

## 27. LÜNEBURGITE $[\text{Mg}_3 (\text{PO}_4)_2 \text{B}_2\text{O} (\text{OH})_4 \times 6 \text{H}_2\text{O}]$ IN UPPER MIOCENE SEDIMENTS OF THE EASTERN MEDITERRANEAN SEA

Jens Müller and Frank Fabricius, Lehrstuhl für Geologie, Technische Universität, München, West Germany

### ABSTRACT

Upper Miocene dolomitic marls drilled at Site 374 (Messina Abyssal Plain, Ionian Sea) contain small white mm-sized spherules which have been identified by X-ray, chemical, and IR-spectrometry techniques as lüneburgite  $[\text{Mg}_3 (\text{PO}_4)_2 \text{B}_2\text{O} (\text{OH})_4 \times 6 \text{H}_2\text{O}]$ .

We assume that the lüneburgite formed as a secondary product by upward migrating brines from the Miocene evaporites which contain highly soluble Mg- and B- salts. Enrichment of phosphorus may be the result of concentration in residual brines from the evaporites or to diagenetic reactions such as leaching of apatite or decomposition of organic compounds of the host sediment in a reducing environment.

### INTRODUCTION

The unconsolidated upper Miocene sediments recovered at Site 374 (Messina Abyssal Plain) contain small white spherules. These spherules are scattered sporadically throughout Cores 12 and 15. The majority of spherules are about one millimeter in diameter; the largest one observed was four millimeters in diameter.

The dominant form is subspherical to spherical; flattened chip-like particles occur only rarely. The surface of the spherules is even (Figure 1). SEM investigation of freshly broken areas from the interior showed 5 to  $10\mu\text{m}$  large plates of prismatic, or in some cases, pseudo-hexagonal habit (Figure 2). In some areas these plates are subparallel within the spherule. However, within the specimen studied, the subparallel arrangement of the single crystals does not appear to be parallel to the outer surface of the spherule.

### METHODS

Specimens were handpicked (from Samples 374-14-1; 374-13, CC; and 374-15-1, 100-102 cm) for X-ray and chemical analysis and IR-spectrometry.

X-ray diffraction and Guinier camera analyses gave a number of sharp reflections and the calculated d-spacings obtained by the different methods are in good agreement. A sample of lüneburgite from Lüneburg, West Germany (Kalkberg) was run separately and gave d-values identical with those of the white spherules from the eastern Mediterranean Sea (Figure 3). A comparison with the d-spacings reported by Lohse (1958) for lüneburgite shows a similar pattern. Some of the small differences and additional lines not obtained in our analysis may be caused by impurities of the specimens analyzed by Lohse (1958). We believe the differences in crystallinity are the cause of variations of intensities observed in the different specimens analyzed. D-spacings (in Å) are listed in Table 1.

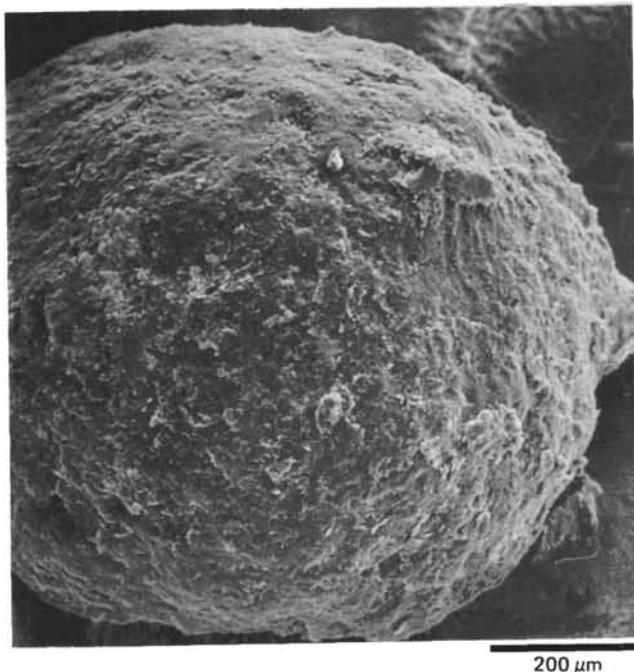


Figure 1. Outer surface of Lüneburgite-spherule from Sample 374-15-1, 120-121 cm (SEM No. 69590).

