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## COMPOSITION OF THE MELILITE GROUP

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### INTRODUCTION

Many workers have made studies of the interesting series of minerals comprising the melilite group in the attempt to get satisfactory end members to explain their composition. Schaller<sup>1</sup> in 1916, summarized the previous work and contributed a careful study of all the existing analyses. Later Ferguson and Buddington<sup>2</sup> prepared a series of synthetic equivalents of the members of the melilite group in which they showed that  $\text{Ca}_2\text{MgSi}_2\text{O}_7$  and  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  were completely miscible. Then Buddington<sup>3</sup> using these two end members and adding the sarcolite molecules, as interpreted by Schaller, made an elaborate study of synthetic mixtures, with only partial verification of the validity of the sarcolite molecules, as given by Schaller. In 1924 Winchell,<sup>4</sup> for the first time considered the melilite group from the standpoint of volume isomorphism. He recognized the fact that all melilites are essentially of the formula  $\text{R}_5\text{O}_7$  with R equal to all the bases, including silicon. He also pointed out the improbability that such dissimilar molecules as Schaller and Buddington had suggested could enter into the melilite composition. In his study in addition to the åkermanite and gehlenite members, as suggested by Buddington he proposed the molecules  $\text{Na}_2\text{Si}_3\text{O}_7$  and  $\text{Ca}_3\text{Si}_2\text{O}_7$ , in agreement with his general  $\text{R}_5\text{O}_7$  formula.

The study of this group was undertaken by the author in the belief that the theory proposed by Winchell was essentially correct but that the simplification of the composition of the group did not adequately explain the analyses. A study by the author on all the available analyses has led to a somewhat different interpretation of the group, due mainly to the fact that more information on the composition of the silicates has recently been disclosed by

x-ray structure studies on some of the more complex minerals. W. Wahl<sup>5</sup> and B. Gossner<sup>6</sup> have in recent papers attempted to write structural formulae for this series. It is the opinion of the author that a more direct means of studying the structure of the silicates is available in the x-ray methods of Bragg<sup>7</sup> and his school, who are at this time making a careful study of such complex silicates as the amphiboles and pyroxenes, topaz, andalusite, sillimanite, etc., with results that seem to justify the treatment accorded the melilites in this paper.

All of the available analyses of melilites have been collected in Table I. With each analysis is given the calculated composition according to the theory proposed in this paper, and also the differences between the reduced analyses and the theoretical composition. There is also given, for comparison, the discrepancies obtained by the use of Schaller's theoretical end members.

In Table II the analyses are given in terms of the atomic composition with a constant number of oxygen atoms. The numbers refer to the analyses numbers in Table I. Both the found and theoretical atomic compositions are given in the same table to facilitate comparison. A detailed discussion of this table is given in the theoretical part of the paper.

Table III gives the molecular percentage composition of the analyses according to the end members adopted in this paper.

### I. THEORY

All the available analyses (Table I) of members of the melilite group have been reduced to their atomic ratios on the basis of 70 oxygen atoms, as has been suggested by Winchell's  $R_5O_7$  formula, and by the two most likely end members, åkermanite  $Ca_2MgSi_2O_7$  and gehlenite  $Ca_2Al_2SiO_7$ . That this is a fundamentally sound procedure, is verified, in the author's opinion, by the results obtained in Table II which is a list of the analyses in this manner. If the artificial åkermanite, gehlenite series is a series corresponding to the natural melilites, then there is a constant value for  $Mg+Al+Si$  of 30 atoms to 70 atoms of oxygen, and any intermediate members having Mg, Al, Si, will have as their total 30 atoms. This fact is amply borne out by Table II. The sum of  $Mg+Al+Si$  is in all cases very close to 30 when the oxygen atoms are taken as 70. The deviation from 30 is significant in but a very few analyses and is within the limits of error in most.

TABLE I. ANALYSES OF MELLILITES.

