0.009	0.011	0.19	0.01	43.85	67.51
8	51.13	4.03	0.17	0.08	0.005	0.003	0.009	0.02	0.01	44.29	12.69
11	52.57	0.99	3.27	0.22	0.005	0.012	0.014	0.05	0.01	42.44	53.10
13	53.72	1.47	0.44	0.08	0.002	0.002	0.007	0.05	0.01	43.67	36.54
14	54.48	0.66	1.44	0.09	0.002	0.003	0.006	0.02	0.01	43.13	82.55
17	33.37	18.73	0.15	0.15	0.004	0.003	0.007	0.03	0.01	46.71	1.78
18	53.07	2.53	0.07	0.06	0.006	0.003	0.005	0.01	0.01	42.29	20.98
20	53.44	1.54	1.15	0.12	0.01	0.033	0.013	0.12	0.01	43.58	34.70
22	49.35	0.65	9.38	0.21	0.004	0.095	0.03	0.56	0.01	39.7	75.92
23	53.99	2.2	0.38	0.12	0.007	0.005	0.006	0.02	0.01	43.78	24.54
27	44.14	9.85	0.12	0.16	0.007	0.003	0.012	0.04	0.02	45.28	4.48
30	52.93	2.52	0.01	0.05	0.003	0.003	0.007	0.01	0.01	44.11	21.00
31	54.51	0.96	0.06	0.06	0.005	0.006	0.005	0.02	0.01	43.88	56.78
33	53.97	1.43	0.33	0.04	0.007	0.006	0.004	0.02	0.02	43.78	37.74
36	54.45	0.6	0.67	0.22	0.011	0.011	0.024	0.16	0.01	43.31	90.75
38	52.54	2	1.01	0.15	0.005	0.005	0.013	0.04	0.01	43.39	26.27
39	44.98	7.1	2.73	0.52	0.039	0.039	0.064	0.23	0.02	43.34	6.34
42	29.73	16.14	4.1	0.92	0.168	0.168	0.034	1.51	0.02	43.41	1.84
44	54.53	0.94	0.08	0.05	0.006	0.01	0.003	0.02	0.01	43.62	58.01
46	30.22	21.27	0.19	0.44	0.01	0.018	0.017	0.09	0.03	46.74	1.42
48	33.28	18.34	0.42	0.68	0.016	0.038	0.029	0.24	0.05	46.06	1.81
49	34.21	18.44	0.03	0.33	0.009	0.003	0.012	0.26	0.02	46.78	1.86
50	52.26	2.13	0.22	0.38	0.004	0.012	0.006	0.18	0.01	43.22	24.54
52	35.03	17.29	0.55	0.1	0.008	0.07	0.015	0.02	0.02	45.78	2.03
54	32.56	19.9	0.6	0.33	0.011	0.018	0.01	0.04	0.12	46.27	1.64
56	52.57	0.8	3.87	0.42	0.013	0.096	0.02	0.51	0.04	41.58	65.71
58	32.49	19.68	0.15	0.51	0.012	0.013	0.013	0.03	0.02	46.29	1.65
60	54.68	0.61	1.41	0.2	0.008	0.053	0.007	0.13	0.01	43.13	89.64
62	34.17	18.18	0.48	0.32	0.01	0.026	0.011	0.14	0.02	45.88	1.88
64	53.28	0.71	2.12	0.31	0.008	0.19	0.02	0.66	0.05	42.43	75.04
65	52.43	0.41	3.7	0.41	0.02	0.2	0.04	0.9	0.48	41.56	127.88
66	32.34	18.9	1.51	0.67	0.009	0.02	0.02	0.26	0.04	45.59	1.71
69	55.23	0.47	0.13	0.1	0.002	0.001	0.002	0.03	0.01	43.76	117.51
71	52.3	2.68	0.3	0.08	0.004	0.002	0.004	0.03	0.01	43.9	19.51
72	54.12	1.14	0.38	0.11	0.005	0.006	0.006	0.05	0.01	43.65	47.47
75	36.17	1.04	30.57	1.29	0.01	0.25	0.03	1.64	0.06	28.95	34.78
76	33.98	17.83	1.31	0.36	0.01	0.06	0.02	0.37	0.07	45.91	1.91
87	27.11	0.49	48.56	1.34	0.007	0.1	0.02	0.52	0.04	21.47	55.33
90	32.96	18.99	0.42	0.29	0.006	0.01	0.02	0.04	0.06	46.6	1.74
Average	45.85	6.74	3.07	0.30	0.01	0.04	0.02	0.23	0.03	43.15	37.47
Min	27.11	0.41	0.01	0.04	0.002	0.001	0.002	0.01	0.01	21.47	1.42
Max	55.23	21.27	48.56	1.34	0.168	0.25	0.064	1.64	0.48	46.78	127.88
SD	9.93	7.97	8.78	0.31	0.03	0.06	0.01	0.37	0.07	4.49	35.98

within the range of 52.57 to 54.68 wt. %, with average value of 53.39 wt. %. (Table 5.2). The Ban Nong Hin Member of totally 200-250 metre-thick is lithologically characterized by partially dolomitic cherty limestone sequence. Altogether 6 representative limestone samples show the CaO content in the range of 32.56 to 54.45 wt. % with average of 46.06 wt. % (Table 5.3). Stratigraphically, the Phu Pha Kao Member is characterized as pure carbonate sequence of 250-300 metres thick. Altogether 32 carbonate rock samples are representing this member. The CaO contents vary between 27.11 and 55.23 wt. % with the average of 45.11 wt. % (Table 5.4).

The characteristic of CaO contents of the three members are summarized and presented in Table 5.5 and Fig. 5.1.

Magnesium contents

The magnesium content, MgO of totally 41 carbonate rock samples shows a drastic variation between 0.41 and 21.27 wt.% with the average of 6.74 wt. %. Three rock samples from the Tham Suae Mop Member show values narrowly ranging from 0.61 to 1.16 wt. % with the average of 0.92 wt. %. The Ban Nong Hin Member displays a great variation from 0.53 to 19.9 wt. % of MgO contents, and the average of 6.80 wt. % of totally 6 samples. The succession of the Phu Pha Khao member exhibits a high degree of variation of MgO contents from 0.41 to 21.27 wt. % with the average of 7.27 wt. % from 32 carbonate rock samples (see also Tables 5.1 to 5.4).

The characteristics of MgO contents of these three members are summarized and presented in Table 5.6 and Fig. 5.1.

Table 5.2 Chemical composition of carbonate rocks (wt. %)

of the Tham Suae Mop Member.

Sample no	CaO	MgO	SiO2	Fe2O3	Na2O	K2O	MnO	Al2O3	P2O5	LOI	Ca/Mg
1	52.91	1.16	1.42	0.17	0.005	0.056	0.021	0.16	0.01	43.22	45.61
11	52.57	0.99	3.27	0.22	0.005	0.012	0.014	0.05	0.01	42.44	53.10
60	54.68	0.81	1.41	0.2	0.008	0.053	0.007	0.13	0.01	43.13	89.64
Average	53.39	0.92	2.03	0.20	0.006	0.04	0.01	0.11	0.01	42.93	62.78
Min	52.57	0.81	1.41	0.17	0.005	0.01	0.01	0.05	0.01	42.44	45.61
Max	54.68	1.16	3.27	0.22	0.008	0.06	0.02	0.16	0.01	43.22	89.64
SD	1.13	0.28	1.07	0.03	0.002	0.02	0.01	0.06	0.00	0.43	23.56

Total analyses 3 samples

Table 5.3 Chemical composition of carbonate rocks (wt. %)

of the Ban Nong Hin Member.

Sample no	Cao	MgO	SiO2	Fe2O3	Na2O	K2O	MnO	Al2O3	P2O5	LOI	Ca/Mg
4	54.17	0.53	1.84	0.12	0.004	0.037	0.016	0.12	0.01	42.96	102.21
22	49.35	0.65	9.38	0.21	0.004	0.095	0.03	0.56	0.01	39.7	75.92
36	54.45	0.6	0.67	0.22	0.011	0.011	0.024	0.16	0.01	43.31	90.75
48	33.28	18.34	0.42	0.68	0.016	0.038	0.029	0.24	0.05	46.06	1.81
54	32.56	19.9	0.6	0.33	0.011	0.018	0.01	0.04	0.12	46.27	1.64
56	52.57	0.8	3.87	0.42	0.013	0.096	0.02	0.51	0.04	41.58	65.71
Average	46.0633	6.80	2.80	0.33	0.01	0.05	0.02	0.27	0.04	43.31	56.34
Min	32.56	0.53	0.42	0.12	0.004	0.011	0.01	0.04	0.01	39.7	1.64
Max	54.45	19.9	9.38	0.68	0.016	0.096	0.03	0.56	0.12	46.27	102.21
SD	10.34	9.55	3.48	0.20	0.00	0.04	0.01	0.21	0.04	2.55	44.10

Total analyses 6 samples

Table 5.4 Chemical composition of carbonate rocks (wt. %) of the Phu Pha Khao Member.

