ART. XLV.—*The Constitution of Melilite and Gehlenite* ;*
by FRANK WIGGLESWORTH CLARKE.

ALTHOUGH many attempts have been made to determine the chemical constitution of melilite and gehlenite, no one of them can be accepted as absolutely conclusive. The analyses of the two minerals vary widely, showing that they are not true species but crystalline mixtures analogous to those found in the feldspar series, the micas, the scapolites, and the garnet group. The problem is, to determine the individual components of melilite and gehlenite, and in such a way as to show their relations to each other, and to all minerals of similar chemical composition or type.

The most recent, and decidedly the most successful attempt to interpret the constitution of these minerals is due to W. T. Schaller.† He regards melilite and gehlenite as mixtures of four definite silicates, namely, åkermanite, $Mg_4Ca_2Si_5O_{30}$; sarcolite, $Al_2Ca_2Si_2O_{12}$; soda sarcolite, $Al_2Na_2Si_2O_{12}$, and "velardenite," $Al_2Ca_2SiO_7$. The last of these silicates is well known as an artificial compound, but not definitely as a natural mineral. All four silicates are tetragonal, and Schaller has shown that their formulæ can be adjusted to the analyses of melilite and gehlenite with a remarkable degree of accuracy. The crystallographic and chemical data are in harmony, but unfortunately, they do not cover the whole ground. The relations of melilite and gehlenite to other minerals, such as anorthite, garnet, zoisite, vesuvianite, and meionite, are not indicated by Schaller's method of formulation, and so the fundamental problem is incompletely solved. A great advance has been made, but much still remains to be done. The present communication represents an effort to find a more general interpretation of the lime-alumina silicates, not only with regard to their chemical composition, but also with reference to their associations in nature, their mode of origin, and their alterations.

To Schaller's formulation of melilite and gehlenite there are obvious objections, which, however, he has shown to be not absolutely insuperable. The four primary compounds of his scheme can be represented by a single type of formula, but to that procedure there are alternatives which seem to be more reasonable. The compounds are not alike chemically; for åkermanite is non-aluminous, "velardenite" is extremely basic, and sarcolite is most simply formulated as a normal orthosilicate. The other lime-alumina silicates which have already

* Published by permission of the Director of the U. S. Geological Survey.

† U. S. Geol. Survey, Bull. 610, pp. 106-126. Schaller gives a good summary of earlier interpretations, which need not be repeated here.

been mentioned are also orthosilicates, and the true components of melilite and gehlenite ought in all probability to follow the same rule. The tetragonal sarcolite, for example, has the same molecular ratios as the isometric garnet, and a probable structural difference between the two species is easy to represent graphically. Including an analogous compound, prehnite, the following constitutional formulæ are at least probable:

Natural sarcolite is a mixture of the lime salt and the soda salt, but the replacement of lime by soda is not necessarily complete. The formulation given here fits best into the general scheme, which will be developed presently. The two sarcolites, however, as Schaller has shown, are probable components of melilite and gehlenite. That is an important step forward.

On comparing the trustworthy analyses of melilite and gehlenite two striking differences appear. In melilite the ratio of oxygen to silicon is slightly lower than that required for the orthosilicate radicle SiO_4 ; and for that reason trisilicate molecules may be assumed as possibly present. This assumption is justified by familiar analogies as in the isomorphism of albite and anorthite, and of the scapolitic minerals marialite and meionite. In each of these pairs a trisilicate and an orthosilicate are morphologically equivalent. In gehlenite, on the other hand, the oxygen is largely in excess of the orthosilicate, and basic molecules must be taken into account. This condition is satisfied by assuming the presence in gehlenite of the

univalent group $-\text{Al} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{Ca}$; which in Schaller's system is characteristic of his basic silicate, "velardenite." In the present discussion its function will be differently shown. Furthermore, natural melilite always contains soda, presumably as soda

sarcolite, while gehlenite contains little or none. Weinschenk's fuggerte is an exceptional mineral, lying near the boundary between melilite and gehlenite, and showing affinities for both species. It is best classified as a sodic variety of gehlenite.

