GEOLOGINEN TUTKIMUSLAITOS

BULLETIN
DE LA
COMMISSION GÉOLOGIQUE
DE FINLANDE

N:o 158

THERMOCHEMICAL INVESTIGATION OF THE ÅKERMANITE-GEHLENITE SERIES

BY

K. J. NEUVONEN

HELSINKI 1952

GEOLOGINEN TUTKIMUSLAITOS
BULLETIN DE LA COMMISSION GÉOLOGIQUE DE FINLANDE N:o 158

THERMOCHEMICAL INVESTIGATION OF THE ÅKERMANITE-GEHLENITE SERIES

BY

K. J. NEUVONEN

HELSINKI 1952

Helsinki 1952. Valtioneuvoston kirjapaino

TABLE OF CONTENTS

PREFACE

The present work originated during the writer's stay as a Visiting Investigator at the Geophysical Laboratory of the Carnegie Institution of Washington, D. C., U. S. A., in the period 1948—1950. This opportunity was generously offered by the Trustees of the Institution at the instigation of Dr. L. H. Adams, Director of the Laboratory, and Dr. Vannevar Bush, President of the Institution. While engaged in the synthesis of the samples investigated calorimetrically, instructions and technical advice was given by the staff members of the Laboratory, specially by Dr. N. L. Bowen, Dr. J. F. Schairer, and Dr. F. C. Kracek. The hydrothermal quenching apparatus was placed at the writer's disposal by Dr. O. F. Tuttle. The calorimetric operation technique was introduced by Dr. Kracek who also offered fruitful advice in discussions of the problem. The X-ray diffraction technique was demonstrated by Dr. Hatten S. Yoder, and samples for comparison in the X-ray examination were kindly given by Dr. Schairer. The point counter technique used in estimation of the amount of impurities in the natural melilite samples was showed by Dr. Felix Chayes.

After having returned to Finland, the work was continued at the Institute of Geology, University of Helsinki, were the newly built solution calorimeter was placed at the writer's disposal by Dr. Th. G. Sahama. He also contributed assistance and suggestions during the investigation and in the preparation of the manuscript.

A natural melilite specimen was kindly sent by Dr. C. D. Wentworth, Board of Water Supply, Honolulu, T. H. A number of other melilite-bearing rock specimens were received from different persons. For the present work, these have been used only for comparison. Some of the mineralogical results obtained on these specimens will be published later.

A natural brucite specimen was obtained through the courtesy of Dr. Adolf Pabst, of the University of California, Berkeley, Calif.

The publication of this work in the »Bulletin de la Commission géologique de Finlande» was made possible by Professor Aarne Laitakari, who also gave a leave of absence for the period from 1948 to 1950. Much encouragement during the work was also given by Dr. Ahti Simonen who is in charge of the geological mapping of Finland, at the Geological Survey of this Country.

The chemical analyses published in this paper were made by Mr. H. B. Wiik of the Geological Survey of Finland.

The figures in the paper have been drawn by Miss Thyra Åberg and Mrs. Toini Mikkola, both of the Geological Survey of Finland.

Constructive criticism of the English used in the manuscript was offered by Professor Etta MacDonald.

To all the persons mentioned the writer likes to express his most sincere thanks.

The writer.

INTRODUCTION

The importance of the application of physical chemistry to geology has been generally accepted by the petrologists since the days of professor J. H. L. Vogt. During the last fifty years the ideas concerning petrological processes greatly developed primarily as a result of the increased knowledge of physical properties of rock making minerals. Because of the need of experimental data on these minerals, a new school arose among the petrologists who began to use laboratory equipment in addition to pick and hammer. A new method and technique for studying liquid-solid equilibrium in the silicate systems was developed at the Geophysical Laboratory of the Carnegie Institution of Washington. The use of these methods during the last forty years has produced results which every petrologist in the field has to note. On the other hand this method like any other has its limitations. The major limitation is that reactions in silicate systems mostly cannot be examined in the absence of a liquid or vapor phase because of the slowness of ions diffusing through a solid.

The application of quantitative thermodynamics may be thought to offer aid in the study of the subsolidus field in silicate systems. For doing this the heat of formation, heat content, and entropy data are needed for minerals. The heat of formation of silicates are obtained through heat of solution measurements using hydrofluoric acid (or acid mixtures containing HF) as dissolving agent. In case of silicate minerals, it is convenient to express the heat of formation of a mineral from the component oxides and is evaluated from the heat of solution of the mineral and from the heats of solution of the corresponding oxide components.

One of the most important ternary silicate systems is the system CaO-MgO-SiO_2, in which many significant rock making minerals occur. The heat of formation has been previously determined for the following crystalline phases in this system: $CaSiO_3$, $MgSiO_3$, Mg_2SiO_4 (Torgeson and Sahama, 1948), Ca_2SiO_4, Ca_3SiO_5 (King, 1951), $CaMgSiO_4$, $Ca_3MgSi_2O_8$ (Neuvonen, 1952). The only crystalline compounds in the system for which the heat-of-formation values are not known are $CaMg(SiO_3)_2$ (diopside), $Ca_3Si_2O_7$, and $Ca_2MgSi_2O_7$ (åkermanite). It is now one of the principal purposes of the present study to determine the heats of formation of diopside and åkermanite. Åkermanite does not occur in nature as a pure compound, $Ca_2MgSi_2O_7$, but it does occur in solid solution with gehlenite, $Ca_2Al_2SiO_7$, and with other compounds as the mineral group melilite. It is therefore understood that these two minerals must be investigated together.

The isomorphic mixture of åkermanite and gehlenite offers one of the best examples of a complete solid solution among the silicate minerals, as shown by Ferguson and Buddington (1920). Two solid solution series of silicate minerals, *viz.* Mg-Fe olivines and Mg-Fe orthopyroxenes have been previously studied thermochemically by Sahama and Torgeson (1949). As stated by these authors, the heat-of-solution values obtained indicate that the isomorphism in both these solid solution series approaches ideality. The present investigation of the åkermanite-gehlenite series was undertaken in order to find out whether or not the method is able to detect possible deviations from ideality.

It was first planned to use only natural melilite samples. Artificial samples had to be used, however, because of the lack of sufficient number of natural melilites that could be considered close enough representatives of the binary system in question.

METHODS

PURIFICATION OF THE NATURAL MINERALS USED

In purifying the natural minerals for calorimetry, the corresponding rock specimens were first ground to approximately the same grain size or finer than that of the rock. After grinding, the finest portion of the powder, which remained suspended, was washed out with hot water. The separation proper began with centrifuging the material in Clerici's solution of a suitable specific gravity. From several successive centrifugations a fraction was obtained that was virtually free from grains of foreign minerals. This fraction, however, still contained numerous small inclusions, detectable on examining the powder under the microscope. To liberate these inclusions, the material was pulverized in a porcelain ball mill. The material, now sufficiently fine-grained, was subjected to further purification with the centrifuge and Clerici's solution. A technical limit for the separation is given by the grain size required and by the viscosity of the Clerici's solution employed.

The amount of impurities contained in the final fractions to be analyzed was estimated by counting a large number of grains (about 2 000) in a microscopic preparation made in a liquid with an index of refractivity close to that of the mineral. The counting was made with a point counter, and using separate counting keys for »pure», »impure», and »foreign» grains the percentage of impurities was evaluated. The amount of inclusions in the impure grains was roughly estimated from the areal ratio of the inclusions to the whole grain.

PREPARATION OF SYNTHETIC ÅKERMANITE-GEHLENITE SAMPLES

The preparation of the synthetic samples of the åkermanite-gehlenite series was done at the Geophysical Laboratory of the Carnegie Institution of Washington. The general technique applied, and the starting materials were those used in syntheses at this Laboratory. These are as follows:

SiO_2: Quartz of the regular Geophysical Laboratory supply of Lake Toxaway mineral, leached with hydrochloric acid. The residue from evaporation with HF and H_2SO_4 amounts to 0.04 percent (Dr. J. W.

Greig, of the Geophysical Laboratory, personal communication). To invert the quartz to cristobalite and to eliminate water, the material was heated for one hour at 1 500°C.

MgO: Reagent grade material obtained from J. T. Baker Chemical Co., lot No. 82 735, containing 0.2 percent total alkalis. This material was heated for one hour at 1 500° C.

Al_2O_3: »Tabular Alumina T 61, free from iron», obtained from the Aluminum Company of America. The following impurities are reported by the manufacturer: SiO_2 0.02, Fe_2O_3 0.03, TiO_2 0.02, and Na_2O 0.02 percent. This material was heated for three hours at 1 300° C.

$CaCO_3$: Reagent grade material obtained from J. T. Baker Chemical Co., lot No. 10 641. To eliminate moisture it was heated at 130° C for 100 hours.

Calculated amounts of starting materials, corresponding to five or ten grams of the product, were weighed into a platinum crucible. After mixing, the material was slowly heated to 1100° C and kept at that temperature for 12 hours. The samples were melted by heating in a compressed air gas furnace for one hour at 1600°—1700° C and quenched to glass. The melting and quenching procedure was repeated as many times as was necessary to give a homogeneous product. Homogeneity was tested under the microscope using dark field illumination and an immersion liquid with an appropriate index of refractivity. If the weight of the product after driving off the CO_2 or after the first quenching deviated more than 0.05 percent from the calculated weight, the material was discarded. Between the quenchings, the glass was crushed in a diamond mortar and the pieces of iron were picked out by means of a strong hand magnet.

Following the technique described above, several portions of each desired mixture were prepared. The final samples varied in amount from 15 to 30 grams.

For crystallization, approximately ten grams of each glassy sample was heated for one or more hours at a temperature of about 30° C below the corresponding solidus temperature in the åkermanite-gehlenite series as determined by Ferguson and Buddington (1920) and later corrected by Osborn and Schairer (1941). Microscopic examination showed that the crystallization was complete and that no foreign grains were present in the material.

CALORIMETRIC TECHNIQUE

The first experiments of measuring the heat of solution of the synthetic melilites were undertaken at the Geophysical Laboratory, using 20 percent hydrofluoric acid as dissolving agent. The calorimeter used was that built by Dr. F. C. Kracek (Adams, 1949), of that Laboratory. In this acid, however, a precipitate was formed in the calorimeter and, accordingly, the results could not be reproduced with reasonable accuracy.

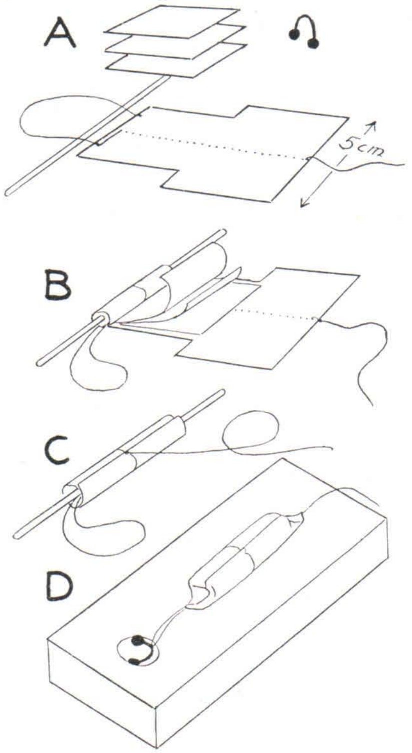
Later, the work was continued at the Institute of Geology, University of Helsinki, Finland, using the newly built solution calorimeter, and the general technique briefly described by Sahama and Neuvonen (1951). After some preliminary tests it was found necessary to lower the HF content of the acid as much as possible. The acid mixture selected for the work contained 5 percent by weight of hydrofluoric acid and 20 percent by weight (actually 19.95 %) of hydrochloric acid. In this acid mixture no precipitate was formed in any of the solution experiments, provided that the amount of CaO content of the sample did not exceed about 300 milligrams. In most cases it also was possible to dissolve two fair size samples in one acid filling (856 ± 0.5 grams of the acid mixture).

Pure åkermanite, contained in a gelatin capsule, dissolved in the acid mixture mentioned without any difficulties. The more gehlenite rich members of the series, however, did not dissolve at all or dissolved much too slowly, when contained in a gelatin capsule. Being very easily soluble in acids the melilite powder reacts so vigorously that a gelatinous silicic acid, liberated in the reaction, forms a mantle around the clumpy material, thus preventing further reaction. The gelatinous silica once formed dissolves too slowly to give good reproducible results.

Considerably shorter runs and better reproducible results were obtained by a method in which the powdered material was contained in folded paper envelope instead of a gelatin capsule. This paper envelope was folded in a way easily opened by means of silk yarn when immersed in the acid. If the grain size of the material was not too fine (coarser than 65 mesh), this method worked quite well.

According to the final procedure, used for most of the samples, the material to be dissolved was spread as a thin layer on a filter paper of suitable form and size, and the paper was rolled to a firm roll easily opened by itself when wetted by the acid. As an extra precaution, a silk yarn was attached to the paper to improve opening of the roll. This form of a container proved to be very reliable and useful also for materials that showed no tendency to form silicic acid mantle around the grains. In fact, the writer is of the opinion that the dissolution of quartz in this acid mixture was made possible by the use of this type of container. A more detailed description of the method might, therefore, be desirable.

A piece of filter paper, treated with hydrochloric and hydrofluoric acid by the manufacturer, is cut in a form of a broad »T» (Fig. 1 A). Using a needle and silk thread a loop is formed at the lower end of the »T» and the thread, continuing under the paper, is fastened to the top edge of the paper with a knot. The thread exceeds the knot in length with about 30 cm. and is marked to indicate the distance from the surface of the acid to the top of the capsule tube.



← Fig. 1. Making the filter paper container. A. Materials assembled, loop sewed in the T-shaped paper. B. Papers rolled on the glass rod. C. Roll completed. D. Container completed, platinum weight attached, lying on plastic mount.

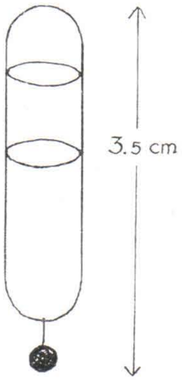


Fig. 2. Platinum skeleton for gelatin capsules.

The material to be dissolved is spread on the surface of the lower part of the »T». If necessary, additional layers of material may be applied separated by thin sheets of paper. The folio so formed, is rolled around a glass rod (Fig. 1, B and C), the rod removed, and the ends of the paper roll are closed by a firm twisting. A platinum weight is fastened to the loop of the silk thread (Fig. 1, D). If the material is hygroscopic, it is advisable to keep the filled container in a desiccator up to the moment of dropping into the calorimeter. As it is dropped, one gives a firm pull to the silk yarn at the moment when the sample gets immersed in the acid. This insures a fast opening of the container. As is seen from the figure, the platinum weight was fastened outside the paper container.

If a gelatin capsule was used, it was placed inside a skeleton made of platinum wire. A drawing of this weight is shown in Fig. 2.

All materials to be dissolved except CaO and Al_2O_3 were dried at 130° C and cooled in a desiccator before weighing. The treatment for CaO and Al_2O_3 was somewhat different and is described later.

Weighing of the calorimetric acid was made with an accuracy of 0.1 gram, using hydrochloric and hydrofluoric acid of exactly known concentration, to give 856 grams of the desired acid mixture. A calibration of the calorimeter was made for every individual heat-of-solution measurement. When two subsequent runs were made in the same acid filling, a common calibration for the two runs was used.

The thermal leakage calculations were based on the method of Regnault-Pfaundler (White, 1928, p. 40) and the area $\int_{t_0}^{t} f\,(x) \cdot d\,x$ was evaluated using the trapeze formula.

The galvanometer readings were taken every two minutes during the rating periods and every one minute during the solution or heating period. The temperature rise, measured in absolute microvolts, was converted to defined calories using the individual calibration values (joules/microvolt) and the relationship: 1 defined calorie = 4.1840 international joules.

CORRECTIONS APPLIED

The heat-of-solution values given in the next chapter, include several corrections. These corrections must be briefly described.

