研究報文

A NICKELIFEROUS SEPIOLITE FROM THE ŌEYAMA
NICKEL MINE, KYOTO PREFECTURE, JAPAN

MASATOMO MUCHI

Fukuoka University of Education

YOSHIAKI HOSHINO and ISAO FURUSATO

Kurosaki Ceramic Co. Ltd.

Abstract: The light green mineral from the Ōeyama nickel mine has been identified to be nickeliferous sepiolite being a very rare mineral by means of chemical analysis, electron micrographs, thermal curves and x-ray diffraction. Its occurrence seems to be the first recorded in Japan. The mineralogical properties generally agree with those of fibrous type sepiolites described in the literatures, but the thermal effects on this mineral are somewhat different from those on the fibrous type. From the electron micrographs and X-ray analyses, it has been confirmed that the Ōeyama nickeliferous sepiolite is composed of fibrous particles which are not uniform in length and have higher crystallinity than that of the sepiolite from this mine described recently. The chemical formula for this mineral was $12 \text{SiO}_2 \cdot 8 (\text{Ni}, \text{Fe}, \text{Mg})\text{O} \cdot 17 \text{H}_2\text{O}$. Of this $17 \text{H}_2\text{O}$ obtained from the chemical analysis $3\text{H}_2\text{O}$ were considered to be possibly hygroscopic water in comparison with the Preisinger formula.

INTRODUCTION

Peridotite and serpentine rock fragments with various sizes have deposited stepwise at the foot of the cliff on the northeastern side of Akaishi-dake (the chief peak of the Ōeyama mountains). The weathering of these accumulations which formed the piedmont upland has considerably proceeded, and in the consequence, a lateritic appearance has well been displayed by dark- and red-brown soil or clay materials formed at or near the surface.

Kinoshita and Takimoto (1939) described that beneath the reddish brown clay, the so-called "blue caly" tinged with green

usually occurred with somewhat clear boundary below the ground water table, and that the partially weathered serpentine fragments were intermingled with such clays. And also they confirmed that the upper part of the reddish brown clay included a very little amount of nickel, because it was leached out by rain water with soluble materials, while, in the "blue clay" and intermingled parts, the nickel content remarkably increased; and designated such nickel-bearing sub-soil and clayey materials as "caly nickel ore" (composed essentially of nickel serpentine and nickel chlorite).

One of the authors happened to find the small fragments of light greenish clay resembling with usual garnierite in appearance in highly weathered debris accumulating on the southeastern side of this mine, and the sample is shown in Fig. 1. This clay accompanies deep greenish clay material on its outer side. The work of this clay material will be published later. It has been confirmed that the light greenish clay is not composed of garnierite, but of nickeliferous sepiolite. Nickeliferous sepiolite is a very rare mineral in the world, there being only one occurrence at New Caledonia, which is described by Caillere (1936) till now.

Therefore, the occurrence of nickeliferous sepiolite from this mine is very noticeable. The origin of this mineral would be due to the reaction between serpentine and descending water with dissolved salts.

The density measured by using the heavy liquid (a mixture of bromoform and bromobenzene) was about 2.15 to 2.20. In thin section the fibrous particles have straight extinction and a moderate index of $n=1.55-1.56$.

CHEMICAL ANALYSIS

The result of chemical analysis of the Ōeyama nickeliferous sepiolite is given in Table 1 with those of the nickeliferous sepiolite from New Caledonia and the fibrous type sepiolite from Ampandrava. The magnesia content of this nickeliferous sepiolite is a little lower and also the H_2O is a little higher, in comparison with those of the New Caledonia one. The water content, particularly H_2O (—) content, considerably fluctuates among specimens as shown in the literature. Many problems for the fluctuating water have yet been left unproved, although the fluctuation is thought to be caused, to some extent, by the variation of the degrees of crystallinity or the quantitative difference of the two type sepiolites (fibrous and compact type ones) included in each specimen even if the specimen

Fig. 1. (A) The general view of the light greenish clay composed of nickeliferous sepiolite.
(B) The detailed view of the central portion of (A).

is pure, as shown later on.