The spherules were ground and dissolved in hydrochloric acid in preparation for the chemical analysis. Presence of magnesium and calcium was determined by atomic absorption,  $\text{PO}_4$  and B by titration. The results are reported in Table 2, together with the results obtained by Noellner (1870) and Biltz and Marcus (1912).

An IR-spectrum of the lüneburgite spherules is shown in Figure 4, together with that of the reference sample from Lüneburg which shows good agreement. The respective wavelengths are comparable with those reported by Moenke (1962).

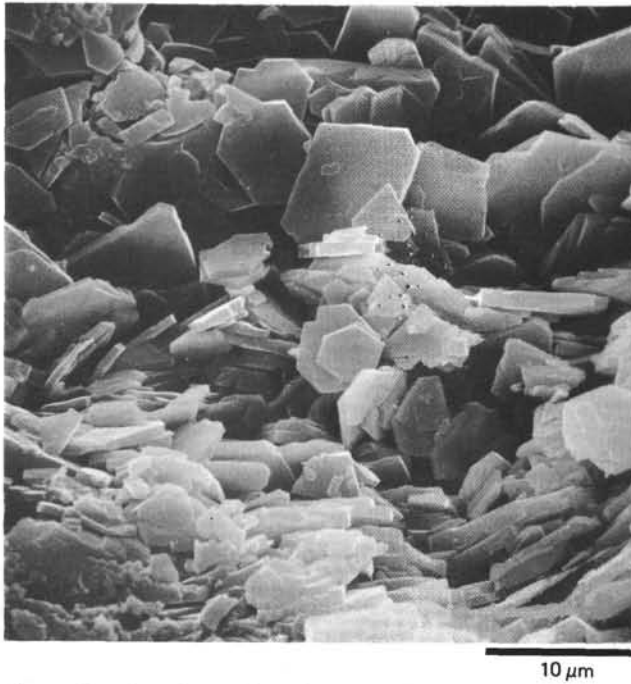


Figure 2. Interior of lüneburgite-spherule (same sample). Note prismatic and pseudo-hexagonal habit of crystals and their parallel arrangement in the lower section.

**DISCUSSION**

The consistent results obtained by comparing X-ray data, chemical composition analyses, and IR-spectra of the white spherules from the eastern Mediterranean with those of lüneburgite from Lüneburg enable us to identify the spherules as lüneburgite  $Mg(PO_4)_2 \cdot B_2O_3 \cdot (OH)_4 \cdot 6H_2O$ , a rare "semi-salinar" mineral which was first described and analyzed by Noellner in 1870.

No traces of lüneburgite were detected in the surrounding sediments by X-ray techniques. Sediments (as analyzed from Sample 374-13-1, 71-73 cm) consist chiefly of authigenic Ca-dolomite ( $Ca_{55}Mg_{45}$ ) and the detrital components quartz, feldspar, smectite, illite, kaolinite, chlorite, and traces of (?)attapulgitite. The fine-grained black sediment is slightly enriched in organic carbon (0.3-0.7%; Sigl, this volume) and when fresh, expels a bituminous odor. Secondary(?) gypsum occurs within the sequence containing lüneburgite. These homogeneous sediments were deposited as a transitional facies between the formation of evaporites and deposition of more open marine sediments (Site 374 Report, this volume).

Lüneburgite has been reported only from a few places. According to a recent summary by Kuehn (1972), it has been found:

- a) in upper Permian (Zechstein) sediments from Lüneburg, West Germany where it forms several cm-sized nodules (Noellner, 1870; 1872);
- b) as pseudo-hexagonal 0.1-mm flakes disseminated in carnallite (Biltz and Marcus, 1912);
- c) as in (b) in salt deposits from New Mexico and Texas together with halite, sylvite, and clay (Schaller and Henderson, 1932);