All the heat-of-solution values are given for materials at 25° C dissolved in the acid mixture at 75° C. Therefore, a correction was applied for the deviation of the actual temperature of the sample from 25° C at the time of dropping the capsule. The following figures were used for the heat capacities of the dissolved materials, calculated on the basis of the heat capacity equations listed by Kelley (1949):

	Cp
Gehlenite	0.193 cal/gram/degree
Åkermanite	0.241*)
Quartz	0.176
Calcium oxide	0.189
Diopside	0.189
Brucite	0.311

If gelatin capsules were used, an error was introduced because of the heat of reaction of gelatin with the acid. This error was corrected by measuring the heat of solution of gelatin in the acid mixture, and subtracting this value from the observed heat-of-solution value. The five runs made gave:

Run No.	Heat of solution of gelatin in the acid mixture used.
1.	+ 10.14 cal/gram
2.	+ 11.07
3.	+ 10.73
4.	+ 10.79
5.	+ 10.41
Average:	+ 10.63 ± 0.32 cal/gram.

---

*) Experimental measurements of the heat capacity of åkermanite not being available, this figure was calculated on the basis of the assumed relationship:
$C_{p_{\text{åkermanite}}} = C_{p_{Ca_2SiO_4}} + C_{p_{MgSiO_3}}$. The error introduced thereby is negligible.

This average value for gelatin at 25° C dissolved in acid at 75° C was used for corrections. An additional correction due to deviation of the temperature of gelatin from 25° C was also applied using 0.5 cal/degree/gram as the heat capacity of gelatin.

Filter paper, used for capsules, did not show any heat of reaction with the acid. Thus the only correction caused by the paper was that due to the difference in heat content between the paper at the temperature at the moment of dropping and at the temperature of acid. The mean heat capacity of the paper for that temperature range was determined by dropping considerably large samples of paper into the calorimeter. Four measurements gave:

Mean heat capacity of filter paper »No. 41, W. and R. Balston» in the temperature range 25°-75° C.

Run No. 1.	0.217 cal/gram/degree
2.	0.212
3.	0.219
4.	0.221
Average:	0.217 ± 0.003 cal/gram/degree.

The correction due to deviation of the temperature of the platinum weight from the temperature of the acid was made in a similar manner than that applied for the filter paper. For the heat capacity of platinum the figure 0.032 cal/gram/degree was used.

Corrections caused by the water content of the samples and by other deviations from the theoretical composition are described in connection with the listed heat-of-solution values of dissolved materials.

Of each sample, at least four reliable heat-of-solution runs were made. The arithmetic average of these individual measurements was adopted for the calculations. The uncertainty was computed according to the relationship:

$$\text{Uncertainty} = 2\sqrt{\frac{\Delta^2{}_1 + \Delta^2{}_2 + \Delta^2{}_3 + \ldots + \Delta^2{}_n}{n\,(n-1)}}$$

in which Δ equals the deviation of an individual measurement from the average and n indicates the number of runs included.

MATERIALS

NATURAL MELILITES

Two natural melilite minerals were separated and purified following the technique described above.

1. Melilite from melilite basalt, Honolulu, Hawaii, belonging to the Sugar Loaf Series (Cross, 1915). This specimen was obtained through

the courtesy of Dr. C. D. Wentworth, Board of Water Supply, Honolulu, Hawaii.

Melilite grains occur in the rock in association with olivine, nepheline, magnetite, some augite, and accessories. Chemical analysis listed in Table I, shows that the mineral is very rich in soda. The estimated amount of impurities in the sample and the optical properties of the mineral are also given in Table I.

2. Melilite, derived from a massive melilite (»gehlenite») specimen purchased from Ward's Natural Science Establishment, Inc., and originating from Luna County, New Mexico. The chemical analysis, optical properties, and an estimation of the amount of impurities of the sample are given in Table I.

Table I. Chemical composition and optical properties of two melilites used for calorimetric measurements. Analyst H. B. Wiik.

Melilite from melilite basalt, Sugar Loaf Series, Honolulu, Hawaii.				Melilite, Luna County, New Mexico.			
Weight percent		Atomic ratio multiplied by 10,000		Weight percent		Atomic ratio multiplied by 10,000	
SiO_2	42.81	Si	7 128	SiO_2	32.60	Si	5 428
Al_2O_3	6.59	Al	1 293	Al_2O_3	18.10	Al	3 551
Fe_2O_3	1.90	Fe^{3+}	238	Fe_2O_3	0.95	Fe^{3+}	119
FeO	3.06	Fe^{2+}	426	FeO	0.92	Fe^{2+}	128
MnO	0.08	Mn	11	MnO	0.02	Mn	3
MgO	7.48	Mg	1 855	MgO	6.91	Mg	1 714
CaO	33.27	Ca	5 933	CaO	40.08	Ca	7 147
Na_2O	3.75	Na	1 210	Na_2O	0.18	Na	58
K_2O	0.33	K	70	K_2O	0.21	K	44
TiO_2	0.12	Ti	15	TiO_2	0.00	Ti	—
P_2O_5	n. d.	P	—	P_2O_5	0.00	P	—
H_2O+	0.43	OH	477	H_2O+	0.48	OH	533
H_2O-	0.00			H_2O-	0.00		
Total	99.82			Total	100.45		
Total impurities		½ percent			½ percent		
ω	1.630				1.656		
ε	1.637				1.654		

Using the »Norelco» Geiger Counter recording X-ray spectrometer, Type No. 12021, of the North American Philips Co., Inc., with Cu-K radiation and Ni-filter, powder diffraction patterns were obtained for both natural melilites. These patterns show a full similarity with those obtained for synthetic preparations given on p. 16. All the critical »peaks» in the patterns were sharp and clear, indicating that zoned structure was not present in the samples in detectable amounts. Unit cell dimensions, measured directly from the charts, without any internal standard, are for the two natural samples:

Melilite, Honolulu, Hawaii.	$a_0 = 7.78$,	$c_0 = 5.02$ Å
Melilite, Luna County, New Mexico.	$a_0 = 7.77$,	$c_0 = 5.05$ Å

SYNTHETIC SAMPLES OF ÅKERMANITE-GEHLENITE SERIES

Employing the preparation technique described above, glassy and crystalline samples of pure åkermanite, pure gehlenite, and of isomorphic mixture corresponding to 85, 74, 50, and 25 molecular percent of åkermanite, respectively, were synthesized.

The composition of the preparations was tested by optical and X-ray methods. The optical properties of the glassy and crystalline samples are shown in Table II and in Fig. 3. For comparison, the optical properties of the åkermanite-gehlenite series, as determined by Ferguson and Buddington (1920), are plotted in the diagram in Fig. 3. The agreement between the values is very close.

Table II. Index of refraction of the synthetic melilites for Na-light.

Molecular composition	ω	ε	n_{glass}
Å	1.631	1.638	1.640
$Å_{85}$	1.637	1.643	1.639
$Å_{74}$	1.643	1.647	1.639
$Å_{50}$	1.653	1.671	1.638
$Å_{25}$	1.663	1.665	1.637
$Å_0 = G$	1.667	1.657	1.636

X-ray powder diffraction patterns were obtained for all crystalline preparations, using the »Norelco» recording spectrometer. The d-spacings were assigned indices applying the unit cell dimensions given by Andrews (1948). Because of some deviation from his values, the unit cell dimensions were determined for all the crystalline preparations by measuring the d-spacings of several (hk0) and (00l) planes, utilizing the counting circuit of the instrument. For this purpose some additional samples, originating from the work on the ternary system pseudowollastonite-åkermanite-gehlenite by Osborn and Schairer (1941), were kindly placed at the writer's disposal by Dr. J. F. Schairer.

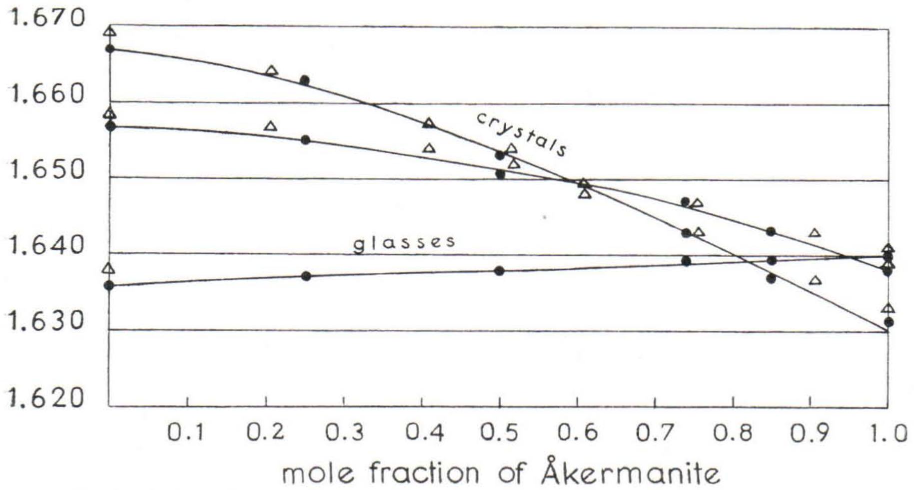


Fig. 3. Index of refractivity in the åkermanite-gehlenite series for Na-light.
△ after Ferguson and Buddington (1920).
● present determinations.

The dimensions of the unit cell and the ratio c_0/a_0 are shown in Table III and plotted against composition in Fig. 4.

Table III. Unit cell dimensions in Ångström units and the ratio c_0/a_0 in the artificial åkermanite-gehlenite series. Uncertainty ± 0.003 Å.

Mole percent gehlenite	100	75	50	26	0
c_0	5.076	5.060	5.045	5.030	5.015
a_0	7.685	7.720	7.760	7.800	7.840
c_0 / a_0	0.661	0.655	0.650	0.645	0.640

These values obtained are in good agreement with the values given by Ervin and Osborn (1949). No such deviation from linearity as observed by Andrews (1948) can be seen in the present measurements.

In the paper by Ervin and Osborn *(op. cit.)*, diagrams are given for d-spacings of some of the lines plotted against the composition. Since the unit cell dimensions a_0 and c_0 change in opposite directions with changing composition, some of the d-spacings shift towards higher, some towards lower d-values. The distance between two lines, shifting in opposite directions on the chart, serves thus as a more accurate indication of the composition. Furthermore, no internal standard is needed in this method, while it is necessary if absolute d-values are used. Several pairs of lines could be used, the only limitation is the interference of other lines in

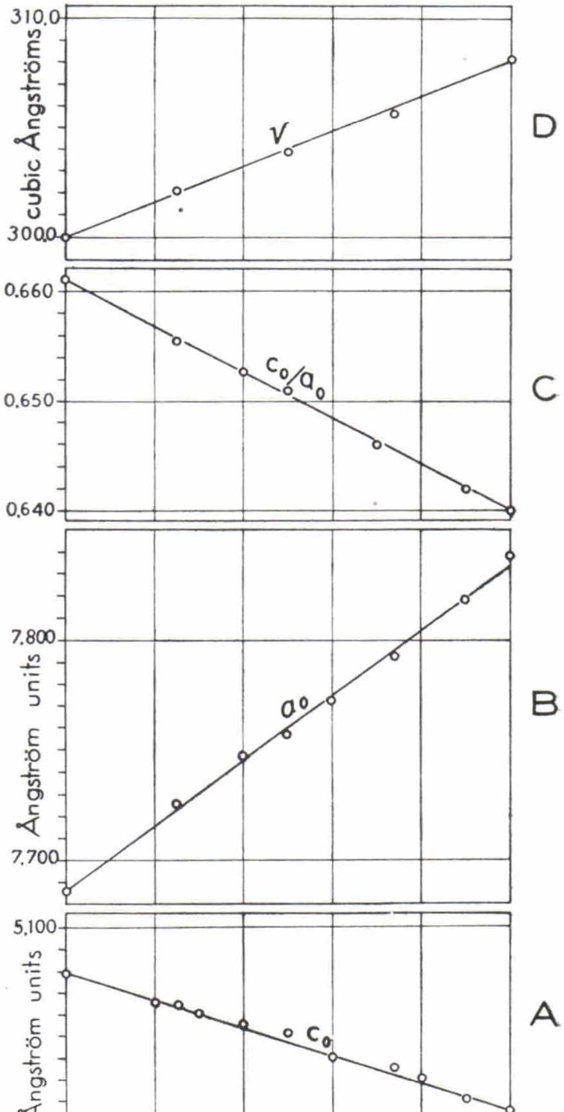


Fig. 4. The dimension of the unit cell, the ratio c_0/a_0, and the unit cell volume of synthetic åkermanite-gehlenite series. A. The length of the c-axis determined from the d-spacings of (004), (002), and (213) in Ångström units. B. The lenght of the a-axis determined from the d-spacings of (400), (440), and (620) in Ångström units. C. The ratio c_0/a_0. D. The unit cell volume in cubic Ångströms.

the pattern. The variation of the distance of the pairs (213)—(440) and (213)—(521), which are useful throughout the series, is shown in Fig. 5.

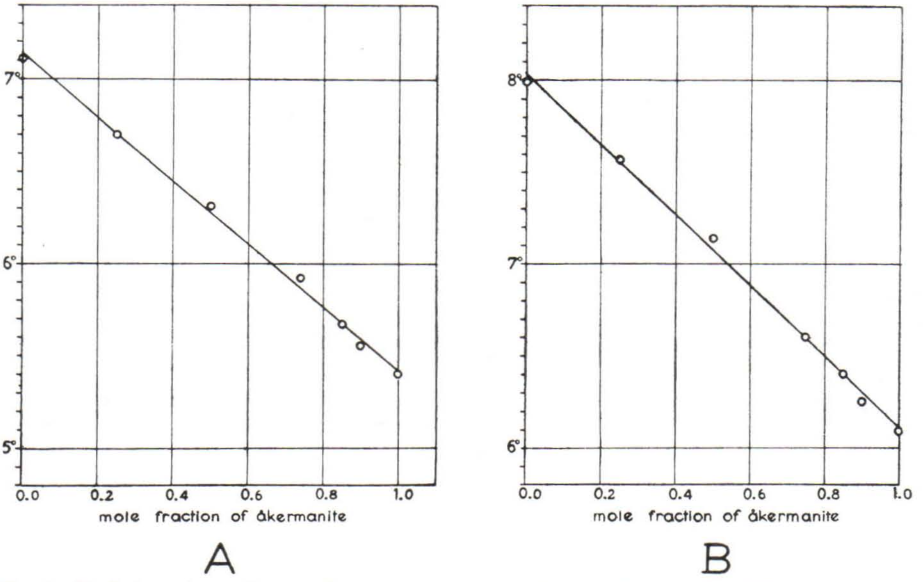


Fig. 5. Variation of the distance between two selected lines in the powder diffraction pattern of the åkermanite-gehlenite series. A. Distance between (213) and (521). B. Distance between (213) and (440).

DIOPSIDE

The diopside sample used, is derived from a limestone from Juva, Finland, recently described by Juurinen and Hytönen (1952). The heat-of-solution measurements were carried out on the original material of these authors. The physical properties and chemical analysis of the material as given by them are reproduced in Table IV.

Table IV. Chemical composition and physical properties of diopside from Juva, Finland.

	Weight percent	Atomic ratio multiplied by 10,000		Calculated composition reduced to one hundred percent		
					Weight percent	Molecular percent
SiO_2	54.66	Si	9 101	$CaSiO_3$	52.70	49.22
Al_2O_3	0.07	Al	14	$MgSiO_3$	46.03	49.74
Fe_2O_3	0.68	Fe^{3+}	85	$MnSiO_3$	0.04	0.03
FeO	0.07	Fe^{2+}	10	$FeSiO_3$	1.23	1.01
MnO	0.02	Mn	3	Total	100.00	100.00
MgO	18.78	Mg	4 658			
CaO	25.85	Ca	4 609			
TiO_2	0.00	OH	244			
H_2O+	0.22					
H_2O-	0.00					
Total	100.35					
$\alpha = 1.664$ $\beta = 1.673$ $\gamma = 1.695$		$2V\gamma = 60°$ $c \wedge \gamma = 38°$		$d_{4°}^{20°} = 3.276$		

OXIDE COMPONENTS

QUARTZ.

The quartz sample used for heat-of-solution measurements was purchased from Mr. Ambrosi Cavenz, Sedrun, Switzerland. The material was in form of clear crystals. Hand picked crystals were crushed and pulverized with a hammer mill. The iron contamination was dissolved out with hydrochloric acid, and fine-grained carbon from the steel of the machinery, remaining in the material, was oxidized by boiling the powder in a concentrated mixture of sulphuric and chromic acids. After filtration and washing with hot water, a snow white product was obtained. According to microscopic examination it was absolutely free from impurities.