Sample no	Cao	MgO	SiO2	Fe2O3	Na2O	K2O	MnO	Al2O3	P2O5	LOI	Ca/Mg
6	54.68	0.81	0.22	0.09	0.006	0.009	0.011	0.19	0.01	43.86	67.51
8	51.13	4.03	0.17	0.08	0.005	0.003	0.009	0.02	0.01	44.29	12.69
13	53.72	1.47	0.44	0.08	0.002	0.002	0.007	0.05	0.01	43.67	36.54
14	54.48	0.66	1.44	0.09	0.002	0.003	0.006	0.02	0.01	43.13	82.55
17	33.37	18.73	0.15	0.15	0.004	0.003	0.007	0.03	0.01	46.71	1.78
18	53.07	2.53	0.07	0.06	0.006	0.003	0.005	0.01	0.01	42.29	20.98
20	53.44	1.54	1.15	0.12	0.01	0.033	0.013	0.12	0.01	43.58	34.70
23	53.99	2.2	0.38	0.12	0.007	0.005	0.006	0.02	0.01	43.78	24.54
27	44.14	9.85	0.12	0.16	0.007	0.003	0.012	0.04	0.02	45.28	4.48
30	52.93	2.52	0.01	0.05	0.003	0.003	0.007	0.01	0.01	44.11	21.00
31	54.51	0.96	0.06	0.06	0.005	0.006	0.005	0.02	0.01	43.88	56.78
33	53.97	1.43	0.33	0.04	0.007	0.006	0.004	0.02	0.01	43.78	37.74
38	52.54	2	1.01	0.15	0.005	0.005	0.013	0.04	0.01	43.39	26.27
39	44.98	7.1	2.73	0.52	0.039	0.039	0.064	0.23	0.01	43.34	6.34
42	29.73	16.14	4.1	0.92	0.168	0.168	0.034	1.51	0.01	43.41	1.84
44	54.53	0.94	0.08	0.05	0.006	0.01	0.003	0.02	0.01	43.62	58.01
46	30.22	21.27	0.19	0.44	0.01	0.018	0.017	0.09	0.03	46.74	1.42
49	34.21	18.44	0.03	0.33	0.009	0.003	0.012	0.26	0.02	46.78	1.86
50	52.26	2.13	0.22	0.38	0.004	0.012	0.006	0.18	0.01	43.22	24.54
52	35.03	17.29	0.55	0.1	0.008	0.07	0.015	0.02	0.02	45.78	2.03
58	32.49	19.68	0.15	0.51	0.012	0.013	0.013	0.03	0.02	46.29	1.65
62	34.17	18.18	0.48	0.32	0.01	0.026	0.011	0.14	0.02	45.88	1.88
64	53.28	0.71	2.12	0.31	0.008	0.19	0.02	0.86	0.05	42.43	75.04
65	52.43	0.41	3.7	0.41	0.02	0.2	0.04	0.9	0.48	41.56	127.88
66	32.34	18.9	1.51	0.67	0.009	0.02	0.02	0.26	0.04	45.59	1.71
69	55.23	0.47	0.13	0.1	0.002	0.001	0.002	0.03	0.01	43.76	117.51
71	52.3	2.68	0.3	0.08	0.004	0.002	0.004	0.03	0.01	43.9	19.51
72	54.12	1.14	0.38	0.11	0.005	0.006	0.006	0.05	0.01	43.65	47.47
75	36.17	1.04	30.57	1.29	0.01	0.25	0.03	1.64	0.06	28.95	34.78
76	33.98	17.83	1.31	0.36	0.01	0.06	0.02	0.37	0.07	45.91	1.91
87	27.11	0.49	48.56	1.34	0.007	0.1	0.02	0.52	0.04	21.47	55.33
90	32.96	18.99	0.42	0.29	0.006	0.01	0.02	0.04	0.06	46.6	1.74
Average	45.11	7.27	3.22	0.31	0.01	0.04	0.01	0.24	0.04	43.14	31.56
Min	27.11	0.41	0.01	0.04	0.002	0.001	0.002	0.01	0.01	21.47	1.42
Max	55.23	21.27	48.56	1.34	0.168	0.25	0.064	1.64	0.48	46.78	127.88
SD	10.18	7.98	9.86	0.34	0.03	0.07	0.01	0.41	0.08	5.00	33.97

Total analyses 32 samples

Table 5.5 CaO contents of the Nam Maholan Formation and its subdivisions.

Lithostratigraphic unit	CaO content (wt. %) Range	Average	Remarks
Phu Pha KHao Member	27.11-55.23	45.11	32 samples
Ban Nong Hin Member	32.56-54.45	46.06	6 samples
Tham Suae Mop Member	52.57-54.68	53.39	3 samples
Nam Maholan Formation	27.11-55.23	45.85	41 samples

Table 5.6 MgO contents of the Nam Maholan Formation and its subdivisions.

Lithostratigraphic unit	MgO content (wt. %) Range	Average	Remarks
Phu Pha KHao Member	0.41-21.27	7.27	32 samples
Ban Nong Hin Member	0.53-19.9	6.8	6 samples
Tham Suae Mop Member	0.61-1.16	0.92	3 samples
Nam Maholan Formation	0.41-21.27	6.74	41 samples

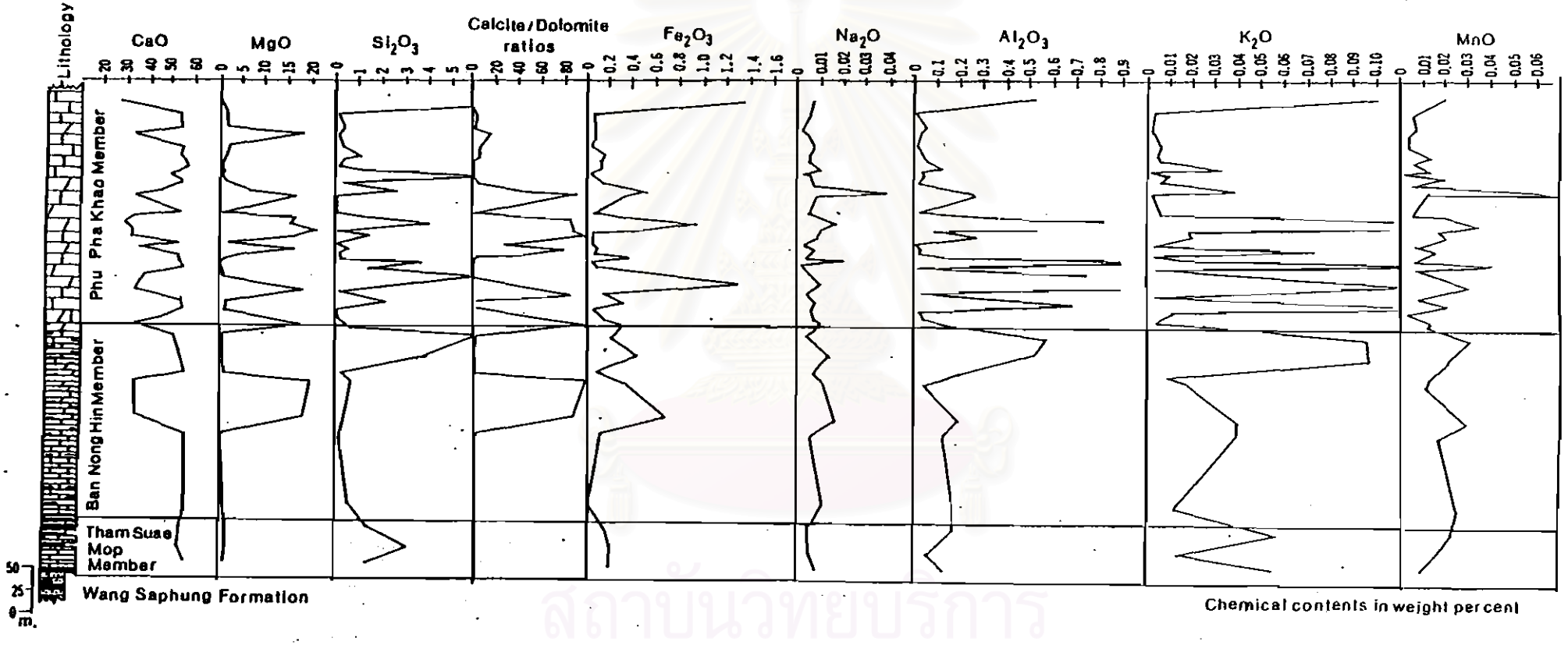


Fig. 5.1 Association of stratigraphy and geochemical characteristics of the Nam Maholan Formation and its subdivisions.

Other geochemical contents

For the analytical results of SiO_2, Fe_2O_3, Al_2O_3, MnO, K_2O, and Na_2O contents of the 3 members of the Nam Maholan Formation under the present investigation, the distribution patterns are as below.

The distribution patterns of these elemental composition of 3 carbonate rock samples of the mixed carbonate-siliciclastic sequence of the Tham Suae Mop Member show relatively low contents with only slightly variation. They are summarized and presented in Table 5.7 and Fig. 5.1.

For the Ban Nong Hin member, the distribution patterns of these geochemical contents show the moderately high variation especially in the upper middle of the partially dolomitic cherty limestone sequence. As a whole, the average contents of these geochemical characteristics are relatively moderately higher than those of the Tham Suae Mop Member (Table 5.7, Fig. 5.1).

Regarding the Phu Pha Khao Member, the geochemical values of these elemental compositions show the highly fluctuated patterns throughout the relatively pure carbonate succession. Besides, the average contents of these elemental compositions are relatively higher than those of the Ban Nong Hin Member and the Tham Suae Mop Member, particularly the SiO_2 and Al_2O_3. Other geochemical contents, notably, Fe_2O_3, MnO, K_2O, and Na_2O, are on average equal or slightly varies between the three members (Table 5.7, Fig. 5.1).

Dolomite contents

The calculation of dolomite content in weight per cent is essentially based on the calcite/dolomite ratios of Tennant and Berger (1975). The overall distribution of dolomite content of the Nam Maholan Formation of totally over 500 metres thick as determined from 41 carbonate rock samples shows a strongly fluctuated pattern (Fig.

