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Helvite from Yagisawa Mine, Nagano Prefecture, Japan*

By

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Introduction

A beautiful green mineral was collected from the manganese ore deposit of the Yagisawa mine, Nagano Prefecture by Professor Toyofumi YOSHIMURA in 1941 (YOSHIMURA, 1952). Recently this mineral was identified by the writer to be a kind of helvite, and was published briefly in Japanese (YOSHIMURA and YOSHINAGA, 1959). Some new data are added here.

Occurrence

The Yagisawa mine is situated at Nagawa-mura, Nishichikuma-gun, about 30 kilometers to the south-west of Matsumoto city, Nagano Prefecture. The manganese ore deposits of the mine are composed of three lenticular ore bodies in a cherty formation of the Paleozoic system. About 2.5 kilometers to the east of the mine, the Paleozoic sediments are seen penetrated by a stock of two-mica granite which is said to have been intruded in later Mesozoic age.

The First level ore body consists of pyrite and chalcopryrite accompanied by a small amount of manganese minerals. The Second and the Third level ore bodies** are characterized by the abundance of rhodonite and/or pyroxmangite ores.

Minerals found in the Second level ore body are rhodonite, pyroxmangite, spessartine, helvite, tephroite (?), dannemorite, rhodochrosite, calcite, huebnerite, alabandite, marmatite, galena, chalcopryrite, fluorite, and quartz. The helvite occurs as coarse grains, 0.5 to 3.0 centimeters in diameter, associating with dannemorite, spessartine, fluorite, and quartz in the rhodonite or pyroxmangite ore.

Physical properties

Helvite crystals are generally anhedral, but sometimes show tetrahedral outlines. Color is amber yellow to siskin green. In thin section it is pale greenish yellow. Specific gravity measured with the pycnometer is $G_{25}^4 = 3.21$. Hardness, H=6. Optically isotropic without anomaly. Refractive index, $N=1.736$.

* Received July 9, 1959

* Partly read at the meeting of the Mineralogical Society of Japan on June 6, 1958.

**These ore bodies belong to the "Kaso type" according to YOSHIMURA's general classification of manganese deposits in Japan (YOSHIMURA, 1952 and 1953).

Chemical properties and chemical composition

The mineral emits sulfurous odour by crushing or grinding. By the acid treatment, the mineral is decomposed expelling sulfur as H_2S . To ascertain the existence of such sulfur in helvite, the staining method developed by GRUNER (1944) is most sensible and helpful. Helvite resembles garnet very much. They look similar even under the microscope. Staining method is rapid and easy to distinguish helvite from garnet.

The results of the chemical analysis of the helvite in question are given in Table 1, Column 1. A little content of CaO may be due to a small amount of fluorite included as impurity. Separation of aluminum from beryllium was based on the 8-hydroxyquinoline method. Sulfur was precipitated as $BaSO_4$ with barium chloride. The chemical formula calculated from the analysis on the basis of 13 (O, S) is:

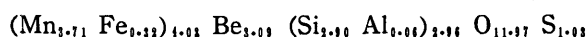


Table 1. Chemical analyses of helvite group minerals

	1	2	3	4	5	6	7	8
SiO ₂	31.29	33.33	31.54	29.48	30.26	32.46	32.25	30.19
Al ₂ O ₃	0.52	0.77	0.37	—	—	—	—	—
TiO ₂	none	—	0.01	—	—	—	—	—
BeO	13.88	14.92	13.60	14.17	12.70	13.52	13.43	12.58
MnO	47.36	44.43	26.51	11.53	1.22	51.12	—	—
FeO	4.19	4.45	18.02	37.53	6.81	—	51.44	—
ZnO	none	—	5.61	4.87	46.20	—	—	54.54
CaO	0.17	—	1.62	tr.	CuO 0.30	—	—	—
MgO	tr.	—	none	—	—	—	—	—
S	5.93	5.03	5.34	5.04	5.49	5.78	5.74	5.37
H ₂ O	0.01	—	0.06	—	0.21	—	—	—
	103.35	102.93	102.68	102.62	103.19	102.88	102.86	102.68
Less O=S	2.96	2.51	2.67	2.52	2.74	2.88	2.86	2.68
Total	100.39	100.42	100.01	100.10	100.45	100.00	100.00	100.00