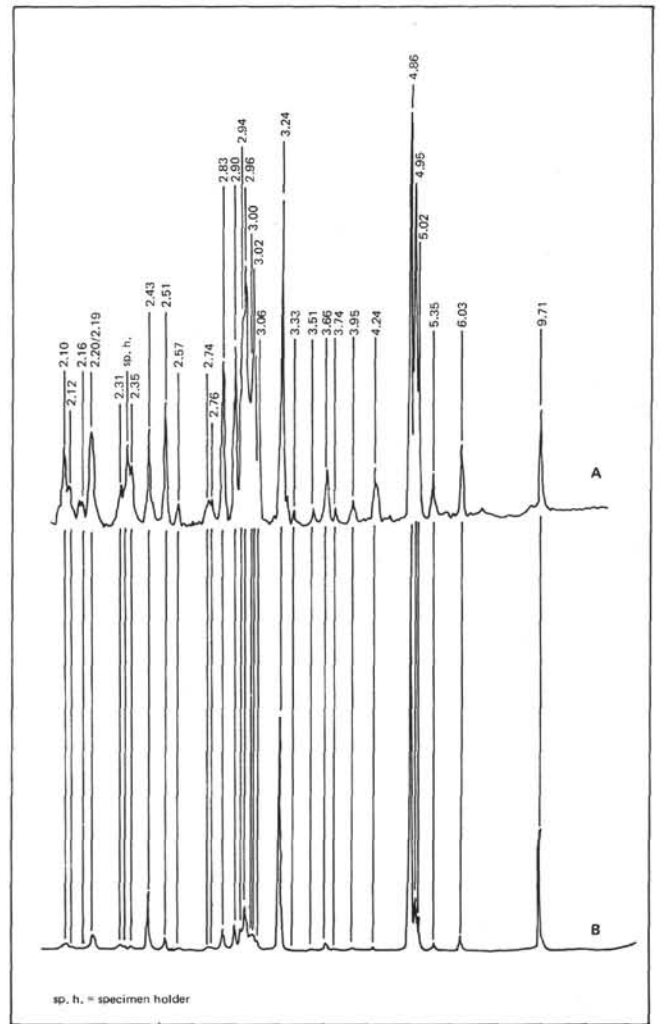


Figure 3. X-ray diffractograms of lüneburgite from the eastern Mediterranean (A) and from Lüneburg, W. Germany (B) with d-spacings in Å.

**TABLE 1**  
List of d-Spacings of Lüneburgite  
 $[Mg_3(PO_4)_2 \cdot B_2O_3 \cdot (OH)_4 \cdot 6H_2O]$

1		2		3		4	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
9.71	32	9.714	m	9.71	30	9.8	12
6.03	20	6.029	m	6.04	5	6.06	40
5.35	10	5.351	w	5.35	2	5.385	30
5.02	51	5.022	s	5.02	7	5.035	100
4.95	71	4.954	vs	4.95	14	4.98	80
4.86	100	4.859	s	4.87	100	4.87	30
-	-	-	-	-	-	4.74	5
4.24	15	4.245	m	4.25	2	4.245	25
3.95	7	3.965	vw	3.96	1	3.985	8
3.74	4	3.728	vw	3.74	<1	3.76	8
3.66	14	3.656	vw	3.66	2	3.665	12
3.51	4	-	-	3.52	<1	3.525	12
3.33	11	-	-	3.34	<1	3.30	5
3.24	89	3.246	m	3.24	58	3.245	30
3.06	28	3.061	w	3.05	2	3.065	40
3.02	46	3.025	m	3.03	4	3.025	40
3.00	32	2.997	vw	3.00	4	-	-
2.96	64	2.969	m	2.96	11	2.975	40