Because of the low HF concentration in the calorimetric acid, it was necessary to use extremely fine quartz powder. For that reason, the coarse particles were removed from the purified powder by eluting the material 20 minutes in water of room temperature, using a beaker 20 cm. high. Before weighing, the material was dried at 300° C for 48 hours.

The water content of quartz dissolved was determined by loss on ignition to be 0.18 percent and the residue from evaporation with HF and H_2SO_4 0.10 percent.

CALCIUM OXIDE.

Calcium oxide was prepared from »Calcium Carbonate, precipitated, for analysis of silicates acc. to Smith, of E. Merck, Darmstadt». The carbonate was transfered to oxide at 1100° C and the material heated after that for two hours at 1400° C. Between the runs, the oxide powder was kept at 1000° C and cooled for weighing in a desiccator for 20 minutes

ALUMINUM OXIDE.

The aluminum oxide used for the heat-of-solution measurements was obtained through the courtesy of Dr. E. F. Osborn, Pennsylvania State College. The material is fine powdered (0.1 micron and less) γ-alumina from Linde Air Product Co. The total content of foreign oxides is 0.017 %, according to an average of spectroscopic analyses of thirteen batches carried out by the manufacturer. According to a test kindly performed by Dr. Osborn, the material gives an X-ray pattern of pure γ - alumina, indicating that there cannot be any greater amounts of corundum present in the sample. No corundum can be detected in the material under the microscope and no residue is remained when the powder is dissolved in calorimetric acid.

Because of the hygroscopic character of the γ-alumina used, a special procedure was necessary in storing and weighing the samples. It is described as follows:

γ-alumina powder dried at 130° C for 40 hours was placed in several small weighing bottles sealed with grease and kept in a desiccator. Material from such a bottle was used for filling of only one gelatin capsule, and the rest of the material was subjected to an immediate water determination. In this way, the content of water of each batch dissolved in the calorimeter was individually determined and the result applied for correcting the value of heat of solution to water-free γ-alumina.

MAGNESIUM HYDROXIDE.

The heat of solution of magnesium oxide itself was not determined, but obtained by dissolving crystalline $Mg(OH)_2$. For this purpose a natural brucite from Wood's Mine, Texas, Lancaster Co., Pennsylvania, U. S. A., was used. This sample of water clear brucite was obtained through the courtesy of Dr. Adolf Pabst, of the Univ. of California, Berkeley, Calif. Hand picked and pulverized material was analyzed. This analysis is shown in Table V.

Table V. Chemical composition of brucite from Wood's Mine, Texas, Lancaster Co., Pennsylvania. Analyst H. B. Wiik.

	Weight percent	Calculated composition reduced to one hundred weight percent	
SiO_2	0.00	$Mg(OH)_2$	98.85
$(Al, Fe)_2O_3$	0.10	$Mn(OH)_2$	1.05
MnO	0.84	$(Al,Fe)_2O_3$	0.10
MgO	68.29	Total	100.00
CaO	0.00		
$H_2O +$	30.65		
$H_2O -$	0.09		
Total	99.97		

RESULTS OF THE HEAT-OF-SOLUTION MEASUREMENTS

In the following, the results are given of calorimetric measurements of heat of solution for the materials described in the previous chapter. The values obtained on individual runs, the corresponding weights of the samples dropped into the calorimeter, and the calculated arithmetic averages and uncertainties are listed for each substance dissolved. All weights are corrected to vacuum. The results, not corrected for chemical composition, are expressed in calories per gram. These observed heat-of-solution values are corrected for deviation of the actual chemical composition from the ideal one. At the present stage of our knowledge of the thermochemistry of natural minerals it seems likely that the most serious uncertainty in the results arises from the fact that natural minerals usually are not pure but contain other elements or compounds in solid solution. Corrections due to these contaminations, whether present as foreign inclusions or belonging to the structure of the mineral itself, are necessarily more or less inaccurate. Therefore, corrections made in the following are described in more detail. The corrected values of heat of solution are expressed in calories per gram and in calories per mole.

The calculated uncertainties in the heat-of-solution measurements are in general 0.1—0.2 percent of the total values. Occasionally, the uncertainties of the measurements are as high as 0.23 percent, but for some substances less than 0.1 percent. While this calculated uncertainty gives an idea of the reproducibility of the measurements proper it does not, however, include errors of methodical and instrumental origin. It was not possible, to compare the results obtained with measurements made by using an entirely different method and apparatus, but some studies were carried out to establish the order of magnitude of errors of this kind.

For that purpose the heat of solution of synthetic åkermanite was determined separately six months apart. Averages of these measurements differ 0.2 percent. The heat of solution of synthetic gehlenite was measured within a period of one month, but no systhematic difference can be observed in the results obtained. No difference was also found in values measured by using different resistance thermometers. In dissolving the crystalline mixture containing 50 molecular percent åkermanite and 50 molecular percent gehlenite, two different batches of synthetic preparations were used, but no systematic difference was observed in the values, despite the fact that these two samples differed also in mode of preparation and in grain size.

Since the results of heat-of-solution measurements are mainly used in a relative manner, it is obvious that the errors of instrumental origin will diminish or entirely disappear. This will be the case not only when conclusions are drawn based on the relative differences in the values obtained but also when the heats of formation are computed by means of the measured heat-of-solution values.

HEAT OF SOLUTION OF QUARTZ

To obtain a reliable value for the heat of solution of quartz in the acid mixture concerned, five runs were made. The results, uncorrected for chemical composition of the quartz sample used, are given below:

	Weight of the sample dissolved.	Heat of solution of quartz. Not corrected for chemical composition.
Run No. 1.	0.3987 grams	—554.34 cal/gram
2.	0.4469	—554.82
3.	0.2894	—554.87
4.	0.3225	—555.07
5.	0.3765	—555.77
Average:		—554.97 ± 0.47 cal/gram

For the residue from evaporation with HF and H_2SO_4 (p. 20) no correction was applied. A correction for the water content (0.18 percent) was performed assuming that water is present in the quartz sample in a form thermally equivalent to ice. Accordingly, the corrected value for the heat of solution of quartz was calculated as follows:

$$-554.97 = 0.9982 \times \triangle H_{\text{Quartz}} + 0.0018 \times (\text{latent heat of fusion of ice}) + 0.0018 \times (\text{heat of solution of liquid water}).$$

In this equation, $\triangle H_{\text{Quartz}}$ denotes the heat of solution of water-free quartz.

The heat of solution of liquid water in the acid mixture was determined in four runs yielding the following results:

	Heat of solution of liquid water.
Run No. 1.	+ 29.55 cal/gram
2.	+ 30.13
3.	+ 30.67
4.	+ 31.18
Average	+ 30.38 ± 0.70 cal/gram or + 547 ± 13 cal/mole.

Using the value of + 30.38 cal/gram for the heat of solution of liquid water and the figure + 79.71 cal/gram for the latent heat of fusion of ice, as given by Osborne (1939), the corrected heat of solution of quartz in the acid mixture is calculated to

$$\triangle H_{\text{Quartz}} = -556.17 \pm 0.50 \text{ cal/gram or}$$
$$= -33{,}400 \pm 30 \text{ cal/mole.}$$

HEAT OF SOLUTION OF CALCIUM OXIDE

All heat-of-solution measurements of calcium oxide were made in an acid mixture in which 0.4 grams of SiO_2 was previously dissolved. The following five runs were made:

	Weight of the sample dissolved.	Heat of solution of calcium oxide.
Run No. 1.	0.1815 grams	— 883.11 cal/gram
2.	0.1820	— 883.96
3.	0.2173	— 884.09
4.	0.2258	— 884.19
5.	0.1730	— 884.60

$$\text{Average: } \triangle H_{\text{CaO}} = -883.99 \pm 0.50 \text{ cal/gram or}$$
$$= -49{,}570 \pm 30 \text{ cal/mole.}$$

The sample of calcium oxide being one hundred percent pure, no corrections for the chemical composition are needed.

HEAT OF SOLUTION OF ALUMINUM OXIDE

The heat-of-solution measurements on aluminum oxide, in form of γ-alumina, were made in an acid mixture in which 0.4 grams of SiO_2 was previously dissolved. As has been mentioned above (p. 21), the water content of each sample dropped into the calorimeter was determined individually. The results of six runs are as follows:

	Weight of the sample dissolved.	Water content of the sample.	Uncorrected heat of solution.	Heat of solution corrected for water.
Run No. 1.	0.1901 grams	3.44 percent	— 796.60 cal/gram	— 828.90 cal/gram
2.	0.1571	3.83	— 793.30	— 829.28
3.	0.1315	3.83	— 794.12	— 830.13
4.	0.1999	3.74	— 795.03	— 830.20
5.	0.2019	3.55	— 797.68	— 831.09

The water correction was made in a manner similar to that on quartz assuming that the water contained in the sample of γ-alumina used is thermally equivalent to ice. The water-corrected heat-of-solution values listed average to:

$$\begin{aligned} \triangle H_{\gamma\text{-alumina}} &= -829.92 \pm 0.77 \text{ cal/gram or} \\ &= -\ 84{,}600 \pm 80 \text{ cal/mole.} \end{aligned}$$

This accounts for aluminum oxide in form of γ-alumina having the thermal properties of the particular sample available for this work.

HEAT OF SOLUTION OF MAGNESIUM HYDROXIDE (BRUCITE)

Of the natural brucite described above (p. 21) six heat-of-solution runs were made in the acid mixture in which 0.4 grams of SiO_2 had been previously dissolved. The results are as follows:

	Weigt of the sample dissolved.	Heat of solution of brucite. Not corrected for manganese.
Run No. 1.	0.2543 grams	— 439.90 cal/gram
2.	0.2496	— 440.51
3.	0.2464	— 441.24
4.	0.2631	— 441.36
5.	0.2473	— 442.55
6.	0.2604	— 442.92
	Average:	— 441.41 ± 0.95 cal/gram.

No correction was applied for the content of $(Al,Fe)_2O_3$ shown by the analysis in Table V to be 0.10 percent by weight. According to this analysis, the mineral contains 1.05 percent by weight $Mn(OH)_2$. This must be corrected for. The correction was made in the following way: According to figures taken from the tables given by Bichowsky and Rossini (1936) the heat of the reaction

$$Mg(OH)_2(cryst.) + MnCl_2(sol.) \rightarrow Mn(OH)_2(cryst.) + MgCl_2(sol.)$$

amounts to $\triangle H_{B\text{-}R} = -400$ cal/mole. Subtracting this reaction from the reaction

$$Mg(OH)_2(cryst.) + 2HCl(sol.) \rightarrow MgCl_2(sol.) + 2H_2O(sol.)$$

yields

$$Mn(OH)_2(cryst.) + 2HCl(sol.) \rightarrow MnCl_2(sol.) + 2H_2O(sol.)$$

with a heat of reaction

$$\triangle H_{Mn(OH)_2} = \Delta H_{Mg(OH)_2} - \Delta H_{B\text{-}R}$$

In this equation $\triangle H_{Mn(OH)_2}$ and $\triangle H_{Mg(OH)_2}$ denote the heat of solution of manganese and magnesium hydroxides in diluted hydrochloric acid, respectively.

The heat of solution of pure magnesium oxide in form of crystalline brucite, $\triangle H_{Mg(OH)_2}$, is now calculated according to the following relationship:

$$-441.41 = 0.9895 \frac{\triangle H_{Mg(OH)_2}}{58.336} + 0.0105 \frac{\triangle H_{Mg(OH)_2} + 400}{88.946}$$

which yields

$$\triangle H_{Mg(OH)_2} = -25{,}850 \text{ cal/mole.}$$

To this value an estimated uncertainty of ± 70 calories must be added. The procedure of correcting for the manganese content was performed on the assumption that diluted hydrochloric acid, instead of the acid mixture, was used as the dissolving agent. The total correction being relatively small in this case, the error introduced through this assumption is considered negligible.

HEAT OF SOLUTION OF MAGNESIUM OXIDE

For obtaining heats of formation of magnesium minerals, an accurate value for the heat of solution of magnesium oxide is needed. For mineralogical purposes, the heat of formation of a compound usually is given from the component oxides. The magnesium oxide on which the heat-of-formation value is based should correspond to the natural mineral periclase. This mineral is, however, not readily soluble in any acid in calorimetric conditions. As shown by Taylor and Wells (1938), both the rate and the heat of reaction of magnesium oxide with hydrochloric acid largely depends on the thermal pre-history of the material to be dissolved. These authors prepared their magnesium oxide through dehydrating magnesium hydroxide at different temperatures and found that the heat evolved in the solution of magnesium oxide in hydrochloric acid decreased as the temperature at which the material was prepared was increased. Also the rate of dissolution decreases on increasing temperature of preparation. Natural periclase obviously corresponds to fused or »dead-burned» synthetic magnesium oxide. Accordingly, the magnesium oxide used for reference in computing heat-of-formation values for magnesium minerals should be prepared at as high a temperature as possible. Taylor and Wells *(op. cit.)* prepared a sample of magnesium oxide at 1425° C that was still soluble in hydrochloric acid. They also regard it very probable that the difference in heat of solution between this material and fused magnesium oxide will be relatively small. The sample of magnesium oxide prepared at this temperature apparently is closest to the natural periclase in thermal properties. The corresponding value of the heat of solution of this material in hydrochloric acid reported by the said authors is, therefore, adopted in the following.

The heat of solution of magnesium oxide in the acid mixture concerned was computed from the heats of the following reactions:

A) MgO (cryst., 25° C; dehydrated 2.5 hours at 1425° C) + H_2O (liquid, 25° C) $\rightarrow$ $Mg(OH)_2$ (brucite, 25° C)

According to Taylor and Wells *(op. cit.)* the heat of this reaction amounts to

$$\triangle H_A = -9{,}080 \pm 30 \text{ cal.}$$

B) $Mg(OH)_2$ (brucite, 25° C) + $2HCl$ (sol., 75° C) $\rightarrow$ $MgCl_2$ (sol., 75° C) + $2H_2O$ (liquid, 75° C)

The heat of this reaction, given on p. 25, amounts to

$$\triangle H_B = -25{,}850 \pm 70 \text{ cal.}$$

C) H_2O (liquid, 25° C) → H_2O (sol., 75° C)

The heat of this reaction, given on p. 23, yields

$$\triangle H_C = +550 \pm 15 \text{ cal.}$$

The value for $\triangle H_C$ was rounded up to the next ten calories.

The heat of solution of magnesium oxide, *viz.* the heat of the following reaction

$$\text{MgO (cryst., 25° C; dehydrated 2.5 hours at 1425° C)} +$$
$$\text{2HCl (sol., 75° C)} \rightarrow \text{MgCl}_2 \text{ (sol., 75° C)} + \text{H}_2\text{O (sol., 75° C)}$$

is computed as

$$\triangle H_{MgO} = \Delta H_A + \Delta H_B - \Delta H_C = -35{,}480 \pm 80 \text{ cal/mole.}$$

This value accounts for the heat of solution of magnesium oxide, prepared through dehydrating magnesium hydroxide 2.5 hours at 1425° C, in the acid mixture of 20 percent HCl and 5 percent HF by weight.

HEAT OF SOLUTION OF THE SYNTHETIC GLASSY AND CRYSTALLINE MELILITES

Heats of solution in the acid mixture for the synthetic melilite glasses are given in Table VI and for the synthetic crystalline melilites in Table VII. In these tables as well as later in the text of this paper, the composition of a synthetic glassy or crystalline melilite preparation is indicated by a subscript giving the molecular percentage of åkermanite in that preparation. Thus $Å_{74}$ denotes a glassy or crystalline melilite containing 74 molecular percent of åkermanite and 26 molecular percent of gehlenite. The synthetic preparations being made of chemically pure starting materials, no corrections due to chemical composition are necessary.

Table VI. Heat of solution of synthetic melilite glasses of varying åkermanite-gehlenite ratio in an acid mixture containing 20 percent by weight HCl and 5 percent by weight HF.