	CaO	Na <sub>2</sub> O (K <sub>2</sub> O)	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO etc.	Total	REFERENCES
1. Åkermanite, anal. (a) (b) reduced av. calc. diff. diff. by W. T. S.	39.62		13.38	1.09	46.70		0.12	100.79	F. Zambonini, <i>Miner. Vesuv.</i> , p. 255, 1910. From Vesuvius.
	39.30		13.30	.96	46.55			100.23	
	39.27		13.31	1.02	46.40				
	39.70		13.29	.77	46.24				
	+0.43		-0.02	-0.25	-0.16				
-0.42		-0.00	+0.08	+0.34					
2. Åkermanite, anal. (Humboldtite A.) reduced calc. diff. diff. by Buddington	35.58	2.95	7.60	11.37	39.86	0.50	1.78	100.26	H. S. Washington, <i>Analyst. Am. J. Sc.</i> , 5th Ser., Vol. 3, 1922, p. 77. Monte Somma.
	35.69	2.98	9.44	11.91	39.98		H <sub>2</sub> O = .59		
	36.44	2.76	8.68	11.38	40.74				
	+0.75	-0.22	-0.76	-0.53	-0.76				
	+1.13		-0.35	-0.69	+0.02				
3. Åkermanite, anal (Humboldtite B.) reduced calc. diff. diff. by Buddington	32.82	5.44	5.32	9.59	41.69	.76	3.75	99.71	H. S. Washington, <i>Anal.</i> Ref. same as 2. Monte Somma.
	33.02	5.48	9.14	10.42	41.94				
	33.55	4.63	7.84	10.70	43.28				
	+0.53	-0.85	-1.30	+ .28	+1.34				
	+0.63		+ .09	+ .36	-0.69				
4. Åkermanite, anal. (Humboldtite) reduced cal. diff. diff. by Buddington	34.71	3.64	6.56	12.04	40.36	.75	1.53	100.51	H. S. Washington, Ref. same as 2. Humboldtite. Monte Somma.
	34.85	3.65	8.14	12.84	40.52				
	35.25	3.57	7.64	12.73	40.81				
	+0.40	-0.08	-0.50	-0.11	+0.29				
	+0.84		+0.18	-0.10	-0.40				

TABLE I. ANALYSES OF MELILITES.

	CaO	Na <sub>2</sub> O (K <sub>2</sub> O)	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO etc.	Total	REFERENCES
5. Melilite, anal. reduced calc. diff. diff. by W. T. S.	35.41	3.24	4.15	10.30	42.07	.50	2.18	100.40	MnO, P <sub>2</sub> O <sub>5</sub> , CO <sub>2</sub> etc. =2.35.
	34.98	3.43	5.78	11.25	44.56				W. T. Schaller, Anal.
	33.29	4.51	6.62	11.25	44.33				Ref. Jour. Wash.
	-1.69 +0.26	+1.08	+0.84	0.0 -1.97	-0.23 +1.71				Acad. Sci., Vol. 4, p. 473, 1914, Colorado.
6. Melilite, anal. reduced calc. diff.	29.85	5.27	4.72	9.86	41.68	2.61	4.32	100.07	H. S. Washington, Anal. Am. J. Sci., 14, 1927, p. 192. Villa Seuni.
	30.13	.78	4.76	9.95	42.06	2.63	4.36		
	30.59	5.79	4.28	9.91	42.83	2.92	3.68		
	+0.46	-0.32	-0.48	-0.04	+0.77	+0.29	-0.68		
7. Melilite reduced calc. diff. diff. by W. T. S.	32.98	2.18	6.33	6.47	40.14	9.95	.53	100.34	H <sub>2</sub> O=.27. F. Zambonini, ana- lyst. Zeit. Kryst., Vol. 41, p. 266, 1906. Capo di Bove.
	34.45	1.49	6.92	13.40	41.93				
	34.63	3.48	6.78	13.38	41.73				
	+0.18 +0.90	+0.18	-0.14	-.02 -.60	-.20 -.30				
8. Melilite, anal. reduced calc. diff.	33.92	3.25	6.02	10.47	41.07	3.80		99.57	Millosevich, Anal. Am. Jour. Sci., p. 192, 1927. Albano.
	34.07	1.04	6.05	14.33	41.25				
	33.86	4.40	6.50	13.41	42.28				
	-0.21	3.95	+0.45	-.92	+1.03				

TABLE I. ANALYSES OF MELLILITES.

	CaO	Na <sub>2</sub> O (K <sub>2</sub> O)	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO etc.	Total	REFERENCES
9. Mellilite, anal.	34.78	3.40	5.87	10.93	41.09	3.40	H <sub>2</sub> O = .24	100.39	Bodlaender, Analyst. <i>Neues Jahrbuch</i> , p. 15, 1893. Capo di Bove.
reduced	35.24	.68	5.95	13.28	41.63				
calc.	34.03	3.90	6.49	13.76	41.77				
diff.	-1.21	+0.05	+0.54	+0.48	+0.14				
diff. by W. T. S.	-0.65			+0.61	+0.04				
10. Mellilite, anal.	32.47	1.95	6.44	6.42	39.27	10.17		98.18	Damour, Analyst. See Dana-System <i>Min.</i> p. 475. Capo di Bove.
reduced	34.54	1.46							
calc.	34.85	3.09	6.85	13.75	41.77				
diff.	+0.31	3.25	6.63	13.76	41.51				
diff. by W. T. S.	+0.99	+0.16	- .22	+0.01	- .26				
11. Mellilite, anal.	31.81	4.43	5.75	10.88	40.69	4.43		98.35	Damour, Analyst. Dana-Syst. <i>Min.</i> p. 475. Monte Somma.
reduced	32.92	1.36							
calc.	32.82	4.83	5.95	14.19	42.11				
diff.	- .10	4.89	6.05	14.18	42.06				
diff. by W. T. S.	+0.96	+0.06	+0.10	- .01	- .05				
12. Mellilite, anal.	32.18	2.21	6.41	7.56	39.20	11.34	H <sub>2</sub> O = .21	100.56	Same reference as No. 7, Capo di Bove.
reduced	33.60	1.45							
calc.	33.83	3.31	6.69	15.47	40.93				
diff.	+0.23	4.06	5.73	15.50	40.88				
diff. by W. T. S.	+1.93	+0.75	- .96	+0.03	- .05				
				-1.42	- .51				