Table 5.7 Other geochemical contents of the Nam maholan Formation and its subdivisions.

Lithostratigraphic units	Sio2 (wt. %)		Fe2O3 (wt. %)		Al2O3 (wt. %)		MnO (wt. %)		K2O (wt. %)		Na2O (wt. %)		Remarks
	range	average	range	average	range	average	range	average	range	average	range	average	
Phu Pha Khao Member	0.01-48.56	3.22	0.04-1.34	0.31	0.01-1.64	0.24	0.002-0.064	0.01	0.001-0.25	0.04	0.002-0.168	0.01	32 samples
Ban Nong Hin Member	0.42-9.38	2.8	0.12-0.68	0.33	0.04-0.56	0.27	0.01-0.03	0.02	0.011-0.096	0.05	0.004-0.016	0.01	6 samples
Tham Suae Mop Member	1.41-3.27	2.03	0.17-0.22	0.2	0.05-0.16	0.11	0.01-0.02	0.01	0.01-0.06	0.04	0.005-0.008	0.007	3 samples
Nam Maholan Formation	0.01-48.56	3.07	0.04-1.34	0.3	0.01-1.64	0.23	0.002-0.064	0.02	0.001-0.25	0.04	0.002-0.168	0.01	41 samples

5.1). The dolomite content generally varies between 0 to over 90 per cent with average of 28.90 per cent (Table 5.8).

For the Tham Suae Mop member of mixed carbonate-siliciclastic sequence, no dolomite is detected in 3 carbonate rock samples. However, for the Ban Nong Hin Member which overlies the Tham Suae Mop Member, the dolomite contents, as obtained from 6 samples, varies from 0 to over 90 per cent with the average of 29.88 per cent. It is noted that the zone of high dolomite content is present in the upper middle part of the partially dolomitic cherty limestone sequence, whereas the rest of the sequence is the zone without any dolomite. With respect to the Phu Pha Khao Member, the distribution pattern of dolomite contents as obtained from 32 samples varies drastically in the range of 0 to over 90 per cent, with the average of 29.88 per cent throughout the relatively pure carbonate sequence (Table 5.8, Fig. 5.1).

Discussion

It is apparent that the dolomitization is very selective only in the upper middle part of the Ban Nong Hin Member, whereas the Phu Pha Khao Member has been variably dolomitized almost throughout the sequence. The cross-plot between dolomite contents versus MgO contents of the samples obtained from three members have apparently exhibited the positive linear relationships (Fig. 5.2A). The cross-plot between calcite/dolomite ratios with MgO contents shows three separated components of these carbonate rocks (Fig. 5.2B).

With respect to the SiO_2 contents, it is believed that the SiO_2 contents have been contributed by the presence of chert, or detrital clay, or both. The cross-plot between the SiO_2 and Al_2O_3 contents shows all the three possibilities (Fig. 5.3A). The relationship of calcite/dolomite ratios with Al_2O_3 and SiO_2 contents (Figs. 5.3B, C) shows impurity of possibly derived clay and chert.

Table 5.8 Dolomite contents of the Nam Maholan Formation and its subdivisions.

Sample no.	Lithostratigraphic units	Calcite/dolomite ratios	Dolomite %	Calcite %	Remarks
6		100.0	0	100	
8		1.5	40	60	
13		49.0	2	98	
14		100.0	0	100	
17		0.2	85	15	
18		24.0	4	96	
20		100.0	0	100	
23		19.0	5	95	
27		0.8	56	44	
30		2.7	27	73	
31		100.0	0	100	
33		15.7	6	94	
38		19.0	5	95	
39		1.4	42	58	
42		0.1	88	12	
44		100.0	0	100	
46		0.1	89	11	32 samples
49	Phu Pha Khao	0.1	90	10	Range 0->90
50	Member	32.3	3	97	Average 29.88
52		0.3	79	21	
58		100.0	0	100	
62		0.1	89	11	
64		100.0	0	100	
65		100.0	0	100	
66		0.0	100	0	
69		100.0	0	100	
71		5.3	16	84	
72		100.0	0	100	
75		100.0	0	100	
76		0.2	86	14	
87		100.0	0	100	
90		0.2	85	15	
4		100.0	0	100	
22		100.0	0	100	6 samples
36	Ban Nong Hin	100.0	0	100	Range 0->90
48	Member	0.1	88	12	Average 31.30
54		0.0	100	0	
56		100.0	0	100	
1	Tham Suae Mop	100.0	0	100	3 samples
11	Member	100.0	0	100	Range -
60		100.0	0	100	

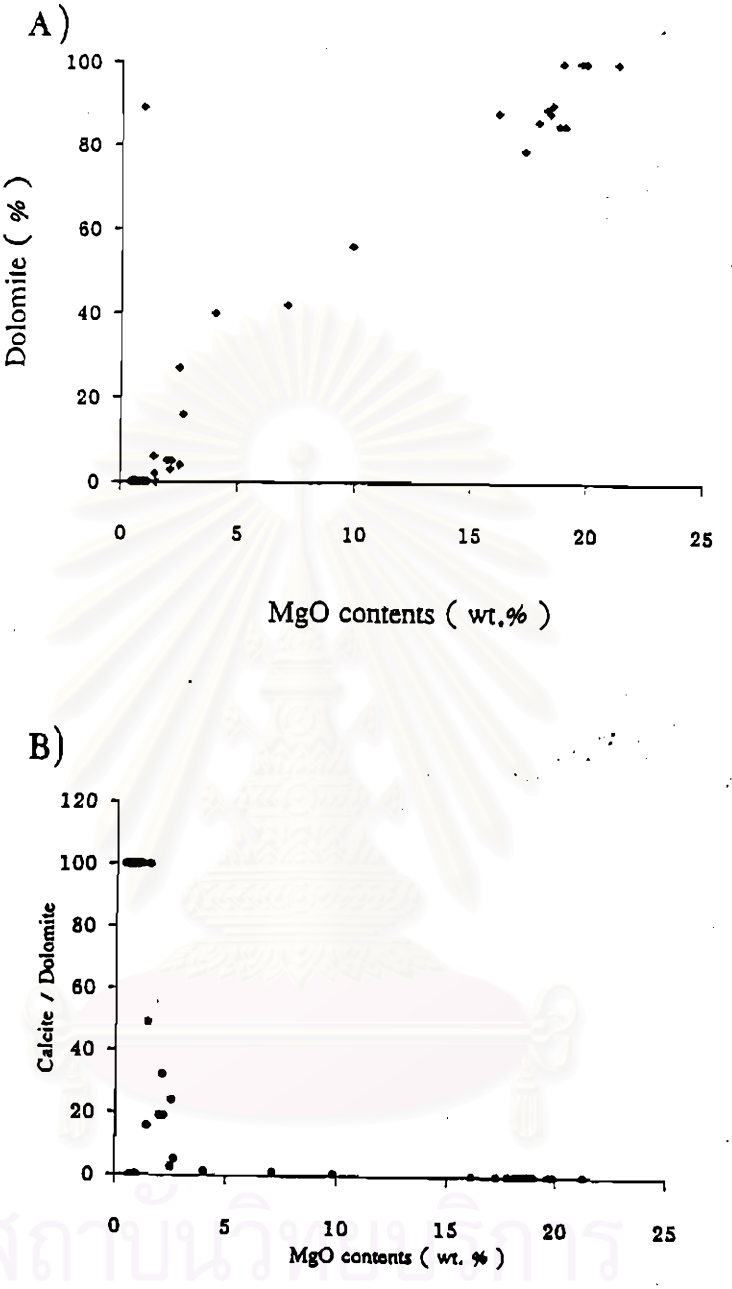


Fig. 5.2 Relationships of geochemical compositions of carbonate rocks of the Nam Maholan Formation in the study area (data from Table 5.1).

A) MgO contents and Dolomite contents.

B) MgO contents and Calcite / Dolomite ratios.