1. Helvite from Yagisawa mine, Nagano Prefecture, Japan. Analyst: M. YOSHINAGA (this paper).
2. Helvite from Schwarzenberg, Saxony. Analyst: H. A. MIERS and G. T. PRIOR (MIERS and PRIOR, 1892).
3. Helvite from Iron Mountain, New Mexico. Analyst: R. E. STEVENS (GLASS and others, 1944).
4. Danalite from Redruth, Cornwall. Analyst: H. A. MIERS and G. T. PRIOR (MIERS and PRIOR, 1892).
5. Genthelvite from West Cheyenne Cañon, Colorado. Analyst: F. A. GENTH (GENTH, 1892).
6. Theoretical composition of helvite.
7. Theoretical composition of danalite.
8. Theoretical composition of genthelvite.

This formula shows good agreement with the general formula for the helvite group, $R_4 Be_3 Si_3 O_{12} S$, given by GLASS and others (1944), where R is Mn, Fe, and Zn. For the helvite group three end members are given, i. e. helvite (R=Mn), danalite (R=Fe), and genthelvite (R=Zn). But none of them is known in nature in a pure state. The chemical composition of all the known minerals is the mixture of the three end members, or of helvite and danalite. Triangular diagram of the helvite group is shown in Figure 1. The mineral from the Yagisawa mine (solid dot) falls

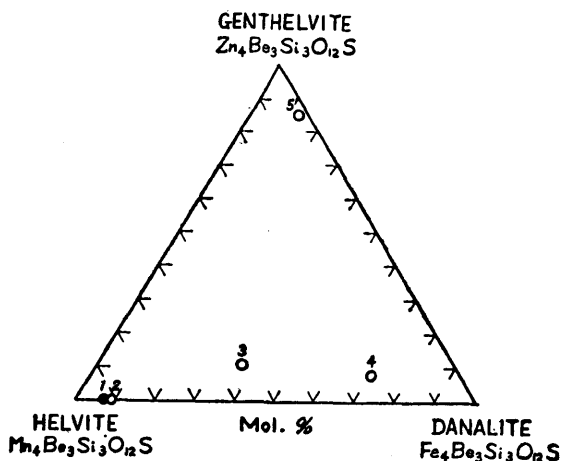


Figure 1. Chemical composition of the helvite group
 1. Helvite from Yagisawa mine (this paper).
 2. Helvite from Schwarzenberg, Saxony.
 3. Helvite from Iron Mountain, New Mexico.
 4. Danalite from Redruth, Cornwall.
 5. Genthelvite from West Cheyenne Cañon, Colorado.

nearest to the helvite end of the helvite-danalite series. The number given on each dot shows the column number in Table 1 respectively.

X-ray powder pattern

The X-ray powder diffraction data for Fe $K\alpha$ are given in Table 2, Column 1, and are compared with the data for helvite from Iron Mountain (Column 2) and danalite from Needle-point Mountain (Column 3; THOMPSON, 1957). The indices of reflection in Table 2 are those given by THOMPSON (1957).