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	CaO	Na <sub>2</sub> O (K <sub>2</sub> O)	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO etc.	Total	REFERENCES
13. Mellilite, anal.	32.05	2.12	6.71	8.61	38.34	10.02		99.36	Damour, analyst. Dana p. 475. Capo di Bove.
reduced		1.51							
calc.	33.65	3.28	7.04	15.77	40.26				
dif.	33.83	4.06	5.73	15.50	40.88				
dif. by W. T. S.	+0.18	+0.78	-1.31	-.27	+0.62				
	+1.93			-2.40	+0.47				
14. Gehlenite, anal.	33.19	4.18	3.12	12.89	37.84	1.13	5.66	100.33	C. E. Tilley, H <sub>2</sub> O = 1.66, TiO <sub>2</sub> = .66. <i>Geol.</i> <i>Mag.</i> , Vol. LXVI No. 782, p. 347-352, 1929. Co. Antrim, Ireland.
reduced	33.64	4.23	3.16	13.06	39.02	1.15	5.74		
calc.	33.95	3.71	9.35	13.88	39.11				
dif.	+0.31	-0.52	+0.45	-0.33	+0.09				
15. Gehlenite, anal. (Fuggarite)	37.65	2.04	4.89	17.97	34.04	3.49	insol = .12	100.20	E. Mayr, Analyst. <i>Zeit. Kryst.</i> , Vol. 27, p. 577, 1896. Mon- zoni.
reduced	38.10	2.06	4.94	20.45	34.45				
calc.	37.28	2.29	5.20	20.74	34.49				
dif.	-0.82	+0.23	+0.26	+0.29	+0.04				
dif. by W. T. S.	-0.62			+0.48	+0.14				
16. Gehlenite, anal.	37.90		3.88	22.02	29.78	3.22	1.63	100.00	Ign. by dif. = 1.38. Rammelsberg, Ana- lyst. Dana-Syst. <i>Min.</i> , p. 476. Mon- zoni.
reduced	39.21		5.07	24.91	30.81		MnO = .19		
calc.	40.17		4.29	24.77	30.77				
dif.	+0.96		-0.78	-0.14	-0.04				
dif. by W. T. S.	+0.95			-1.18	+0.23				

TABLE I. ANALYSES OF MELLITES.

	CaO	Na <sub>2</sub> O (K <sub>2</sub> O)	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO etc.	Total	REFERENCES
17. Gehlenite, anal. reduced calc. diff. diff. by W. T. S.	36.74		3.77	21.33	30.01	3.56	Ign. 4.72	100.13	Lemberg, Analyst. Dana-Syst. Min., p. 476. Monzoni.
	39.03		4.01	25.08	31.88				
	39.55		3.72	24.90	31.83				
	+0.52		-0.29	-0.18	-0.05				
	+0.72		-0.84	+0.12					
18. Gehlenite, anal. reduced calc. diff.	38.11	0.33	2.20	19.80	31.60	5.97	(H <sub>2</sub> O)1.53	99.54	Damour, Analyst. Dana-Syst. Min., p. 476. Monzoni.
	39.76	0.34	2.29	24.64	32.97				
	38.53	0.35	3.14	24.85	33.13				
	-1.23	+0.01	+0.85	+0.21	+0.16				
19. Gehlenite, anal. (velardernite) reduced calc. diff.	40.86		4.18	25.52	27.88	1.59	0.43	100.80	E. V. Shannon, Ana- lyst. Proc. U. S. National Museum, Vol. 60, Art. 22, p. 1-4. H <sub>2</sub> O=0.34. Tulare Co., Calif.
	40.67		4.17	25.40	27.75	1.58			
	40.91		4.26	26.46	28.37				
	+0.24		-.34	-0.52	+0.62				
20. Gehlenite, anal. (Velardernite) reduced calc. diff. diff. by W. T. S.	39.55	0.31	2.44	27.82	26.33	1.43	0.51	100.27	H <sub>2</sub> O=1.85 Allen, Analyst. Am. Jour. Sci., Vol. 5, p. 527, 1908. Velar- denia.
	40.19	0.31	2.99	29.72	26.79				
	40.53	0.23	2.94	29.46	26.84				
	+0.34	-0.08	-0.05	-0.26	+0.05				
	-.33		+0.22	+0.11					

