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SEPIOLITES IN LIUYANG, HUNAN PROVINCE, CHINA

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Abstract

Mineralogical study of sepiolite deposits, which occur in Liuyang, Hunan Province, China, has been conducted. These deposits could be classified into two types, namely, the primary rock type deposit and the clay type deposit. They consist predominantly of fairly crystallized sepiolite with small amounts of talc, calcite and quartz. Presence of marine fossils such as anthozoa, brachiopoda and Fusulina within the deposits indicates their formation under a shallow marine environment.

Introduction

Although sepiolite has been well-studied, some researchers put forth slightly different structure models for the interpretation of their data. The Nagy-Bradley model of sepiolite (Nagy and Bradley, 1955) differs from the later model of Brauner and Preisinger (1956). According to the Nagy-Bradley model, the structure could be either orthorhombic or monoclinic with the preferred space group given as the monoclinic $C2/m$, whereas Brauner and Preisinger (1956) and Preisinger (1959) proposed an orthorhombic structure of space group $Pncn$. With regards to the formation mechanism of sepiolite, several problems remain unsolved. However, the occurrences and the environmental condition in the formation of sepiolites in Liuyang, Hunan Province are clearly observed. This observations lead to the discussion of the formation mechanism of sepiolite in general.

Geological setting

The sepiolite deposits present in the marly section of lower Permian in Liuyang, Hunan Province, China. The ore belt which is 2-14 meters thick is about 6 kms' long elongating from east to west and 0.5-1.7 kms' wide from south to north. The ore bodies exhibit stratified or lenticular shapes. In some parts, the content of sepiolite is more than 20%. Marine fossils such as anthozoa, brachiopods, cephalopods, fusulinids, foraminifers, etc., are rich in sepiolite clay. The ore can be divided into two types, primary rock type and clay type. The primary rock type deposits are composed of massive grey to dark-grey sepiolite-bearing magnesium shales and marls. The content of sepiolite is more than 5%.

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Small amounts of celestite and pyrite are present.

The clay type deposits were formed from primary rock type deposits by weathering. They show various colors such as grey, grey-white, brown-grey and earthy. Sepiolite, talc, calcite and quartz are the main minerals, whereas smectite, kaolinite, muscovite, chlorite, zeolite, and palygorskite occur as secondary minerals. Horizontal beddings rich in marine fossils are mostly present in the ore bodies.

Mineralogical characteristics of sepiolite

1. X-ray analysis

X-ray powder diffraction patterns and the x-ray diffraction data for the two types of sepiolites are given in Fig. 1 and Table 1, respectively. The x-ray powder diffraction data are listed together with Brindley's data (1959). A reflection of $d(110) = 12.2 \text{ \AA}$ which is a characteristic reflection of sepiolite is strong. Lattice constants for sepiolites calculated by using powder data are listed in Table 2. Orthorhombic structure of the Brauner-Preisinger model could be explained all of the observed reflections.