The chemical analysis of this specimen indicates a ratio of SiO_2 : MgO : H_2O =3: 1.998: 4.191 as shown in Table 1. The ratio SiO_2/MgO of this specimen closely agrees with those of usual sepiolites in the literature, and its chemical formula is shown as follows: $12 \text{SiO}_2 \cdot 8 \text{ octahedral metal oxides} \cdot 17 \text{H}_2\text{O}$.

Nagy and Bradley (1955), and Presinger (1959) postulated the idealized chemical formula of sepiolite to be $12\text{SiO}_2 \cdot 8\text{MgO} \cdot 14\text{H}_2\text{O}$, but there are differences between the numbers of water molecules belonging to the structure respectively. Of the seventeen water molecules obtained by the chemical analysis, about three of them

are considered to be hygroscopic water. Assuming that 32 oxygens are included in the half-unit cell of sepiolite, the structural formula is given as follows:

Table 1. Chemical compositions of nickeliferous sepiolites from the Oeyama nickel mine and from New Caledonia, and the fibrous type sepiolite from Ampandrandava, Madagascar, after S. Caillere

	Nickeliferous sepiolite from the Oeyama nickel mine, Kyoto Prefecture		Nickeliferous sepiolite from New Caledonia and fibrous type sepiolite from Ampan- drandava, Madagascar, after S. Caillere		
	wt%	Molecule ratio × 1000	(1) wt%	(2) wt%	
SiO ₂	50.48	841	SiO ₂	50.40	52.50
Al ₂ O ₃	0.34	2			0.60
Fe ₂ O ₃	0.28	1	0.73	2.90	0.70
FeO					
MgO	20.03	497	*	20.28	21.31
CaO	trace	64			
NiO	7.60			9.70	
Na ₂ O	0.11				
K ₂ O	0.06				
H ₂ O (+)	9.71	1178	H ₂ O	8.68	9.21
H ₂ O (-)	11.50			9.92	12.06
Total	100.11			99.79	99.75

(1) Nickeliferous sepiolite from New Caledonia (S. Caillere).

(2) Fibrous type sepiolite from Ampandrandava, Madagascar (").

* : Octahedral metal oxides.

ELECTRON MICROGRAPHS

The electron micrographs of this specimen are shown in Fig. 2. From the observation under a polarization microscope or electron microscope, it is recognized that sepiolite particles can be generally classified into two types. The one is fibrous, tubular and rod-like, being designated as alpha-sepiolite or para-sepiolite (Fersman 1908, quoted by Davis 1951). The other is flake-like, spherical and irregular, being considered to be amorphous, and it is called beta-sepiolite by Winchell (1951) and Davis (1951).

Under the highly magnified electron microscope, this specimen seems to be composed of poorly developed fibers on the whole, and somewhat rounded flaky particles are also observed. It may be

characteristic that the two types occur together in this specimen. The pictures well display that the individual tubes considerably vary in length and width, and the small particles in Fig. 2 D reveal the rather stubby nature. Some long bundles are surrounded by considerably shorter tubes which may be due in part to breakage caused by the heat of the electron beam.

A few cross sections are clearly observed at terminations of tubes, indicating somewhat angular or polygonal forms besides circular ones. Some tubes have fuzzy material on both outside and inside, and such forms appear to be cylindrical rather than lath-like. Similar material is frequently observed on chrysotile and halloysite particles. The width obtained from the measurement on 220 tubes in the pictures ranges from 0.01 to 0.05 microns with the mean value of 0.03 microns. This value is considerably smaller than the mean width of hydrated-halloysite particles measured by Bates, Hildebrand and Swineford, 1950 (860 Å), but is more similar to the average of outside diameters of chrysotile particles measured by Bates and Comer, 1959 (250 Å).

These particles yield the longitudinal striations parallel to the length of the fiber, as frequently seen for alpha-sepiolites and other tubular minerals. And also tubes interlace with irregularly-shaped particles having fine projections or "amorphous appearing material" as observed on the poorly-crystallized sepiolite particles from this mine described by authors (1965).