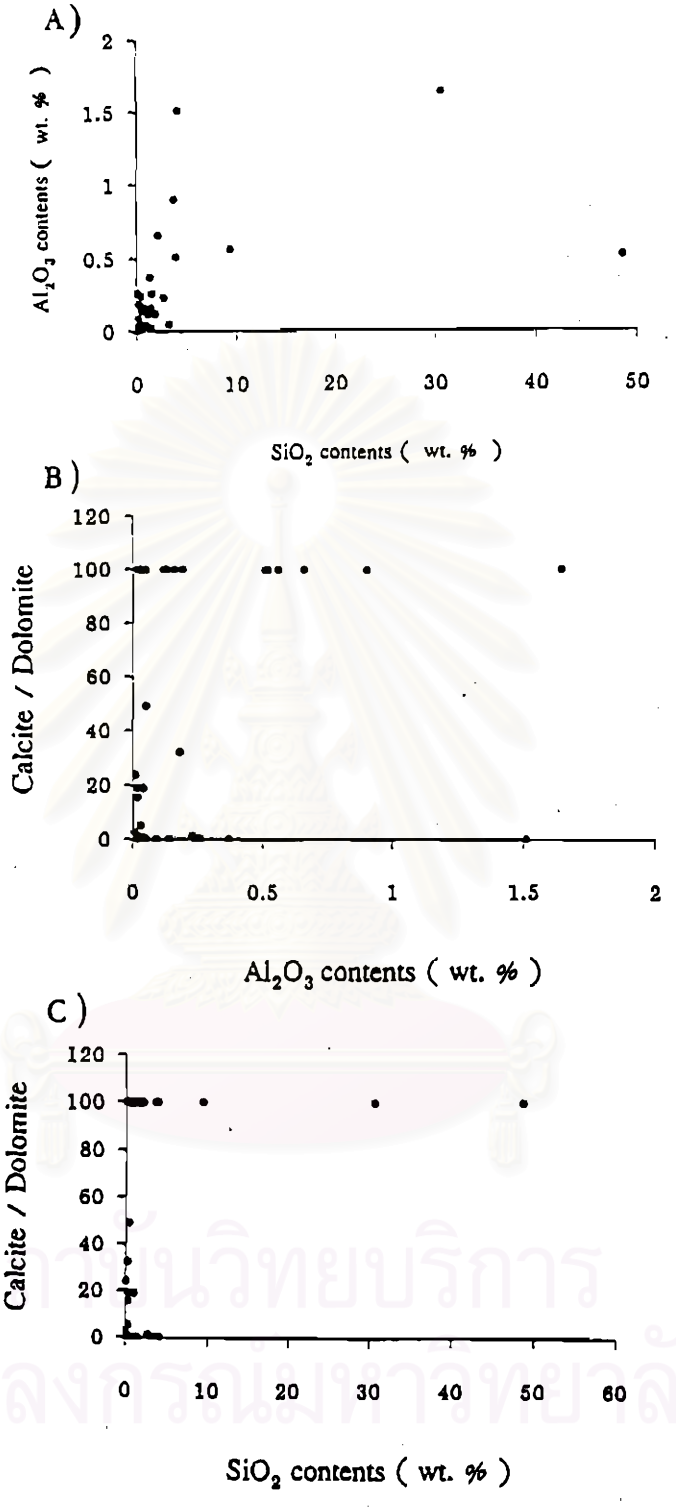


Fig. 5.3 Relationships of geochemical compositions of carbonate rocks of the Nam Maholan Formation in the study area (data from Table 5.1).

A) SiO_2 contents and Al_2O_3 contents

B) Al_2O_3 contents and Calcite / Dolomite ratios.

C) SiO_2 contents and Calcite / Dolomite ratios.

Stable isotopes

The uses of stable isotopes of oxygen and carbon in fossils and limestone to access environmental determinations, such as to distinguish between carbonate of different origins, salinity determination, and palaeotemperature diagnosis, have been attempted by many workers (Boggs, 1987; Shackleton, 1968; Keith and Weber, 1964; Clayton and Degens, 1959 etc.). Generally, the applications of stable carbon and oxygen isotopes investigation to geological problems have been dealt primary with the paleotemperature and paleosalinity determination (Flugel, 1982; Bowen, 1965; Urey, 1947). These are based mainly on the premise principle that fresh waters are depleted in both heavy carbon (^{13}C) and heavy oxygen (^{18}O) relative to marine water, then both values of ^{13}C and ^{18}O in fresh water carbonate are conventionally lower than those of the marine carbonate (Rollinson, 1993; Boggs, 1987; Faure, 1986; Flugel, 1982, etc.).

The isotopic compositions of oxygen are reported in terms of $^{18}O/^{16}O$ ratio ($\delta^{18}O$) relative to the two standard; the SMOW and PDB. The SMOW (Standard Mean Ocean Water) was originally hypothetical water sample with oxygen and hydrogen isotope ratios similar to those of standard ocean water. The SMOW was defined by Craig (1961) with reference to a large volume of distilled water that distributed by the National Bureau of Standard in the United States (Fuare, 1986). The PDB standard was originally used by Urey and his colleagues at the university of Chicago for express the isotope composition of oxygen in carbonates, particularly palaeotemperature determinations based on CO_2 produced from Cretaceous Belemnite of the Peedee Formation in South Carolina (Rollinson, 1993: Faure, 1986). The conversion of resulting between the SMOW and PDB values have been illustrated by Friedman and O'Neil (1977) as

$$\delta^{18}O_{SMOW} = 1.03086\ \delta^{18}O_{PDB} + 30.86$$

The carbon isotope composition of calcium carbonate is subsequently presented in term of the relative abundance between ^{13}C and ^{12}C ratios ($\delta^{13}C$) comparing with PDB standard as well as of $\delta^{18}O$ values.

Isotopic analysis

The results of carbon and oxygen values are given in the usual per mil deviation of $^{18}O/^{18}O$ and $^{13}C/^{12}C$ in relative to standard samples. All analyses of the present study are performed by the geosciencetist staff at laboratory of Chengdu Institute of Geology and Mineral Resources, Sichuan Province, People Republic of China.

Four kinds of samples were selected for isotopic analysis. These include whole-rock, fusulinacean, brachiopod, and dolomite specimens. The isotopic standards used in this study are those of China including GBW 04405 ($\delta^{13}C$ 0.57, $\delta^{18}O$ -8.49) and GBW 04406 ($\delta^{13}C$ -10.85, $\delta^{18}O$ -12.45). The standard values in laboratory is 811# ^{13}C -3.33, ^{18}O -10.62. Those values of standards are correlated to PDB.

Isotopic results

Oxygen isotope

Totally 21 isotopic results of the whole rocks analysis (Table 5.9) representing the stratigraphy of the Nam Maholan Formation in the study area displays the oxygen isotopic ratios from -9.95 to -4.51 per mil (PDB) with average of -7.5 per mil (PDB). The 2 analytical results of the Tham Suae Mop Member are -5.13 and -7.38 per mil (PDB). The 3 values of the Ban Nong Hin Member are ranging from -7.34 to -5.46 per mil (PDB) and also the 16 analytical results from the Phu Pha Khao Member show the values between -9.95 to -4.51 per mil (PDB).

Table 5.9 Analytical results for carbon and oxygen isotopes of the whole-rock analysis in Carboniferous-Permian limestones of the Nam Maholan Formation.

Sample no.	^{13}C‰	^{18}O‰	^{18}O SMOW‰
1#	4.13	-7.38	23.25
2*	5.01	-6.87	23.78
8	4.52	-8.38	22.22
9#	5.19	-5.13	25.57
13	3.5	-8.36	22.24
15	1.36	-9.4	21.17
21*	4.68	-5.46	25.23
22	4.22	-7.8	22.82
28*	4.38	-7.34	23.29
33	4.99	-5.83	24.85
34	2.74	-8.13	22.48
36	1.6	-9.07	21.51
38	4.11	-6.69	23.96
52	2.91	-8.19	22.42
53	2.87	-4.51	26.21
65	-0.12	-9.29	21.28
72	3.08	-6.42	24.24
75	3.62	-7.62	23.00
78	-0.76	-8.2	22.41
82	0.27	-7.7	22.92
87	2.08	-9.95	20.60
Average	**3.07**	**-7.51**	**23.12**
Maximum	5.19	-4.51	26.21
Minimum	-0.76	-9.95	20.60
SD	1.45	1.82	1.88

1# the Tham Suae Mop Member 1* the Ban Nong Hin Member

1 the Phu Pha Khao Member Total analyses 21 samples

The 16 analytical results of fusulinaceans in carbonate rocks (Table 5.10) show the isotopic values from -9.11 to -4.61 per mil (PDB) with average of -7.19 per mil (PDB). The 5 analytical results of the Tham Suae Mop Member exhibit values from -7.61 to -5.8 per mil (PDB). The Ban Nong Hin Member displays 2 values of the isotope ratios at -8.88 and -6.52 per mil (PDB). The Phu Pha Khao Member show the isotope values between -9.11 and -4.61 per mil (PDB).

The 13 oxygen isotope ratios of brachiopods ranging from -8.86 to 5.51 per mil (PDB) with average of -7.18 per mil (PDB) are shown in Table 5.11. The analysis of 2 samples from the Tham Suae Mop Member shows isotope values at -5.68 and -5.16 per mil (PDB). The 11 analytical results from the Phu Pha Khao Member are between -8.86 and -5.34 per mil (PDB).

The 9 dolomite samples (Table 5.12) displays the value of the oxygen isotope ratio from -8.41 to -1.02 per mil (PDB) with average of -6.20 per mil (PDB). The 8 analystical results from the Phu Pha Khao Member show values ranging from -8.41 to -1.02 per mil (PDB). A sample of dolomite from the Ban Nong Hin Member displays the value at -1.55 per mil (PDB).

Carbon isotope

A total of 21 whole-rock analytical values (Table 5.9) show the carbon isotopic values ranging from -0.76 to +5.19 per mil (PDB) with on average of +3.07 per mil (PDB). The values are +4.13 and +5.19 per mil (PDB) from the 2 analytical results of the Tham Suae Mop Member. The 3 samples of the Ban Nong Hin Member shows isotope values from +4.38 to +5.01 per mil (PDB), and values ranging between -0.76 and +5.19 per mil (PDB) are displayed from 16 analyses of the Phu Pha Khao Member.

Analystical results from 16 fusulinacean samples (Table 5.10) in limestone displays the carbon isotope values range from -4.02 to +5.71 per mil (PDB) with an

Table 5.10 Analytical results for carbon and oxygen isotopes of fusulinaceans in Carboniferous-Permian limestones of the Nam Maholan Formation.