Table 2. X-ray powder data for helvite and danalite

hkl	1		2		3	
	d (Å)	I	d (Å)	I	d (Å)	I
002					4.087	1
012	3.71	2	3.68	2	3.678	4
112	3.38	10	3.36	10	3.347	10
022	2.93	½	2.91	½	2.897	1
013	2.62	3	2.61	3	2.591	3
222	2.386	2	2.377	2	2.368	2
023	2.287	1	2.284	1	2.274	1
123	2.213	5	2.198	5	2.193	5
	2.152	½	2.137	½	2.129	1
004	2.066	½	2.053	½	2.052	1
033, 114	1.949	7	1.940	8	1.932	7
024	1.849	2	1.836	2	1.833	2
124	1.803	1	1.795	1	1.790	1
224	1.689	3	1.680	3	1.678	3
015, 134	1.621	2	1.613	2	1.607	2
025, 234	1.536	1	1.526	1	1.524	1
125	1.513	2	1.501	2	1.498	2
044	1.462	4	1.453	4	1.451	4
035, 334	1.418	3	1.411	3	1.410	3
006, 244	1.380	4	1.372	4	1.368	3
116, 235	1.342	4	1.337	4	1.333	3
026			1.299	½	1.297	½
145	1.277	4	1.269	4	1.268	4
226	1.246	1	1.243	1	1.237	½
036, 245	1.233	1	1.225	½	1.224	½
136	1.219	1	1.211	½	1.208	½
444	1.1950	1	1.1891	½	1.185	½
017, 055, 345	1.1691	1	1.1636	1	1.162	1
027, 146	1.1342	½	1.1283	½	1.128	½
127, 255	1.1259	5	1.1202	5	1.118	5
037	1.0866	2	1.0810	2	1.079	2
056, 346	1.0591	½	1.0527	1	1.051	1
237, 156	1.0508	5	1.0462	5	1.043	5
118, 147, 455	1.0181	4	1.0139	4	1.012	6
028, 446	1.0031	3	0.9989	2	0.9966	3
128, 247					0.9887	2
	$a_0=8.272$		$a_0=8.238$		$a_0=8.196$	

1. Helvite from Yagisawa mine. Unfiltered Fe K_α radiation, $\lambda=1.9373\text{\AA}$. Camera radius 28.65 mm (this paper).
2. Helvite from Iron Mountain, New Mexico. Unfiltered Fe K_α radiation, $\lambda=1.9373\text{\AA}$. Camera radius 28.65 mm (this paper).
3. Danalite from Needle-point Mountain, British Columbia. Filtered Fe K radiation. Camera radius 28.65 mm (THOMPSON, 1957).

The lattice dimensions of the helvites from the Yagisawa mine and Iron Mountain were determined by the graphical extrapolation method: They are $a_0 = 8.272$ and 8.238 . The extrapolation function used is $1/2 \cdot (\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$. After GLASS and others (1944) the extrapolated values of a_0 for the end members are 8.27, 8.18 and 8.10 respectively for helvite, danalite, and genthelvite. a_0 value of helvite from the Yagisawa mine shows that it is a purer manganese member, while the specimen from Iron Mountain belongs to iron-rich helvite.

Associated minerals

Minerals found intimately associated with helvite are as follows; rhodonite, pyroxmangite, spessartine, rhodochrosite, dannemorite, huebnerite, fluorite, marmatite, and quartz.

(i) Dannemorite

Dannemorite is found sometimes associated with helvite. Pale brown fibers less than 1.0 millimeter in length. The X-ray powder diffraction data are given in Table 3. They were compared with the data for dannemorite* of the Renge mine,

Table 3. X-ray powder data for dannemorite from Yagisawa mine

d (Å)	I	d (Å)	I
8.36	7	1.869	1
4.55	½	1.786	½
4.18	½	1.750	½
3.92	½	1.702	½
3.66	½	1.654	5
3.43	2	1.623	1
3.27	3	1.591	½
3.08	10	1.558	1
2.97	1	1.513	½
2.84	3	1.487	½
2.75	4	1.450	½
2.62	3	1.411	7
2.53	3	1.393	½
2.31	1	1.376	1
2.25	½	1.352	½
2.19	5	1.333	½
2.09	½	1.301	1
2.03	½	1.292	2
1.973	½	1.185	3

Unfiltered Fe K α radiation, $\lambda = 1.9373 \text{ \AA}$. Camera radius 28.65 mm.

Yamaguchi Prefecture (YOSHIMURA and SHIROZU, 1947), cummingtonite from Holland (ASTM Cards No. 7-382), and grunerite from France (ASTM Cards No. 7-394).

* The X-ray powder photographs were taken by the writer in the course of this study.

The specimen from the Yagisawa mine was identified with dannemorite.

(ii) Huebnerite

Huebnerite was found as platy crystals associated with coarse grains of pyroxmangite. This mineral is reddish black in color. Reddish brown when powdered. A crystal is 6×4 millimeters in size and other smaller grains. The X-ray diffraction patterns shown in Table 4 agree well with those reported of huebnerite in Japan (LEE, 1955), (KATO, 1958).

