

The crystal structure of synthetic soda melilite, $\text{CaNaAlSi}_2\text{O}_7$

By S. JOHN LOUISNATHAN

Department of the Geophysical Sciences, The University of Chicago, Chicago

(Received 25 August 1969)

Auszug

Die Kristallstruktur von synthetischem Natriummelilith wurde aus Diffraktometerdaten bis $R = 5,1\%$ verfeinert. Die Verbindung hat die gleiche Struktur wie die übrigen, natürlich vorkommenden Melilithe. Die Aluminium- und Siliciumatome sind in der Struktur geordnet, die Calcium- und Natriumatome statistisch verteilt.

Abstract

The crystal structure of synthetic soda melilite was refined to $R = 5.1\%$ from three-dimensional diffractometer data. Soda melilite is isostructural with the other naturally-occurring melilites. Aluminum and Si atoms are ordered in the structure while Ca and Na atoms are disordered.

1. Introduction

The literature on the melilite group of minerals with a discussion of the various proposed end-members was reviewed by CHRISTIE (1961*a* and *b*; 1962). After prolonged discussion it is now generally accepted that $\text{CaNaAlSi}_2\text{O}_7$, called soda melilite, can be established as an end member, partly represented in some natural melilites. YODER (1964) showed that pure soda melilite is stable only at pressures in excess of 4 kbar. Its optical properties were determined by SCHAIRER, YODER and TILLEY (1965).

The crystal-structure determination of soda melilite was undertaken as a part of a systematic structural study of the melilite group. The general composition of a melilite can be written as $(\text{Ca,Na})_2(\text{Mg,Al})(\text{Al,Si})_2\text{O}_7$. Order-disorder of Mg, Al and Si among the tetrahedral sites and diadochy of Ca, Na etc. in the 8-coordination sites are of principal interest in this group of minerals as explained by SMITH (1953).

2. Experiments

The specimen was prepared by YODER from glass at 1150°C, 10 kbar, 70 hours. The product is more than 95% soda melilite with some glass and rare wollastonite needles. Traces of platinum from the sealing tube were also present.

A diffractometer powder pattern using Ni-filtered Cu radiation, and a photographic powder pattern using Mn-filtered Fe radiation were made using spectroscopically pure silicon as internal standard. Of the 56 lines, four weak lines agreed with four of the stronger lines of wollastonite, and two weak lines with two of the stronger lines of platinum. The remaining 50 lines (Table 1) were readily indexed on a tetragonal cell with cell dimensions determined by the least-squares technique: $a = 7.6344 \pm 0.0006 \text{ \AA}$ and $c = 5.0513 \pm 0.0006 \text{ \AA}$.

Table 1. Powder pattern of soda melilite, $\text{CaNaAlSi}_2\text{O}_7$.

hkl	I_o	d_{obs}	d_{calc}	hkl	I_o	d_{obs}	d_{calc}	hkl	I_o	d_{obs}	d_{calc}	hkl	I_o	d_{obs}	d_{calc}
001	89	5.058 \AA	5.051 \AA	311	4	2.178 \AA	2.178 \AA	303	6	1.4041 \AA	1.4038 \AA	602	w	1.1361 \AA	1.1364 \AA
101	11	4.218	4.213	212	24	2.027	2.030	313	11	1.3814	1.3810	503	m	1.1510	1.1511
111	4	3.691	3.688	400	19	1.908	1.909	521	8	1.3646	1.3650	514	s	1.1190	1.1189
210	7	3.415	3.414	222	6	1.844	1.844	512	22	1.2875	1.2879	324	m	1.0850	1.0845
201	33	3.045	3.045	312	37	1.744	1.745	004	17	1.2628	1.2627	354	vw	1.0340	1.0337
211	100	2.827	2.829	420	3	1.707	1.707	522	*vw	1.2363	1.2363	721	w	1.0266	1.0268
220	4	2.699	2.699	003	11	1.684	1.684	333	vw	1.2291	1.2286	603	vw	1.0148	1.0151
002	39	2.526	2.525	103	8	1.644	1.644	611	w	1.2187	1.2181	730	m	1.0028	1.0025
310	17	2.415	2.414	421	6	1.618	1.617	423	w	1.1978	1.1987	115	w	0.9931	0.9930
102	62	2.398	2.398	113	17	1.606	1.607	214	m	1.1837	1.1843	623	w	0.9810	0.9809
221	17	2.383	2.381	203	4	1.539	1.540	621	w	1.1749	1.1741	504	w	0.9731	0.9731
112	26	2.287	2.288	213	24	1.5097	1.5100	341	m	1.1608	1.1604				
301	22	2.271	2.273	223	8	1.4281	1.4285	224	vw	1.1442	1.1438				