THERMOBALANCE CURVE AND DIFFERENTIAL THERMAL ANALYSIS CURVE

The thermogravimetric analysis for this specimen was carried out for about 0.2 grams, using the Honda thermobalance apparatus; and the record was obtained by the periodical reading at intervals of approximately one minute. The sample was heated from room temperature to 1000°C at a heating rate of 5°C per minute. The curve is shown in Fig. 3.

The water in this specimen is dehydrated in four temperature regions with considerably steep inflections as indistinctly seen on this curve, such a loss often appearing on those of fibrous type sepiolities, but it is not clear in general. This thermobalance curve is similar to those of the nickeliferous sepiolite and fibrous type material published by Caillere and Henin (1957), mostly resembling the curve having four regions of water loss for the Vallecas sepiolite worked by Martin-Vivaldi and Cano-Ruiz (1956). However,

on the curve of the Vallecas sepiolite the temperature commencing the dehydration in the third region from the low temperature side is rather lower than that of this specimen, and on the curve of the New Caledonia nickeliferous sepiolite, the temperature beginning the second inflection is more higher, and the third inflection is not

Fig. 2.

so remarkable. On this thermobalance curve, a weight loss of about thirteen per cent which would seem to be due to adsorbed and zeolitic water simultaneously occurs between room temperature and 250°C. And then in the second stage, the relatively quick loss of about four per cent follows in the 250°–450°C region, and the following cliff displaying a weight loss of about seventeen per cent clearly appears in the region of 450°–650°C, being sharp and characteristic for this specimen, although the cliff in this temperature region is generally small and not distinct as shown in the literature. The water loss of two types subdivided in the region of 250°–650°C, corresponding to the bound water, total 5.7 per cent against the loss of 5.5 per cent expected from the Bauner-Preisinger model. Above 650°C, the final dehydration slowly begins at first, then suddenly at 750°C, and again slowly above 900°C. The weight loss in this temperature region is about 2.5 per cent comparable to the one of 2.7 per cent expected from the model.

The differential thermal analysis curve of this specimen is shown in Fig. 4. The curve was obtained by using the Shimazu D.T.A. apparatus and the sensitivity was adjusted to give 12mV and 100 uV to X- and Y-axis respectively. The heating rate was approximately 10°C per minute. Although this curve is rather different from that of the New Caledonia nickeliferous sepiolite as shown later on, this exhibits certain similarities to those of the fibrous type sepiolites. The first endothermic effect is very remarkable and forms two peaks at 130° and 150°C. The fibrous type sepiolites often show this double peak. Between 250° and 450°C, no remarkable endothermic

Fig. 2. Electron micrographs of nickeliferous sepiolite from the Ōeyama Nickel Mine.

A and B: These pictures show long tubes and bundles of elongated fibers surrounded by much shorter ones which may occur as the result of breakage. The longitudinal striations parallel along the lengths of the fibers well develop. A large subhedral lath is observed at the upper left in the (B) figure.

h: Hexagonal cross section,

c: Tubes and laths with circular terminations,

s: Subhedral lath,

C and D: These pictures are characterized by considerably short, rather flaky particles associated with long tubes.

Polygonal and circular cross sections are often seen, and partial unrolling is observed at the lower right in the (C) figure.

p: Polygonal cross section,

c: Circular cross section,

peak is recognized but replaced by a dome-like exothermic peak which gives a flattened culmination in the region of 295° and 405°C, though the fibrous sepiolite from Ampandrandava shows a small endothermic peak in this temperature region as described by Caillere and Henin (1957). Thereafter a weak and gently-elongated endothermic peak proceeds to about 600°C, it being negligible, but

Fig. 3. Thermobalance curve for the Ōeyama nickeliferous sepiolite.