Sample no.	^{13}C ‰	^{18}O ‰	$^{18}O_{SMOW}$ ‰
4*	-0.42	-8.88	21.71
6	4.02	-8.07	22.54
7	4.47	-7.64	22.98
10#	4.99	-6.04	24.63
11#	3.81	-7.61	23.02
20	4.99	-4.84	25.87
23	5.71	-4.61	26.11
29	4.9	-7.85	22.77
50	2.86	-9.11	21.47
69	1.26	-8.05	22.56
70	2.63	-8.83	21.76
73	4.5	-7.74	22.88
83*	2.98	-6.52	24.14
84#	4.8	-5.8	24.14
85#	3.51	-7.33	23.30
98#	3.75	-6.12	24.55
Average	**3.67**	**-7.19**	**23.40**
Maximum	5.71	-4.61	26.11
Minimum	-0.42	-9.11	21.47
SD	2.9	2.0	2.0

1# the Tham Suae Mop Member 1* the Ban Nong Hin Member

1 the Phu Pha Khao Member Total analyses 16 samples

Table 5.11 Analytical results for carbon and oxygen isotopes of brachiopod from limestones of the Nam Maholan Formation.

Sample no.	^{13}C ‰	^{18}O ‰	$^{18}OSMOW$ ‰
12#	4.08	-5.68	25.00
20	4.27	-7.6	23.03
25	5.06	-6.05	24.62
31	4.31	-8.4	22.20
43	-3.22	-5.42	25.27
44	5.64	-5.34	25.36
51	3.46	-8.14	22.47
60#	5.63	-5.16	25.54
71	3.32	-8.73	21.86
80	3.44	-8.23	22.38
86	3.18	-6.87	23.78
91	4.32	-8.86	21.73
92	2.66	-8.82	21.77
Average	**3.55**	**-7.18**	**23.46**
Maximum	5.64	-5.16	25.54
Minimum	-3.22	-8.86	21.73
SD	1.00	2.22	2.29

Total analyses 13 samples

Table 5.12 Analytical results for carbon and oxygen isotopes from dolomite of the Nam Maholan Formation.

Sample no.	^{13}C ‰	^{18}O ‰	$^{18}OSMOW$ ‰
17	3.52	-8.41	22.19
42	3.12	-1.02	29.81
46	0.45	-6.6	24.06
49	0.55	-8.27	22.33
52	2.91	-8.19	22.42
54*	2.99	-1.55	29.26
62	3.37	-6.83	23.82
76	1.78	-7.54	23.09
90	4.16	-7.43	23.2
Average	**2.54**	**-6.20**	**24.46**
Maximum	4.16	-1.02	29.81
Minimum	0.45	-8.41	22.19
SD	0.45	0.69	0.71

12# the Tham Suae Mop Member
12 the Phu Pha Khao Member
54* Ban Nong Hin Member
Total analyses 9 samples

average of +3.67 per mil (PDB). The 5 carbon isotope ratios range from +3.51 to +4.99 per mil (PDB) represent the Tham Suae Mop Member. The ratios are range from -0.42 to 2.98 per mil (PDB) from the analyses of the 2 samples of the Ban Nong Hin Member, and present the isotope ratios between +1.26 and +4.99 per mil (PDB) of the 9 samples from the Phu Pha Khao Member.

For the brachiopod, the carbon isotopic values between -3.22 and +5.64 per mil (PDB) with an average of +3.55 per mil (PDB) are represented by 13 samples analyses. The 2 results from the Tham Suae Mop Member are +4.08 and +5.63 per mil (PDB). The 11 analystical results from the Phu Pha Khao Member are between -3.22 and +5.64 per mil (PDB).

The 9 dolomite samples show the range of carbon isotope between +0.45 and +4.16 per mil (PDB) with an average of +2.54 per mil (PDB). A sample from the Ban Nong Hin Member shows the carbon isotope ratio at 2.99 per mil (PDB). The 8 results of the Phu Pha Khao Member are ranging from +0.45 to +4.16 per mil (PDB).

Stable isotope interpretation

Various isotopic values suggest a possible differentiated convection system. Negative values of $\delta^{18}O$ may suggest to interaction of meteoric water and/or slight influence of diagenesis, most likely in a bacterial mediated environment in the zone of oxygen reduction. High values of $\delta^{13}C$ in carbonate succession are explained by high biota productivity in marine depositional basin, regarding to photosynthesis derived CO_2 from fauna, such as abundance of algae.

The $\delta^{13}C$ values suggested that the carbon forming carbonate was provided by respiration of bacterial or organic oxidation rather than those production of tectonic activity, according to the carbonates forming from CO_2 have been derived by the geothermal process must be strongly enriched in ^{12}C relative to total organic matter in

sedimentary rocks. These are advocated by $\delta^{13}C$ values that display the range between -14 and -28 per mil (PDB) of cooling lava flow, and geothermal methane have $\delta^{13}C$ value between -20 and -30 per mil on PDB scale (Rollinson, 1993). Additionally, $\delta^{13}C$ values for such rocks were reported at -36.2 ± 6.2 per mil (PDB) from cap rocks of Salt Dome in the Gulf Coast area of the United States (Cheney and Jeasen, 1965; 1976), and average value at -22.5 ± 4.0 per mil (PDB) from calcite associated organic material in the uranium deposits of the Win River Formation in the Gas Hills, Wyoming, USA, and also sulfer-bearing limestone from Sicily have $\delta^{13}C$ at -28.7 ± 8.9 per mil on the PDB scale (Faure, 1986). These indicate that geothermal methane may be enriched amount in ^{12}C relative to methane derive from hydrocarbon of biogenic origin.

The fluctuated values of both stable oxygen and carbon isotope ratios of these carbonate rocks may point to shallow marine origin with fresh-water influx and/or meteoric water supply during accumulation. Low $\delta^{18}O$ values in marine water indicate to a mixed water model (Moor *et al.*, 1988). In addition, traditionally, the isotope compositions of carbon in carbonate rocks tend to show constancy with geologic ages (Viezer and Hoefs, 1976; Faure, 1986, *etc.*) and stable isotope values of both oxygen and carbon have been shown fairly constant in open ocean environment (Taft, 1967). Consequently, the fluctuation of the isotope values of the carbonate succession of the Nam Maholan Formation possibly suggests to partly restricted water circulation of the depositional environment.

Carbonate origin

Marine carbonates are commonly show positive $\delta^{18}O$ values, whereas the non-marine are generally less enrichment $\delta^{18}O$ values. The carbonate succession in the study area is considered as a carbonate of marine origin, and displays average $\delta^{18}O$ value at 23.61 per mil with the maximum and the minimum values at 29.81 and 20.60 per mil on SMOW scale, respectively. These analogous to marine

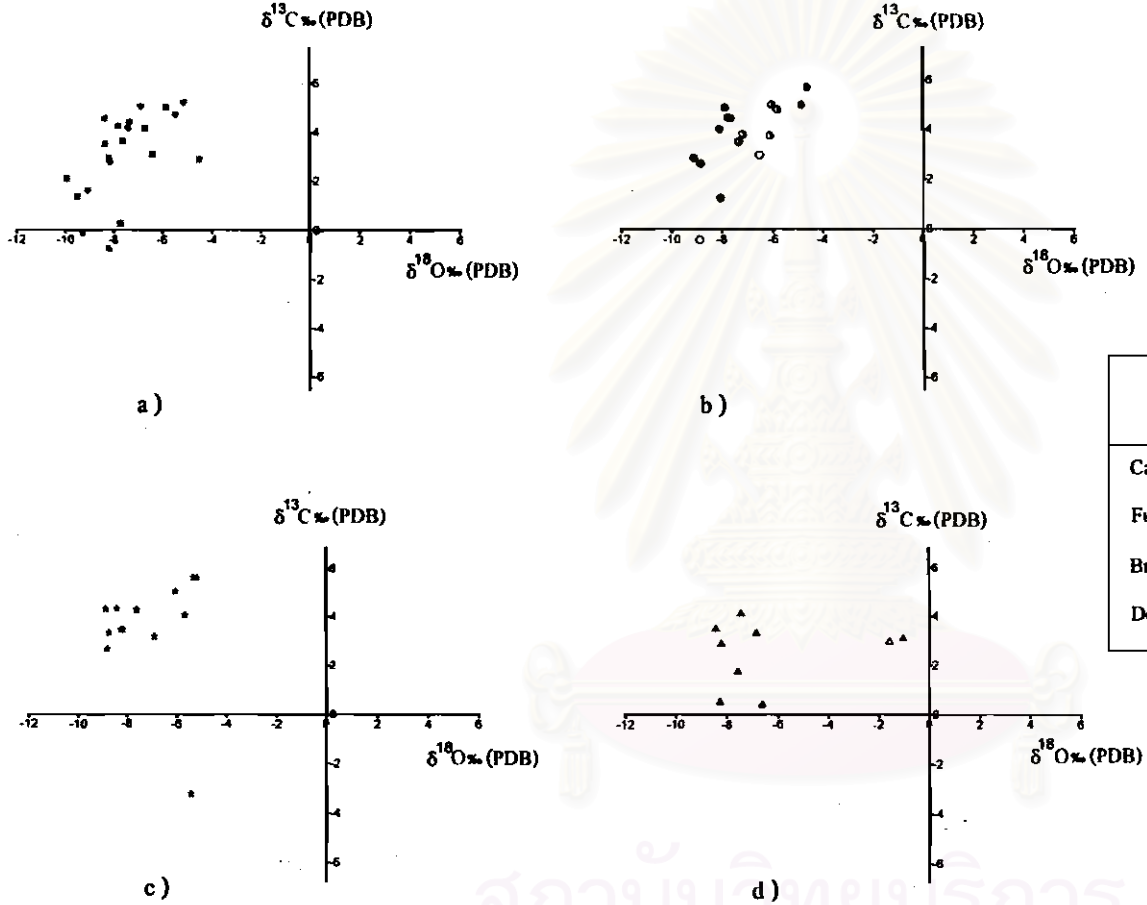
carbonate that generally illustrates positive $\delta^{18}O$ values between +20 per mil and +30 per mil relative to SMOW (Faure, 1986). Subsequently, the analytical values of $\delta^{18}C$ (-0.76 to +5.19 with average of +3.07 per mil on PDB scale) are assigned as marine limestone values corresponding to values reported by Munnich and Vogel (1962) and Deggen (1965).