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	CaO	Na <sub>2</sub> O (K <sub>2</sub> O)	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO etc.	Total	REFERENCES
21. Sarcolite, anal. reduced calc. diff. diff. by W. T. S.	33.70	4.43	0.36	21.63	39.34			99.46	A. Pauly, analyst. <i>Centr. Min.</i> , p. 266, 1906. Monte Somma.
	33.88	4.45	.36	21.75	39.56				
	31.96	4.12	1.53	22.31	40.08				
	-1.92	-.33	+1.17	+0.56	+0.52				
	-.74		+0.21	+0.53					
22. Sarcolite, anal.  reduced calc. diff. diff. by W. T. S.	32.36	3.30		21.54	40.51			98.91	Rammelsberg, Ana- lyst. <i>Pogg. Ann.</i> , Vol. 109, p. 570, 1850. Monte Somma.
		1.20							
	32.85	4.16		21.87	41.12				
	31.23	3.57		23.54	41.66				
	-1.62		+1.67	+0.54					
	+0.51		+0.69	+0.69	-1.20				
23. Sarcolite, anal.  reduced calc. diff. diff. by W. T. S.	32.43	2.93		24.50	42.11			101.97	Scacchi, Analyst. Dana-Syst. <i>Min.</i> , 5th ed., p. 318, 1842. Monte Somma.
	31.80	2.88		24.03	41.29				
	32.06	2.86		23.91	41.17				
	+0.26	-0.02		-0.12	-0.12				
	+2.78		-1.45	-1.45					

TABLE II.  
ATOMIC COMPOSITION OF THE MELLILITES

Anal. No.	Mineral name	Calculated						Found							
		Ca	Na	Mg	Al	Si	O	Ca	Na	Mg	Al	Si	O		
1	Åkermanite	19.1		8.9	.4	20.7	70	18.8		8.9	0.5	20.7	70	Ca+Al+Si	30.1
2	Åkermanite (Humboldtite)	17.6	2.4	5.8	6.0	18.2	70	17.3	2.4	5.9	6.1	18.1	70	Ca+Na	30.1
3	Åkermanite (Humboldtite)	16.0	4.0	5.2	5.6	19.2	70	16.2	4.6	5.1	5.4	19.1	70	Ca+Na	29.6
4	Åkermanite (Humboldtite)	16.9	3.1	5.1	6.7	18.2	70	16.9	3.1	5.1	6.7	18.2	70	Ca+Al+Si	30.0
5	Mellite	15.9	2.9	4.4	5.9	19.7	70	16.6	2.9	3.8	5.9	19.7	70	Ca+Al+Si	29.4
6	Mellite	14.9	5.1	4.3	6.3	19.4	70	14.8	5.2	4.9	6.2	19.2	70	Ca+Al+Si	30.3
7	Mellite	16.4	2.8	4.5	7.0	18.5	70	16.5	3.0	4.5	7.0	18.5	70	Ca+Al+Si	30.0
8	Mellite	16.1	3.4	4.3	7.0	18.7	70	16.5	3.4	4.1	6.9	18.6	70	Ca+Al+Si	29.6
9	Mellite	16.2	3.4	4.3	7.2	18.5	70	16.9	3.4	4.0	7.0	18.5	70	Ca+Al+Si	29.5
10	Mellite	16.6	2.8	4.4	7.2	18.4	70	16.4	2.7	4.5	7.2	18.4	70	Ca+Al+Si	30.1
11	Mellite	15.6	4.2	4.0	7.2	18.6	70	15.6	4.2	4.0	7.4	18.6	70	Ca+Al+Si	30.0
12	Mellite	16.1	3.5	3.8	8.1	18.1	70	15.9	2.8	4.4	8.1	18.1	70	Ca+Al+Si	30.6
13	Mellite	16.1	3.5	3.8	8.1	18.1	70	16.0	2.8	4.7	8.2	17.8	70	Ca+Al+Si	30.7
14	Gehlenite	16.7	3.3	4.6	7.5	17.9	70	16.7	3.7	4.4	7.5	17.9	70	Ca+Al+Si	29.8
15	Gehlenite (Fuggarite)	18.0	2.0	3.5	11.0	15.5	70	18.4	1.8	3.4	10.9	15.5	70	Ca+Al+Si	29.8
16	Gehlenite	19.5		2.9	13.2	13.9	70	19.0		3.4	13.2	13.9	70	Ca+Al+Si	30.5
17	Gehlenite	19.1		2.5	13.2	14.3	70	18.8		2.7	13.2	14.3	70	Ca+Al+Si	30.2
18	Gehlenite	18.5	0.3	2.1	13.1	14.8	70	19.0	0.3	1.5	13.1	14.8	70	Ca+Al+Si	29.4
19	Gehlenite	20.0		2.9	14.2	12.9	70	20.0		3.0	14.3	12.7	70	Ca+Al+Si	30.0
20	Gehlenite (Vielardenite)	19.8	0.2	2.0	15.8	12.2	70	19.8	0.2	1.9	15.7	12.2	70	Ca+Al+Si	29.8
21	Sarcolite	15.0	3.5	1.0	11.5	17.5	70	16.0	3.8	0.2	11.3	17.4	70	Ca+Al+Si	28.9
22	Sarcolite	14.5	3.0		12.0	18.0	70	15.4	3.5		11.3	18.0	70	Ca+Al+Si	29.3
23	Sarcolite	14.9	2.4		12.2	17.8	70	14.8	2.4		12.2	17.8	70	Ca+Al+Si	30.0