* All lines above this were obtained from Cu-Ni diffractometer pattern, this line and all the following lines were obtained from Fe-Mn photographic powder pattern

Precession and Weissenberg photographs of a [001] cleavage fragment of $0.06 \times 0.1 \times 0.2 \text{ mm}$ dimensions were made yielding space-group extinctions compatible with $P\bar{4}2_1m$. Four hundred and ninety one independent intensities, representing the layers $h0l$ to $h6l$, were measured on a manual scintillation-counter diffractometer of Weissenberg geometry, using Zr-filtered $\text{MoK}\alpha$ radiation. The observed intensities were corrected for Lorentz, polarization, transmission, and absorption ($\mu = 16.4 \text{ cm}^{-1}$) effects.

3. Structure determination and refinement

It was assumed that soda melilite is isostructural with the other melilites, with Al and Si ordered in the tetrahedral sites $\text{Al}_{1.0}$ in $\text{T}_{1,2}$ and $\text{Si}_{1.0}$ in T_{3-6} following the notation of LOUISNATHAN (1970)* and Ca and Na disordered ($\text{Ca}_{0.5}\text{Na}_{0.5}$) in the 8-coordination sites. Using the appropriate half-ionized scattering functions, calculation of structure amplitudes with the atomic coordinates obtained for

* $\text{T}_{1,2}$ tetrahedra are at $\bar{4}$, and T_{3-6} tetrahedra are at m point symmetry.

gehlenite (LOUISNATHAN, 1970) gave an initial agreement factor of $R = 0.24$.

The structural parameters were refined by the least-squares technique using the SORFLS program [a local modified version of the ORFLS program of BUSING, MARTIN and LEVY (1962)]. Six cycles of refinement varying the scale factor, positional and isotropic thermal-vibrational parameters of the atoms brought R to 0.14. At this stage a calculation of interatomic distances showed that the T_1 —O(3) distance was 1.75 ± 0.02 Å and the mean T_3 —O distance 1.61 ± 0.01 Å, indicating clear separation of Al into T_1 from Si into T_2 . Further refinements used a weighting scheme based on the ratio of peak to background intensity, with

$$w = \left[x + \left(\frac{y}{I-B} \right) \left(\frac{I+B}{I-B} \right) \right]^{-1},$$

where I is the number of counts obtained for the peak without the background, B the number of background counts, with x and y taken as unity. Such a weighting scheme assigned weights between 1.0–2.0 for reflections with F_{obs} in the range of 60–20 (scale factor being close to unity) and weights between 2 and 10 reflections with F_{obs} in the range of 20 to nearly zero. Such a weighting scheme appeared to be justifiable, since the quantity $g = \{\Sigma[w(F_{\text{obs}} - F_{\text{calc}})^2]/(N_o - N_v)\}^{\frac{1}{2}}$, (where N_o is the number of observations, N_v the number of parameters varied) was always close to unity (HAMILTON, 1964). Different scale factors for each k layer, anisotropic temperature factors for all atoms, and anomalous-scattering corrections with $f' = f'' = 0.1$ for the tetrahedral sites and $f' = 0.1$ and $f'' = 0.25$ for the 8-coordination sites were introduced. Refinement was continued varying also the site-occupancies of the cation sites. After six cycles of refinement R was 0.10 and weighted R (R') 0.07. Further cycles involved two parallel sets of refinements one on hkl set and the other on $\bar{h}\bar{k}\bar{l}$, in order to minimize the polar dispersion errors in interatomic distances. After four cycles of adjustment the refinements converged giving the following agreement factors:

set	R	R'	g
$\bar{h}\bar{k}\bar{l}$	0.081	0.052	0.9
hkl	0.080	0.051	0.9

The differences in the positional coordinates of atoms between the two polarities were within the estimated errors in these quantities.