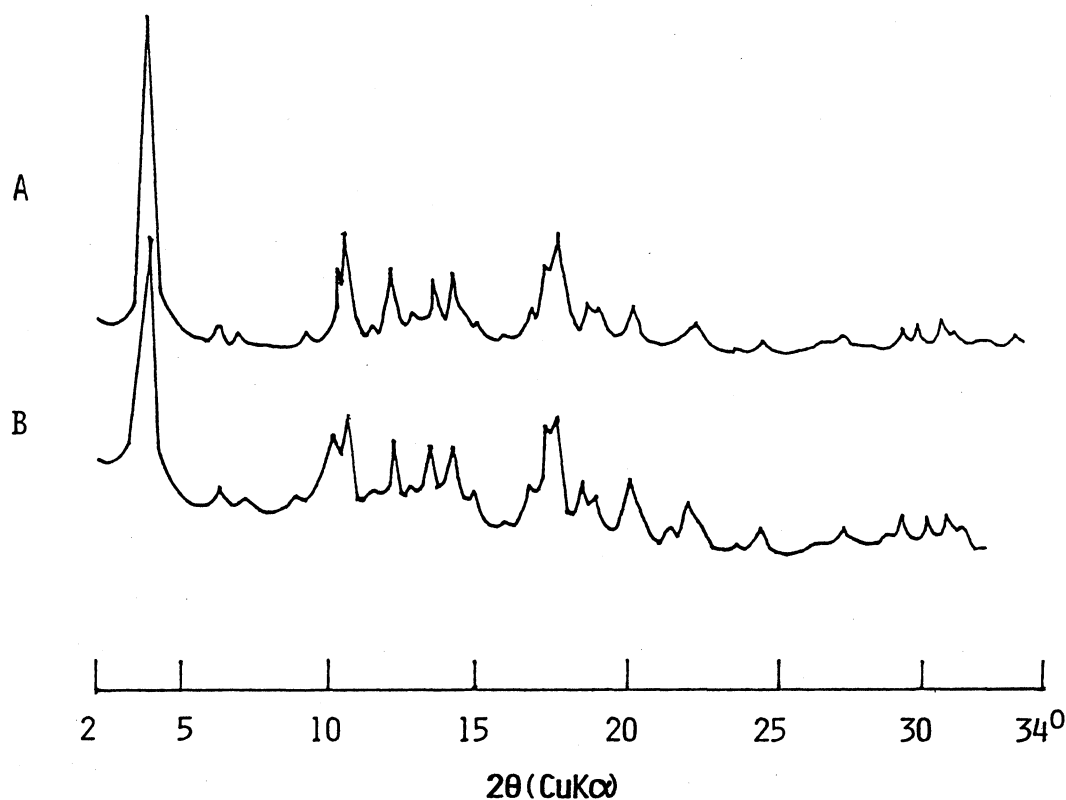


Fig. 1. X-ray powder diffraction patterns for the sepiolites.
A. sepiolite from the primary rock type deposit.
B. sepiolite from the clay type deposit.

Table 1. X-ray powder diffraction data for sepiolites

hkl	1		2		3	
	d(A)	I	d(A)	I	d(A)	I
110	12.05	100	12.2	100	12.25	100
130	7.47	10	7.53	12	7.48	10
200	6.73	5	6.720	10	6.718	8
040						
150	5.01	7	5.000	6	4.988	8
060	4.498	25	4.501	25	4.480	25
131	4.306	40	4.312	40	4.300	40
330	4.022	7	3.988	8	3.989	7
260	3.750	30	3.755	30	3.752	30
241	3.533	12	3.525	10	3.530	10
080	3.366	30	3.365	25	3.360	30
331	3.196	35	3.200	25	3.198	30
261	3.050	12	3.000	10	3.040	10
370	2.932	4				
081	2.825	7	2.825	7	2.826	8
421	2.771	4				
0,10,0	2.691	20	2.690	15	2.680	15
510						
441	2.617	30	2.620	10	2.618	20
281						
530	2.586	NR				
112						
371	2.560	55	2.562	35	2.560	40
191						
132	2.479	5				
202	2.449	25	2.450	20	2.445	20
042						
1,11,0						
222	2.406	15	2.406	10	2.410	10
461						
062						
312	2.263	30	2.263	20	2.260	20
2,10,1						
620						
570	2.206	3				
332						
640						
2,12,0	2.125	7	2.123	5	2.120	8
4,10,0						
082	2.069	20	2.068	10	2.069	15
571	2.033	4				
192	1.957	4	1.960	3	1.957	3
0,14,0	1.921	2	1.920	2	1.920	2
3,13,0						
0,10,2	1.881	7	1.880	1	1.880	1
382						
472	1.818	2			1.815	2
482	1.760	6			1.765	2
492	1.700	10	1.700	10	1.698	10
612						
4,10,2	1.637	3	1.640	1	1.640	1
5,13,0						
3,12,2	1.592	10	1.590	10	1.591	10
662						
403	1.550	15	1.550	10	1.555	10
0,14,2						
682	1.518	15	1.516	10	1.510	12
4,16,0	1.502	8	1.500	10	1.498	12
880						
0,10,3	1.468	4	1.466	10	1.468	10
960	1.416	9				

1. After G. W. Brindley (1959).
 2. Sepiolite from the primary rock type deposit.
 3. Sepiolite from the clay type deposit.
- NR signifies not resolved.