Molecular composition of the glass	Molecular weight	Weight of the sample dissolved gram	Heat of solution cal/gram	Average	
				cal/gram	cal/mole
$Å_{100}$	272.60	0.5487 0.5403 0.5617 0.5681 0.5701 0.5390	— 605.28 — 605.35 — 606.03 — 606.82 — 607.85 — 608.37	— 606.62 ± 1.06	— 165,360 ± 290

Å$_{74}$	273.01	0.2880 0.4070 0.5938 0.3622	— 644.52 — 645.26 — 646.81 — 647.57	— 646.04 ± 1.40	— 176,380 ± 380
Å$_{50}$	273.38	0.3765 0.4777 0.4172 0.4121	— 673.10 — 673.40 — 673.55 — 675.00	— 673.76 ± 0.85	— 184,190 ± 230
Å$_{25}$	273.77	0.4395 0.3496 0.3730 0.3301 0.3680	— 697.43 — 697.64 — 698.01 — 698.24 — 699.04	— 698.07 ± 0.56	— 191,110 ± 150
Å$_0$ = G	274.16	0.4596 0.4361 0.4935 0.3736 0.3953	— 709.34 — 710.28 — 710.89 — 711.10 — 712.63	— 710.85 ± 1.08	— 194,890 ± 300

Table VII. Heat of solution of synthetic crystalline melilites of varying åkermanite-gehlenite ratio in an acid mixture containing 20 percent by weight HCl and 5 percent by weight HF.

Molecular composition of melilite	Molecular weight	Weight of the sample dissolved gram	Heat of solution cal/gram	Average	
				cal/gram	cal/mole
Å$_{100}$	272.60	0.4708 0.3054 0.5651 0.3853 0.3734	— 577.31 — 577.38 — 578.07 — 578.69 — 579.11	— 578.11 ± 0.71	— 157,590 ± 190
Å$_{85}$	272.83	0.4071 0.3888 0.3891 0.4171	— 586.22 — 587.86 — 588.63 — 588.68	— 587.85 ± 1.15	— 160,380 ± 310
Å$_{74}$	273.01	0.3275 0.3815 0.2514 0.2737	— 599.44 — 600.47 — 601.25 — 601.63	— 600.70 ± 0.97	— 164,000 ± 260
Å$_{50}$	273.38	0.4167 0.4368 0.3452 0.3827	— 625.45 — 626.24 — 626.50 — 627.07	— 626.32 ± 0.68	— 171,220 ± 190
Å$_{25}$	273.77	0.6816 0.3032 0.4945 0.6658	— 649.65 — 650.97 — 651.22 — 651.30	— 650.79 ± 0.77	— 178,170 ± 210
Å$_0$ = G	274.16	0.4527 0.4207 0.3041 0.2847	— 665.69 — 667.81 — 667.95 — 668.20	— 667.41 ± 1.16	— 182,980 ± 320

HEATS OF SOLUTION OF THE TWO NATURAL MELILITE SAMPLES

The heats of solution of the melilites from Honolulu and from Luna County were determined in the acid mixture. The results of four runs on each of the minerals are as follows:

	Weight of the sample dissolved.	Heat of solution. Melilite from Honolulu.
Run No. 1.	0.2601 grams	— 553.66 cal/gram
2.	0.2316	— 554.56
3.	0.2553	— 554.78
4.	0.2375	— 556.48
	Average:	— 554.87 ± 1.17 cal/gram

	Weight of the sample dissolved.	Heat of solution. Gehlenite from Luna County.
Run No. 1.	0.4079 grams	— 606.28 cal/gram
2.	0.4374	— 606.36
3.	0.3675	— 607.00
4.	0.3920	— 607.26
	Average:	— 606.73 ± 0.48 cal/gram.

The chemical compositions of these two natural melilites, expressed in terms of hypothetical melilite end members, are somewhat complicated. Therefore, the corrections due to the chemical composition of the minerals will be discussed later in connection with the interpretation of the heat-of-solution measurements.

HEAT OF SOLUTION OF THE DIOPSIDE FROM JUVA

The heat of solution of the diopside sample in the acid mixture was determined in five runs:

	Weight of the sample dissolved.	Heat of solution. Diopside from Juva. Not corrected for chemical composition.
Run No. 1.	0.2501 grams	— 534.79 cal/gram
2.	0.3738	— 534.80
3.	0.2487	— 536.10
4.	0.2920	— 536.13
5.	0.3024	— 537.21
	Average:	— 535.81 ± 0.92 cal/gram.

This value must be corrected to correspond to pure $CaMg(SiO_3)_2$. The analysis of the diopside from Juva given in Table IV, p. 19, shows a very slight deficiency of calcium metasilicate with respect to the metasilicates of magnesium, ferrous iron, and manganese. Although this deficiency apparently is of such an order of magnitude that it might simply be due to analytical errors, it is corrected for the following calculations. The corrections were performed as follows. According to the analysis, the composition of the diopside from Juva may be expressed as follows:

$CaMg(SiO_3)_2$	98.25	percent by weight
$MgSiO_3$	0.48	
$MnSiO_3$	0.04	
$FeSiO_3$	1.23	
Total	100.00	

The heat of solution of pure $CaMg(SiO_3)_2$ is thus calculated from the equation:

$$-535.81 = 0.9825 \times \Delta H_{CaMg(SiO_3)_2} + \frac{0.0048}{100.38} \Delta H_{MgSiO_3} + \frac{0.0004}{130.99} \Delta H_{MnSiO_3} + \frac{0.0123}{131.91} \Delta H_{FeSiO_3}$$

In this equation $\Delta H_{CaMg(SiO_3)_2}$, ΔH_{MgSiO_3}, ΔH_{MnSiO_3}, and ΔH_{FeSiO_3} denote the heats of solution of the corresponding pure compounds in the acid mixture. The heats of solution of $MgSiO_3$, $MnSiO_3$, and $FeSiO_3$ in the acid mixture concerned have not been measured experimentally. The heat of solution of $MgSiO_3$ may be computed from the heats of solution of MgO and SiO_2 given in this paper on p. 27 and 23, and on the basis of the value for the heat of formation of $MgSiO_3$ from the component oxides as given by Torgeson and Sahama (1948) *viz.* — 8,690 ± 150 cal/mole. The calculation yields $\Delta H_{MgSiO_3} = -60{,}190 \pm 180$ cal/mole.

The heat of solution of $FeSiO_3$ may be calculated on the basis of the reaction $Fe_2SiO_4 + SiO_2 \rightarrow 2\ FeSiO_3$, for which Sahama and Torgeson (1949) give the heat of reaction $\Delta H = -310 \pm 210$ cal. The heat of solution of Fe_2SiO_4 was estimated on the basis of two preliminary experiments in the acid mixture used to amount to — 76,100 cal/mole. Using these figures and the heat-of-solution value of quartz given above the heat of solution of $FeSiO_3$ in the acid mixture is calculated to amount to $\Delta H_{FeSiO_3} = -54{,}600$ cal/mole.

Sahama and Torgeson *(op. cit.)* measured the heat of solution of $MnSiO_3$ to be 240 cal/mole less than that of $FeSiO_3$. Because the heat of solution of quartz is almost identical in both acids, it may be assumed that this difference is about the same also in the present acid mixture. According to this assumption, the heat of solution of $MnSiO_3$ may be estimated to $\Delta H_{MnSiO_3} = -54{,}360$ cal/mole. This estimation is considered close enough for purpose of correction. Substituting these figures in the equation above gives — 537.09 cal/gram for the heat of solution of pure $CaMg(SiO_3)_2$. This figure must still be corrected for the 0.22 percent water shown by the analysis. The water correction, made in a similar manner as for quartz, yields

$$\Delta H_{\mathrm{diopside}} = -538.51 \text{ cal/gram or}$$
$$-116{,}600 \text{ cal/mole.}$$

To this value an uncertainty of ± 250 cal/mole must be added.

INTERPRETATION OF THE RESULTS OF HEAT-OF-SOLUTION MEASUREMENTS ON SYNTHETIC MELILITE PREPARATIONS

The values for heat of solution in the acid mixture obtained for synthetic melilite glasses and crystalline melilites, given in Tables VI and VII, are plotted against åkermanite-to-gehlenite ratio in Fig. 6. The size of the circles around the points indicates the calculated uncertainty of the respective measurements. Smooth curves are drawn in the figure through the points representing the melilite glasses and the crystalline melilites, respectively. These curves illustrate the dependence of the magnitude of heat of solution upon the åkermanite-to-gehlenite ratio of the sample dissolved.

For both glassy and crystalline melilites, the curves shown in Fig. 6 clearly deviate from the straight lines connecting the corresponding points for pure åkermanite and pure gehlenite. For the glassy melilites, the deviation from linearity is very pronounced and is not readily explained by either experiment or systematic instrumental errors associated with the method.

The curve drawn through the points for the crystalline melilites exhibits a rather peculiar S-shaped form. The point corresponding to the sample $Å_{74}$ lies on the line between the pure end members within the uncertainty of the measurements. The point for $Å_{85}$ is definitely below and, on the other hand, those for $Å_{50}$ and $Å_{25}$ are well above the straight line.

It is admitted that, especially for the crystalline melilites, additional points corresponding to other åkermanite-gehlenite solid solutions would be desirable. However, the values obtained can hardly be interpreted as being accidental. As has been pointed out in the previous chapter, there is no evidence according to the X-ray and optical methods that the chemical composition of the synthetic preparations does not correspond to the compositions given. Because the uncertainty of the measurements on the different samples, at least for purpose of relative comparison with each other, is definitely of a smaller order of magnitude than the deviations from linearity observed, there seems to be a thermal reason for this deviation.

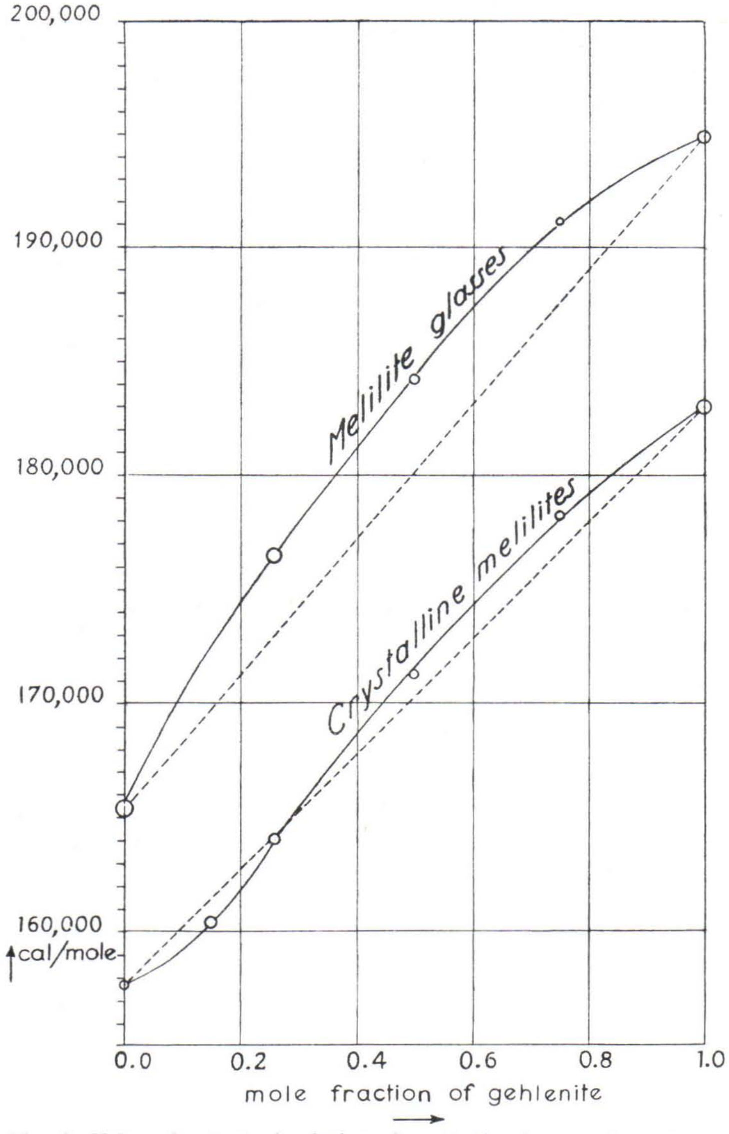


Fig. 6. Values for heat of solution of synthetic glassy and crystalline melilites of the åkermanite-gehlenite series.

From a thermochemical point of view, a deviation of the kind observed may indicate that the formation of the åkermanite-gehlenite solid solutions is accompanied by a heat effect. This may, on the other hand, be interpreted to mean deviation from the ideal behaviour.

It is possible, however, that the observed deviation from linearity in heat of solution for glassy melilites is caused by a different degree of order in the glasses originating from differences in thermal pre-history. Such differences may be caused by variation in quenching technique. The order of magnitude of such effect is not known, but it alone would hardly be enough to cause the observed deviation. The fact that two separate preparations of the crystalline mixture $Å_{50}$, used for calorimetric measurements, gave identical values for heat of solution, indicates that the thermal pre-history of the sample is not responsible for the deviation from linearity observed for the crystalline melilites.

In addition to the heat effect, a nonideal mixing of components is accompanied with a change in volume. This should be seen in the densities and in the unit cell dimensions of the solid solutions. According to Ferguson and Buddington (1920), the densities of the synthetic glasses and of the crystalline preparations of the åkermanite-gehlenite series exhibit linear relationships between density and composition. A deviation from Vegard's law was found by Andrews (1948) in the unit cell dimensions of the åkermanite-gehlenite series. Later more accurate studies made by Ervin and Osborn (1949) have not confirmed his observation. No systematic deviation from linearity can be seen in the values obtained by the present writer either.

The lack of deviation from Vegard's law contradicts the thermal behavior observed. It would be interesting, therefore, to find out the order of magnitude of the deviation in structural dimensions able to cause the found heat effect upon mixing. A possibility for doing this is offered by application of Born's theory of lattice energy.

The lattice energy of an ionic crystal may be defined as the energy change in the process of bringing the ions from infinity to the positions they occupy in the crystal. According to Born, between the ions of an ionic crystal the attractive Coulomb forces and the repulsive forces, rapidly changing with distance, are in equilibrium. The potential Φ of a system of ions with the interionic distance r is given by the equation

$$\Phi = -a/r + b/r^n$$

in which a equals the Coulomb forces and b equals the repulsive forces in the system, and $n > 1$. This function has a minimum for Φ. Assuming that this minimum value of the potential indicates stability in the system, Born and Landé marked the corresponding value for the interionic distance r_0, and derived a formula which gives the lattice energy U_0 of an ionic crystal per mole:

$$U_0 = \frac{A}{r_0}(1-1/n).$$

In this equation, A denotes a constant depending only on the nature and number of ions present and on the structural type of the crystal and is independent of the interionic distance.

Later, more exact expressions have been introduced for lattice energy including both the van der Waal's attractive forces and more correct expressions for the repulsive potential (Born, 1940; Wasastjerna, 1949). In discussing the order of magnitude of the structural effect, for the present purpose the accuracy of the original formula may be considered sufficient.

We may assume that an ideal solid solution differs from a real one only in slightly different structural dimensions corresponding to a small difference in heat content. If these two crystals are identical in all other respects, the lattice energies are

$$U_1 = A/r_1\ (1-1/n) \text{ and } U_2 = A/r_2\ (1-1/n)$$

and the difference of the lattice energies of these two crystals is

$$\begin{aligned} U_1 - U_2 &= A\ (1-1/n)\ (1/r_1 - 1/r_2) \\ &= A/r_1\, r_2 \,.\, (1-1/n)\ (r_2 - r_1) \end{aligned}$$

and, since $A/r_1\ (1-1/n) = U_1$,

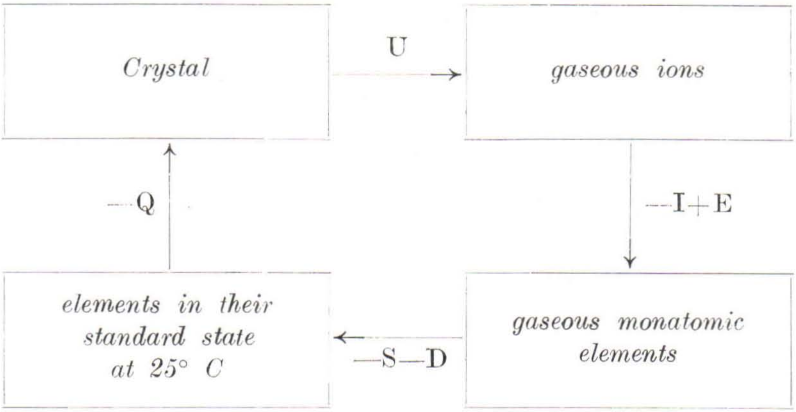
then $$U_1 - U_2 = -\, U_1/r_2 \,.\, (r_1 - r_2).$$

The difference in the lattice parameters $r_1 - r_2$ may be referred to Δ r. The difference in lattice energies of these two solid solutions may be set equal to Δ H, the observed deviation from linearity in the heat-of-solution values. Accordingly,

$$\Delta H = \frac{-U_1 \Delta r}{r_2}$$

This equation gives the mutual relationship between the heat effect (heat of formation of mixed crystal from the end members) and corresponding change in the structure upon mixing. For numerical solution of this equation U_1 and r_2 should be known.

