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四川甘溪泥盆系观雾山组白云岩特征与其形成条件的关系

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内容提要　本文通过沉积环境分析，X射线衍射、扫描电镜、同位素及阴极发光分析，讨论了甘溪泥盆系观雾山组白云石的晶体形态及大小、有序度、碳酸钙克分子含量，同位素特征及阴极发光特征与形成条件的关系。中晶白云岩及细晶白云岩分别产于生物层及潮坪环境，为成岩早期地下淡水与海水混合白云岩化作用的产物。低的碳酸钙克分子含量，中—弱的阴极发光强度及低的$\delta^{18}O$、$\delta^{13}C$值。微晶白云岩形成于泻湖环境。白云石具他形粒状晶，差的有序度，高的碳酸钙克分子含量，强的阴极发光强度及高的$\delta^{18}O$、$\delta^{13}C$值，为准同生期高Mg^{2+}/Ca^{2+}值卤水交代碳酸钙软泥形成。

主题词　生物层　泻湖　潮坪　白云岩　有序度　碳酸钙克分子含量　阴极发光

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THE CORRELATION BETWEEN THE DOLOMITES AND THEIR FORMING CONDITIONS IN THE GUANWUSHAN FORMATION (MIDDLE DEVONIAN) GANXI, SICHUAN, CHINA

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INTRODUCTION

It is known that most of natural dolomites are not ideal ones having a ordering three-layered arrangement and being stoichiometric, which range approximately from 0.3 to 1 in ordering degree and from 58 to 50 mole percent $CaCO_3$ in composition.Since the metastable dolomite phase is less stable than structurally and pcompositionally ideal dolomite,it will gradually stablize into the ideal one wh ich has the lowest free energy possible for any combination of subequal amounts of $CaCO_3$ and $MgCO_3$ under sedimentary conditions.

The structure and composition of dolomites were controlled by varied geological conditions and the concerned specialists have not yet fully answered the question: what are the most important conditions under which this stablization takes place? In the case studied in this paper,dolomites with the same age from one depositional system, does there exist a corelation between the circumstances in which the dolomites were formed and the strcture, composition and other mineralogical characters? In an attempt to answer part of this question we examined the ordering degree, $CaCO_3$ mole content, crystal sizes and forms, cathodoluminescing intensity and isotope values of dolomites formed in various depositional environments from the Guanwushan Formation of Middle Devonian of Ganxi section, located in Beichuan County, Sichuan Province, South China. We will discuss the relationship between the crystal sizes and forms, ordering degree, CaCO 3 mole content, cathodoluminescing intensity, isotope values and th eir forming conditions of the dolomites.

DEPOSITIONAL ENVIRONMENT

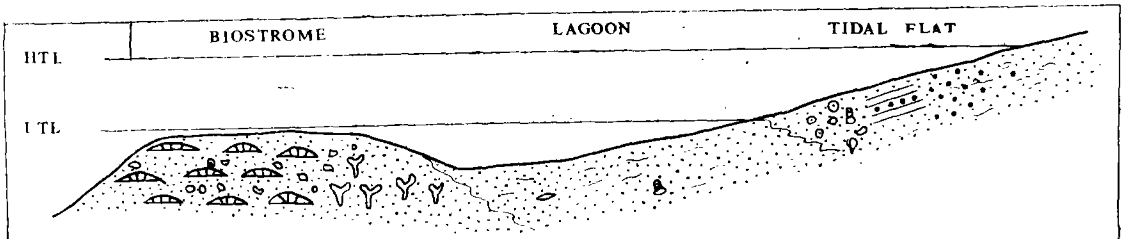
The Guanwushan Formation of the Ganxi section can be subdivided into threeparts: a lower lagoonal part, a middle biostromal part and a upper intertidal part (Fig. 2).