Table 2. Lattice constants for the sepiolites.

	Primary rock type sepiolite	Clay type sepiolite
a	13.403 Å (±0.015 Å)	13.343 Å (±0.01 Å)
b	26.868 Å (±0.013 Å)	26.848 Å (±0.01 Å)
c	5.253 Å (±0.025 Å)	5.267 Å (±0.002 Å)

2. Chemical composition

The chemical analyses data for the sepiolites are listed in Table 3. CaO content in the primary rock type ore is very high. Due to the presence of calcium minerals, the primary rock type ore is high in CaO but relatively low in SiO₂, MgO, Fe₂O₃ and Al₂O₃. Generally speaking, Al₂O₃ content in sepiolites in the studied area is high as compared with previously reported values (Kauffman, 1943 ; Nagy and Bradley, 1955 ; Caillere and Henin, 1961 ; Takahashi, 1966 ; Otsuka et al., 1966 ; Imai et al., 1966 ; Yang, 1980), this is probably attributed to weathering.

Table 3. Chemical analyses data for the sepiolites.

	SiO ₂	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃	FeO	K ₂ O	Na ₂ O	TiO ₂	MnO	CO ₂	H ₂ O(+)	H ₂ O(-)	Total
Primary rock type sepiolite	30.62	1.98	11.63	33.44	0.68	0.28	0.03	0.02	0.05	0.001	8.68	4.52	7.84	99.771%
Clay type sepiolite	46.92	2.85	14.13	10.44	1.25	0.11	0.33	0.15	0.02	0.004	8.76	5.96	8.84	99.764%

3. Dehydration and high temperature phases

Differential thermal analysis curves for the sepiolites are shown in Fig. 2. The curves are almost same. First large endothermic peak is at 114°C for the primary rock type and at 120°C for the clay type.

Endothermic peaks at 340°C, 563°C and 843°C appear at the same temperatures for both specimens.

Thermogravimetric analysis curves for the sepiolites are shown in Fig. 3. Both curves show similar patterns. For the clay type sepiolite, the first weight loss of 8.75% occurs at lower than 250°C, and the weight loss between 250°C and 520°C is 2.75%. Weight loss between 520°C and 840°C is 1.5%, and that above 840°C is 1.05%. The weight loss of 8.75% is attributed to the loss of water, which is physically bounded and absorbed on the external surface of sepiolite and, in the structural channels like zeolitic water. Therefore,

the first weight loss is influenced by the relative humidity. An endothermic peak at 340°C in the DTA curve is attributed to the loss of two of the four water molecules which are weakly bounded. The third endothermic peak at about 563°C is due to the loss of the two others which are more strongly bounded than the former. These water loss did not produce any apparent structural changes, but the sepiolite heated at 340°C could rehydrate and recover its original structure. Sepiolite anhydride obtained at 563°C was irreversible, and the result agreed with that obtained by Nagata et al. (1974). At 843°C, a sharp endothermic peak appears due to the loss of constitutional water or hydroxyl groups. Immediately after the endothermic peak an exothermic peak occurs. It is attributed to the development of magnesium silicate phase. This phase is probably the pre-crystalline phase of enstatite. Enstatite starts crystallizing before 1000°C, and increases in amount up to 1350°C (Grim, 1968). Above this temperature β -cristobalite is formed and this phase lasts until about 1500°C.