The relationship of $\delta^{18}O$ and $\delta^{13}C$ plots of the Nam Maholan isotopic values (Fig. 5.5) are mostly located in field of limestone and marble of marine origin with partly performance of oceanic-ridge hydrothermal effect (Fig. 5.6). As shown in Fig. 5.7, the Nam Maholan carbonate Formation displays low negative $\delta^{18}O$ values and positive $\delta^{13}C$ values which are located in field of shallow marine origin and tend to fresh water limestone field.

Possible palaeosalinity

In order to determine palaeosalinity, organisms actually indicated different salinity, particularly in fossiliferous rocks. This feature is generally supplemented by geochemical criterions, such as the interpretation of boron content and stable oxygen isotope significant (Flugel, 1982). The boron content is generally an investigation in palaeosalinity determination, but it is not sensitive to rapid salinity changes in marine water (Boggs, 1987). Isotopically, the fractionation of ^{18}O and ^{16}O during evaporation of surface ocean water is also used in salinity determination. These premise on the decreasing $\delta^{18}O$ values with increasing temperature are based on the constancy of salinity condition. To calculation, the equation which proposed by Epstein and Mayeda (1953) with subsequently modified by Craig and Gordon (1965) have been referred as

$$\delta^{18}O = -21.2 + 0.61\ S$$ where S is the salinity in per mil.



Symbols

	Rock Member		
	Tham Suae Mop	Ban Nong Hin	Phu Pha Khao
Calcite	✱	✲	✱
Fusulinacean	◑	○	●
Brachiopod	⁂		★
Dolomite		△	▲

Fig. 5.5 Variation of $\delta^{18}O$ and $\delta^{13}C$ values of the Nam Maholan Formation.
a) Whole rocks b) Fusulinacean c) Brachiopod and d) Dolomite

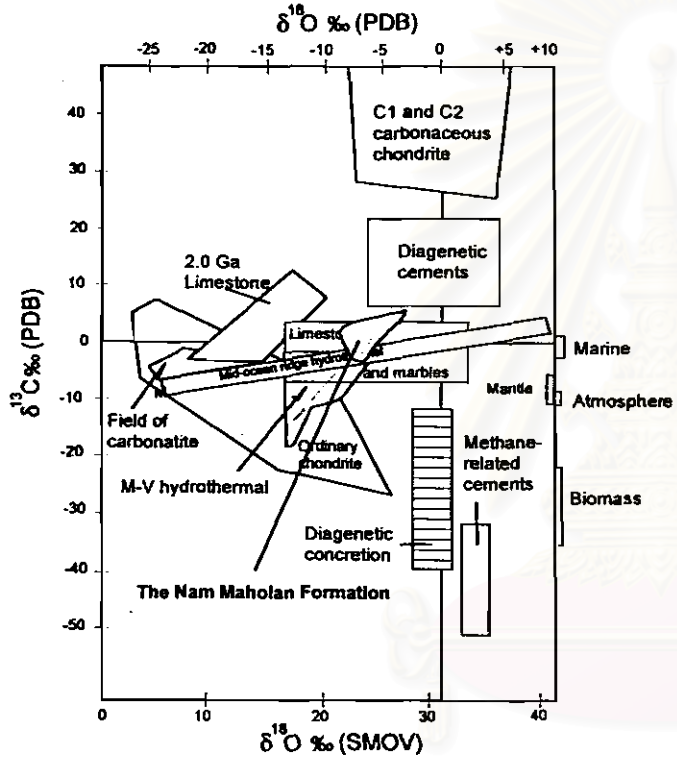


Fig. 5.6 $\delta^{18}O$ vs $\delta^{13}C$ plot showing the composition of carbonate from a variety of environments. The Nam Maholan Formation is located in field of limestone and marble of marine origin with partly Mid-ocean ridge hydrothermal effected.
(diagram after Rollinson, 1993)

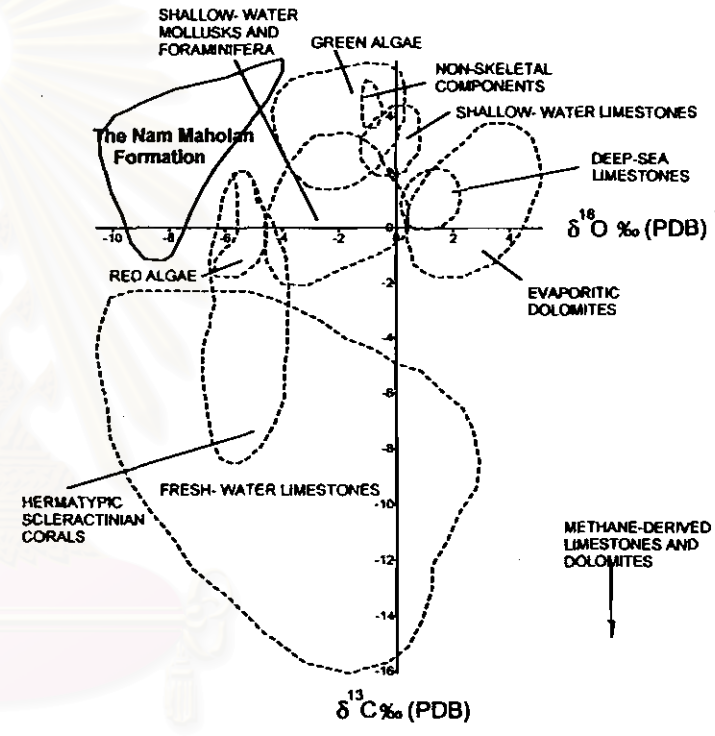


Fig. 5.7 Variation of $\delta^{18}O$ and $\delta^{13}C$ plot illustrated the Nam Maholan Formation display mostly positive $\delta^{13}C$ values and negative values of $\delta^{18}O$. The formation is located in field of shallow marine limestone tend to fresh water limestone field.
(diagram after Boggs, 1987)

For the calculation of salinity based on the $\delta^{18}O$ values by equation above, the Nam Maholan Formation displays the average salinity range between 22.4 and 24.58 per mil with the overall variation values range between 18.44 and 33.08 per mil. These are arrange in normal marine salinity (Flugel, 1982). The illustration of wide variation may suggest contamination of meteoric water that has been interpreted as occasionally fresh water influx, probably indicating the very shallow depositional environment beside terrane that could supply abundant fresh water from the land and/or meteoric in prevailed humid climate condition. In addition, some palaeo-exposures with slightly restricted water circulation is also considered. The calculated salinity values of each carbonate member indicate normal marine and display slightly variation of average values from the Tham Suae Mop Member, the Ban Nong Hin Member, to the Phu Pha Khao Member.

Probable paleotemperature

The accuracy of paleotemperature determination of skeletal calcium carbonate is limited by several important conditions, such as 1) the $\delta^{18}O$ value of carbonate precipitate with surrounding sea water are neighter crystallization nor diffusion in initial isotope ratios, 2) the calcium carbonate secreted by some organisms is not in isotopic equilibrium with water, and 3) the effect of the mineral composition of carbonate on the fractionation of oxygen (Rollinson, 1993; Taft, 1967; Degens, 1965).

In order to calculate the paleotemperature, the equation expressed by Epstein *et al.* (1953) and modified by Craig (1965) has been adopted to determine temperature based on the $\delta^{18}O$ values of skeletal calcium carbonate (Faure, 1987). This equation is

$$t^{\circ}C = 16.9 - 4.2 (\delta c - \delta w) + 0.13 (\delta c - \delta w)^2$$

where δc is the corrected $\delta^{18}O$ of CO_2 obtained from the carbonate by reaction with phosphoric acid at 25°C with respect to the mass spectrometer working standard gas.

The δw is the corrected $\delta^{18}O$ of CO_2 equilibrated isotopically at 25°C where the carbonate was precipitated measured against the same mass spectrometer working-standard gas used for the carbonate analysis.

According to the heaviest oxygen isotope ratio, the calculated accumulating temperatures of the Nam Maholan Formation from whole rocks, fusulinaceans, and brachiopods, display paleotemperature at 36.56 °C, 36.61 °C, and 42.03 °C, respectively. They may not suggest original temperatures of carbonate precipitation. However, they probably imply carbonate precipitation under re-equilibrium condition at relatively elevated temperatures.

The dolomite displays 25.64 °C and 21.31 °C of calculated temperatures of the heaviest isotope ratio from the the Ban Nong Hin and Phu Pha Khao Members. These values may point to the difference of original stage and re-equilibrium of dolomitization.

Isotopic values with associated stratigraphy

The varion of oxygen isotope values in sea water where the calcium carbonate precipitation depends largely on the $\delta^{18}O$ value of sea water at the site of deposition (Rollinson, 1993).