An approximation for the lattice energy of solid solutions in the åkermanite-gehlenite series may be evaluated by means of the Born-Haber thermochemical cycle (Sherman, 1932). According to this procedure, the lattice energy of a crystal can be related to measurable thermal data. The principle of the cycle is as follows:



In the first step of this cycle the lattice energy U is liberated. This energy must now equal the energy absorbed in the cycle forming the crystal. The energy change in the second step corresponds to the ionization potential of the cations (— I) and to the electron affinity of anions (+ E). In the third step the energy change of the system consists of heat of sublimation of the metals (— S) and of heat of dissociation of oxygen (— D). In the last step the crystal is reformed from the elements in the standard state and the energy change equals the heat of formation of the crystal (— Q). Now,

$$U = Q + S + I + D - E.$$

Figures for the ionization potential and heat of sublimation of calcium and magnesium, for heat of dissociation and electron affinity of oxygen, and for heat of formation of CaO may be obtained from Bichowsky and Rossini (1936). Recent values for ionization potential and for heat of sublimation of Si and Al, and heat of formation of SiO_2 and Al_2O_3 are available from the tables of selected thermodynamic properties published by U. S. National Bureau of Standards. The most reliable value for heat of formation of MgO is given by Kelley (1945). The data needed for computing the lattice energy for åkermanite and gehlenite may be completed by using the heat-of-formation values for these minerals as obtained from the component oxides given below (p. 41). These data are summarized in table VIII.

Table VIII. Thermal data for calculating the lattice energy for åkermanite and gehlenite. kcal/mole.

	I	S	D	E	Q
Ca	— 412.9	— 47.8	—	—	—
Mg	— 520.8	— 36.3	—	—	—
Al	— 1 307.4	— 75.0	—	—	—
Si	— 2 469.4	— 88.0	—	—	—
O	—	—	— 59.1	+ 225	—
Åkermanite	—	—	—	—	— 901.9
Gehlenite	—	—	—	—	— 927.8

The lattice energy for åkermanite calculated on the basis of the Born-Haber cycle, using figures from Table VIII amounts to

$$U_{\text{Å}} = -9484.0 \text{ kcal/mole}$$

and that of gehlenite to

$$U_G = -9160.0 \text{ kcal/mole}$$

These figures may be in error by not more than 10 percent due to the inaccuracy of the energy values used. As an average, we may consider that U_1 is of the order of magnitude of $-9 \cdot 10^6$ cal/mole. If r_2 is taken as the edge of a cube having the same volume as the unit cell in the åkermanite-gehlenite series, it will amount to 6.7 Ångström units. The maximum deviation from linearity in the heat-of-solution curve for crystalline samples is about 1600 calories. Hence, substituting these numerical values to the equation

$$\Delta H = -\frac{U_1 \Delta r}{r_2}$$

yields

$$1600 \sim \frac{9 \cdot 10^6 \cdot r}{6.7}$$

from which

$$r \sim 1.2 \cdot 10^{-3} \sim 0.001 \text{ Ångström units.}$$

The methodical accuracy in determing structural dimensions is about ± 0.003 Å, if a »Norelco» type X-ray spectrometer is used. It is therefore understood that the deviation clearly observed in the thermal studies, cannot be found in the unit cell dimensions.

Since the change in the density corresponding to a change of a structural dimension of 0.001 Å amounts to about 0.0015, it is evident that no deviation from linearity can be seen in the density values measured.

The result obtained was calculated numerically for melilites. Since the order of magnitude of the lattice energy is about the same for all complex silicates of equal number of atoms in the formula weight, it is evident that the mutual relationship between the structural and thermal deviation from linearity just obtained for melilite solid solutions holds in general. This fact justifies the postulation that solution calorimetry offers an accurate tool for investigating the degree of ideality of isomorphism in silicate minerals. Very few solid solution series of silicates have been calorimetrically investigated so far, but the results obtained indicate (Sahama and Torgeson, 1949) that the ideality may in some cases be so complete that no deviation can be seen in the heat-of-solution values measured.

One more physical property of minerals which possibly could be used in detecting ideality of mixed crystals is the index of refractivity. The mutual relationship between the optical properties and other characteristics of mixed crystals is, however, so complicated (Barth, 1930) that it is at present impossible to state anything about the order of magnitude of the influence of nonideal mixing to the refractive indices. It is expected, however, that a clear deviation from ideality would cause a deviation from linearity in variation of the indices with the composition, although such a feature can also originate from a change of chemical bonds as emphasized by Barth *(op. cit.)*.

As stated above, the deviation from linearity of the heat-of-solution curve for the crystalline melilites indicates a heat effect upon formation of the solid solutions from pure end members. This heat of the reaction

$$\text{Åkermanite} + \text{Gehlenite} \rightarrow \text{Solid solution phase}$$

may be calculated on the basis of the measured heat-of-solution values for the solid solutions dissolved. The results of these calculations are given in Table IX.

Table IX. Heat of formation of the crystalline åkermanite-gehlenite solid solutions from pure crystalline end members at 25° C.

	Heat of formation at 25° C cal/mole	Uncertainty cal
$Å_{85}$	— 1 020	380
$Å_{74}$	— 190	340
$Å_{50}$	+ 940	320
$Å_{25}$	+ 1 540	360

The heat of formation of solid solution formed from the end members is zero within the accuracy of measurements for the mixture corresponding to the minimum melting point, while the heat effect is positive near the gehlenite-rich end and negative near the åkermanite-rich end of the series. The large positive heat of formation of some of the solid solutions may indicate that an immiscibility gap exists at lower temperatures in the system. However, in lack of sufficient thermal data a more detailed thermodynamic examination of the problem cannot be performed at present.

INTERPRETATION OF HEAT OF SOLUTION OF THE NATURAL MELILITES

In listing the heat-of-solution values in a previous chapter no correction was performed for the heats of solution of the natural melilites dissolved. For correction purposes the compositions of these two melilites, given in Table I, p. 15, may be expressed in the following manner:

	Melilite, Sugar Loaf series, Honolulu, Hawaii.	Melilite, Luna County, New Mexico.
Åkermanite-gehlenite solid solution	68.28	94.63
Alkali melilite [1]	15.61	1.30
$FeSiO_3$	5.62	1.68
$MnSiO_3$	0.14	0.04
Fe_2O_3	1.90	0.94
Ca_2SiO_4	8.02	0.93
H_2O+	0.43	0.48
Total	100.00	100.00

The composition of the åkermanite-gehlenite solid solution of the specimen from Hawaii amounts to about 74 molecular percent åkermanite and that of the specimen from Luna County to about 50 molecular percent åkermanite.

For correcting the heat of solution, it can be assumed that the observed heat of solution equals the sum of the heats of solution of the components. This makes it possible to calculate an approximation for the heat of solution of a hypothetical melilite solid solution consisting of åkermanite, gehlenite, and alkali melilite provided that the heat-of-solution values of all the other components may be evaluated. Estimated heat-of-solution values for $FeSiO_3$ and $MnSiO_3$ were calculated in the present paper (p. 30). For Ca_2SiO_4, an estimation can be obtained assuming that the heat of solution of åkermanite equals the sum of the heats of solution of $MgSiO_3$ and Ca_2SiO_4, yielding $\Delta H_{Ca_2SiO_4} = -365.3$ cal/gram. For Fe_2O_3 a rough value may be calculated on the basis of figures from Bichowsky and Rossini (1936) for the reaction: Fe_2O_3 (cryst.) + 6 HCl (sol.) → 2 $FeCl_2$ (sol.) + 3 H_2O (sol.), and gives $\Delta H_{Fe_2O_3} = -170$ cal/gram. Using all of these figures the heat of solution of the natural melilite from Hawaii, may be corrected according to the following equation:

$$-554.87 = 0.8389\, \Delta H_{\text{solid sol.}} + 0.0562\, \Delta H_{FeSiO_3} + 0.0014\, \Delta H_{MnSiO_3} + 0.0190\, \Delta H_{Fe_2O_3} + 0.0802\, \Delta H_{Ca_2SiO_4} + 0.0043\, \Delta H_{\text{water}}$$

From which $\Delta H_{\text{solid sol.}} = -599.5$ cal/gram.

---

[1] The composition of alkali melilite is taken from Berman (1929) and Goldsmith (1948) as $(Na,K)_2Si_3O_7$.

This value is for a melilite solid solution consisting of 81.4 weight percent of mixture $Å_{74}$ and of 18.6 weight percent of alkali melilite and is 1.2 cal/gram lower than the value for the pure solid solution $Å_{74}$.

In a similar manner, the heat of solution of the natural melilite from Luna County may by corrected to give

$$\Delta H_{\text{solid sol.}} = -621.6 \text{ cal/gram.}$$

This value, then, is for a melilite solid solution consisting of 98.6 weight percent of mixture $Å_{50}$ and of 1.3 weight percent of alkali melilite and is 4.7 cal/gram lower than the measured value for the synthetic mixture $Å_{50}$.

Both of these calculated heat-of-solution values are lower than the heat of solution of the corresponding synthetic samples having the same åkermanite-to-gehlenite ratio. This might suggest that the alkali content in melilite structure makes the structure more stable with respect to the pure åkermanite-gehlenite solid solutions. The constant occurence of alkali content in natural melilite minerals also indicates the same.

HEAT OF THE REACTION CRYSTAL → GLASS FOR THE ÅKERMANITE GEHLENITE SOLID SOLUTIONS

The heat-of-solution data given above in Tables VI and VII for melilite glasses and crystalline melilites are sufficient for computing the heat of reaction

$$\text{Crystal } (25° \text{ C}) \rightarrow \text{Glass } (25° \text{ C})$$

for different åkermanite-gehlenite solid solutions. The results of the computation are given in Table X.

Table X. Heat of the reaction Crystal → Glass at 25° C for åkermanite-gehlenite series.

Åkermanite, $Å_{100}$	$\Delta H = + 7{,}770 \pm 350$ cal/mole
$Å_{74}$	$+ 12{,}380 \pm 460$
$Å_{50}$	$+ 12{,}970 \pm 300$
$Å_{25}$	$+ 12{,}940 \pm 260$
Gehlenite, $Å_0$	$+ 11{,}910 \pm 440$

As is seen from the figures in Table X, the heat of the reaction Crystal → Glass for åkermanite-gehlenite solid solutions at 25° C is positive and varies but slightly throughout the series with exception of the åkermanite end.

Because of lack of data for high temperature heat content, it is not possible to evaluate the heat of the corresponding reaction at elevated temperatures. Thus the latent heats of fusion cannot be calculated for åkermanite, gehlenite, or for the solid solution corresponding to the minimum melting point.

HEAT OF FORMATION DATA

The heat-of-solution values given in the previous chapter allow the calculation of the heat of formation of the corresponding minerals. These data and some additional heat-of-formation values from literature, needed in the discussion of the decomposition of åkermanite, are listed below.

HEATS OF FORMATION OF CRYSTALLINE ÅKERMANITE-GEHLENITE SOLID SOLUTIONS FROM THE COMPONENT OXIDES

For åkermanite, the heat of formation is calculated from the following reactions the heats of which are known:

I. $Ca_2MgSi_2O_7$ (cryst., 25° C) + 18 HF (sol., 75° C) → $2\,CaF_2$ (sol., 75° C) + MgF_2 (sol., 75° C) + $2H_2SiF_6$ (sol., 75° C) + 7 H_2O (sol., 75° C)

$\Delta H_I = -157{,}590 \pm 190$ cal/mole.

II. CaO (cryst., 25° C) + 2 HF (sol., 75° C) → CaF_2 (sol., 75° C) + H_2O (sol., 75° C)

$\Delta H_{II} = -49{,}570 \pm 30$ cal/mole.

III. MgO (cryst., 25° C; dehydrated 2.5 hours at 1425° C) + 2HF (sol., 75° C) → MgF_2 (sol., 75° C) + H_2O (sol., 75° C)

$\Delta H_{III} = -35{,}480 \pm 80$ cal/mole.

IV. SiO_2 (quartz, 25° C) + 6HF (sol., 75° C) → H_2SiF_6 (sol., 75° C) + $2H_2O$ (sol., 75° C)

$\Delta H_{IV} = -33{,}400 \pm 30$ cal/mole

Subtracting reaction I from the sum of (2 II + III + 2 IV) yields

V. 2CaO (cryst., 25° C) + MgO (cryst., 25° C; dehydrated 2.5 hours at 1425° C) + $2SiO_2$ (quartz, 25° C) → $Ca_2MgSi_2O_7$ (cryst., 25° C)

with the heat of reaction

$$\Delta H_V = 2\,\Delta H_{II} + \Delta H_{III} + 2\,\Delta H_{IV} - \Delta H_I = -43{,}830 \pm 220 \text{ cal/mole.}$$

This value represents the heat of formation of åkermanite from the component oxides as defined above at 25° C.

In the equation for the heat of formation of åkermanite given above, ΔH_{I}, ΔH_{II}, ΔH_{III}, and ΔH_{IV} denote the heats of solution of åkermanite and of its component oxides, respectively, in the same acid. The equation may, of course, be generalized. The heat of formation of a complex silicate from the component oxides is obtained by subtracting the heat of solution of the silicate from the sum of the heats of solution of the oxides in corresponding stoichiometric ratio. Strictly speaking, this rule holds only if the heats of solution of the individual oxides are not influenced by other ions simultaneously in solution. The more dilute the solution is, the better the requirement is fulfilled. Errors due to the mutual influence of the ions in solution are avoided by using relatively small samples and by using an acid mixture carrying a small amount of silica in solution in determining the heats of solution of the oxide components.

Following the procedure applied for obtaining the heat of formation of åkermanite, the heats of formation of the åkermanite-gehlenite solid solutions may be derived from the general equation:

$$\Delta H = n\Delta H_{CaO} + m\Delta H_{MgO} + p\Delta H_{Al_2O_3} + q\,\Delta H_{SiO_2} - \Delta H_{Ca_nMg_mAl_{2p}Si_qO_7}$$

The general chemical formula of the åkermanite-gehlenite solid solutions is indicated in this equation by $Ca_nMg_mAl_{2p}Si_qO_7$. The results computed according to this equation are shown in Table XI.

Table XI. Heats of formation of crystalline åkermanite-gehlenite solid solutions from the component oxides at 25° C.

Molecular composition	n	m	p	q	Heat of formation cal/mole	Uncertainty
$Å_{100}$	2.00	1.00	0.00	2.00	—43,830	220
$Å_{85}$	2.00	0.85	0.15	1.85	—43,400	330
$Å_{74}$	2.00	0.74	0.26	1.74	—41,510	290
$Å_{50}$	2.00	0.50	0.50	1.50	—38,060	220
$Å_{25}$	2.00	0.25	0.75	1.25	—35,040	240
$Å_0 = G$	2.00	0.00	1.00	1.00	—34,160	350

All these heat-of-formation values refer to following crystalline component oxides:

SiO_2: natural low quartz,
MgO: dehydrated from $Mg(OH)_2$ at 1425° C 2,5 hours,
CaO: obtained through decomposition of $CaCO_3$ at
1100° C, ignited two hours at 1400° C,
Al_2O_3: γ-alumina, manufactured under unknown conditions, dried at 130° C for 40 hours.

γ-alumina had to be used because corundum is insoluble in acids. This is unfortunate, because γ-alumina shows varying degree of order in the structure as recently suggested by Ervin (1952), and does not have unique thermochemical properties (Kelley and collaborators, 1946). For this reason, the heats of formation evaluated, except that for pure åkermanite, cannot be used except for comparison with other heat-of-formation data for aluminum minerals based on the same batch of γ-alumina. Because of the lack of uniformity in the thermal properties of γ-alumina, the heat of reaction γ-alumina → Corundum is very inaccurately known. It is, therefore, not possible to recalculate the heat-of-formation values given in Table XI of åkermanite-gehlenite solid solutions on the basis of corundum.