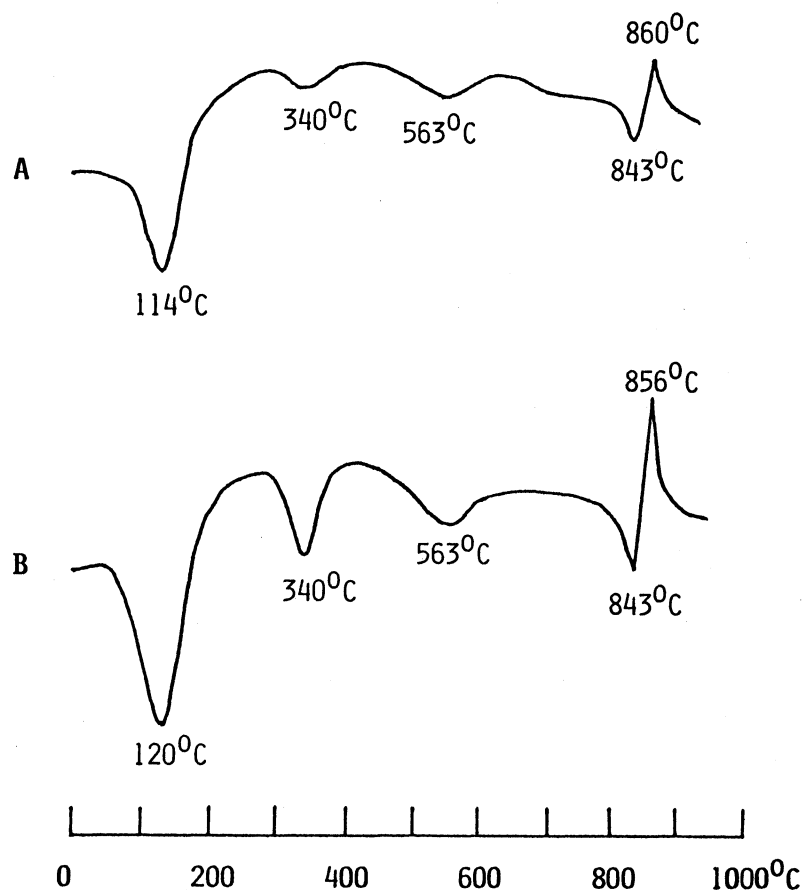


Fig. 2. Differential thermal analysis curves for the sepiolites.
 A. sepiolite from the primary rock type deposit.
 B. sepiolite from the clay type deposit.