Table 4. X-ray powder data for huebnerite from Yagisawa mine

d (Å)	I	d (Å)	I
5.72	2	1.644	½
4.80	6	1.595	1
3.75	6	1.523	5
3.66	4	1.507	1
(β) 3.27	1	1.495	½
2.99	10	1.482	1
2.94	10	1.468	5
2.87	3	1.450	2
(β) 2.74	½	1.442	6
2.48	7	1.402	½
2.41	2	1.383	6
2.23	1	1.349	1
2.20	4	1.341	1
2.08	½	1.327	5
2.05	1	1.321	1
2.02	1	1.2943	1
(β) 1.967	½	1.2786	1
1.919	1	1.2473	2
1.881	2	1.2301	3
1.843	2	1.2027	5
1.781	8	1.1876	3
1.746	5	1.1768	½
1.719	6	1.1517	1
1.676	1	1.1441	3

Unfiltered Fe K_α radiation, λ=1.9373Å. Camera radius 28.65 mm.

(iii) Fluorite

Fluorite is also seen closely associated with helvite. It is found widely distributed in the rhodonite and pyroxmangite ores of this mine. Colorless crystals with refraction index, N=1.434.

Acknowledgments

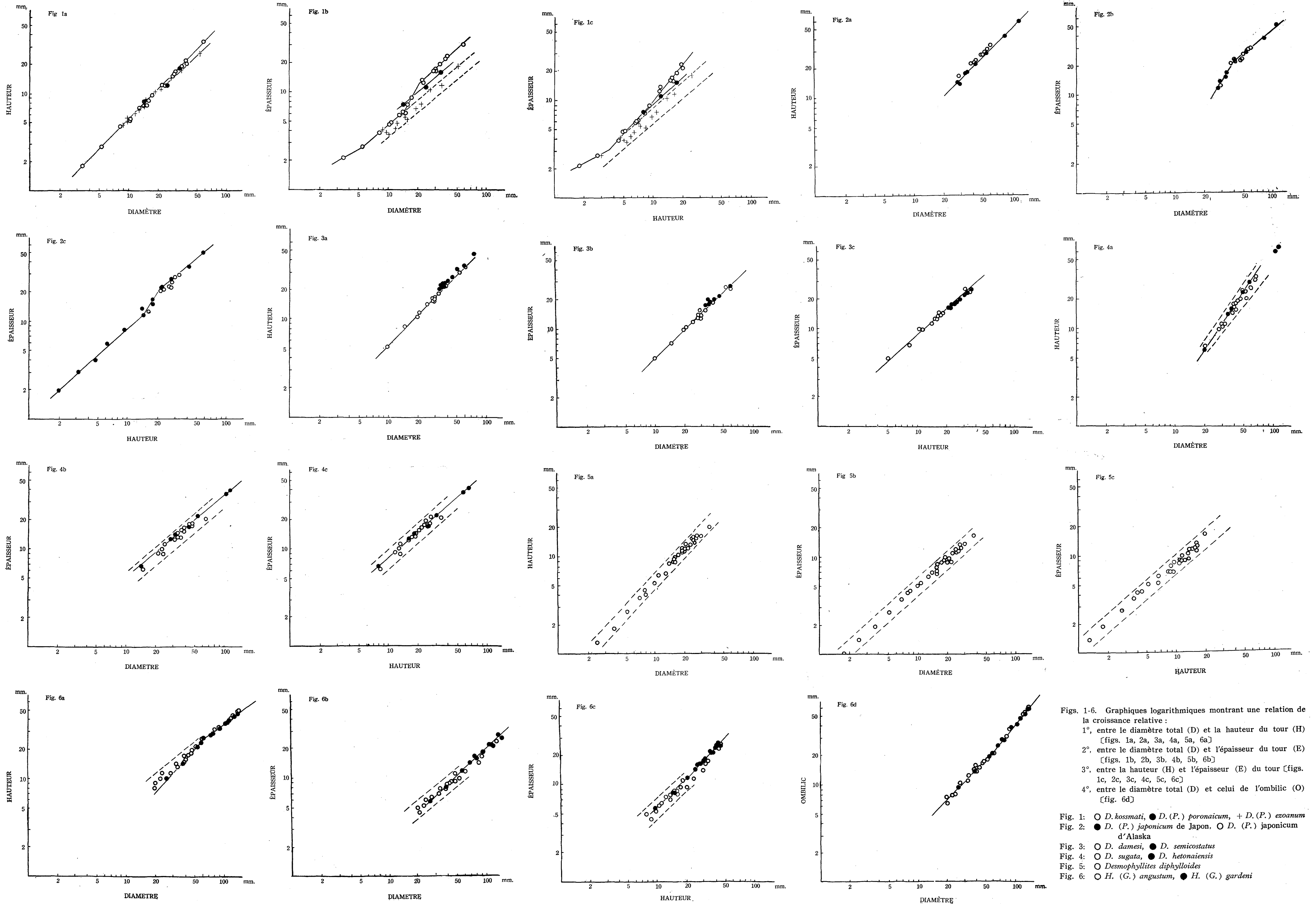
The writer wishes to express his thanks to Professor Toyofumi YOSHIMURA of Kyushu University for his kind guidance and critical reading of this paper in manu-