The isotopic results of whole rock analysis relationship with stratigraphy are illustrated in Fig. 5.8. Both oxygen and carbon isotope values display subsequently decreasing upward stratigraphicallty and fluctuation. The heaviest

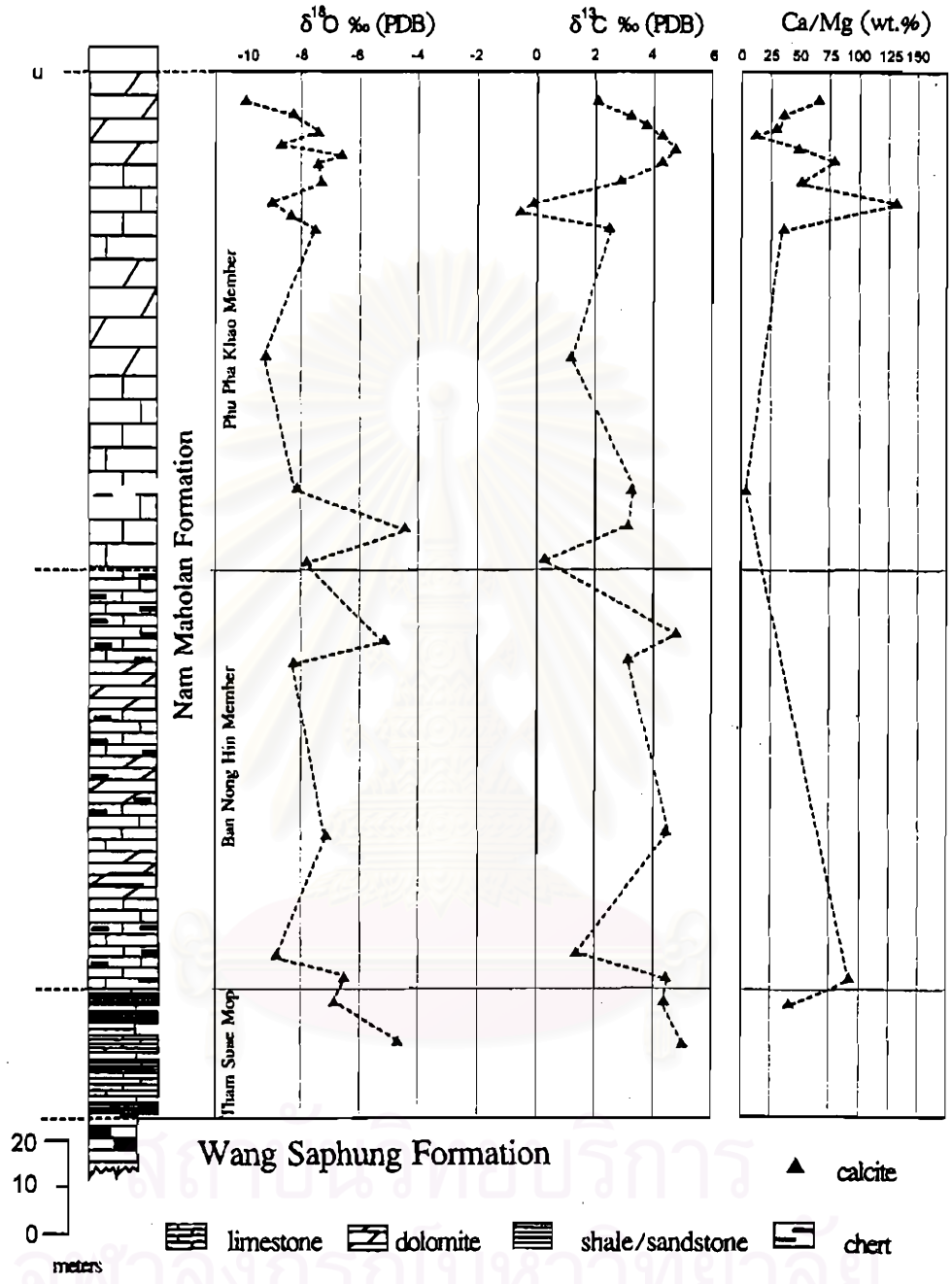


Fig. 5. 8 Isotope values of whole-rock analysis demonstrating fluctuation of the values throughout the stratigraphic column and tend to decline upward stratigraphy. Ca/Mg ratios display fluctuation values at the top of the Phu Pha Khao Member.

carbon isotope value is identified at the middle part of the Tham Suae Mop Member and the heaviest value of oxygen isotope is identified at the lower part of the Phu Pha Khao Member. The isotopic ratios are always shown abundant declining values near the boundaries of members. The abundant decline abruptly values are present near the boundary between bottom of the Phu Pha Khao Member and the top of the Ban Nong Hin member as well as between the bottom of the Ban Nong Hin and top of the Tham Suae Mop Member.

The heaviest isotopic value of fusulinacean is located at the middle part of the Phu Pha Khao Member (sample no. 23). The lowest value of carbon isotope is located at the middle part of the Ban Nong Hin Member, whereas the lowest oxygen isotope is located at the uppermost part of the Phu Pha Khao Member (Fig. 5.9). These isotope values tend to decline in an upward sequence with a wide variation and fluctuation. However, located at the lower part of the formation, the Tham Suae Mop Member displays increasing isotope value to the top of the member with small fluctuation.

The isotope values of brachiopod shows slightly decreasing values from the bottom to the top of stratigraphy (Fig. 5.10). The abruptly low anomalous values of carbon and oxygen isotope ratios are located near the lower boundary of the Phu Pha Khao Member. The 2 analytical results from the upper part of the Tham Suae Mop Member shows their trend increasing upward stratigraphically.

The isotope values of dolomite exhibit abruptly low anomalous values from the top of the Ban Nong Hin Member to the bottom of the Phu Pha Khao Member (Fig. 5.11). The high anomalous values are illustrated at the middle part of the Phu Pha Khao Member. These isotope values exhibit tend to decline in an upward stratigraphic sequence.

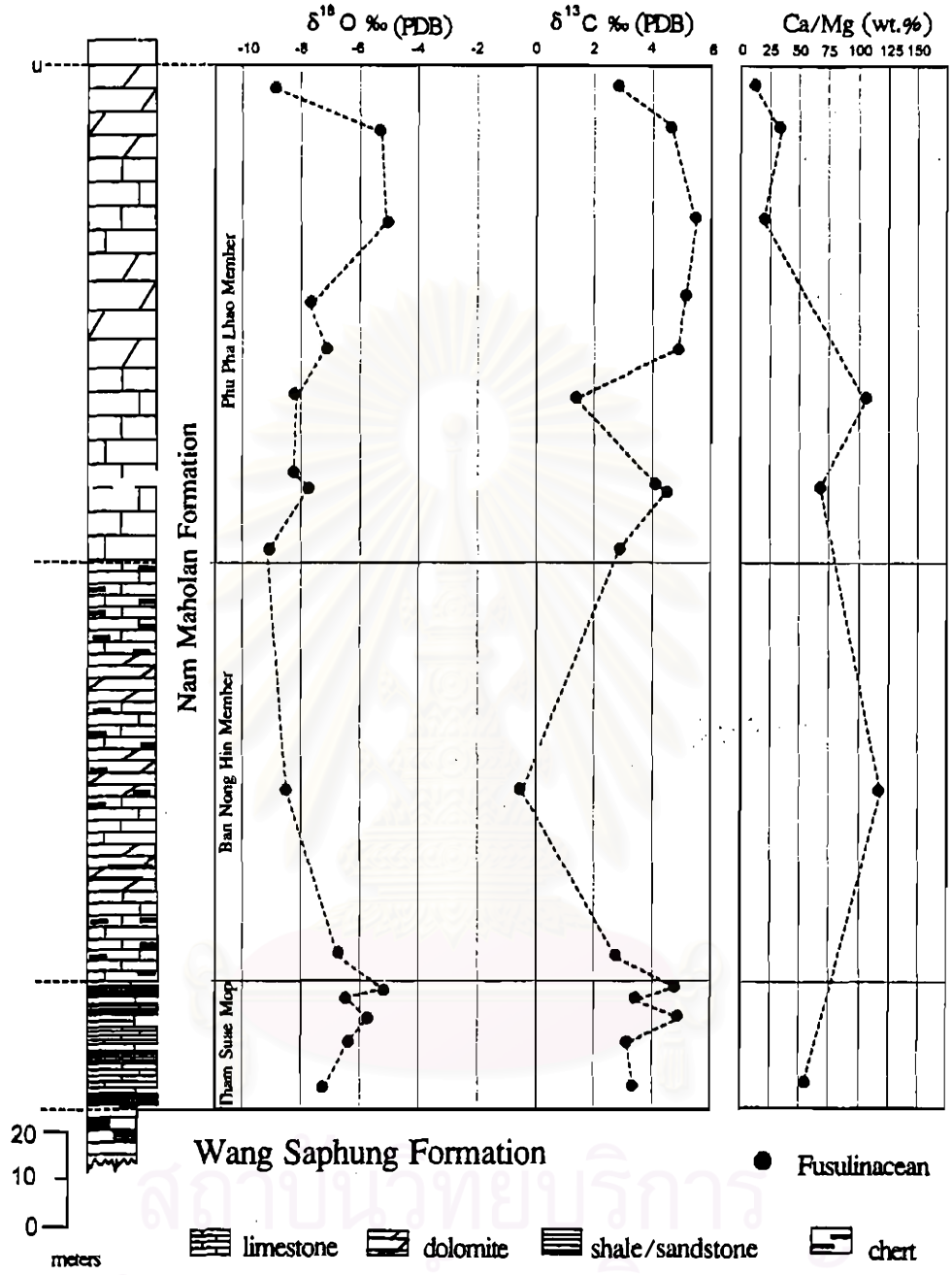


Fig. 5. 9 Isotope values of fusulinacean in correlation with the composite column. Both oxygen and carbon isotope values tend to decline upward stratigraphy as well as Ca/Mg ratios.