HEAT OF FORMATION OF DIOPSIDE

The heat of formation of diopside, evaluated from the heat-of-solution data given in the previous chapter of this paper, is computed according to the following equation:

$$\Delta H = \Delta H_{CaO} + \Delta H_{MgO} + 2\Delta H_{SiO_2} - \Delta H_{diopside} = \\ - 35{,}250 \pm 220 \text{ cal/mole.}$$

This value is for the pure mineral of composition $CaMg(SiO_3)_2$.

OTHER HEAT-OF-FORMATION DATA NEEDED

The heats of formation of tricalcium silicate and calcium orthosilicate (β) have been determined by King (1951):

$$\Delta H_{Ca_3SiO_5} = -26{,}980 \pm 220 \text{ cal/mole}$$
$$\Delta H_{Ca_2SiO_4\,(\beta)} = -30{,}190 \pm 230 \text{ cal/mole.}$$

These values are based on natural quartz and on calcium oxide prepared from calcium carbonate by ignition for 12 hours at 1100° C.

The heats of formation of wollastonite, clinoenstatite, and forsterite have been determined by Torgeson and Sahama (1948) as follows:

$$\Delta H_{CaSiO_3} = -21{,}250 \pm 130 \text{ cal/mole,}$$
$$\Delta H_{MgSiO_3} = -\ \ 8{,}690 \pm 150 \text{ cal/mole, and}$$
$$\Delta H_{Mg_2SiO_4} = -15{,}120 \pm 210 \text{ cal/mole.}$$

All these values are for pure minerals having the theoretical composition, and are based on natural quartz, on calcium oxide prepared at 1150° C, and on magnesium oxide which was obtained from dehydrating magnesium hydroxide for one hundred hours in temperatures rising gradually from 400° through 1000° C.

The heats of formation of monticellite and merwinite measured by Neuvonen (1952) are:

$$\Delta H_{CaMgSiO_4} = -27{,}560 \pm 140 \text{ cal/mole and}$$
$$\Delta H_{Ca_3Mg(SiO_4)_2} = -57{,}020 \pm 380 \text{ cal/mole.}$$

These are based on the same component oxide materials as described in the present paper. The values account for pure theoretical compositions.

DECOMPOSITION OF ÅKERMANITE

On cooling a melt of the åkermanite composition very slowly, Carsten and Kristoffersen (1931) found the crystalline product obtained to consist of åkermanite and of small amount of diopside. Bowen, Schairer, and Posnjak (1933) observed that åkermanite glass that crystallized at 1375°C as a single phase åkermanite, gives a crystalline complex with Ca_2SiO_4 as one of the phases when it is crystallized at 1050° C. On heating large homogeneous crystals of åkermanite Osborn and Schairer (1941) found that the crystals remained homogeneous at temperatures above 1325° C. At temperatures below 1325° C, very small euhedral crystals grew within the åkermanite crystals. These crystals had approximately the indices of refraction and general appearance of diopside. No crystals were found with optical characteristics of Ca_2SiO_4. Preliminary investigations made by these authors showed that solid solutions åkermanite-gehlenite near åkermanite end become unstable at much lower temperatures.

Although the fact that åkermanite is unstable at low temperatures is shown clearly by the observations mentioned it is not definitely known to what components åkermanite inverts when subjected to heating at temperatures below its stability field.

As is seen from the diagram in Fig. 7 indicating the possible silicate phases in the ternary system CaO-MgO-SiO_2, the decomposition of åkermanite to two crystalline phases may proceed according to the following three reactions:

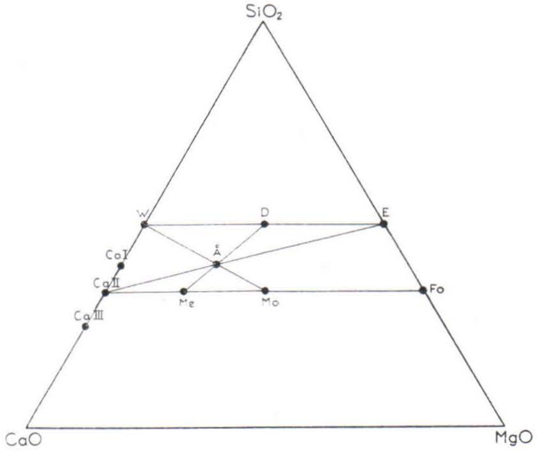


Fig. 7. The crystalline silicate phases in the system CaO-MgO-SiO_2.

A. Åkermanite.
Ca I. $Ca_3Si_2O_7$.
Ca II. Ca_2SiO_4.
Ca III. Ca_3SiO_5.
D. Diopside.
E. Enstatite (clinoenstatite).
F. Forsterite.
Me. Merwinite.
Mo. Monticellite.
W. Wollastonite (pseudowollastonite).

1. Åkermanite → Diopside + Merwinite.
2. Åkermanite → Monticellite + Wollastonite.
3. Åkermanite → Clinoenstatite + Calcium orthosilicate.

The heats of formation from the component oxides for the minerals included in the above reactions at 25° C are given in a previous chapter of this paper (p. 42 and p. 43). On the basis of these data the heats of reaction may be calculated to yield the following values:*

$$\begin{aligned} \text{Reaction 1.}\quad & \Delta H_1 = -2{,}310 \pm 300 \text{ cal/mole} \\ 2.\quad & \Delta H_2 = -4{,}980 \pm 300 \\ 3.\quad & \Delta H_3 = +4{,}950 \pm 360 \end{aligned}$$

The heats of reaction 1. and 2. are negative, and that of reaction 3. is positive. The figures are given for one mole of åkermanite.

The reaction 1. may proceed further due to hypothetical decomposition of diopside to wollastonite and enstatite, and due to decomposition

---

*) The heat-of-formation values measured by Torgeson and Sahama *(op. cit.)* and by King *(op. cit.)* are based on component oxides prepared slightly different from those used by the writer. The error introduced will not change the discussion, however.

of merwinite to monticellite and wollastonite. A limit for such further decomposition is determined by the mineralogical phase rule, according to which the number of phases cannot exceed three in the present case. The heat of decomposition of diopside is positive and would decrease the negative value of the heat of reaction 1. The heat of reaction merwinite → monticellite + Ca_2SiO_4 amounts to — 730 cal, thus giving the heat of the reaction

1 a. Åkermanite → Diopside + Monticellite + Ca_2SiO_4

$$\Delta H_{1a} = -2{,}670 \pm 300 \text{ cal/Åkermanite mole.}$$

The further decomposition of monticellite to Ca_2SiO_4 and Mg_2SiO_4 has a strongly positive heat of reaction and would accordingly decrease the negative value for the heat of reaction 1 a. and also would decrease that of the heat of reaction 2. Decomposition of merwinite to Ca_3SiO_5 and enstatite, is accompanied with a positive heat of reaction, thus also causing a decrease in the heat of reaction 1.

To judge whether or not the reactions above are possible from a thermodynamic point of view, the change of free energy should be known for each reaction. Calculation of the free energy change according to the relationship $\Delta F = \Delta H - T\Delta S$ would presuppose experimental values for the entropies of the minerals concerned. For magnesium orthosilicate, magnesium metasilicate (Kelley, 1943), wollastonite (Wagner, 1932), tricalcium silicate, and calcium orthosilicate (Todd, 1951) the entropy values are known at 25° C. For åkermanite, merwinite, and monticellite, however, no entropy values are given in literature. Therefore, accurate free energy calculations must await until these are known. It is to be expected, on the other hand, that the entropy increment in the reactions concerned is relatively small.

An exception to this rule is given by the reaction: albite + nepheline → jadeite for which the change of the entropy, according to the measurements made by Kelley (Yoder and Weir, 1951), amounts to $\Delta S_{25^\circ C} = -14.7$ entropy units. Such a large entropy increment is obviously not common in reactions between silicate minerals.

To calculate the free energy change for the reactions mentioned at elevated temperatures, high temperature heat content data are needed for all the minerals in consideration. Unfortunately, these data are given in literature for only a few of the compounds concerned (Kelley, 1949). For first approximation, the effect of temperature is but relatively small. Accordingly, in lack of adequate entropy and heat content data the heats of the reactions given above may be used to indicate the direction of the reactions given. According to this assumption, the reactions 1., 1 a., and 2. having a negative heat of reaction at 25° C, are theoretically possible from the thermodynamic point of view.

Using the hydrothermal quenching apparatus built by Tuttle (1948) the writer performed some experiments to decompose åkermanite. The pressure in all these experiments was about 2000 kg/cm^2 and the temperature varied from 400° to 900° C. In microscopic examination of the materials subjected to hydrothermal heating, it was observed that small quantities of tiny crystals had grown within the crystalline melilite when pure åkermanite was used. Small grain size did not enable indentification of these crystals under the microscope. The material was, therefore, subjected to further investigation with the »Norelco» type X-ray spectrometer. The low percentage of the decomposition products, present in the sample, made the extra lines (in addition to the åkermanite lines) in the pattern weak and broad. As is seen from Table XII summarizing the hydrothermal experiments, several extra lines appeared in the materials. The values of d-spacings measured for these extra lines are accurate only within 0.05—0.1 Kx units.

Table XII. Powder diffraction lines of the products of decomposition of åkermanite.

Starting Material	Pressure kg/cm^2	Temperature °C	Time Hours	Extra lines found, in order of intensity. Kx units.
Åkermanite glass	2 000	400 700	4	2.97 3.32, 3.22, 3.15, 2.67 1.67
Åkermanite cryst	2 000	700	32	2.97
Åkermanite glass	2 000	900	2	2.57 3.22, 3.15, 2.97 1.67

If these extra d-spacings found are compared with the x-ray powder diffraction lines given by Clark (1946) for different crystalline compounds in the system CaO-MgO-SiO_2, it becomes evident that there are different possibilities for interpretation. The only mineral among the hypothetical decomposition products of åkermanite, the presence of which cannot be established on the basis of the d-spacings is monticellite. Accordingly, the X-ray study made of the decomposition products, indicates that the decomposition follows the reaction:

$$\text{Åkermanite} \rightarrow \text{Merwinite} + \text{Diopside.}$$

This result contradicts the thermodynamic calculations according to which the formation of monticellite and wollastonite, or monticellite, diopside, and Ca_2SiO_4 from åkermanite was more probable. It is to be kept in mind, on the other hand, that the free energy change, and not the heat of reaction should have been used in judging the probability of the different reactions. In addition the present calculations are made for reactions at 25° C while the decomposition of the åkermanite in all the experiments made has taken place at considerably higher temperatures. It is possible that these facts are sufficient to explain the disagreement. The stability of merwinite is not fully known (Osborn, 1943), but its mode of occurrence in nature suggests that it is formed at high temperatures (Bowen, 1940). It seems evident therefore that the decomposition of åkermanite proceeds in the following steps with decreasing temperature:

$$\text{Åkermanite} \xrightarrow{1325\ \text{C}^\circ} \text{Diopside} + \text{Merwinite} \rightarrow$$
$$\text{Diopside} + \text{Monticellite} + Ca_2SiO_4 \rightarrow$$
$$\text{Monticellite} + \text{Wollastonite}.$$

In the present connection, it is interesting to note that the solid solution $Å_{50}$ did not show any sign of decomposition after a hydrothermal treatment. This agrees with the statement made by Osborn and Schairer *(loc. cit.)* according to which the stability of the solid solution extends to lower temperatures with increasing gehlenite content.

SUMMARY

The present paper deals with the thermochemical investigation of the åkermanite-gehlenite solid solutions by means of solution calorimetry.

The methods of preparing natural melilite specimens and synthetic glassy and crystalline åkermanite-gehlenite solid solutions are described. The calorimetric measurements have been made using a mixture of hydrochloric and hydrofluoric acid as the dissolving agent at 75° C. The calorimetric technique and the corrections required are discussed. Difficulties due to slow dissolving rate of the samples were overcome by using paper containers of special form.

The materials used for the study were examined by microscopic and X-ray methods. Unit cell dimensions were determined and found to agree with the values given by earlier investigators. An alternative method is suggested for evaluating the composition of åkermanite-gehlenite solid solution by means of powder diffraction pattern.

Heats of solution in the acid mixture were measured for synthetic and natural melilites, for diopside, for quartz, for calcium oxide, for γ-alumina, and for natural brucite. Values of heat of solution obtained for synthetic glassy and crystalline melilites are plotted against composition. The relationship between heat of solution and the åkermanite-to-gehlenite ratio is not linear, indicating a nonideal isomorphism between

the end members. The possibility of using solution calorimetry for investigation of the character of isomorphism is discussed.

Latent heats of crystallization of the åkermanite-gehlenite solid solutions are computed from the heat-of-solution data.

Heats of formation from the component oxides are given for åkermanite, gehlenite, and for their mutual solid solutions as well as for diopside.

The decomposition of åkermanite below its stability field is discussed on the basis of the thermal data obtained.

REFERENCES

Adams, L. H. (1949) Annual report of the director of the Geophysical Laboratory. Carnegie Inst. Wash. Year Book 48, p. 29.

Andrews, K. W. (1948) The lattice parameters and interplaner spacings of some artificially prepared melilites. Mineralog. Mag. 28, p. 474.

Barth, Tom F. W. (1930) Optical properties of mixed crystals. Am. J. Sci. 19, p. 135.

Berman, H. (1920) Composition of the melilite group. Am. Mineral. 14, p. 389.

Bichowsky, F. R., and Rossini, F. D. (1936) The thermochemistry of the chemical substances. New York.

Born, Max (1940) On the stability of crystal lattices. Proc. Cambridge Phil. Soc. 36, p. 160.

Bowen, N. L. (1940) Progressive metamorphism of siliceous limestone and dolomite. J. Geol. 48, p. 225.

Bowen, N. L., Schairer, J. F., and Posnjak, E. (1933) The system, CaO-FeO-SiO_2. Am. J. Sci. 26, p. 193.

Carstens, C. W., and Kristoffersen, Kr. (1931) Schlackenstudien mit besonderer Berücksichtigung der manganhaltigen Schlacken. Neues Jahrb. Mineral. Geol., Beilage-Bd. 62 A, p. 163.

Clark, C. B. (1946) X-ray diffraction data for compounds in the system CaO-MgO-SiO_2. J. Am. Ceram. Soc. 29, p. 25.

Cross, W. (1915) Lavas of Hawaii and their relations. U. S. Geol. Survey, Profess. Paper 88.

Ervin, Guy Jr. (1952) Structural interpretation of the diopside-corundum and boehmite - γ - Al_2O_3 transitions. Acta Cryst. 5, p. 103.

Ervin, Guy Jr., and Osborn, E. F. (1949) X-ray data on synthetic melilites. Am. Mineral. 34, p. 717.

Ferguson, J. B., and Buddington, A. F. (1920) The binary system åkermanite-gehlenite. Am. J. Sci. 50, p. 131.

Goldsmith, Julian, R. (1949) Some melilite solid solutions. J. Geol. 56, p. 437.

Juurinen, Aarno, and Hytönen, Kai (1952) Diopside from Juva, Finland. Compt. rend. Soc. géol. Finlande 25; Bull. Comm. géol. Finlande 157 (in press).

Kelley, K. K. (1943) Specific heats at low temperatures of magnesium orthosilicate and magnesium metasilicate. J. Am. Chem. Soc. 65, p. 339.

—»— (1945) Energy requirements and equilibria in the dehydration, hydrolysis, and decomposition of magnesium chlorite. U. S. Bur. Mines Tech. Paper 676.

—»— (1949) Contributions to the data on theoretical metallurgy. X. High-temperature heat-content, heat-capacity, and entropy data for inorganic compounds. U. S. Bur. Mines Bull. 476.

Kelley, K. K., Shomate, C. H., Young, F. E., Naylor, B. F., Salo, A. E., and Huffman, E. H. (1946) Thermodynamic properties of ammonium and potassium alums and related substances, with reference to extraction of alumina from clay and aluminate. U. S. Bur. Mines Tech. Paper 688.

King, E. G. (1951) Heats of formation of crystalline calcium orthosilicate, tricalcium silicate and zink orthosilicate. J. Am. Chem. Soc. 73, p. 656.

Neuvonen, K. J. (1952) Heat of formation of merwinite and monticellite. Am. J. Sci. (Bowen-volume, in press).