script, and to Doctors Yohachiro OKAMOTO and Kin'ichi SAKURAI for providing the samples of helvite from Iron Mountain used in this study. His thanks are also due to Professor Takeo WATANABE of the University of Tokyo, and Assistant Professor Haruo SHIROZU of Kyushu University for their kind advices.

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Figs. 1-6. Graphiques logarithmiques montrant une relation de la croissance relative :

- 1°, entre le diamètre total (D) et la hauteur du tour (H) [figs. 1a, 2a, 3a, 4a, 5a, 6a]
- 2°, entre le diamètre total (D) et l'épaisseur du tour (E) [figs. 1b, 2b, 3b, 4b, 5b, 6b]
- 3°, entre la hauteur (H) et l'épaisseur (E) du tour [figs. 1c, 2c, 3c, 4c, 5c, 6c]
- 4°, entre le diamètre total (D) et celui de l'ombilic (O) [fig. 6d]

Fig. 1: ○ *D. kossmati*, ● *D. (P.) poronaicum*, + *D. (P.) ezoanum*
 Fig. 2: ● *D. (P.) japonicum* de Japon, ○ *D. (P.) japonicum* d'Alaska
 Fig. 3: ○ *D. damesi*, ● *D. semicostatus*
 Fig. 4: ○ *D. sugata*, ● *D. hetonaiensis*
 Fig. 5: ○ *Desmophyllites diphyloides*
 Fig. 6: ○ *H. (G.) angustum*, ● *H. (G.) gardeni*