(1) Biostrome

The rocks of the lower part of Guanwushan Formation were deposited in a biostrome environment. The individual thick beds cover large area in very similar lithofacies and hence do not represent proper reefs. The principal lithology is bindstone, bafflestone, bioclastic packstone, a small amount of wackestone and a lenticular body of oolitic grainstone. Usually the bindstone and bafflestone display massive bedding (photo. 1). The main fossils are tabular, spherical and dendritic Stromatoporoids, Corals, Brachiopods, Crinoids, Bivalves, Gastropods and others. Stromatoporoids, in life position, are the prevailing biostrome-forming organisms. A strong dolomitization is very common throghout the rocks in this environment, forming medium crystalline dolomite which preserves most sedimentary structures and also considerable amounts of the above fossils (Photo. 2)

(2) Lagoon

The rocks of the middle part of Guanwushan Formation were deposited in lagoonal environment. The interbedding of mudstone, a small amount of wackestone and micrite dolomite make up this part. All these dark coloured rocks contain few fossils.The pyrite (single crystals and framboidal aggregates, Photo. 3—4)



	BIOSTROME		LAGOON	TIDAL FLAT
prevailing Rock types	Bindstone, Bioclastic Bafflestone Packston, Dolomite	Wackestone Dolomite	Mudstone, Argillaceos Mudstone Wackestone, Dolomite	Wackestone Mudstone, Dolomite
Fossils and othere Grains	Tabular + Spherical Stromatoporoids Corals Brachiopobs Crinoids Bivalves Gastropods	Dendritic Stromatoporoids Corals Brachiopods Crinnoids Bivalves Gastropods	Brachiopods Crinoids Bivalves Ostracods Gastropods Corrals a few Onkoidz	Brachiopods Corals Crinoids Ostracods Calcisphere Pellets and a few Onkoids
Fossils Content	Abundant		Few	Some
Sedimentary Structures	Thick Bedded		Horizontal laminated bedding	Banded Bedding, horizontal Laminaten Bedding, Fenestrol Laminated Bedding
Ordering degree of Dolomite	Good (Average, 0.99)		Pooor (Average, 0.59)	Good (Average, 0.97)
$CaCO_3$ Mole Content of Dolomite	50.5		53.2	50.3
$\delta^{18}O$ average‰)	−6.06		−2.18	−5.81
$\delta^{13}C$ (average‰)	+1.57		+1.94	+0.807
Horizon	Lower most part of the Guanwushan Formation	Lower most part of the Guanwushan Formation	iddle part of the Guanwushan Formation	Upper part of the Guanwushan Formation

Fig. 1 The deposional pattern of the Guanwushan Formation, Middle Devonian of Ganxi, Sichuan, China

was frequently found in both limestone and dolomite of this environment. The laminated bedding is the most common structure in the rocks. It is obvious that the lagoon was a restricted and reducing environment with lower energy and salinity.

(3) Tidal flat

The rocks of the upper part of Guanwushan Formation were deposited in a tidal flat environment. The prevailing rock types are pelletic and bioclastic wackestone, mudstone and fine crystalline dolomite. The main fossils are Crinoids, rals, Brachiopods and calcispheres. Spores (Photo. 5) were often found in the rocks. Both banded bedding and laminated bedding are very common structures. However, we did not find the exposed structures, such as mud cracks and birds eyes, so there was no supratidal zone developed in this area during the Guanwushan period.

METHODS EMPLOYED

Each sample of dolomite for X-ray diffraction analysis was crushed and powdered into the size less than 20μm in diameter. Consequently, the powders were leached in 2% acetic acid for ten days in order to remove the calcite remained in dolomite. Finally the powders were filtered and dried in an oven below 60℃. The diffraction pattern of every sample was registered upto 46° (2θ). In order to determine the intensity ratio of 015 and 110 (I015/I110) more exactly, the interval from 33° (2θ, Cu, Kα) to 40° (2θ, Cu, Kα) was enlarged. To determine the CaCO3 mole content of dolomite, sodium chloride was used as internal standard. Part of the X-ray diffraction diagrams are shown in Fig. 2.