TABLE III  
MOLECULAR PERCENTAGE COMPOSITION OF THE MELILITE GROUP

No.	Anal. Mineral	A	B	C	D	Schaller's anal. no.
	A. $\text{Ca}_2\text{Al}_2\text{SiO}_7$ Gehlenite molecule.					
	B. $\text{Ca}_2\text{MgSi}_2\text{O}_7$ Åkermanite molecule.					
	C. $\text{Na}_2\text{Si}_3\text{O}_7$ Soda-melilite molecule.					
	D. $\text{CaSi}_3\text{O}_7$ Sub-melilite molecule.					
1.	Åkermanite	2.0	90.7	0.0	7.3	4 and 5
2.	Åkermanite (Humboldtite)	30.6	58.6	10.8	0.0	
3.	Åkermanite (Humboldtite)	28.7	53.1	18.2	0.0	
4.	Åkermanite (Humboldtite)	34.3	51.7	14.0	0.0	
5.	Melilite	30.9	45.8	13.4	9.9	16
6.	Melilite	32.8	45.1	22.1	0.0	
7.	Melilite	36.1	46.1	13.7	4.1	13
8.	Melilite	36.2	44.2	15.5	4.1	
9.	Melilite	37.1	44.1	15.5	3.3	11
10.	Melilite	37.2	45.2	12.8	4.8	12
11.	Melilite	38.7	41.6	18.0	1.7	10
12.	Melilite	41.8	38.9	15.9	3.4	15
13.	Melilite	41.8	38.9	15.9	3.4	14
14.	Gehlenite	50.9	37.2	11.9	0.0	
15.	Gehlenite (Fuggarite)	55.7	35.3	9.0	0.0	17
16.	Gehlenite	66.8	29.2	0.0	4.0	7
17.	Gehlenite	67.3	25.4	0.0	7.3	8
18.	Gehlenite	67.3	21.5	1.4	9.8	9
19.	Gehlenite	71.1	28.9	0.0	0.0	
20.	Gehlenite (Velardeite)	79.2	19.9	0.9	0.0	6
21.	Sarcolite	62.8	10.4	18.5	8.3	3
22.	Sarcolite	64.5	0.0	14.3	21.2	2
23.	Sarcolite	65.6	0.0	11.4	23.0	1

However the expected total of  $\text{Ca} + \text{Na} = 20$  is not in evidence for most analyses although the assumed end members have each 20 atoms of calcium. There is the significant fact evident, however, that the total of  $\text{Ca} + \text{Na}$  does not materially exceed 20 atoms in any analysis. This deficiency it seems cannot be explained by error

in analyses and must be accounted for in an adequate explanation of the series. A general formula of the melilites may from these deductions be written for the whole group, as follows:



From the analyses as given, the probable limits of  $x$ ,  $y$ ,  $z$ , can be stated as follows:

(a)  $x$  may be 0 or some small number probably not greater than 3 (in any known melilite).

(b)  $y$  may have as its maximum value 10 and its minimum value 0. This corresponds in the first case to a melilite composed entirely of the end member åkermanite, and where  $Mg=0$  to a melilite with no åkermanite present; it is evident that a value greater than 10 Mg would necessitate more than 20 atoms in the  $Ca+Na$  member, and this is not found in the series.

(c)  $z$  varies from 0 to 15.7 in the series. This variation indicates that the gehlenite molecule ( $Ca_2Al_2SiO_7$ ) is absent in some melilites and that velardeñite (#20) is an almost pure gehlenite, the pure molecule having 20 atoms. The value 20 may be taken as the maximum Al content of the melilites since more aluminum would necessitate more than 20  $Ca+Na$  atoms.

(d) The silicon as given in the general formula is  $30-(y+z)$  atoms. Inspection of the table shows that the minimum number of silicon atoms is ten. The maximum number of atoms noted in the table is 20.7. If however  $y$  and  $z$  could both be zero then the maximum number would have to be 30. In Winchell's hypothetical soda melilite this value is used and the formula is  $Na_{20}Si_{30}O_{70}$ . This molecule will be discussed in another section of this paper. There is another possibility of using the theoretically maximum amount of silicon in a formula such as  $Ca_{10}Si_{30}O_{70}$ . This formula has only 10 Ca atoms rather than 20 (or a number near 20) and therefore cannot be considered as a true melilite molecule. However, it can be used to explain the fact that the total  $Ca+Na$  is in most cases less than 20, as will be shown later.