Table 2. *The observed and calculated structure amplitudes in the synthetic soda melilite*
The table contains 493 reflections. The overall scale factor is 1.16×10^{-2}

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	
0 0 2	4098	3974	10 0 7	1353	1233	2 2 4	3461	3593	4 3 8	1216	1224	8 4 6	1567	1343	
3	4030	4025	1 1 1	3451	3369	5	3175	3461	9	443	136	7	1493	1308	
4	6568	6656	2	2690	2743	6	1607	1425	5 3 0	2004	2124	8	861	698	
5	1357	717	3	3350	3424	7	1974	1964	1	980	1031	9 4 0	8	1287	1343
6	3113	3101	4	353	333	8	903	803	2	1832	2110	1	1480	1523	
7	1676	1566	5	2762	2828	9	1452	1410	3	1069	1206	2	774	632	
8	400	211	6	1514	1454	3 2 0	346	101	4	1647	1604	3	514	239	
9	2096	1867	7	2526	2626	1	2199	2063	5	961	1093	4	751	459	
10	583	176	8	647	541	2	2558	2502	6	2853	1776	5	1030	796	
1 0 2	4379	4278	9	1220	1241	3	2437	2639	7	1395	1159	6	691	435	
3	2079	1885	10	782	942	4	788	569	8	981	838	7	540	105	
4	1124	1318	2 1 0	2734	2820	5	788	703	9	699	441	10 4 0	2897	3109	
5	467	160	1	7430	7456	6	1494	1424	6 3 0	1745	1631	1	1404	1454	
6	2344	2441	2	3571	3411	7	734	445	1	1007	1178	2	1801	1992	
7	1216	1028	3	4605	4361	8	708	627	2	1540	1757	3	1056	794	
8	1175	1175	4	657	735	9	987	494	3	870	780	4	1541	1520	
9	398	391	5	1825	1921	4 2 0	5552	5396	4	1240	1357	5	534	226	
10	531	344	6	2077	1969	1	1945	1939	5	443	96	6	813	668	
2 0 0	594	506	7	760	441	2	2382	2418	6	2013	1919	7	776	217	
1	4443	4439	8	1434	1543	3	2046	2053	7	694	453	8	154	563	
3	2112	2192	9	768	454	4	2172	2183	8	986	1017	9	729	721	
4	262	446	10	1217	1086	5	1523	1604	9	884	697	2	2027	2059	
5	2520	2454	3 1 0	5167	5159	6	1708	1499	7 3 0	5483	6374	3	3976	3910	
6	825	686	1	1734	1621	7	1355	1273	1	1995	2031	4	1704	1889	
7	1585	1542	2	6758	6776	8	665	522	2	3846	3812	5	213	2269	
8	513	225	3	3389	3250	9	803	630	3	1084	940	6	793	688	
9	1193	950	4	1169	1057	5 2 0	3155	3073	4	3374	3303	7	1757	1836	
10	203	357	5	1288	1176	1	6327	6449	5	565	173	8	946	920	
3 0 1	8794	8849	6	1268	1135	2	2097	2138	6	848	973	6 5 0	1725	1916	
2	825	935	7	1172	1063	3	3353	3194	7	1002	757	1	2167	2345	
3	3462	3269	8	583	278	4	671	674	8	719	150	2	833	702	
4	5055	4852	4 1 0	3182	3299	5	2119	2021	8 3 0	608	419	3	1748	1732	
5	1351	1282	1	3381	3263	6	1632	1461	1	530	861	4	726	634	
6	2790	2615	2	1130	1156	7	816	482	2	302	865	5	634	517	
7	620	21	3	4288	4410	8	1853	1705	3	1520	1489	6	971	691	
8	1118	1464	4	2319	2384	9	939	594	4	1119	1012	7	439	317	
9	201	139	5	1232	1032	6 2 0	1623	1621	5	1028	935	8	794	593	
4 0 0	7232	7093	6	2477	2350	1	3026	2937	6	1353	1058	7 5 0	166	308	
1	1288	1259	7	1005	807	2	1717	1567	7	883	618	1	1907	1704	
2	1565	1558	8	753	746	3	5255	2451	8 3 0	1263	1378	2	1466	1615	
3	1569	1946	9	655	270	4	1258	1193	1	1749	1820	3	2650	2422	
4	2166	2010	5 1 0	1259	1110	5	2809	2699	2	706	529	4	507	738	
5	2160	2071	1	2400	2452	6	1571	1457	3	2217	2360	5	807	569	
6	411	560	2	1847	1967	7	1741	1694	4	1004	789	6	942	628	
7	2278	2204	3	3746	4052	8	646	334	5	1644	1460	7	861	636	
8	942	991	4	1686	1513	9	885	670	6	855	636	8	746	446	