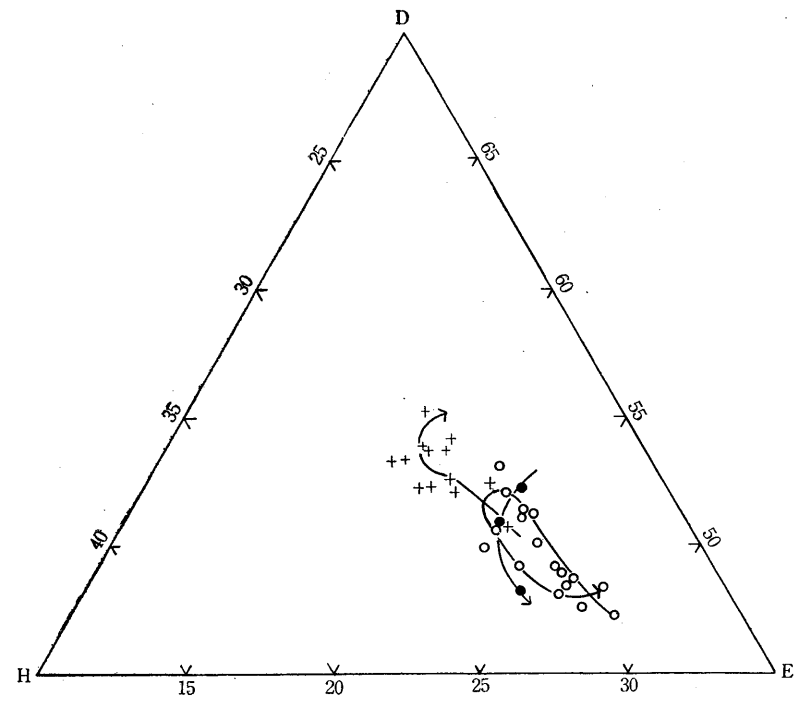


Fig. 7

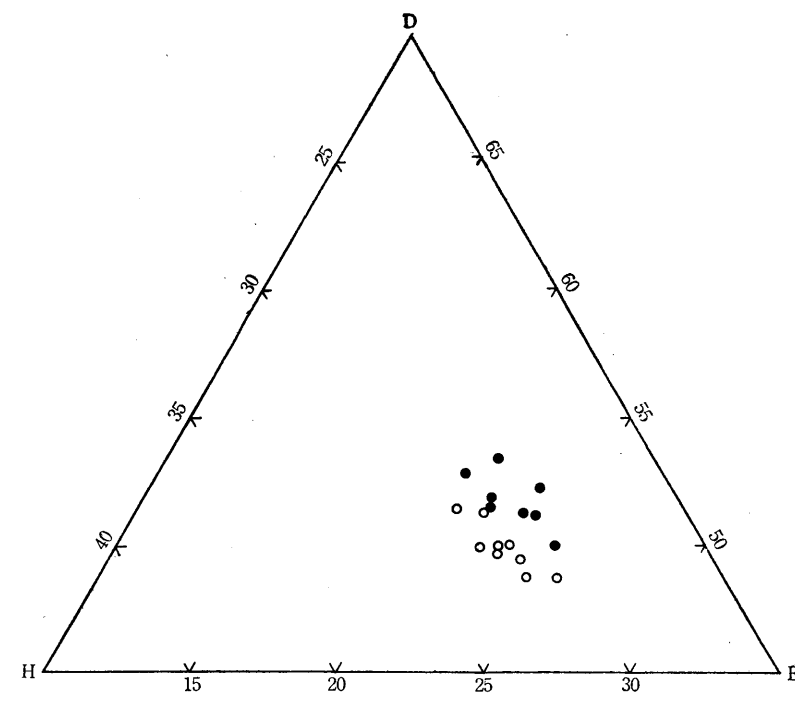


Fig. 8

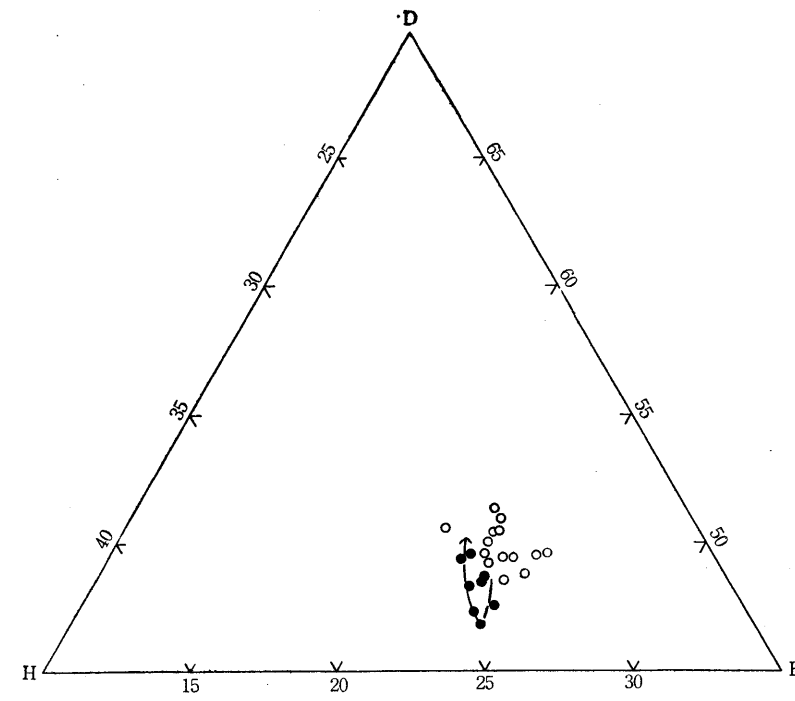


Fig. 9

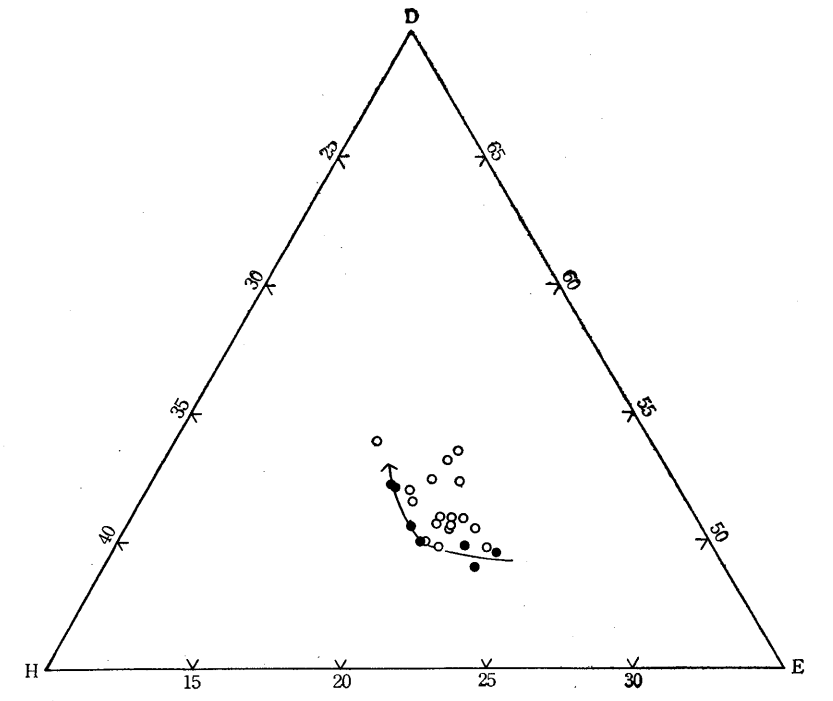


Fig. 10

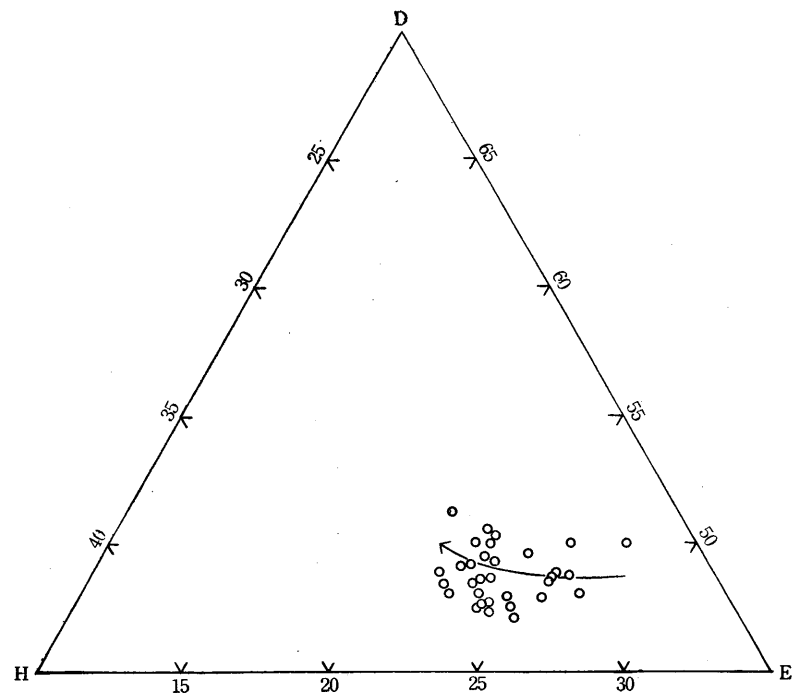


Fig. 11

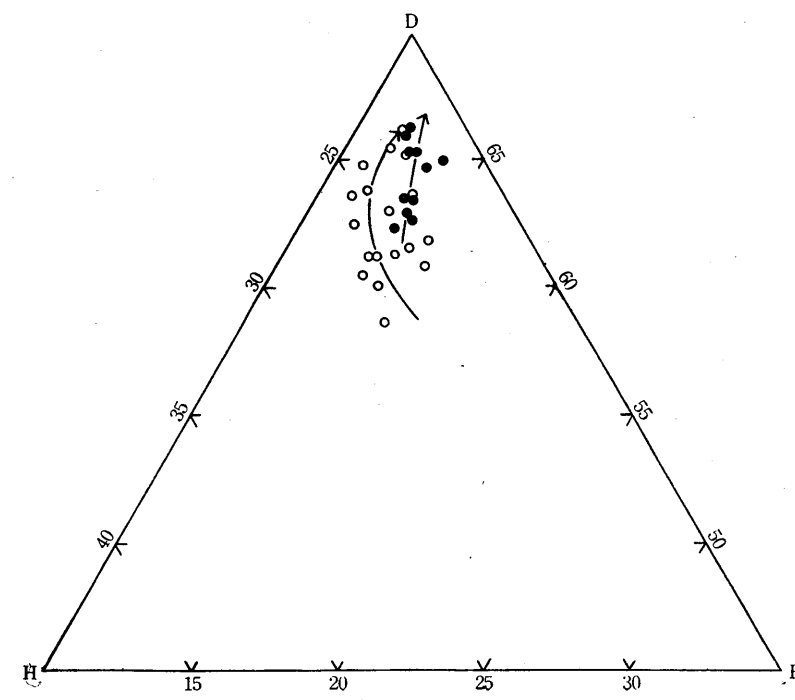


Fig. 12