TABLE 1 — Continued

1		2		3		4	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
2.94	48	2.941	m	2.94	5	2.942	40
2.90	41	2.901	m	2.90	6	2.905	20
2.83	35	2.825	vs	2.83	5	2.833	100
2.76	7	—	—	2.76	<1	—	—
2.73	11	2.737	vw	2.73	<1	2.736	12
—	—	—	—	—	—	2.688	5
2.57	5	2.575	vw	2.57	<1	2.583	8
2.51	37	2.510	s	2.51	3	2.516	80
—	—	—	—	—	—	2.486	5
—	—	—	—	—	—	2.453	8
2.43	23	2.431	vw	2.43	14	2.434	8
—	—	—	—	—	—	2.41	5
—	—	—	—	—	—	2.39	5
2.35	16	2.350	vw	2.35	1	2.360	35
2.31	11	—	—	2.31	1	2.322	8
—	—	—	—	—	—	2.293	5
—	—	—	—	—	—	2.233	5
2.20	25	2.201	vw	2.20	5	2.205	12
2.19	25	2.193	vw	2.19	—	—	—
2.16	6	2.160	vw	2.16	<1	2.165	12
—	—	2.135	vw	—	—	2.130	12
2.12	9	2.121	vw	2.12	<1	—	—
2.10	21	2.104	w	2.10	2	2.108	30
2.08	5	—	—	2.08	1	2.092	8
2.01	19	2.009	w	2.01	1	2.017	235
—	—	—	—	—	—	1.994	20
—	—	—	—	—	—	1.987	5
—	—	—	—	—	—	1.975	8
—	—	—	—	—	—	1.965	12
1.94	32	1.942	m	1.94	14	1.928	17
1.92	5	—	—	1.92	<1	1.920	8
1.89	18	1.890	m	1.89	2	1.897	20
1.86	5	1.859	w	1.86	<1	1.866	12
1.81	7	1.816	vw	1.81	1	1.819	10
—	—	—	—	—	—	1.792	8
1.76	5	—	—	1.76	<1	1.768	20
1.74	6	—	—	1.74	<1	1.744	5
—	—	—	—	—	—	1.734	10
—	—	—	—	—	—	1.686	10
1.65 <sub>b</sub>	13	1.657	vw	1.65	1	1.657	35
—	—	1.650	w	—	—	—	—
1.62	5	—	—	1.62	<1	1.628	8
—	—	—	—	—	—	1.615	10
1.60	5	—	—	1.60	<1	1.602	5
1.57 <sub>b</sub>	12	1.580	vw	1.57	<1	1.583	20
—	—	1.572	w	—	—	1.570	35
1.55	5	—	—	1.55	<1	1.554	12
1.54	5	—	—	1.54	<1	1.540	8
1.51	5	—	—	1.51	1	1.511	30
—	—	—	—	—	—	1.502	8
1.47	5	—	—	1.47	<1	1.476	20
1.45	5	—	—	1.45	<1	1.455	8

Note: 1 = Lüneburgite from Sample 374-15-1, 100-102 cm (eastern Mediterranean Sea) diffractometer record; 2 = As in (1) diffraction pattern of Guinier camera. 3 = Lüneburgite from Lüneburg (W. Germany) diffractometer record, 4 = Lüneburgite from Lüneburg d-spacings by Lohse (1958).

d) as idiomorphic mm-sized crystals with inclusions of anhydrite and clay, together with boracite in "anhydritischem Hartsalz" of upper Permian (Zechstein) sediments, and within halite associated with thrust faults (Stassfurt/Zechstein), together with boracite, quartz, celestite, pyrite, marcasite, and fluorspar (Braitsch, 1961);

TABLE 2  
Chemical Analyses of Lüneburgite

	1	2	3	4
MgO	25.2	25.38	25.3	25.13
CaO	0.1	—	—	0.15
P <sub>2</sub> O <sub>5</sub>	27.6	29.78	29.8	29.61
B <sub>2</sub> O <sub>3</sub>	13.7	14.61	12.7	12.9
H <sub>2</sub> O	N.D.	30.23	32.2	32.16

Note: 1 = 1. from the eastern Mediterranean; 2 = theoretical composition calculated after the formula Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> B<sub>2</sub>O (OH)<sub>4</sub> × 6 H<sub>2</sub>O; 3 = analyses by Noellner (1870); 4 = analyses by Blitz and Marcus (1912). N.D. = not determined.

e) as mm-sized nodules composed of thin spherulitic plates in a fissure filling in a carnallitic layer (Thüringen/Zechstein) together with boracite (Heide and Bader, 1964);

f) in borax-lakes from Tibet (Noellner, 1872).

Previous workers (Braitsch, 1961; Kuehn, 1972) have assumed that, in some instances, lüneburgite formed as a secondary product by upward migrating brines originating either from underlying evaporites or which were associated with oil deposits enriched in boron and phosphorus as described by Herrmann and Hofmann (1961). Also, Kuehn (1972) noted that leaching of apatite by boric acids or reworking of detrital phosphates could be a possible source of phosphorus and thus lead to a reaction forming lüneburgite as suggested by experiments by Berdesinski (1951, 1952).