The reported syntheses of melilite are not altogether satisfactory, and need not be discussed here. There are, however, melilites of artificial origin which are very significant as regards chemical composition. For example, the melilite crystals obtained by Bodländer* from Portland cement, have very nearly the composition represented by the formula $\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6\text{Mg}_3$; which may be written structurally thus:

Another crystalline melilite isolated by Stahl† from furnace slag has very nearly the same molecular ratios. In this instance, however, the general formula $\text{Al}_2(\text{SiO}_4)_6\text{R}_6$ includes a large proportion of ferrous iron and some zinc among the components of R. With these clues we may write the following series of formulæ:

These expressions are to be qualified by the evident fact that in melilite as in garnet ferric molecules may be commingled with those of alumina, and ferrous or magnesian molecules with those of lime. In natural melilite we have, apparently, a crystalline mixture of the *normal* melilite, as written above, with sarcolite, soda sarcolite, and a small proportion of a trisilicate, $\text{Al}_4(\text{Si}_3\text{O}_{10})_6\text{Ca}_4\text{Na}_4$, equivalent to sarcolite. A study of the available analyses of melilite will serve to show how closely this scheme fits the facts.

Analyses of Melilite

1.	Damour analyst.	From Vesuvius.
2.	" "	Capo di Bove, yellow.
3.	" "	" " brown.
4.	Bodländer "	" " "
5.	Zambonini "	" " yellow.
6.	" "	" " brown.
7.	Schaller "	Iron Hill, Uncompahgre quadrangle, Colorado.†

* Neues Jahrb., 1892, vol. i, p. 53.

† Berg-u.-Hüttenmännische Zeitung, lxiii, 273, 1904. Discussed by Zambonini in Zeitschr. Kryst., xli, 226, 1906.

‡ See Larsen and Schaller, Journ. Wash. Acad., iv, 473, 1914.

	1	2	3	4	5	6	7
SiO ₂	40·69	39·27	38·34	41·09	40·14	39·20	42·07
TiO ₂	-----	-----	-----	-----	trace	trace	·20
Al ₂ O ₃	10·88	6·42	8·61	10·93	6·47	7·56	10·50
Fe ₂ O ₃	4·43	10·17	10·02	3·40	9·95	11·34	·30
FeO	-----	-----	-----	-----	·53	-----	2·18
MnO	-----	-----	-----	-----	trace	trace	·16
CaO	31·81	32·47	32·05	34·78	32·98	32·18	35·41
MgO	5·75	6·44	6·71	5·87	6·33	6·41	4·15
Na ₂ O	4·43	1·95	2·12	3·40	2·18	2·21	3·24
K ₂ O	·36	1·46	1·51	·68	1·49	1·45	trace
H ₂ O	-----	-----	-----	·24	·27	·21	·47
P ₂ O ₅	-----	-----	-----	-----	-----	-----	·82
CO ₂	-----	-----	-----	-----	-----	-----	·90
	<hr/> 98·35	<hr/> 98·18	<hr/> 99·36	<hr/> 100·39	<hr/> 100·34	<hr/> 100·56	<hr/> 100·40

Reducing these analyses to standard form, by computing Fe₂O₃ into its equivalent of Al₂O₃; FeO, MnO, and MgO into CaO; K₂O into Na₂O, and recalculating to 100 per cent, the data become comparable as shown in the next table. The P₂O₅ and CO₂ of the Colorado mineral are reckoned as representing calcium phosphate and carbonate, and rejected.

Reduced analyses of melilite.