Uncovered polished thin sections were used for cathodoluminescent analysis. The instrument employed for cathodoluminescence is "III X II—TYPE" made in Chengdu College of Geology, and "LEITZ VARIO ORTHINAT 2" with automatic microscope camera and "LABORLUX 12" microscope. The oper-ating voltage ranged from 10kv until 18kv and the current density from 400uA until 700uA.

RESULTS AND INTERPRETATION

The dolomites of the Guanwushan Formation were classified into three types according to their crystal sizes and to the environments where they occurred: medium cryystalline dolomite in biostromes, micrite dolomite in lagoons and fine crystalline dolomite in tidal flats. The main characters and the analysis resultsof them are shown in Table 1.

Micrite dolomite which occurred in lagoon has 5-60μm crsytal sizes, hypidiomorphic to xenomorphic crystal forms (Photo.6), poor ordering degree (average: 0.59) and high $CaCO_3$ mole content (average: 53.2%). Its $\delta^{18}O$ values range from −0.04‰ to −4.53‰ (PDB), average −2.18‰, and $\delta^{13}C$ values from +1.28‰ to +2.63‰, average: +1.94‰. As described before, the lagoon where this type of dolomite was formed was a restricted and reducing environment with low energy and abnormal salinity. The Mg^{2+}/Ca^{2+} ratio in it must be higher than that in normal sea water. The dolomitization under these conditions probably took place during penecontemporaneous stage. The nucleation rate, therefore, must be high due to the easy access of the water having a high Mg^{2+}/Ca^{2+}ratio through the soft sediment. For this reason the crystal size is small, and for the same reason of high nucleation rate, the calcium, magnesium and carbonate ions had no enough time to arrange themselves structurally and compositionally in the lowest energy law, so this type of dolomite has a very poor ordering degree and a high $CaCO_3$ mole content.

On the other hand, medium crystalline dolomite which occurred in biostromes has relatively coarse crystal sizes, 100—500μm, excellent rhombohedral crystal forms(Photo.7), very good ordering degree (average: 0.99) and lower, almost stoi chiometric $CaCO_3$ mole content (average: 50.5%). The $\delta^{18}O$ values range from −1.85‰ to —9.14‰, average −6.06‰, $\delta^{13}C$ values are from +0.24‰ to +2.45‰, average +1.57‰. This type of dolomite, containing abundant reef-forming organ-