An examination of the group formula indicates that sodium replaces calcium and that Mg, Al, Si are replaceable to the extent noted above. In the tables of ionic radii of Goldschmidt,<sup>8</sup> which are now generally accepted, the calcium and sodium ions are of the

same order of magnitude, the Mg, Al, Si are considerably smaller and of comparative similar radii among themselves. Oxygen is the largest of the atoms present in the composition of the series. There is then an adequate reason for the relationship established. There are seemingly two kinds of basic elements, the Ca and Na together, and the Mg, Al, Si elements in another set. Thus Winchell's  $R_3O_7$  is really  $X_2Y_3O_7$  which is the less exact form of the author's general formula as given above.

The question as to the replaceability of calcium and sodium atom for atom cannot be definitely answered by the data in this paper because there is no real constancy in the number of atoms of both in the melilites. However, in other recent treatments of the relationship of these two atoms in isomorphous compounds there is little doubt left but that these two elements can substitute for each other, atom for atom, provided the valences are balanced after substitution by some further change such as for example an attendant substitution of magnesium for aluminum. The amphiboles, pyroxenes, feldspars,<sup>9</sup> etc. are evidences of this type of replacement.

As to the replacement of Mg, Al, and Si there seems to be excellent evidence in the actual analyses of this series that this has taken place. It is gratifying to the author that while this paper was in preparation, that further evidences of this type of replacement were pointed out in tourmaline<sup>10</sup> and the amphiboles and pyroxenes<sup>11</sup> by F. Machatschki in two very recent papers. The problem of composition and isomorphism is treated in a manner similar to that given in this paper.

That the atomic volume relationships are not the only determining factors in isomorphism is obvious. What the other factors may be are not as yet known, but it is safe to say that volume isomorphism is one of the most important considerations in the study of a series such as the melilites, or, as Machatschki has pointed out, in the tourmalines and amphiboles and probably all other silicates.

The end members adopted by the author have been chosen to agree with the general formula as follows:

- |                    |                       |
|--------------------|-----------------------|
| A. $Ca_2Al_2SiO_7$ | Gehlenite             |
| B. $Ca_2MgSi_2O_7$ | Åkermanite            |
| C. $Na_2Si_3O_7$   | Soda melilite         |
| D. $CaSi_3O_7$     | Sub-melilite molecule |

The molecules A and B can enter into combination in all proportions as indicated by the analyses of natural melilites and by the work of Ferguson and Buddington on synthetic preparations.  $\text{Na}_2\text{Si}_3\text{O}_7$  enters only to a limited extent as indicated in the analyses. This hypothetical molecule does not occur in the natural melilites to a greater extent than about 23 per cent.

$\text{CaSi}_3\text{O}_7$ , the sub-melilite molecule can be used to show the extent to which the formula falls short of having  $(\text{Ca} + \text{Na}) = 20$ . This molecule is usually of very minor importance in the composition exceeding 10 per cent in only two analyses. This type of molecule is interpreted by the author as being an indication that part of the melilite structure is open, because all the negative charges of oxygen have already been satisfied by  $\text{Mg} + \text{Al} + \text{Si}$ , which is constant and more firmly bound in the structure, and ionic equilibrium, so to speak, has been reached without filling up the holes which normally would be occupied by Ca or Na. That this can occur to only a limited extent without the breakdown of the structure is evident, so that such a molecule could only be expected to be present in limited amounts.  $\text{CaSi}_3\text{O}_7$  need not be of the same structural type as the other members of the group, and still enter in the solid solution to the limited extent noted in the analyses of the natural occurrences. It is doubtful whether  $\text{CaSi}_3\text{O}_7$ , prepared artificially, would be a true melilite.

## II. Other THEORIES

The principal theories advanced to explain the composition of the melilite group have been those of Schaller, Buddington and Winchell.

Schaller proposed as end members the following:

Sarcolite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ or $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Soda-sarcolite	$3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ $\text{Na}_6\text{Al}_2\text{Si}_3\text{O}_{12}$
Åkermanite	$4\text{MgO} \cdot 8\text{CaO} \cdot 9\text{SiO}_2$ $\text{Mg}_8\text{Mg}_4\text{Si}_9\text{O}_{30}$
Velardeñite	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ $\text{Ca}_2\text{Al}_2\text{SiO}_7$

Winchell has pointed out that the compounds proposed by Schaller are much dissimilar in character and not likely to be end members of the same group. In general Schaller's end members give calculated compositions about as well as those of the author. Soda sarcolite, in small amounts combined with a large amount of sar-

colite gives agreement with the end members  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ,  $\text{Na}_2\text{Si}_3\text{O}_7$  and  $\text{CaSi}_3\text{O}_7$  proposed by the author. The other two end members are essentially the same as the author's molecules. An objection which may be raised against Schaller's molecules is that sarcolite ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) and velardeñite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) are composed of the same elements in slightly differing amounts. That the melilites can have two end members of such similarity seems unlikely.