Osborn, E. F. (1943) The compound merwinite ($3CaO \cdot MgO \cdot 2SiO_2$) and its stability relations within the system CaO-MgO-SiO_2 (Preliminary report). J. Am. Ceram. Soc. 26, p. 231.

Osborn, E. F., and Schairer, J. F. (1941) The ternary system pseudowollastonite-åkermanite-gehlenite. Am. J. Sci. 239, p. 715.

Osborne, Nathan S. (1939) Heat of fusion of ice. A revision. Nat. Bur. Stand. J. Res. 23, p. 643.

Sahama, Th. G., and Neuvonen, K. J. (1951) A solution calorimeter for silicates. Compt. rend. Soc. Géol. Finlande 24; Bull. Comm. géol. Finlande 154, p. 177.

Sahama, Th. G., and Torgeson, D. R. (1949) Thermochemical study of the olivines and orthopyroxenes. U. S. Bur. Mines Repts. Invest. 4408.

Sherman, Jack (1932) Crystal energy of ionic compounds and thermochemical applications. Chem. Rev. 11, p. 93.

Taylor, Kenneth, and Wells, Lansing S. (1938) Studies of heat of solution of calcium and magnesium oxides and hydroxides. U. S. Nat. Bur. Stand. J. Res. 1121, p. 133.

Todd, S. S. (1951) Low-temperature heat capacity and entropies at 298.16 °K of crystalline calcium orthosilicate, zink orthosilicate and tricalcium silicate. J. Am. Chem. Soc. 73, p. 3277.

Torgeson, D. R., and Sahama, Th. G. (1948) A hydrofluoric acid solution calorimeter and the determination of the heats of formation of Mg_2SiO_4, $MgSiO_3$, and $CaSiO_3$. J. Am. Chem. Soc. 70, p. 2156.

Tuttle, O. F. (1948) A new hydrothermal quenching apparatus. Am. J. Sci. 246, p. 628.

Yoder, H. S., and Weir, C. E. (1951) Change of free energy with pressure of the reaction nepheline + albite → 2 jadeite. Am. J. Sci. 249, p. 683.

Wagner, Hubert (1932) Zur Thermochemie der Metasilikate des Calciums und Magnesiums und des Diopsids. Z. anorg. und allgem. Chem. 208, p. 1.

Wasastjerna, J. A. (1949) On the theory of the heat of formation of solid solutions. Soc. Sci. Fenn., Comm. Phys.-Math. 15, No. 3.

White, Walter, P. (1928) The modern calorimeter. New York.

U. S. National Bureau of Standards. Tables of selected values of chemical thermodynamic properties.

Bulletin de la Commission géologique de Finlande.

*N:o 1.	Ramsay, Wilhelm und Nyholm, E. T. Cancrinitsyenit und einige verwandte Gesteine aus Kuolajärvi. S. 1—12. 4 Fig. 1895	60: —
*N:o 2.	Sederholm, J. J. Ueber einen metamorphosirten praecambrischen Quarzporphyr von Karvia in der Provinz Åbo. S. 1—16. 12 fig. 1895	—
N:o 3.	Ramsay, Wilhelm, jemte Bihang 1 af Hackman, Victor och 2 af Sederholm, J. J. Till frågan om det senglaciala hafvets utbredning i Södra Finland. S. 1—44. 1 karta. Résumé en français: La transgression de l'ancienne mer glaciaire sur la Finlande méridionale. 1896	100: —
*N:o 4.	Frosterus, Benj. Ueber einen neuen Kugelgranit von Kangasniemi in Finland. S. 1—38. 11 Fig. 2 Taf. 1896	—
*N:o 5.	Berghell, Hugo. Bidrag till kännedomen om Södra Finlands kvartära nivåförändringar. S. 1—64. 16 fig. 1 plansch. 1 karta. Deutsches Referat: Beiträge zur Kenntniss der quartären Niweauschwankungen Süd-Finlands. 1896	—
*N:o 6.	Sederholm, J. J. Über eine archäische Sedimentformation im südwestlichen Finland und ihre Bedeutung für die Erklärung der Entstehungsweise des Grundgebirges. S. 1—254. 97 Fig. 5 Taf. 2 Karten. 1897	—
*N:o 7.	Ailio, Julius. Über Strandbildungen des Litorinameeres auf der Insel Mantsinsaari. S. 1—43. 8 Fig. 1898	—
*N:o 8.	Andersson, Gunnar. Studier öfver Finlands torfmossar och fossila kvartärflora. S. 1—210. 21 fig. 4 tafl. Deutsches Referat: Studien über die Torfmoore und die fossile Quartärflora Finlands. 1898	—
N:o 9.	Sederholm, J. J. Esquisse hypsométrique de la Finlande. P. 1—17. 1 carte. 1899	100: —
N:o 10.	Sederholm, J. J. Les dépôts quaternaires en Finlande. P. 1—28. 2 fig. 1 carte. 1899	100: —
*N:o 11.	Hackman, Victor. Neue Mitteilungen über das Ijolithmassiv in Kuusamo. S. 1—45. 7 Fig. 1 Taf. 2 Karten. 1899	—
*N:o 12.	Ramsay, Wilhelm und Borgström, L. H. Der Meteorit von Bjurböle bei Borgå. S. 1—28. 20 Fig. 1902	—
*N:o 13.	Frosterus, Benj. Bergbyggnaden i sydöstra Finland. S. 1—168. 18 fig. 8 tafl. 1 karta. Deutsches Referat: Der Gesteinsaufbau des südöstlichen Finland. 1902	—
*N:o 14.	Borgström, Leon. H. Die Meteoriten von Hvittis und Marjalahti. S. 1—80. 8 Taf. 1903	—
N:o 15.	Hackman, Victor. Die chemische Beschaffenheit von Eruptivgesteinen Finlands und der Halbinsel Kola im Lichte des neuen amerikanischen Systemes. S. 1—143. 3 Tab. 1905	120: —
*N:o 16.	Sundell, I. G. On the Cancrinite-Syenite from Kuolajärvi and a Related Dike Rock. P. 1—20. 1 plate. 1905	—
*N:o 17.	Fircks, Curt. On the Occurrence of Gold in Finnish Lapland. P. 1—35. Frontispiece. 15 fig. 1 map. 1906	80: —
*N:o 18.	Tanner, V. Studier öfver kvartärsystemet i Fennoskandias nordliga delar. I. Till frågan om Ost-Finmarkens glaciation och nivåförändringar. S. 1—165. 23 fig. 6 tafl. Résumé en français: Études sur le système quaternaire dans les parties septentrionales de la Fenno-Scandia. I. Sur la glaciation et les changements de niveau du Finmark oriental. 1906	200: —

---

*) Loppuunmyyty.
Out of print.

*N:o 19.	Trüstedt, Otto. Die Erzlagerstätten von Pitkäranta am Ladoga-See. S. 1—333. 80 Fig. 19 Taf. 1 Karte. 1907	—
N:o 20.	Tanner, V. Zur geologischen Geschichte des Kilpisjärvi-Sees in Lappland. S. 1—23. 3 Fig. 2 Taf. 1 Karte. 1907	60: —
N:o 21.	Tanner, V. Studier öfver kvartärsystemet i Fennoskandias nordliga delar. II. Nya bidrag till frågan om Finmarkens glaciation och nivåförändringar. S. 1—127. 10 fig. 6 tafl. Résumé en français: Études sur le système quaternaire dans les parties septentrionales de la Fenno-Scandia. II. Nouvelles recherches sur la glaciation et les changements de niveau du Finmark. 1907	200: —
N:o 22.	Borgström, L. H. Granitporphyr von Östersundom. S. 1—20. 3 Fig. 1 Taf. 1907	60: —
*N:o 23.	Sederholm, J. J. Om granit och gneis, deras uppkomst, uppträdande och utbredning inom urberget i Fennoskandia. S. 1—110. 11 fig. 8 tafl. 1 planteckn. 1 karta. English Summary of the Contents: On Granite and Gneiss, their Origin, Relations and Occurrence in the Pre-Cambrian Complex of Fenno-Scandia. 1907	—
*N:o 24.	Sederholm, J. J. Les roches préquaternaires de la Fennoscandia. P. 1—39. 20 fig. 1 carte. 1910	—
N:o 25.	Tanner, V. Über eine Gangformation von fossilienführendem Sandstein auf der Halbinsel Långbergsöda-Öjen im Kirchspiel Saltvik, Åland-Inseln. S. 1—13. 5 Fig. 2 Taf. 1911	60: —
*N:o 26.	Mäkinen, Eero. Bestimmung der Alkalien in Silikaten durch Aufschliessen mittelst Chlorkalzium. S. 1—8. 1911	—
N:o 27.	Sederholm, J. J. Esquisse hypsométrique de la Finlande. P. 1—21. 5 fig. 1 carte. 1911	80: —
*N:o 28.	Sederholm, J. J. Les roches préquaternaires de la Finlande. P. 1—27. 1 carte. 1911	—
*N:o 29.	Sederholm, J. J. Les dépôts quaternaires de la Finlande. P. 1—23. 5 fig. 1 carte. 1911	80: —
*N:o 30.	Sederholm, J. J. Sur la géologie quaternaire et la géomorphologie de la Fennoscandia. P. 1—66. 13 fig. 6 cartes. 1911	—
N:o 31.	Hausen, H. Undersökning af porfyrblock från sydvästra Finlands glaciala aflagringar. S. 1—34. 9 fig. Deutsches Referat. 1912	80: —
N:o 32.	Hausen, H. Studier öfver de sydfinska ledblockens spridning i Ryssland, jämte en öfversikt af is-recessionens förlopp i Ostbaltikum. Preliminärt meddelande med tvenne kartor. S. 1—32. Deutsches Referat. 1912	80: —
N:o 33.	Wilkman, W. W. Kvartära nivåförändringar i östra Finland. S. 1—40. 9 fig. Deutsches Referat. 1912	100: —
N:o 34.	Borgström, L. H. Der Meteorit von St. Michel. S. 1—49. 1 Fig. 3 Taf. 1912	100: —
N:o 35.	Mäkinen, Eero. Die Granitpegmatite von Tammela in Finnland und ihre Minerale. S. 1—101. 23 Fig. 1913	120: —
N:o 36.	Eskola, Pentti. On Phenomena of Solution in Finnish Limestones and on Sandstone filling Cavities. P. 1—50. 15 fig. 1913	100: —
N:o 37.	Sederholm, J. J. Weitere Mitteilungen über Bruchspalten mit besonderer Beziehung zur Geomorphologie von Fennoskandia. S. 1—66. 27 Fig. 1 Taf. 1913	140: —
N:o 38.	Tanner, V. Studier öfver kvartärsystemet i Fennoskandias nordliga delar. III. Om landisens rörelser och afsmältning i finska Lappland och angränsande trakter. S. 1—815. 139 fig. 16 tafl. Résumé en français: Études sur le système quaternaire dans les parties septentrionales de la Fennoscandia. III. Sur la progression et le cours de la récession du glacier continental dans la Laponie finlandaise et les régions environnantes. 1915	600: —
N:o 39.	Hackman, Victor. Der gemischte Gang von Tuutijärvi im nördlichen Finnland. S. 1—41. 9 Fig. 1914	80: —
*N:o 40.	Eskola, Pentti. On the Petrology of the Orijärvi region in Southwestern Finland. P. 1—277. 55 fig. 6 plates. 2 maps. 1914	—
N:o 41.	Borgström, L. H. Die Skapolithlagerstätte von Laurinkari. S. 1—30. 7 Fig. 1913	60: —

---

*) Loppuunmyyty.
Out of print.

N:o 42.	Hackman, Victor. Über Camptonitgänge im mittleren Finnland. S. 1—18. 3 Fig. 1914	60: —
N:o 43.	Wilkman, W. W. Kaleviska bottenbildningar vid Mölönjärvi. S. 1—36. 11 fig. Résumé en français. 1915	80: —
N:o 44.	Eskola, Pentti. Om sambandet mellan kemisk och mineralogisk sammansättning hos Orijärvitraktens metamorfa bergarter. S. 1—145. 5 fig. English Summary of the Contents. 1915	120: —
N:o 45.	Ailio, Julius. Die geographische Entwicklung des Ladogasees in postglazialer Zeit und ihre Beziehung zur steinzeitlichen Besiedelung. S. 1—158. 51 Abb. 2 Karten. 1915	200: —
N:o 46.	Laitakari, Aarne. Le gisement de calcaire cristallin de Kirmonniemi à Korpo en Finlande. P. 1—39. 14 fig. 1916	80: —
N:o 47.	Mäkinen, Eero. Översikt av de prekambriska bildningarna i mellersta Österbotten i Finland. S. 1—152. 25 fig. 1 karta. English Summary of the Contents. 1916	200: —
N:o 48.	Sederholm, J. J. On Synantetic Minerals and Related Phenomena (Reaction Rims, Corona Minerals, Kelyphite, Myrmekite, &c.). P. 1—148. 14 fig. in the text and 48 fig. on 8 plates. 1916	240: —
N:o 49.	Wilkman, W. W. Om en prekalevisk kvartsitformation i norra delen af Kuopio socken. S. 1—18. 7 fig. Résumé en français. 1916	60: —
N:o 50.	Sauramo, Matti. Geochronologische Studien über die spätglaziale Zeit in Südfinnland. S. 1—44. 5 Abb. 4 Taf. 1918	120: —
N:o 51.	Laitakari, Aarne. Einige Albitepidotgesteine von Südfinnland. S. 1—13. 5 Abb. 1918	60: —
N:o 52.	Brenner, Th. Über Theralit und Ijolit von Umptek auf der Halbinsel Kola. S. 1—30. 4 Fig. 1920	60: —
N:o 53.	Hackman, Victor. Einige kritische Bemerkungen zu Iddings' Classifikation der Eruptivgesteine. S. 1—21. 1920	60: —
N:o 54.	Laitakari, Aarne. Über die Petrographie und Mineralogie der Kalksteinlagerstätten von Parainen (Pargas). S. 1—113. 40 Abb. 3 Taf. 1921	120: —
N:o 55.	Eskola, Pentti. On Volcanic Necks in Lake Jänisjärvi in Eastern Finland. P. 1—13. 1 fig. 1921	60: —
N:o 56.	Metzger, Adolf A. Th. Beiträge zur Paläontologie des nordbaltischen Silurs im Ålandsgebiet. S. 1—8. 3 Abb. 1922	60: —
*N:o 57.	Väyrynen, Heikki. Petrologische Untersuchungen der granitodioritischen Gesteine Süd-Ostbothniens. S. 1—78. 20 Fig. 1 Karte. 1923	—
*N:o 58.	Sederholm, J. J. On Migmatites and Associated Pre-Cambrian Rocks of Southwestern Finland. Part I. The Pellinge Region. P. 1—153. 64 fig. 8 plates. 1 map. 1923	—
N:o 59.	Berghell, Hugo und Hackman, Victor. Über den Quartzit von Kallinkangas, seine Wellenfurchen und Trockenrisse. Nach hinterlassenen Aufzeichnungen von Hugo Berghell zusammengestellt und ergänzt von Victor Hackman. S. 1—19. 19 Fig. 1923	60: —
N:o 60.	Sauramo, Matti. Studies on the Quaternary Varve Sediments in Southern Finland. P. 1—164. 22 fig. in the text. 12 fig., 1 map and 2 diagrams on 10 plates. 1923	200: —
N:o 61.	Hackman, Victor. Der Pyroxen-Granodiorit von Kakskerta bei Åbo und seine Modifikationen. S. 1—23. 2 Fig. 1 Karte. 1923	60: —
N:o 62.	Wilkman, W. W. Tohmajärvi-konglomeratet och dess förhållande till kaleviska skifferformationen. S. 1—43. 15 fig. 1 karta. Deutsches Referat. 1923	80: —
N:o 63.	Hackman, Victor. Über einen Quartzsyenitporhyr von Saariselkä im finnischen Lappland. S. 1—10. 2 Fig. 1923	60: —
N:o 64.	Metzger, Adolf A. Th. Die jatulischen Bildungen von Suojärvi in Ostfinnland. S. 1—86. 38 Abb. 1 Taf. 1 Karte. 1924	120: —
N:o 65.	Saxén, Martti. Über die Petrologie des Otravaaragebietes im östlichen Finnland. S. 1—63. 13 Abb. 5 Fig. auf 1 Taf. 2 Karten. 1923	120: —
N:o 66.	Ramsay, Wilhelm. On Relations between Crustal Movements and Variations of Sea-Level during the Late Quaternary Time, especially in Fennoscandia. P. 1—39. 10 fig. 1924	80: —

---

*) Loppuunmyyty.
Out of print.