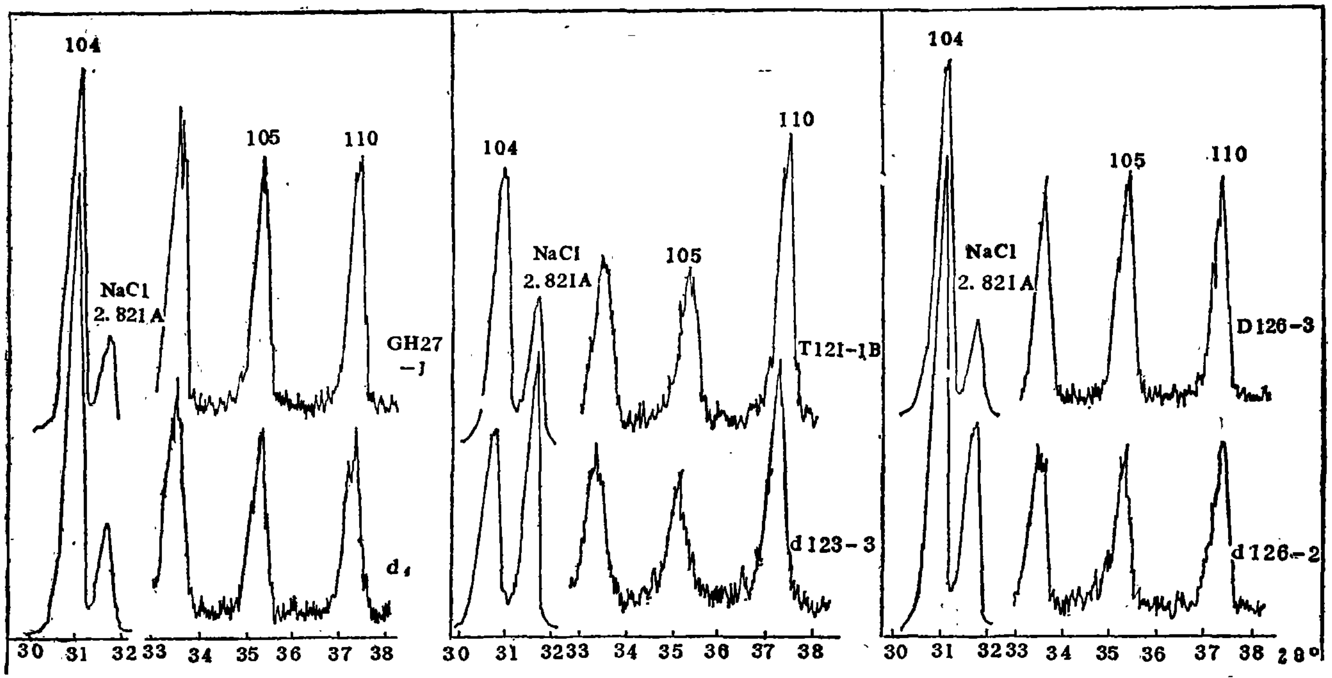


Fig. 2 X-ray diffraction diagrams. From 30° to 32° (2θ), sodium chloride was used as internal standard and from 33° to 38° (2θ) the intensity was enlarged. The samples, GH27-1 and d4 are biostromal dolomite, the samples, T121-1B and d123-3 are lagoonal dolomite and the samples, d126-3 and d126-2 are intertidal dolomite

Table 1 The main characters of the three dolomite types in the Guanwushan Formation

Samples Number	Lithology	Petrological Characters of The Dolomite Stone: The Original Rocks	Sedimentary Structures	Fossils and other Grains	Depos Envir	Mineralogical Characters of the Dolomite: Crystal Morphology	Crystal sizes (μ)	The Data of X-ray Diffraction: d104(Å)	CaCO₃(%)	I015	I110	The Degree of Order	Isotopic Data (PDB‰): δO¹⁸	δC¹³
d4	Medium Crystalline Dolomite	Boundstone	Massive Bedding	Tabular, Spheric aland Dendritic stromatopo-roids, Corals Brachiop-oPs, Crinoid, Bivalves	Biostrome and Patch Reef	Euhedral Rhombi Crystals	100—500	2.888	50.6	7.61	7.68	0.991	-5.81	+2.45
G13-1		Boundstone						2.885	49.5	6.70	6.71	0.999	-1.85	+0.245
GH27-1		Wackestone						2.890	51.2	4.99	4.91	0.998		
Bd119-1		Bafflestone						2.888	50.6	6.75	7.07	0.954	-9.05	+1.39
d119-3		Packstone						2.888	50.6	9.15	9.15	1.00	-4.54	+1.52
Average									50.5			0.99	*-6.06	*+1.57
T121-1B	Micrite Dolomite	Mudstone	Laminated Bedding and intercalated Marls	Almost no Fossils a few Onkoids	Lagoon	Hypidiomorphic-Xenomorphic Granular Crystals	5—60	2.892	52.0	6.51	11.91	0.517	-4.53	+2.63
T123B		Mudstone						2.892	52.0	9.15	11.71	0.721	-0.04	+1.97
T123C		Mudstone						2.899	54.4	5.11	9.62	0.531		
d123-3		Mudstone						2.898	54.2	5.09	10.49	0.485	-1.95	+1.28
Average									53.2			0.59	*-2.18	*+1.94
d126-2	Fine Crystallnie Dolomite	Mudstone	Banded Bedding Laminated Bedding Fenestra laminated Fabric	Brachiopods Corals Crinoids Pellets, Onkoids	Tidai Fiat	Hypidiomor phic Granular Crystals	40—200	2.888	50.6	7.05	7.05	1.00		
d126-3		Mudstone						2.883	48.9	5.01	5.51	0.909	-7.17	-2.22
T127B		Mudstone						2.890	51.3	7.12	7.18	0.992	-2.51	+2.65
Average									50.3			0.97	*-5.81	*+0.807