The chief difference between the end members proposed by Winchell and those of the author is that Winchell has as one of his compounds  $\text{Ca}_3\text{Si}_2\text{O}_7$ . An examination of this molecule in comparison with the type formula of the author suggests that it is not likely to yield satisfactory results because the 3:2:7 ratio is not found to be present in the natural melilites. When this molecule is used there is an apparent excess of silica in the analyses which may be as high as 9 per cent. The molecule used by the author can be derived from  $\text{Ca}_3\text{Si}_2\text{O}_7$  and silica in the following manner:



$\text{CaSi}_3\text{O}_7$  can therefore be used and no excess of  $\text{SiO}_2$  will be observed in the analysis. The excess silica is explained by Winchell as being interatomic because the silicon and oxygen atoms are small enough to fit into the atoms without disturbing them. At the time that his paper was written there had not been much experimental work to verify the size of the oxygen atoms and it was considered one of the smallest. Present measurements, however, are in general agreement that oxygen is one of the largest of atoms entering into the composition of the silicates, so that this theory seems highly improbable on the basis of later knowledge.

Buddington has attempted to show that the end members proposed by Schaller form solid solutions, by preparing synthetic mixtures corresponding to the end members and studying the properties of the resultant compounds prepared under the proper conditions. As Winchell has pointed out, his evidence is rather inconclusive. There are many cases where nonhomogeneous crystallizations result. In fact, when the sarcolite molecule, proposed by Schaller, was used with artificial åkermanite and gehlenite, the whole series failed to show solid solution. Only when a

charge approximating the actual sarcolite composition was used did homogeneous crystallizations result. This seems, to the author, to indicate that the sarcolite and soda sarcolite molecules are not an adequate explanation of the composition of natural sarcolite. In this paper no attempt has been made to apply the molecules proposed to an analysis of Buddington's synthetic mixtures since some of the components used are, in the author's opinion, not those which occur in the natural melilites and, therefore, out of the scope of this paper, which is concerned only with the natural occurrences.

#### DISCUSSION OF ANALYSES

All the available satisfactory analyses of members of the melilite group are given in Table I. The calculated values given in the table are derived from the theoretical composition as computed from the author's molecules. In reducing the analyses  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are grouped together, as are  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , and also  $\text{FeO}$ ,  $\text{MgO}$  and  $\text{MnO}$ . Only where the  $\text{FeO}$  or  $\text{Fe}_2\text{O}_3$  are important constituents are they calculated separately as iron-åkermanite or iron-gehlenite. Differences between calculated and reduced analyses are given in order to quickly show the divergence of the theoretical composition from the actual analysis. Differences obtained by use of Schaller's molecules are also given for comparison. The numbers of the analyses in Table I are used in Tables II and III for the corresponding atomic and molecular compositions, respectively.

Since there are already adequate names in established use for the various members of the group no new ones will be here proposed. The various members of the group are here defined in terms of their molecular percentages as follows:

(a) Åkermanite—those members of the group giving over 50 per cent of the åkermanite molecule ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) and less than 25 per cent of the soda-melilite and sub-melilite molecules combined ( $\text{Na}_2\text{Si}_3\text{O}_7 + \text{CaSi}_3\text{O}_7$ ).

(b) Gehlenite—those members of the group having over 50 per cent of the gehlenite molecule ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) and less than 25 per cent of the soda-melilite and sub-melilite molecules combined ( $\text{Na}_2\text{Si}_3\text{O}_7 + \text{CaSi}_3\text{O}_7$ ).

(c) Melilite—those members of the group which have neither the åkermanite molecule nor the gehlenite molecule present to the extent of 50 per cent, and have less than 25 per cent of the other two molecules combined.

(d) Sarcolite—those members of the group having over 25 per cent of the soda-melilite and sub-melilite molecules combined.

The above classification is in conformity with the long established nomenclature in the group. The more recent names, velardënite and humboldtilite, are not used. Fuggarite is here considered as a gehlenite. Since this name has been applied to but one member of the group which is within the limits defined for gehlenite there seems to be no reason for retaining the name in the classification.

#### ÅKERMANITE

There are two analyses available of almost pure åkermanite (Anal. 1,—Table I) which are obviously of the same material. The calculated composition agrees very well with the observed percentages. Analyses 2, 3, 4, of Table I (Humboldtilite of Buddington) are also good analyses and agree with the calculated compositions. There is a considerably greater percentage of the gehlenite molecule in these three åkermanites than in the other member noted above.