N:o 67.	Sauramo, Matti. Tracing of Glacial Boulders and its Application in Prospecting. P. 1—37. 12 fig. 1924	80: —
N:o 68.	Tanner, V. Jordskredet i Jaarila. S. 1—18. 2 fig. 10 bild. Résumé en français. 1924	60: —
N:o 69.	Auer, Väinö. Die postglaziale Geschichte des Vanajavesisees. S. 1—132. 10 Fig. 10 Taf. 11 Beil. 1924	200: —
N:o 70.	Sederholm, J. J. The Average Composition of the Earth's Crust in Finland. P. 1—20. 1925	80: —
N:o 71.	Wilkman, W. W. Om diabasgångar i mellersta Finland. S. 1—35. 8 fig. 1 karta. Deutsches Referat. 1924	80: —
N:o 72.	Hackman, Victor. Das Gebiet der Alkaligesteine von Kuolajärvi in Nordfinnland. S. 1—62. 6 Fig. 1 Taf. 1925	120: —
N:o 73.	Laitakari, Aarne. Über das jotnische Gebiet von Satakunta. S. 1—43. 14 Abb. 1 Karte. 1925	120: —
N:o 74.	Metzger, Adolf A. Th. Die Kalksteinlagerstätten von Ruskeala in Ostfinnland. S. 1—24. 9 Abb. 2 Karten. 1925	80: —
N:o 75.	Frosterus, Benj. Ueber die kambrischen Sedimente der karelischen Landenge. S. 1—52. 1 Fig. 1925	120: —
N:o 76.	Hausen, H. Über die präquartäre Geologie des Petsamo-Gebietes am Eismeere. S. 1—100. 13 Fig. 2 Taf. 1926	120: —
N:o 77.	Sederholm, J. J. On Migmatites and Associated Pre-Cambrian Rocks of Southwestern Finland. Part II. The Region around the Barösundsfjärd W. of Helsingfors and Neighbouring Areas. P. 1—143. 57 fig. in the text and 44 fig. on 9 plates. 1 map. 1926	240: —
N:o 78.	Väyrynen, Heikki. Geologische und petrographische Untersuchungen im Kainuugebiete. S. 1—127. 37 Fig. 2 Taf. 2 Karten. 1928	160: —
N:o 79.	Hackman, Victor. Studien über den Gesteinsaufbau der Kittilä-Lappmark. S. 1—105. 23 Fig. 2 Taf. 2 Karten. 1927	160: —
N:o 80.	Sauramo, Matti. Über die spätglazialen Niveauverschiebungen in Nordkarelien, Finnland. S. 1—41. 8 Fig. im Text. 11 Fig., 1 Karte und 1 Profildiagr. auf 7 Taf. 1928	60: —
N:o 81.	Sauramo, Matti and Auer, Väinö. On the Development of Lake Höytiäinen in Carelia and its Ancient Flora. P. 1—42. 20 fig. 4 plates. 1928	60: —
N:o 82.	Lokka, Lauri. Über Wiikit. S. 1—68. 12 Abb. 1928	120: —
N:o 83.	Sederholm, J. J. On Orbicular Granite, Spotted and Nodular Granites etc. and on the Rapakivi Texture. P. 1—105. 19 fig. in the text and 50 fig. on 16 plates. 1928	200: —
N:o 84.	Sauramo, Matti. Über das Verhältnis der Ose zum höchsten Strand. S. 1—17. 1928	40: —
N:o 85.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, I. P. 1—88. 1 stéréogramme. 1929	160: —
N:o 86.	Sauramo, Matti. The Quaternary Geology of Finland. P. 1—110. 39 fig. in the text and 42 fig. on 25 plates. 1 map. 1929	240: —
N:o 87.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, II. P. 1—175. 48 fig. 8 planches. 1929	280: —
N:o 88.	Tanner, V. Studier över kvartärsystemet i Fennoskandias nordliga delar. IV. Om nivåförändringarna och grunddragen av den geografiska utvecklingen efter istiden i Ishavsfinland samt om homotaxin av Fennoskandias kvartära marina avlagringar. S. 1—589. 84 fig. 4 tavl. 1 karta. Résumé en français: Études sur le système quaternaire dans les parties septentrionales de la Fennoscandie. IV. Sur les changements de niveau et les traits fondamentaux du développement géographique de la Finlande aux confins de l'océan Arctique après l'époque glaciaire et sur l'homotaxie du quaternaire marin en Fennoscandie. 1930	600: —
N:o 89.	Wegmann, C. E. und Kranck, E. H. Beiträge zur Kenntnis der Svecofenniden in Finnland. I. Übersicht über die Geologie des Felsgrundes im Küstengebiete zwischen Helsingfors und Onas. II. Petrologische Übersicht des Küstengebietes E von Helsingfors. S. 1—107. 4 Fig. 16 Taf. mit 32 Fig. 1 Übersichtskarte. 1931	160: —

N:o 90.	Hausen, H. Geologie des Soanlahti-Gebietes im südlichen Karelien. Ein Beitrag zur Kenntnis der Stratigraphie und tektonischen Verhältnisse der Jatulformation. S. 1—105. 23 Fig. im Text und 12 Fig. auf 4 Taf. 1930	200: —
N:o 91.	Sederholm, J. J. Pre-Quaternary Rocks of Finland. Explanatory Notes to accompany a General Geological Map of Finland. P. 1—47. 40 fig. 1 map. 1930	120: —
N:o 92.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, III. P. 1—140. 29 fig. 3 planches. 1930	200: —
N:o 93.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, IV. P. 1—68. 12 fig. 6 planches. 1931	160: —
N:o 94.	Brenner, Thord. Mineraljordarternas fysikaliska egenskaper. S. 1—159. 22 fig. Deutsches Referat. 1931	280: —
N:o 95.	Sederholm, J. J. On the Sub-Bothnian Unconformity and on Archæan Rocks formed by Secular Weathering. P. 1—81. 62 fig. 1 map. 1931	200: —
N:o 96.	Mikkola, Erkki. On the Physiography and Late-Glacial Deposits in Northern Lapland. P. 1—88. 25 fig. 5 plates. 1932	200: —
N:o 97.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, V. P. 1—77. 15 fig. 1932	160: —
N:o 98.	Sederholm, J. J. On the Geology of Fennoscandia. P. 1—30. 1 map. 1 table. 1932	120: —
N:o 99.	Tanner, V. The Problems of the Eskers. The Esker-like Gravel Ridge of Čahpatoaiv, Lapland. P. 1—13. 2 plates. 1 map. 1932	60: —
N:o 100.	Sederholm, J. J. Über die Bodenkonfiguration des Päijänne-Sees. S. 1—23. 3 Fig. 1 Karte. 1932	200: —
N:o 101.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, VI. P. 1—118. 17 fig. 5 planches. 1933	200: —
N:o 102.	Wegmann, C. E., Kranck, E. H. et Sederholm, J. J. Compte rendu de la Réunion internationale pour l'étude du Précambrien et des vieilles chaînes de montagnes. P. 1—46. 1933	120: —
N:o 103.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, VII. P. 1—48. 2 fig. 1933	100: —
N:o 104.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, VIII. P. 1—156. 33 fig. 7 planches. 1934	220: —
N:o 105.	Lokka, Lauri. Neuere chemische Analysen von finnischen Gesteinen. S. 1—64. 1934	120: —
N:o 106.	Hackman, Victor. Das Rapakiwirandgebiet der Gegend von Lappeenranta (Willmanstrand). S. 1—82. 15 Fig. 2 Taf. 1 Analysentab. 1 Karte. 1934	140: —
N:o 107.	Sederholm, J. J. † On Migmatites and Associated Pre-Cambrian Rocks of Southwestern Finland. Part III. The Åland Islands. P. 1—68. 43 fig. 2 maps. 1934	160: —
N:o 108.	Laitakari, Aarne. Geologische Bibliographie Finnlands 1555—1933. S. 1—224. 1934	200: —
N:o 109.	Väyrynen, Heikki. Über die Mineralparagenesis der Kieserze in den Gebieten von Outokumpu und Polvijärvi. S. 1—24. 7 Fig. 1 Karte. 1935	80: —
N:o 110.	Saksela, Martti. Über den geologischen Bau Süd-Ostbothniens. S. 1—35. 11 Fig. 1 Titelbild. 1 Taf. 1 Karte. 1935	100: —
N:o 111.	Lokka, Lauri. Über den Chemismus der Minerale (Orthit, Biotit u. a.) eines Feldspatbruches in Kangasala, SW-Finnland. S. 1—39. 2 Abb. 1 Taf. 1935	100: —
N:o 112.	Hackman, Victor. J. J. Sederholm. Biographic Notes and Bibliography. P. 1—29. With a vignette. 1935	80: —
N:o 113.	Sahama (Sahlstein), Th. G. Die Regelung von Quarz und Glimmer in den Gesteinen der finnisch-lappländischen Granulitformation. S. 1—110. 5 Fig. 80 Diagr. 3 Taf. 1936	160: —
N:o 114.	Haapala, Paavo. On Serpentine Rocks in Northern Karelia. P. 1—83. 21 fig. 2 maps. 1936	120: —

N:o 115.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, IX. P. 1—505. 83 fig. 20 planches. 1936	400: —
N:o 116.	Väyrynen, Heikki. Petrologie des Nickelerzfeldes Kaulatunturi—Kammikivitunturi in Petsamo. S. 1—198. 71 Abb. 36 Tab. 1 Karte. 1938	200: —
N:o 117.	Kilpi, Sampo. Das Sotkamo-Gebiet in spätglazialer Zeit. S. 1—118. 36 Abb. 3 Beil. 1937	200: —
N:o 118.	Brander, Gunnar. Ein Interglazialfund bei Rouhiala in Südostfinnland. S. 1—76. 7 Fig. im Texte u. 7 Fig. auf 2 Taf. 1937	160: —
N:o 119.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, X. P. 1—170. 30 fig. 4 planches. 1937	200: —
N:o 120.	Hyyppä, Esa. Post-Glacial Changes of Shore-Line in South Finland. P. 1—225. 57 fig. 21 tab. 2 append. 1937	200: —
N:o 121.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XI. P. 1—166. 47 fig. 8 tab. 2 cartes. 1938	200: —
N:o 122.	Hietanen, Anna. On the Petrology of Finnish Quartzites. P. 1—118. 20 fig. 8 plates. 3 maps. 1938	200: —
N:o 123.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XII. P. 1—107. 20 fig. 3 planches. 1938	200: —
N:o 124.	Väyrynen, Heikki. On the Geology and Tectonics of the Outokumpu Ore Field and Region. P. 1—91. 11 fig. 2 maps. 1939	200: —
N:o 125.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XIII. P. 1—119. 45 fig. 1 planche. 1939 ..	120: —
N:o 126.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XIV. P. 1—140. 60 fig. 4 planches. 1941	150: —
N:o 127.	Mölder, Karl. Studien über die Ökologie und Geologie der Bodendiatomeen in der Pojo-Bucht. P. 1—204. 7 Abb. 1 Karte. 14 Diagr. 14 Tab. 1943	200: —
N:o 128.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XV. P. 1—183. 43 fig. 2 planches. 1943 ..	200: —
N:o 129.	Lokka, Lauri. Beiträge zur Kenntnis des Chemismus der finnischen Minerale. Glimmer, Pyroxene, Granate, Epidote u. a. Silikatminerale sowie melnikowitähnliches Produkt und Shungit. S. 1—72. 48 Tab. 1943	150: —
*N:o 130.	Hietanen, Anna. Über das Grundgebirge des Kalantigebietes im südwestlichen Finnland. S. 1—105. 55 Fig. 8 Tafeln. 1 Karte. 1943	250: —
N:o 131.	Okko, V. Moränenuntersuchungen im westlichen Nordfinnland. S. 1—46. 12 Abb. 4 Tab. 1944	90: —
N:o 132.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XVI. P. 1—196. 41 diagr. 9 tabl. 3 cartes. 3 fig. 1944	200: —
N:o 133.	Rankama, Kalervo. On the Geochemistry of Tantalum. P. 1—78. 1 fig. 8 tabl. 1944	150: —
N:o 134.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XVII. P. 1—91. 59 fig. 1 carte. 1944	150: —
N:o 135.	Sahama, Th. G. Spurenelemente der Gesteine im südlichen Finnisch-Lappland. S. 1—86. 12 Fig. 29 Tab. 1945	150: —
N:o 136.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XVIII. P. I—XXXVIII; 1—67. 3 diagr. 11 tabl. 2 cartes. 11 fig. 2 planches. 1945	200: —
N:o 137.	Rankama, Kalervo. On the Geochemical Differentiation in the Earth's Crust. P. 1—39. 18 tabl. 1946	100: —
N:o 138.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géolo-	

	gique de Finlande, XIX. P. 1—120. 7 diagr. 13 tabl. 9 fig. 1 planche. 1946	100: —
N:o 139.	Brenner, Thord. Om mineraljordarternas hållfasthetsegenskaper. S. 1—77. 11 fig. Summary in English. 1946	120: —
N:o 140.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géeologique de Finlande, XX. P. 1—302. 37 tabl. 103 fig. 7 planches. 2 cartes. 1947	300: —
N:o 141.	Simonen, Ahti. On the Petrochemistry of the Infracrustal Rocks in the Svecofennidic Territory of Southwestern Finland. P. 1—18. 7 tabl. 5 fig. 1948	25: —
N:o 142.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XXI. P. 1—129. 45 fig. 1 planche. 4 tabl. 3 cartes 1948	200: —
N:o 143.	Simonen, Ahti. On the Petrology of the Aulanko Area in Southwestern Finland. P. 1—66. 25 fig. 6 tabl. 1 map. 1948	100: —
N:o 144.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XXII. P. 1—165. 70 fig. 3 planches. 4 cartes. 1949.	200: —
N:o 145.	Salmi, Martti. Physical and Chemical Peat Investigations on the Pinomäensuo Bog, SW. Finland. P. 1—31. 12 fig. 1 table. 1949	50: —
N:o 146.	Mikkola, Aimo. On the Geology of the Area North of the Gulf of Bothnia. P. 1—64. 20 fig. 10 tabl. 1 map. 1949	100: —
N:o 147.	Härme, Maunu. On the Stratigraphical and Structural Geology of the Kemi Area, Northern Finland. P. 1—60. 29 fig. 4 tabl. 1 map. 1949	100: —
N:o 148.	Edelman, Nils. Structural History of the Eastern part of the Gullkrona Basin, SW-Finland. P. 1—48. 16 fig. 2 tabl. 8 plates. 1949	90: —
N:o 149.	Lokka, Lauri. Contributions to the Knowledge of the Chemistry of the Radioactive Minerals of Finland. P. 1—76. 7 fig. 33 tabl. 1950	150: —
N:o 150.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XXIII. P. 1—111. 27 fig. 7 planches. 5 tabl. 2 cartes. 1950	250: —
N:o 151.	Lokka, Lauri. Chemical Analyses of Finnish Rocks. P. 1—75. 1950	150: —
N:o 152.	Kahma, Aarno. On Contact Phenomena of the Satakunta Diabase. P. 1—84. 22 fig. 10 tabl. 5 plates. 1951	200: —
N:o 153.	Seitsaari, Juhani. The Schist Belt Northeast of Tampere in Finland. P. 1—120. 53 fig. 9 tabl. 2 maps. 1951	300: —
N:o 154.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sällskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XXIV. P. 1—241. 95 fig. 3 planches. 24 tabl. 1951	400: —
N:o 155.	Virkkala, K. Glacial Geology of the Suomussalmi area, East Finland. P. 1—66. 26 fig. 1 plate. 1951	150: —
N:o 156.	Marmo, Vladi — Mikkola, Aimo. On Sulphides of the Sulphide-bearing Schists of Finland. P. 1—44. 7 fig. 4 plates. 1951	90: —
N:o 157.	Suomen Geologisen Seuran julkaisuja — Meddelanden från Geologiska Sellskapet i Finland — Comptes Rendus de la Société géologique de Finlande, XXV. In press.	
N:o 158.	Neuvonen, K. J. Thermochemical Investigation of the Åkermanite-Gehlenite Series. P. 1—50. 7 fig. 12 tables. 1952	100: —