* including some other dolomite samples (see Fig.3)

isms and other fossils, was formed by replacement of reef limestone, probably during early diagenesis in the phreatic zone.Since the reef limestones had good porosity and permeability and were the most elevated area of the entire depositional system of that thim, they were easily leached by meteoric waters and sea water.The mixing soluton, having less Mg^{2+}/Ca^{2+} ratio than normal sea water, resulted in a low nucleation rate of dolomite,so the dolomite formed under these circumstances has relatively large crystals.For the same reason of low nucleation rate, the calcium, magnesium and carbonate ions had enough time to arrange themselves structurally and compositionally in the lowest energy conditions. Therefore it also has excellent euhedral rhombohedral crystal forms, a good ordering degree and a low $CaCO_3$ mole content.

Another evidence indicating that the dolomitization in the biostromes was influenced by meteoric waters is the isotope values. The carbon isotopic values are distributed within a narrower range (Fig. 3), from +0.245‰ to +2.65‰,except one sample with -2.22‰. Anyway the average value of $\delta^{13}C$ of dolomite in biostrome is slightly lower than that in the lagoon. The oxygen isotopic values range from -0.04‰ to -9.14‰. The average value of $\delta^{18}O$ of dolomite in biostrome is much lower than that in lagoon (Fig. 3), the former being -6.066‰, the later -2.18‰.

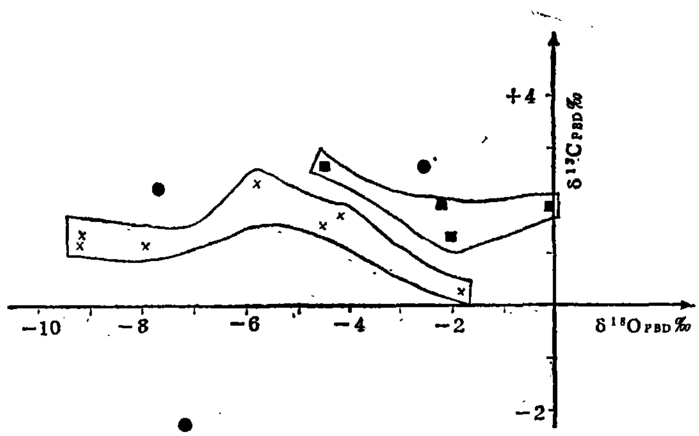


Fig. 3 Distridution of $\delta^{18}O$ and $\delta^{13}C$ values in the three types of dolomite of the Guanwushan Formation.

dolomite in biostrome as mpl marked with cross, dolomite in lagoon samples, markedwith square dolomite in tidal flat.samples marked with solid cirdes

The cathodoluminescence colour of most dolomites in Guanwushan Formation is brick red but the intensity of them is different (Table 2).The cathodoluminescence intensity was measured by means of the time of exposure under the same conditions, that is, the same magnification, same beam voltage and same current density.The brighter the intensity is, the shorter the time of exposure is.The average exposure time of the micrite dolomite in the lagoon is 2.1 minutes and that

Table 2 The time of exposure of different types of dolomite under the same operating conditions for coloured microphotographs of cathodoluminescence (Kodak film 400 ASA)

Sample number	Dolomite types	Magnification	Voltage (kV)	Current (μm)	Exposure time (m)
d 2	medium crystalline, dolomite in biostrome	5 × 10	12.5	500	8.2
d 6					5.8
G11- 2					6.7
T118- 3 A					8.9
T118- 3 B					9.1
T119A					5.0
Bd119-1					5.1
GH27- 1					7.1
average					7.0
T121 A	micrite dolomite in lagoon	5 × 10	12.5kV	500	3.0
d121- 1					0.85
d121- 2					1.9
T123A					2.5
T123B					2.4
T123C					2.1
d123- 1					1.6
d123- 3					2.3
average					2.1
T126A	fine crystalline dolomite in tidal flat	5 × 10	12.5	500	5.6
d126- 1					6.8
T127A					4.8
T127C					7.1
d127- 2					5.6
d127- 3					5.7
average					5.9