Fig. 4. Differential thermal analysis curve for the Ōeyama nickeliferous sepiolite.

the New Caledonia material exhibits a clear and large endothermic peak at the same temperature. The high temperature endothermic effect commences at 750°C, giving the peak culmination at 790°C, and its peak is small and gradually going down toward the high temperature side. This peak is immediately followed by a small exothermic peak which is rather broadened. This weak endothermic-exothermic inversion appears on the curve between 795° and 815°C, being not much sharp as compared with those of some fibrous type sepiolites. The sharpness of this inversion may be considered to be rather pronounced for the compact type sepiolites than the fibrous type ones, as well given by the Ampandrandava sepiolite (compact type) and the poorly crystallized one from this mine. Finally a small endothermic peak with the peak temperature of 825°C closely follows to the inversion and the peak is clearly seen for the New Caledonia nickeliferous sepiolite only in the literature, although the characteristic endothermic peak preceding an exothermic one has not been recognized for that sepiolite.

It is very hard to interpret the co-relation between the thermobalance and differential thermal analysis curves for this nickeliferous sepiolite with precision, for the dehydration processes have not been understood definitely yet.

X-RAY SPECTROGRAMS

The X-ray spectrograms of crude and heated specimens were

Fig. 5. X-ray spectrograms of sepiolites from the Ōeyama nickel mine.

A: Nickeliferous sepiolite.

B: Poorly-crystallized sepiolite.

Fig. 6. Effects of heating on some of characteristic reflections from the Ōeyama nickeliferous sepiolite.

A: Heated at 400°C for one hour.

B: Heated at 600°C for one hour.

C: Heated at 700°C for one hour.

obtained with a geiger counter X-ray diffractometer. Filtered copper radiation (Cu $K\alpha$: 1.418 Å) was used under the following experimental conditions: 35 kV, 15mA, scale factor: 8, multiplier: 1, time constant: 4 seconds, scanning speed 2° per minute.

The spectrograms of crude and heated specimens are shown in Figs. 5 and 6, and observed intensities and measured spacings from the spectrograms are listed in Table 2 together with the data for the Little Cottonwood sepiolite by Brindley (1959).

The X-ray data clearly indicate that this specimen is almost pure, because the diffraction peaks extraneous to sepiolite are not

observed. Generally the diffraction peaks from this specimen are sharper and more resolvable than those of the Eski Chehir and the Ōeyama sepiolites, but are not so well resolved as those of the Little Cottonwood one. Some peaks such as 2.68Å, 2.61Å, 2.06Å and 2.04 Å are somewhat broader.

The thermal behaviours on this specimen generally agree with those mentioned by Caillere and Henin (1961), however some discrepancies have been observed on the spectrograms. Namely, the broad peak with medium intensity appears in the region of 11–9Å (2θ) when heated at 400°C for one hour, it giving the culminations at about 10.6Å and 9.9Å; and on the other hand, the intensity of the 7.5Å peak does not increase, notwithstanding that the enhancement of its peak has been indicated by Cailler and Henin (1961). After heating at 700°C for one hour, the intensity of the diffused 12Å peak remarkably decreased, and the 10.6Å peak shifted to 9.9Å. Also a new peak clearly appeared at about 9.3Å and the intensity was relatively weak. Such a sepiolite anhydride commenced its structural change at 400°C seemed to probably persist up to 700°C, and the diffraction peaks from this specimen disappeared completely at about 850°C. Such changes on the X-ray spectrograms were noticeably different from those of the Ōeyama sepiolite.

CONCLUSION

Light greenish clay mineral found from the Ōeyama nickel mine was identified as a nickeliferous sepiolite by means of chemical analysis, differential thermal analysis, thermogravimetry, electron micrographs and X-ray diffraction. This mineral seems to be very much valuable in its occurrence in this location. The mineralogical properties are summarized as follows:

(1) The H_2O (–) content is somewhat higher than those of other fibrous type sepiolites, and of $17\text{H}_2\text{O}$ obtained from the chemical analysis $3\text{H}_2\text{O}$ is considered to be adsorptive. The structural formula for this specimen is postulated as

(2) In the electron micrographs, the particles of this nickeliferous sepiolite are composed of a mixture of two types of material: the one is fibrous, and the width of fibers ranges from 0.01 to 0.05 microns, taking up the greater part of particles in general; and the other is flake-like and irregular in outline, being interstitial, and seems to be composed of aggregates of very fine or amorphous material.