	1	2	3	4	5	6	7
SiO ₂	41·13	40·67	39·16	40·76	40·84	39·88	43·41
Al ₂ O ₃	13·85	13·36	15·32	13·01	13·03	15·05	10·92
CaO	40·31	42·96	42·33	42·41	42·98	41·86	42·34
Na ₂ O	4·71	3·01	3·19	3·82	3·15	3·21	3·33
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

From these reduced analyses the following formulæ are derived:

1. $7\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 31\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 62\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.
2. $6\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 18\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 6\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6$
+ $70\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.
3. $2\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 24\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 19\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6$
+ $60\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.
4. $7\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 21\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 72\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.
5. $7\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 19\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 1\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6$
+ $73\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.
6. $4\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 22\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 19\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6$
+ $60\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.
7. $13\text{Al}_4(\text{Si}_3\text{O}_8)_6\text{Ca}_4\text{Na}_4 + 14\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 67\text{Al}_2(\text{SiO}_4)_6\text{Ca}_9$.

These correspond to the following calculated analyses:

Calculated analyses of melilite.

	1	2	3	4	5	6	7
SiO ₂	41·21	40·64	39·16	40·99	40·97	40·15	43·36
Al ₂ O ₃	14·13	13·36	15·26	13·04	12·93	15·11	10·96
CaO	39·93	43·00	42·36	42·50	42·88	41·56	42·32
Na ₂ O	4·73	3·00	3·22	3·47	3·22	3·18	3·36
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The agreement between the reduced and calculated analyses is very close. In many cases the *normal* melilite silicate Al₂(SiO₄)₆Ca₃ predominates, forming from 60 to 70 per cent of the mixed crystals. The two sarcolites come next, with the hypothetical trisilicate molecule in subordinate amount. The existence of the trisilicate, however, is subject to some doubt. Melilite is prone to contain impurities, inclusions of other minerals, and the excess of silica shown by the analyses may perhaps be due to their presence. The melilite of Capo di Bove, for example, commonly contains inclusions of leucite,* and it is possible that dissolved silica may sometime be present also. The largest proportion of trisilicate appears in the massive melilite from Colorado, which is more likely to contain impurities than the crystallized mineral. If the excess of silica is really dissolved silica, then the trisilicate molecule would be replaced by an equivalent amount of soda sarcolite, and the formulæ of natural melilite would be simplified. It would then be represented as a crystalline mixture of the two sarcolites with the compound Al₂(SiO₄)₆Ca₃ in varying proportions.

It has already been pointed out that gehlenite differs from melilite in its ratio of silicon to oxygen; and that the difference may be accounted for by assuming the presence in it of the univalent groups—Al $\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ Ca. That is, gehlenite is a basic silicate, and the basic group may be combined in one of several ways. The compound containing it may have the formula Al(SiO₄)₃(AlO₂Ca)₃, or, more probably, a formula derived from that of the melilite silicate, thus:

* See Stelzner, Neues Jahrb., Beil. Bd. ii, 369, 1883.

With these formulæ the two minerals become similar in structure, and, as will be shown later, simply related to many other species. As for natural gehlenite, its analyses are easily reducible to mixtures of the two silicates just given, with sarcolite. In fuggerite a little soda sarcolite also appears.

Analyses of gehlenite.

1. Damour analyst. From Monzoni, Tyrol.
2. Lemberg " " "
3. Rammelsberg " " "
4. Janovsky " Orowitza, Banat
5. Allen " Velardeña mining district, Mexico.*
6. Mayr " Monzoni. Fuggerite.†

	1	2	3	4	5	6
SiO ₂	31.60	30.01	29.78	30.73	26.33	34.04
TiO ₂	----	----	----	----	.03	----
Al ₂ O ₃	19.80	21.33	22.02	22.24	27.82	17.97
Fe ₂ O ₃	5.97	3.56	3.22	.41	1.43	3.49
FeO	----	----	1.63	3.01	.50	----
MnO	----	----	.19	----	.01	trace
MgO	2.20	3.77	3.88	6.10	2.44	4.99
CaO	38.11	36.74	37.90	37.93	39.55	37.65
Na ₂ O	.33	----	----	----	.21	2.04
K ₂ O	----	----	----	----	.10	trace
H ₂ O	----	----	----	----	1.85	----
Ign.	1.53	4.72	[1.38]	.37	----	----
Insolable	----	----	----	----	----	.12
	<hr/> 99.54	<hr/> 100.13	<hr/> 100.00	<hr/> 100.79	<hr/> 100.27	<hr/> 100.20