of the medium crystalline dolomite in biostrome is 7.0 minutes, so the dolomite in lagoon luminesces more brightly than the dolomite in biostrome. The intensity of cathodoluminescence is principally decided by activator and quencher. In carbonate rocks the most important quencher is iron in the carbonate lattice. Iron concentrations in excess of 0.3 percent quenched the Mn^{2+} -induced cathodoluminscence (Lond and Agrell, 1965). Therefore the dolomite in lagoon probably contains less iron than that in biostrome. The reason is probably that the micrite dolomite in lagoon was formed in the earlier diagenetic stage than the medium crystalline dolomite in biostrome.

Most analysis results of fine crystalline dolomite that occurred in tidal flat environment are similar to the dolomite in biostrome (Table 1), which has good ordering degree, low $CaCO_3$ mole content and low $\delta^{18}O$ values, showing the influence of meteoric water. However, the crystal sizes (40—120μm), crystal forms (dominantly hypidiomorphic granular form, Photo.8), and the cathodolumenescing intensity (Table 2) are between those of dolomite in lagoon and in biostrome. This is probably caused by the intensity and timing of the influence of meteric waters in tidal flat environment which is in strength between those found in lagoon and biostrome.

SUMMARY

The Guanwushan Formation consists of three types of dolomite: medium crystal line dolomite which occurred in biostrome environment, micrite dolomite in lagoon and fine crystalline dolomite in tidal flat.

The first type of dolomite, distributed in the lower part of Guanwushan Formation, is characterized as follow:

1) containing abundant reef-forming organisms and other fossils,

2) 100—500μm in size, euhedral rhombohedral crystal forms.

3) very good ordering degree and low $CaCO^3$ mole content,

4) low $\delta^{18}O$ values and

5) dull intensity of cathodoluminescence.

Second type of dolomite, distributed in middle part of Guanwushan Formation, is characterized as follow:

1) containing few fossils but a lot of pyrite,

2) 5—60μm in size, dominantly xenomorphic granular crystal form,

3) poor ordering degree and high $CaCO_3$mole content,

4) relatively high $\delta^{18}O$ values and

5) bright intensity of cathodoluminescence.

Third type of dolomite distributed in the upper part of Guanwushan Formation, is characterized as follow:

1) containing some fossils,

2) 40—200μm in size, dominantly hypidiomorphic granular crystal form,

3) very good ordering degree and lower $CaCO_3$ mole content,

4) relatively low $\delta^{18}O$ values, low $\delta^{13}C$ values and

5) medium intensity of cathodoluminescence.

The micrite dolomite in the lagoon resulted from the dolomitization by the

solution having a high Mg^{2+}/Ca^{2+} ratio during *penecontemporaneous* stage. The medium crystalline dolomite in biostrome and the fine crystalline dolomite in tidal flat resulted from the dolomitization by meteoric ground waters mixing with sea water during the early diagenetic stage.