#### MELILITE

The analyses of these intermediate members of the group are in general agreement with the theory. The substitution of  $\text{Al}_2\text{O}_3$  for  $\text{Fe}_2\text{O}_3$  is not accompanied by any appreciable discrepancy in the calculated composition (see analyses 12, 13). There are some analyses for which the theory does not hold very accurately but in view of the fact that most of the analyses do adequately fit the end members, it seems likely that obvious discrepancies may be explained by impurities in analyzed material, and other sources of error. Table III, giving the molecular composition, shows that these members have about 16 per cent of the soda melilite molecule and about 4 per cent of the sub-melilite molecule.

#### GEHLENITE

There are two modern analyses of this species both of which agree well with the theoretical composition (Anal. 19 and 20). The

others, while older analyses, are in rather good agreement also, with the exception of analysis 18, which has a deficiency of 1.23 per cent of CaO. The gehlenites in general have a low percentage of the minor molecules  $\text{Na}_2\text{Si}_3\text{O}_7$  and  $\text{CaSi}_3\text{O}_7$ .

SARCOLITE

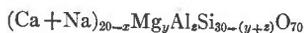
The sarcolites differ from the other members of the group in having a rather large percentage of the soda melilite and sub-melilite molecules. The calculated compositions do not agree especially well with the analyses. The two older analyses are not especially good ones (Anal. 22 and 23, Table I). The more recent one by Pauly, however, does not give good agreement with the theory. The calculated compositions by Schaller are also not in very close agreement with the observed percentages.

The fact that this species has such a large percentage of the sub-melilite molecule as compared to the other members of the group leads to a speculation as to whether it is really a true melilite. An x-ray spectrographic study of sarcolite with this in view will be undertaken later as well as a new analysis. Gossner<sup>12</sup> in a recent paper has shown that sarcolite is not closely related to the melilites but instead is related to the scapolites.

SUMMARY AND CONCLUSIONS

The theory as to the composition of the melilites may be here summed up as follows:

General formula:



where  $x = 0$  to 3

$y = 0$  to 10

$z = 0$  to 20

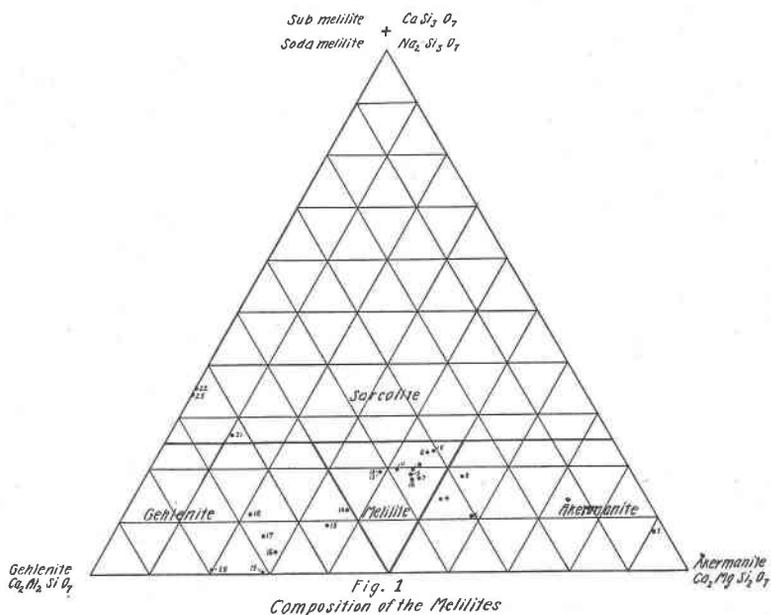
This formula gives rise to the melilite molecules as follows:

Åkermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$
Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$
Soda melilite	$\text{Na}_2\text{Si}_3\text{O}_7$
Sub-melilite	$\text{CaSi}_3\text{O}_7$

The first two of these may be present in any amount. The third (soda-melilite) in the natural occurrences does not exceed

25 per cent, the fourth (sub-melilite molecule) is the least important and with but two exceptions does not exceed 10 per cent.

There are no facilities in this laboratory to conduct experiments on the artificial compounds of the compositions of these end members, it is suggested that this would possibly prove an interesting problem. The study of the space group of melilite and a comparison of the x-ray spectrographs of gehlenite, melilite and sarcolite will be published at a later date.



The optical properties of the various members of the group have not been recorded in this paper because in the artificial  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ — $\text{Ca}_2\text{MgSi}_2\text{O}_7$  series a careful optical study was made.

Since these are the two dominant molecules present the principal optical differences arise from the percentages of these present. An additional reason for omitting an optical study was lack of type material in order to study the effect of the soda melilite and sub-melilite molecules on the optical properties.

A diagram (Fig. 1) shows the composition of the various members of the melilite group. The soda melilite molecule and sub-

melilite molecule have been combined in order to better represent the composition on a plane diagram.

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