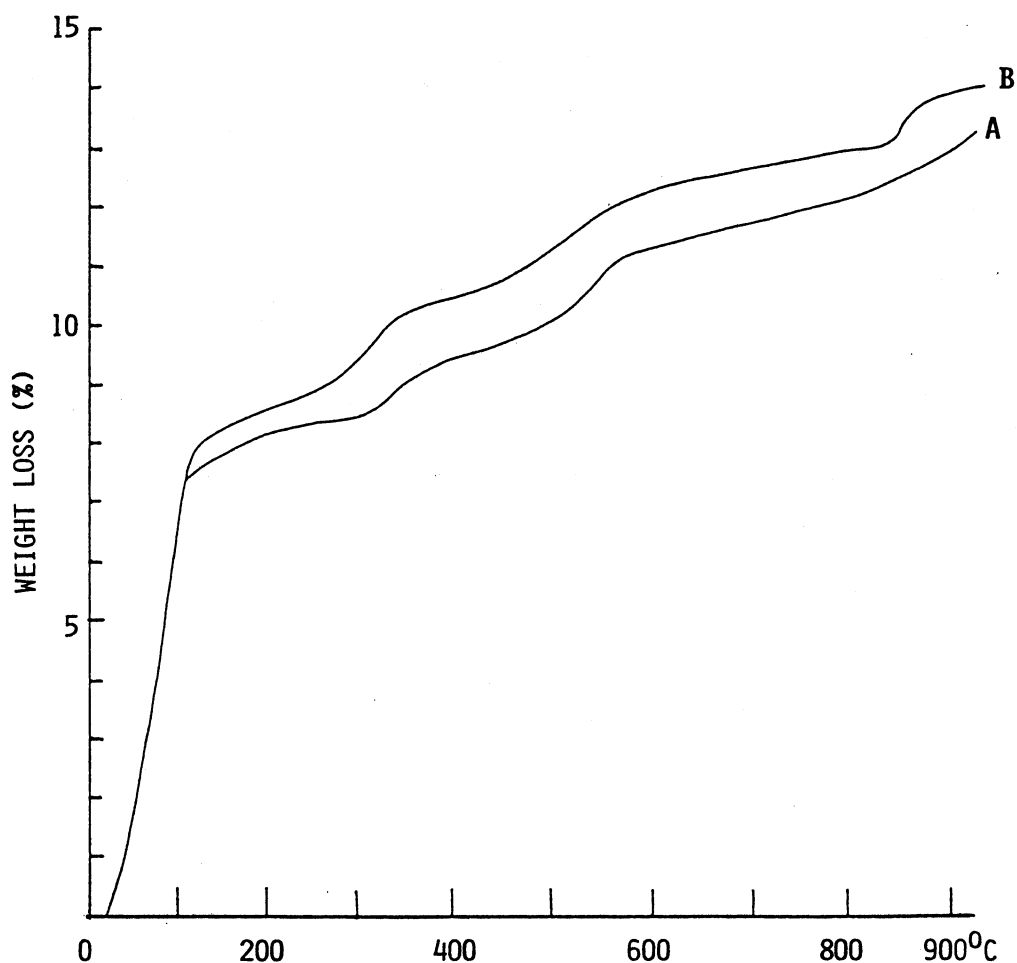


Fig. 3. Thermogravimetric analysis curves for the sepiolites.
 A. sepiolite from the primary rock type deposit.
 B. sepiolite from the clay type deposit.

4. Infrared absorption analysis

As infrared absorption spectra of the two sepiolites are almost same, infrared absorption study for the primary rock type sepiolite was carried out. IR spectrum for the specimen is shown in Fig. 4. A strong absorption band at 3670cm^{-1} is caused by stretching vibration of OH. Absorption bands at 3396cm^{-1} and 3258cm^{-1} may be attributed to zeolitic water (Hayashi *et al.*, 1969). These two absorption bands disappeared when the sample was heated to 450°C , but the 3670cm^{-1} band remained up to 730°C . These results are consistent to those of Hayashi *et al.* (1969). The absorption bands at $1600\text{--}1700\text{cm}^{-1}$ are bending vibration of water. The band at 1658cm^{-1} is due to zeolitic water, and the band at 1631cm^{-1} is mainly attributed to structure water. A very strong absorption band at $1200\text{--}900\text{cm}^{-1}$ is due to Si-O vibration. A strong absorption band between 600 and 400cm^{-1} is due to bending vibration of Si-O.

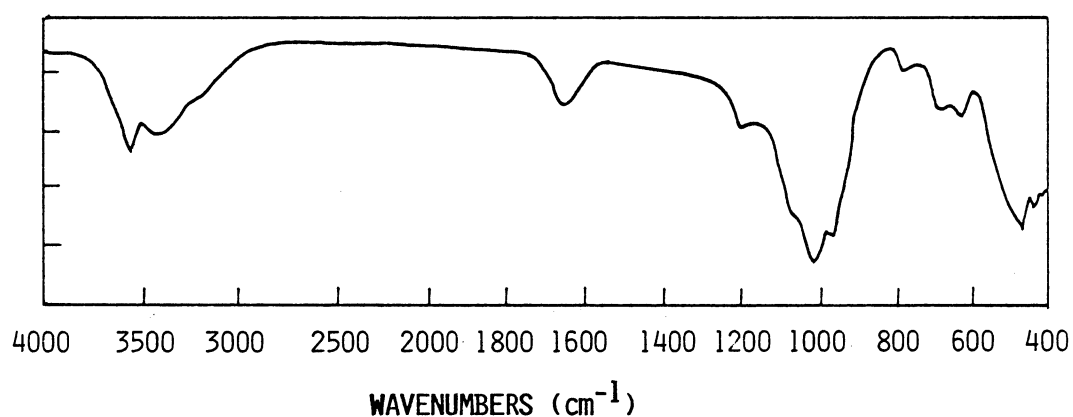


Fig. 4. Infrared absorption spectra of the sepiolite from the clay type deposit.