In all findings listed above, lüneburgite was associated with minerals different from those found in the sediments surrounding the lüneburgite of the eastern Mediterranean. Its paragenesis in the eastern Mediterranean sediments excludes the possibility that it is a synsedimentary primary precipitate, but is instead the result of early diagenetic reactions, although the spherical appearance combined with non-radial and non-concentric structures is reminiscent of a "rolled snowball." As in the case of some of the upper Permian lüneburgite, we assume that ascending brines from the Miocene evaporites which contain highly soluble sulfoborite (Kuehn and Hsü, this volume) were the source of the boron and magnesium. Interstitial waters in these beds contain more than 50 g/l Mg (McDuff and Gieskes, this volume), but no data on boron and phosphorus concentrations are available at present. We have considered several possibilities for the source of phosphorus. First, it might be concentrated in residual brines which were enriched in phosphorus as a result of the evaporation process. Second, leaching of apatite by boric acids or reworking of detrital phosphates as proposed by Kuehn (1972) might be considered as a source. Finally, we cannot exclude the possibility that some of the phosphorus utilized for the formation of lüneburgite came from the host sediment inasmuch as a primary association of phosphorus with organic material (bituminous odor!) in this shale is very likely. Thus, Krejci-Graf (1955) pointed out that phosphorus

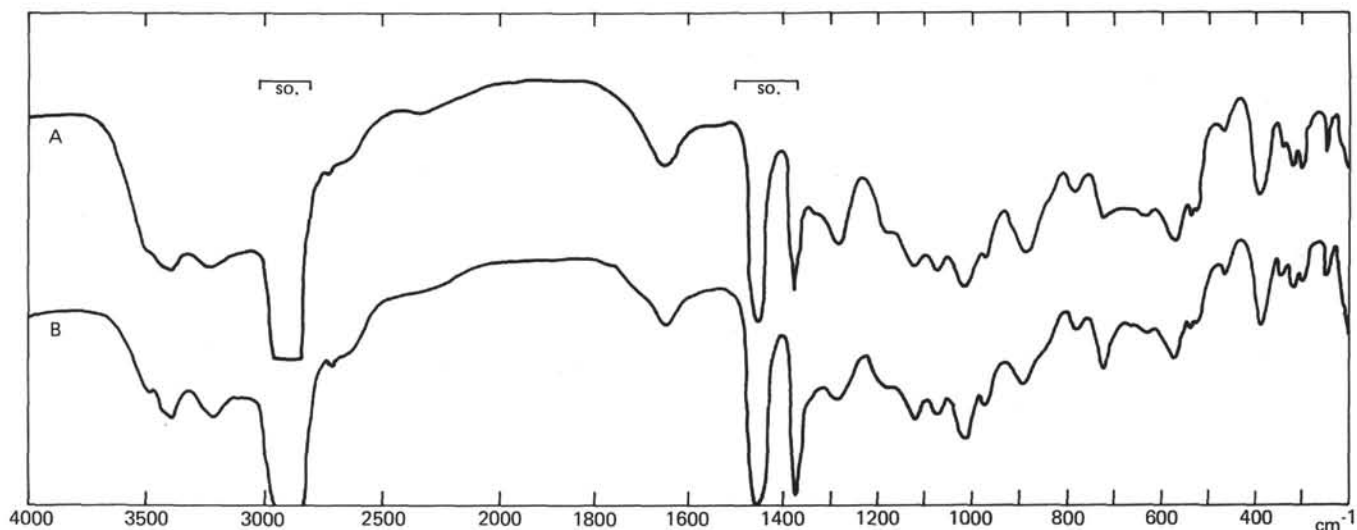


Figure 4. IR-spectra of lüneburgite A = lüneburgite from the eastern Mediterranean; B = lüneburgite from Lüneburg, W. Germany. (so. = solvent)

from P-containing organic matter is mobilized in a reducing environment which leads to enrichment of phosphorus in the interstitial water. With the data at hand, we cannot be certain which factor, or combination of factors, is responsible for the enrichment of phosphorus.

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