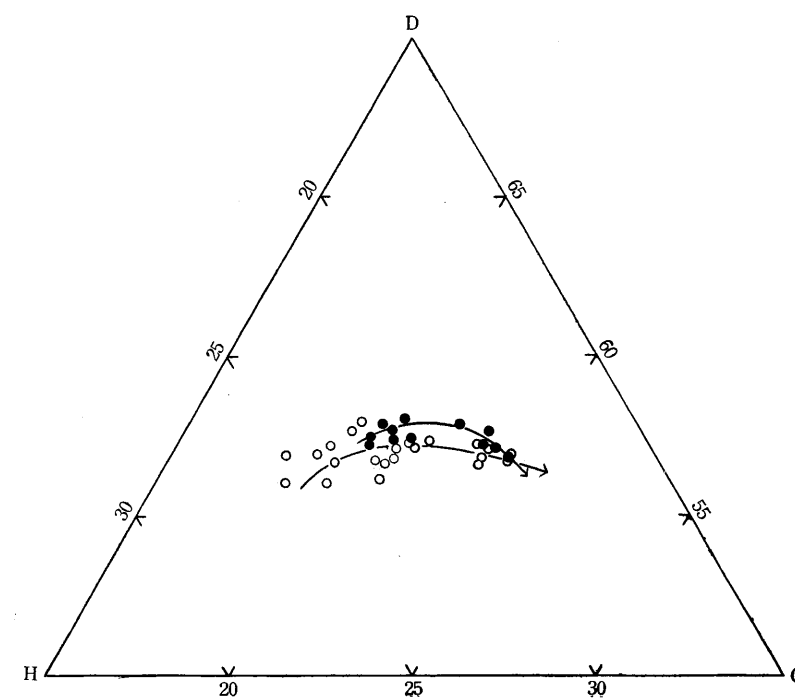


Fig. 13

Figs. 7-13. Diagrammes triangulaires montrant la proportion des dimensions de quelques espèces. Les symboles (D, H, E, O) sont adoptés de même que Figs. 1-6. La courbe de la flèche montre le changement ontogénique de la proportion.

Fig. 7: ○ *D. kossmati*, ● *D. (P.) poronaicum*
+ *D. (P.) ezoanum*

Fig. 8: ● *D. (P.) japonicum* de Japon
○ *D. (P.) japonicum* d'Alaska

Fig. 9: ○ *D. damesi*, ● *D. semicostatus*

Fig. 10: ○ *D. sugata*, ● *D. hetonaiensis*

Fig. 11: ○ *Desmophyllites diphyloides*

Fig. 12: ○ *H. angustum*, ● *H. gardeni*

Fig. 13: ○ *H. angustum*, ● *H. gardeni*