Table 2. X-ray powder data for the Ōeyama nickeliferous sepiolite and the fibrous type sepiolite from Little Cottonwood (Brindley, 1959).

hkl	I		II	
	d (Å)	I	d (Å)	I
110	12.3	98	12.05	100
130	7.5	6	7.47	10
200,040	6.75	4	6.73	5
150	5.07	7	5.01	7
060	4.53	16	4.498	25
131	4.32	17	4.306	40
330	4.07	6	4.022	7
260	3.78	14	3.750	30
241	3.52	10	3.533	12
080	3.37	25	3.366	30
331	3.21	15	3.196	35
261	3.10	10	3.050	12
370	2.95	7	2.932	4
081	2.826	6	2.825	7
421			2.771	4
0,10,0	2.68	12B	2.691	20
510				
441,281	2.61	14B	2.617	30
530			2.586	NR
112,371,191	2.56	18	2.560	55
132	2.47	10	2.479	5
202,042	2.45	12	2.449	25
1,11,0	2.40	10	2.406	15
222,461				
062,312	2.26	11	2.263	30
2,10,1				
620,570,332	2.12	5	2.206	3
640,2,12,0			2.125	7
4,10,0				
082	2.06	6B	2.069	20
571	2.04	6B	2.033	4
	1.875	3	1.957	4
			1.921	2
			1.881	7
			1.818	2
			1.760	6
	1.714	4	1.700	10
			1.637	3
			1.592	10
	1.590	6	1.550	15
	1.552	5		
	1.540	5		
	1.518	8	1.518	15
			1.502	8
	1.416	5	1.416	9
			1.349	6
			1.312	6
			1.299	15

I: Nickeliferous sepiolite from the Ōeyama nickel mine.

II: Fibrous type sepiolite from Little Cottonwood, Utah
(experimented by Brindley, 1959).

"B": Indicates a broad peak.

(3) The thermobalance curve clearly indicated that the water in this sepiolite is lost as if the dehydration occurred in four temperature regions; and on the differential thermal analysis curve, the low temperature endothermic peak is composed of a double peak and also the endothermic peak in the region of 450°–650°C is very small and vague, and the high temperature endothermic effect beginning at about 700°C is relatively weak. The inversion is not so much remarkable and sharper.

(4) The X-ray diffraction peaks closely agree with those of usual sepiolites in the literature, but in its crystallinity, a much larger variation is found in comparison with those.

(5) The thermal effects between 400° and 700°C on the X-ray spectrograms somewhat differ from those of the fibrous type sepiolites, but they are very different from those of the Ōeyama sepiolite.

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京都府大江山ニッケル鉱山産の含ニッケルセピオライト

鞭 政 共
星 野 義 昭
古 里 功

摘 要

大江山ニッケル鉱山より発見された淡緑色の鉱物は、化学分析、電子顕微鏡写真、熱分析曲線およびX線廻折実験の結果から、珍らしいとされている含ニッケルセピオライトであることが判明した。当鉱山産の含ニッケルセピオライトは、日本で最初に記述されたものと思われる。その鉱物学的性質は文献下に示されている繊維状セピオライトのものと一般には一致するが、熱的性質は幾分異っている。電子顕微鏡写真とX線回折の結果とを併用して考察すると、特に長さの不揃いな繊維状の粒子から主としてなっており、大江山産のセピオライトより結晶度は高い。この鉱物の実験式は化学分析の結果、 $12\text{SiO}_2 \cdot 8(\text{Ni}, \text{Fe}, \text{Mg})\text{O} \cdot 17\text{H}_2\text{O}$ で示されるが、この中 $3\text{H}_2\text{O}$ は Preisinger の式と比較すると、恐らく吸着水であろうと思われる。