The iron oxides in the Mexican gehlenite are due to inclusions of magnetite, and should therefore be rejected. With this qualification the reduced analyses are as follows:

Reduced analyses of gehlenite.

	1	2	3	4	5	6
SiO ₂	33.03	31.36	30.52	30.10	27.06	33.65
Al ₂ O ₃	23.61	24.73	23.64	22.08	28.56	20.35
CaO	43.36	43.91	45.84	47.82	44.38	43.98
Na ₂ O	----	----	----	----	----	2.02
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

* See Wright, this Journal (4), xxvi, 575, 1908.

† See Weinschenk, Zeitschr. Kryst., xxvii, 577, 1896. The other analyses are from Dana's System of Mineralogy.

These analyses correspond to the following formulæ :

1. $3\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6 + 1\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6 + 2\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6(\text{AlO}_2\text{Ca})_6$.
2. $4\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6 + 1\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6 + 4\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6(\text{AlO}_2\text{Ca})_6$.
3. $1\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6 + 1\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6 + 2\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6(\text{AlO}_2\text{Ca})_6$.
4. $1\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6 + 9\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6 + 11\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6(\text{AlO}_2\text{Ca})_6$.
5. $1\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6 + 4\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6(\text{AlO}_2\text{Ca})_6$ approximately.
6. $17\text{Al}_4(\text{SiO}_4)_6\text{Ca}_6 + 16\text{Al}_4(\text{SiO}_4)_6\text{Ca}_4\text{Na}_4 + 36\text{Al}_2(\text{SiO}_4)_6\text{Ca}_6(\text{AlO}_2\text{Ca})_6$.

To these formulæ the following calculated analyses correspond :

Calculated analyses of gehlenite.

	1	2	3	4	5	6
SiO_2	33.00	31.37	30.32	29.72	27.03	33.51
Al_2O_3	23.37	24.70	23.62	22.06	27.57	20.40
CaO	43.63	43.93	46.06	48.22	45.40	44.13
Na_2O	----	----	----	----	----	1.96
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The agreement between the reduced and the calculated analyses is satisfactory, except in the case of the Mexican mineral, which seems to have a small excess of alumina.

It has now been shown that melilite and gehlenite can be represented as mixed crystals of a few compounds of precisely similar chemical type. Sarcosite and the melilite silicate are known compounds; the basic gehlenite silicate is hypothetical, and not yet found in the free state. So far the argument is weak, but it is strengthened by other evidence of the most valid kind. The garnets and prehnite have, as we have seen, the same type of structure, and several other lime-alumina silicates can be compared with these. The following formulæ may be taken as illustrative of this fact :

Epidote and its congeners, piedmontite, allanite and hancockite, are of course analogous to zoisite. As for meionite, the carbonate-meionite and sulphate-meionite of Borgström* contain the atomic groups $-\text{Ca}-\text{CO}_3-\text{Ca}-$ and $-\text{Ca}-\text{SO}_4-\text{Ca}-$ replacing the groups $-\text{Ca}-\text{O}-\text{Ca}-$ of the formula given here. Possibly a similar group $-\text{Ca}-\text{SiO}_3-\text{Ca}-$ may account for the excesses of silica shown in some analyses of meionite, which are not always ascribable to marialite.