9	1798	1832	5	2306	2289	7 2 0	419	341	7	1401	1159	8 5 0	175	171	
5 0 1	1611	1562	6	1078	774	1	2076	1976	10 3 0	1158	942	1	3056	2873	
2	1423	1398	7	2116	1973	2	2100	2117	1	855	757	2	157	545	
3	398	429	8	548	303	3	785	621	2	1351	1570	3	2387	2361	
4	800	538	9	1068	954	4	1663	1535	3	1006	804	4	1213	946	
5	611	396	6 1 0	2440	2200	5	1761	1537	4	995	819	5	1101	942	
6	1147	790	1	3039	3110	6	722	446	5	558	181	6	1367	1171	
7	911	959	2	2268	2333	7	579	543	6	1607	1541	7	880	398	
8	470	25	3	1686	1523	8	968	774	7	990	769	8	1273	1040	
9	507	103	4	785	366	8 2 0	1133	1179	4 4 0	7789	7699	9 5 0	1	549	419
6 0 0	7183	7421	5	787	499	1	996	1007	1	3793	3757	2	1258	1147	
1	750	624	6	1794	1660	2	1253	1120	2	3209	3435	3	1892	1803	
2	4938	4791	7	1001	843	3	2033	1961	3	1285	1128	4	1509	1471	
3	664	88	8	1011	991	4	739	810	4	2964	3142	5	1492	1403	
4	3751	3791	9	984	773	5	1842	1666	5	794	776	6	1151	1078	
5	650	518	7 1 0	2385	2712	6	762	1100	6	1301	1107	7	1750	164	
6	1771	1708	1	129	317	7	1624	1653	7	1259	1254	8	1501	1343	
7	943	625	2	560	463	8	780	448	8	575	233	9	632	385	
8	1066	806	3	1456	1416	9 2 0	2081	2410	9	360	706	1	906	719	
9	1005	773	4	646	373	1	2517	2641	5 4 0	1	790	662	2	1003	780
7 0 1	733	740	5	1220	1085	2	834	580	1	3152	3240	3	2906	3119	
2	1817	1675	6	687	547	3	1436	1281	2	1585	1674	4	1488	227	
3	2342	2303	7	1283	1207	4	836	508	3	2433	2510	5	4188	4026	
4	2589	2860	8	996	901	5	856	660	4	1019	834	6	1603	1660	
5	1118	957	8 1 0	1040	817	6	1045	595	5	1176	1018	7	2738	2777	
6	185	1984*	1	2606	2602	7	611	394	6	1418	1357	8	1505	1433	
7	742	528	2	943	803	8	1147	893	7	1099	923	9 6 0	133	283	
8	1345	1254	3	3073	3095	9	1991	1772	8	977	734	1	561	399	
9	2490	2482	4	935	732	10 2 0	1023	1025	9	95	94	2	1171	1136	
1	2751	2848	5	1767	1631	2	1965	1758	6 4 0	1860	1808	3	1075	960	
2	2229	2020	6	1126	680	3	788	571	1	1445	1533	4	1460	1365	
3	2626	2503	7	866	561	4	1239	1127	2	1122	1136	5	616	393	
4	1106	1150	8	1206	1467	5	828	313	3	1680	1466	6 6 0	2132	2251	
5	751	625	9 1 0	1	745	581	6	1430	1212	4	1168	1066	1	2169	2072
6	706	78*	1	2376	2205	7	810	601	5	1841	1912	2	1080	1014	
7	858	514	2	2044	2005	8	799	7910	6	735	566	3	1612	1622	
8	573	20*	3	2258	2194	1	2907	2905	7	1640	1448	4	1289	1051	
9	1175	1016	4	1359	1447	2	2526	2777	8	545	323	5	1512	1361	
2	632	243	5	888	795	3	3224	3430	9 4 0	1171	1060	6	1729	1384	
3	224	217	6	906	693	4	2659	2612	1	3327	1169	7	1386	1338	
4	1537	1353	7	1095	842	5	2789	2948	2	1279	1297	8	1018	863	
5	349	105	8	1387	1095	6	532	332	3	1994	1927	9	1045	881	
6	703	465	9 1 0	1	553	125	7	2121	2423	4	2280	2460	1	900	662
7	1062	596	2	1414	1405	8	573	422	5	1303	1260	2	688	150	
8	583	426	3	659	652	9	2093	2070	6	1751	1584	3	769	488	
10 0 0	1925	1612	4	1425	1190	4 3 0	825	672	7	870	621	4	1274	1066	
1	922	748	5	958	800	1	865	831	8	943	814	5	1221	1125	
2	1872	1660	6	1173	961	2	2230	2335	8 4 0	698	365	6	863	536	
3	766	103	7	710	497	3	2388	2754	1	1006	1045	7	1136	749	
4	1312	1065	8	3511	3464	4	2228	2573	2	94	848	8	1607	1397	
5	1821	1615	9	4441	4552	5	910	827	3	1125	877	9			
6	879	664</													