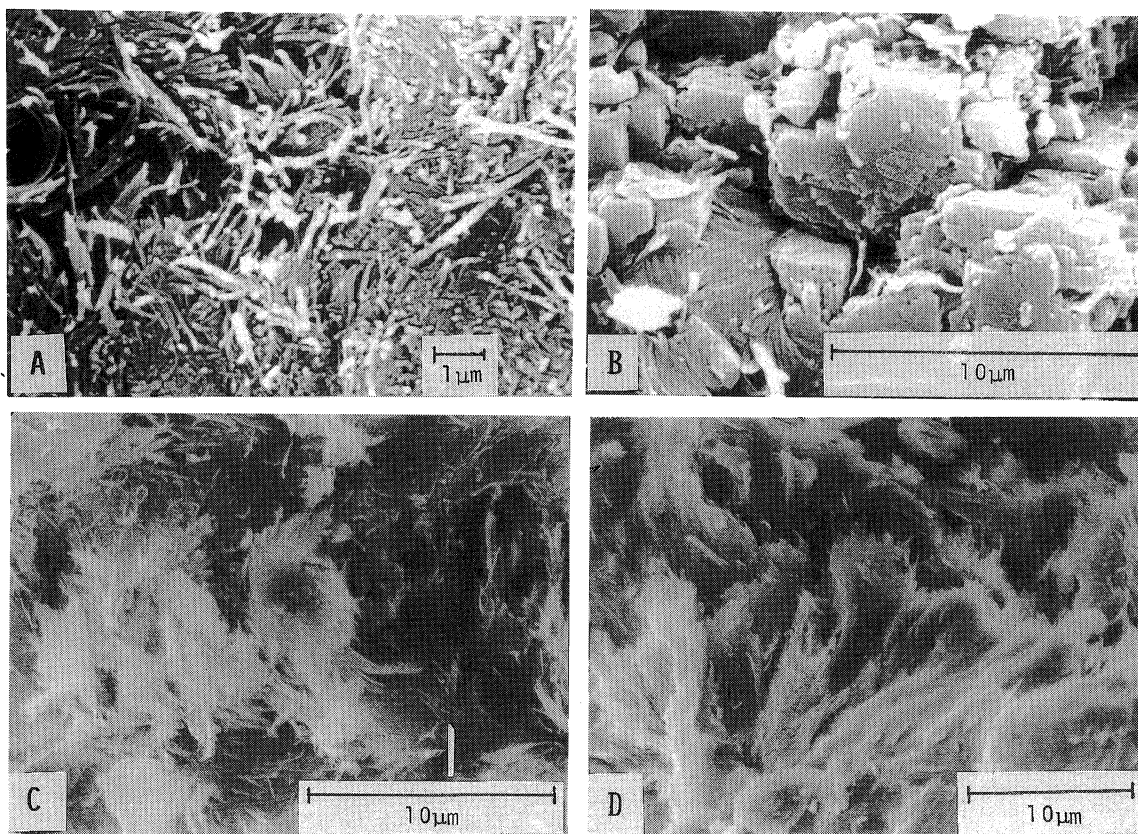


Fig. 5. Scanning electron micrographs of the sepiolites.
 A. sepiolite from the primary rock type deposit.
 B. sepiolite from the clay type deposit.
 C. sepiolite from the primary rock type deposit.
 D. sepiolite from the clay type deposit.

5. Scanning electron micrograph

Scanning electron micrographs of the two sepiolites are shown in Fig. 5. They show fibrous shapes, and some plates are composed of many fibrous crystals. The edge of the plates are often curling.

Discussion

Sepiolite deposits in Liuyang, Hunan Province could be divided into two types, primary rock type deposit and clay type deposit, respectively. The clay type sepiolite has been used for industrial materials, whereas the primary rock type sepiolite has not been used in spite of existing of its large quantity. It is probably because of the presence of impurities in the latter.

With regards to the formation of sepiolite, several problems still remain unsolved, however, it is possible to estimate the environment of formation of sepiolite in Liuyang, Hunan Province. Many shallow marine fossils such as anthozoa, brachiopods, fusulinids and so on are present in both of the sepiolite deposits. This fact indicates that sepiolite was formed under high salinity and weak alkaline condition. Thus, sepiolite was probably deposited at shallow marine or lagoon environment. Celestite, which is present in some parts of the ore beds, does not indicate alkaline condition, and contradicts the estimated environment of formation of sepiolite as mentioned above. However, celestite was probably formed from solution in hydrothermal veins.

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