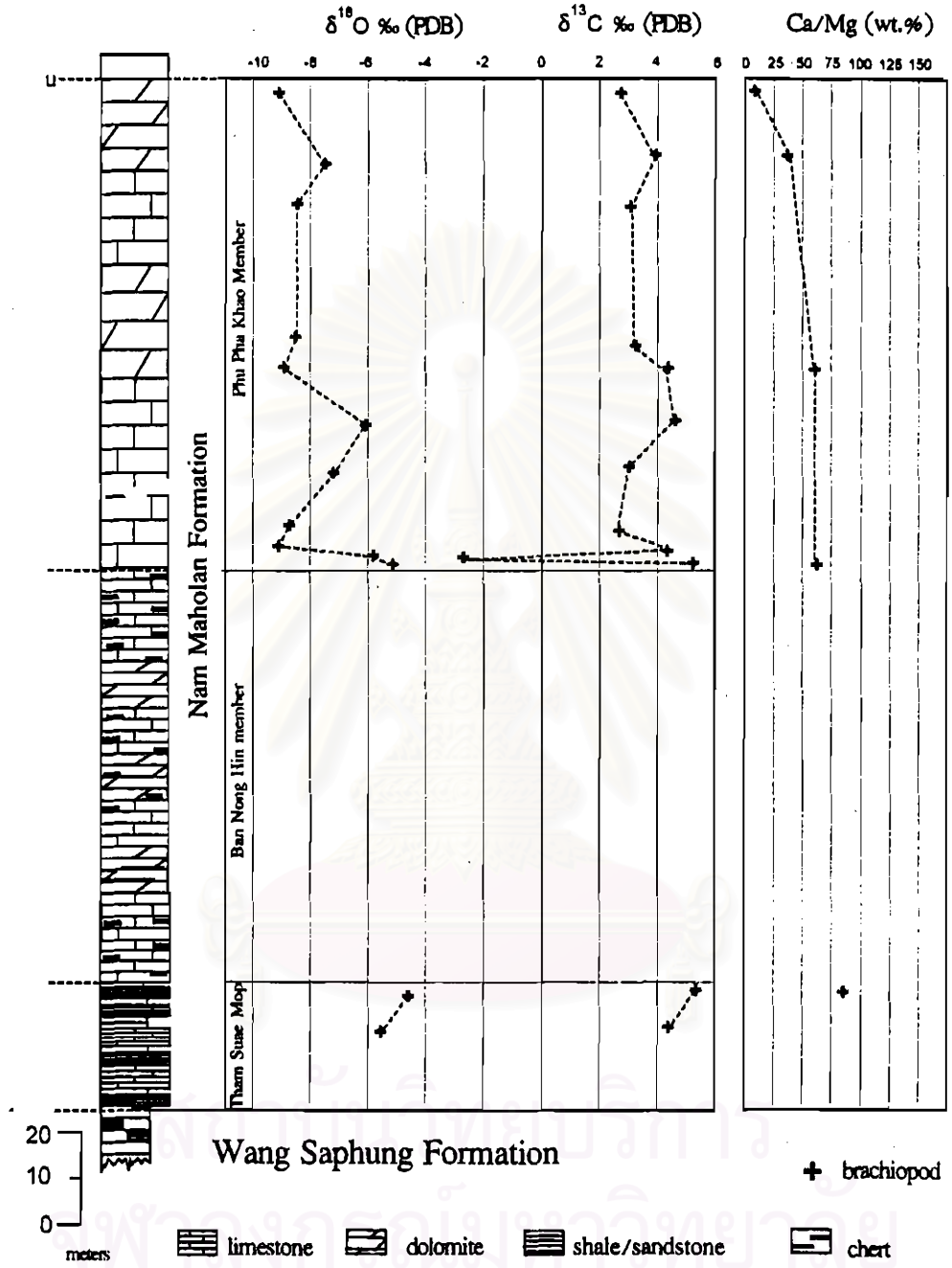


Fig. 5. 10 Variation of isotope values of brachiopod illustrating declination of values upward in the stratigraphic column. Note that the isotope ratios demonstrate abruptly low anomalous values at lower sequence of the Phu Pha Khao Member. Ca/Mg values tend to decline stratigraphically upward.

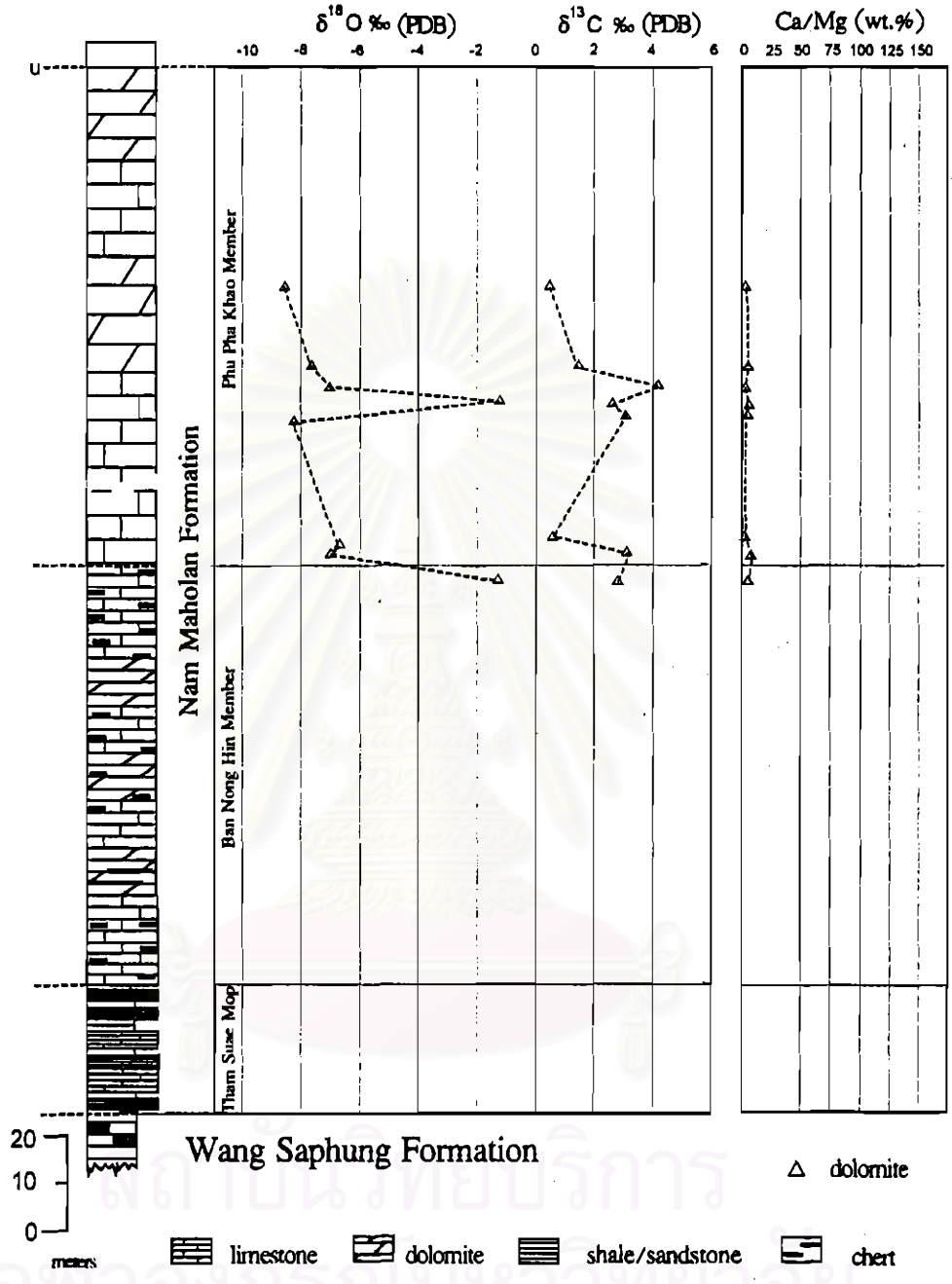


Fig. 5. 11 Isotope values of dolomite illustrating high anormalous values at the middle part of the Phu Pha Khao Member, and between top of the Ban Nong Hin Member and bottom of the Phu Pha Khao Member. The values exhibit the declining upward stratigraphically and fluctuation. Ca/Mg values tend to constancy throughout the stratigraphy.

Summary

The palaeoenvironment is displayed by a continuous sequence of carbonate accumulation in a shallow marine environment. Isotopic results demonstrate the average value of oxygen isotope ratios ranging from -7.51 to -6.20 per mil (PDB) with average of the formation -6.97 per mil (PDB) and carbon isotope values vary from +2.54 to +3.67 per mil (PDB) with average of +3.20 per mil (PDB). These indicate the carbonate of marine origin. The calculation of possible salinity values are between 18.44 and 33.08 per mil. indicating a normal marine salinity with some brackish water. The declined values in an upward stratigraphy and fluctuation may be a result of contamination of occasionally fresh-water influx, regarding to probably palaeo-exposure due to regression and/or slightly uplifted depositional basin. The oxygen isotope values suggest to precipitation of carbonate under re-equilibrium condition relatively elevated temperature. The calculated temperatures are mostly above 35°C, although they may not indicate original accumulating temperature, however, these probably advocate a warm climatic condition during Late Carboniferous (Gzhelian) to late Early Permian (Yahtashian) Period. Additional fluctuation pattern of both oxygen and carbon isotope values probably indicate partly restricted water circulation of the depositional environment.