We now see that melilite and gehlenite fall into place as members of a well-defined group of silicates of similar chemical constitution. Furthermore, they frequently occur in nature as products of contact metamorphism in limestones. That is, they have a common origin. Garnet, epidote, vesuvianite, and scapolites are well-known as associates in such rocks, and anorthite is sometimes found with them. Sarcolite and also vesuvianite are found in the ejected limestone blocks of Monte Somma; but prehnite, presumably a derivative of garnet, is exceptional. I do not find it recorded as an associate of the other species.

At Orawitza gehlenite is found in rolled pebbles containing grains of vesuvianite; and the Colorado melilite is associated with both garnet and vesuvianite, which are products of its alteration. The garnet is probably derived from its isomer, sarcolite; and the vesuvianite appears to be a basic derivative of the melilite silicate, $\text{Al}_2(\text{SiO}_4)_2\text{Ca}_2$.

Anorthite alters into scapolite; vesuvianite and gehlenite to garnet; and garnet to epidote and scapolite. All of these minerals alter into micas, and the magnesian varieties into chlorites also. These facts all strengthen the argument that the several silicates which are considered here are intimately related both structurally and chemically. Their relations, moreover, can be clearly expressed in terms of a general theory.

In a considerable number of publications† issued during the past thirty years, I have shown that many of the aluminous silicates can be regarded constitutionally as substitution derivatives of the normal orthosilicate, $\text{Al}_4(\text{SiO}_4)_3$. This conception may be modified in form, but not in principle, by treating the silicates in question as salts of these aluminosilicic acids,

the numeral prefixes indicating the number of aluminum atoms in each compound. The names are proposed, not as positive contributions to nomenclature, but as devices to avoid circum-

* Zeitschr. Kryst., liv, 238, 1914.

† For a summary of the whole subject see U. S. Geol. Survey. Bull. 588, 1916. The conclusions there given as to melilite and gehlenite are modified in this communication.

location in the following paragraphs. The acids themselves are not definitely known; but the first of the series may be represented by kryptotile, although that is not certain.

In the present discussion we have three fundamental compounds, corresponding with the three acids.

Anorthite is normal calcium trialate, and from it the basic silicate meionite is derived.

Garnet is normal calcium dialate, with sarcolite as an isomeric form. Prehnite is an acid, and zoisite a basic derivative of garnet.

The melilite silicate is normal calcium unalate, with vesuvi-anite and the gehlenite silicate as basic derivatives.

These three fundamental silicates seem to undergo alteration along parallel lines. Anorthite is altered to muscovite, a trialate, garnet into other dialates, such as biotite and the corresponding chlorites; and melilite *probably* follows the same rule. In short, nearly all of the orthosilicates which are characterized as aluminous can be represented as normal, acid, or basic salts of the three alumo-silicic acids. This rule has been sufficiently discussed in my previous publications, and needs no farther development here.

It is interesting to note that in abundance and stability the trialates outrank the other two series. Anorthite is the most abundant of the three calcium salts, and is the only one which can be recrystallized from fusion. Its corresponding mica, muscovite, is also the most abundant and the least alterable. Garnet, upon fusion, breaks down into a mixture of silicates, and anorthite is commonly one of them. The dialate mica, moreover, is easily alterable. As for the pure melilite silicate, its behavior as regards stability is not known, but it is the least abundant of the three calcium compounds. Nephelite, the sodium trialate, is very stable, easily synthesized, and alterable into muscovite. The normal sodium salts of the other alumosilicic acids are not known. Their high proportion of sodium would probably render them too easily alterable for permanence under geochemical conditions. The commonest unalates seem to be among the chloritic minerals, which are basic salts and easily decomposable.

In conclusion a word of caution is necessary. Formulæ such as have been developed in this paper are not to be taken as absolute representations of molecular structure. They are merely graphic expressions of known relations, and as such are legitimate and useful. They show the elementary atoms, moreover, as arranged upon a plane surface, but the true arrangement, the real molecular structure, should be tridimensional. Such an arrangement, which might correlate chemical relations with crystalline form, does not seem to be as yet possible. It may be developed in the future.