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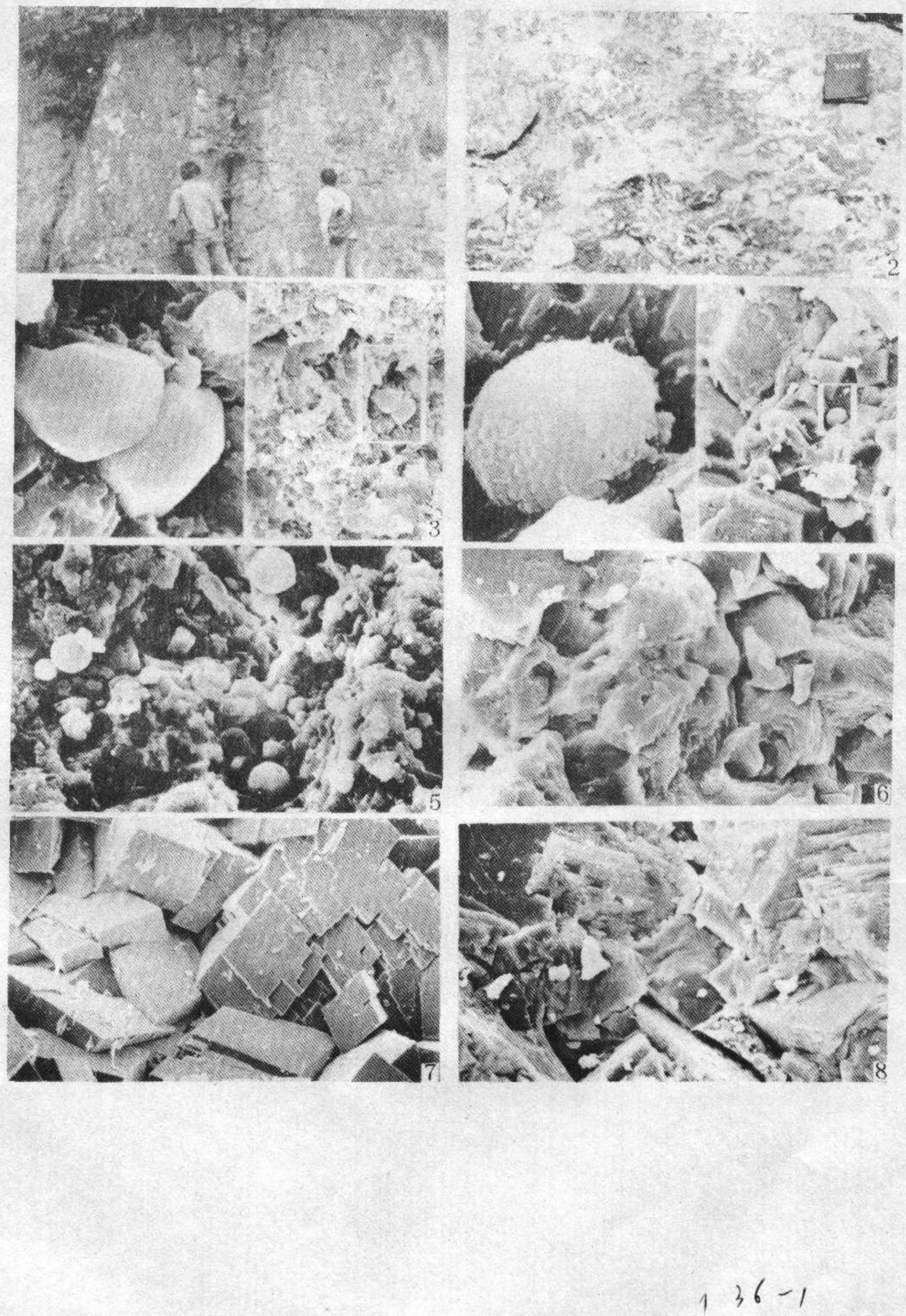

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DOLOMITES AND THEIR FORMING CONDITIONS
ILLUSTRATION OF PHOTOGRAPHS

1. Bindstone, with tabular and spherical Stromatoproids in original growth position, displays massive bedding.

2. Dolomitized in biostrome, medium cristalline, with abundant spherical and tabular Stromatoporoids.

3. Pyrite crystals in lagoonal mudstone, indentified by EDX. SEM-micrograph. Bar scale = 10μm.

4. Framboidal pyrite in lagoonal micrite dolomite. SEM-micrograph. Bar scale = 10μm.

5. The spores in mudstone of tidal flat. SEM-micrograph. Bar scale = 20μm.

6. Showing the excellent rhombohedral crystal form of dolomite in the biostrome. SEM-miorograph. Bar scale = 100μm.

7. Xenomorphic granular crystals of micrite dolomite from the lagoon. SEM-micrograph. Bar scale = 10μm.

8. Hypidiomorphic granular crystal form of the fine crystalline dolomite in tidal flat. SEM-micrograph. Bar scale = 10um.