Table 3. *Coordinates and thermal vibration*
Number in parentheses are the esti-

Atom	x	y	z	β_{11}	β_{22}
(Ca _{1/2} Na _{1/2})	0.3399(2)	$\frac{1}{2} - x$	0.5134(3)	0.0050(2)	β_{11}
Al	0	0	0	0.0018 ^a	β_{11}
Si	0.1416(2)	$\frac{1}{2} - x$	0.9531(3)	0.0009(2)	β_{11}
O(1)	$\frac{1}{2}$	0	0.1687(12)	0.0034(6)	β_{11}
O(2)	0.1428(6)	$\frac{1}{2} - x$	0.2652(9)	0.0074(6)	β_{11}
O(3)	0.0852(4)	0.1747(5)	0.8120(6)	0.0045(6)	0.0035(6)

^a Since different scale factors were used for the different k layers, β_{11} of Al

^b Was not varied as a least-square parameter.

The list of F_{obs} and F_{calc} for the positive polarity is given in Table 2; and the final atomic coordinates, temperature factors and the site-occupancies of cations are given in Table 3.

Table 4. *Bond lengths and bond angles in soda melilite*

Bond lengths		Bond angles	
The [AlO ₄] tetrahedron at point symmetry $\bar{4}$			
4 Al—O(3)	1.762(3) Å	2 O(3)—Al—O(3')	114.8° (2)
2 O(3)—O(3')	2.968(7)	4 O(3)—Al—O(3'')	106.9 (1)
4 O(3)—O(3'')	2.830(7)		
The [Si ₂ O ₇] group at point symmetry $mm2$			
Si—O(1)	1.648(5) Å	Si—O(1)—Si'	136.2° (4)
Si—O(2)	1.577(1)	O(1)—Si—O(2)	104.0 (6)
2 Si—O(3)	1.631(7)	2 O(1)—Si—O(3)	103.2 (2)
O(1)—O(2)	2.680(7)	O(3)—Si—O(3'')	105.2 (3)
2 O(1)—O(3)	2.569(4)	2 O(3)—Si—O(2)	115.7 (2)
O(3)—O(3'')	2.592(7)		
2 O(3)—O(2)	2.716(4)		
The [(Ca, Na) ₈] polyhedron at point symmetry m			
2 (Ca, Na)—O(3)	2.463(4) Å	O(2)—(Ca, Na)—O(3)	66.8° (1)
(Ca, Na)—O(2)	2.470(8)	O(3)—(Ca, Na)—O(3')	63.6 (2)
(Ca, Na)—O(1)	2.453(5)	O(2)—(Ca, Na)—O(2'')	58.8 (1)
2 (Ca, Na)—O(3''')	2.793(3)	O(2)—(Ca, Na)—O(3')	89.7 (3)
2 (Ca, Na)—O(2')	2.572(5)	O(2')—(Ca, Na)—O(3')	84.7 (2)
		O(1)—(Ca, Na)—O(3')	58.4 (1)
		O(1)—(Ca, Na)—O(2'')	107.8 (2)
		O(3'')—(Ca, Na)—O(3''')	139.8 (3)

parameters of atoms in soda melilite
 mated standard deviation ($\times 10^4$)

β_{33}	β_{12}	β_{13}	β_{23}	site occupancies	
				ideal	observed
0.0071(5)	0.0015(3)	0.0009(2)	$-\beta_{13}$	0.50	0.4976(27)
0.0047(7)	0	0	0	0.25	0.2448(21)
0.0010(4)	$-0.0003(2)$	$-0.0002(2)$	$-\beta_{13}$	0.50	0.4554(31)
0.0034(16)	$-0.0023(9)$	0	0	0.25	nv ^b
0.0075(12)	0.0007(10)	$-0.0012(7)$	$-\beta_{13}$	0.50	nv
0.0059(8)	$-0.0013(5)$	0.0013(6)	0.0010(6)	1.00	nv

was not varied.

Interatomic distances and bond angles together with the estimated standard deviations in these quantities were calculated using the SORFFE program [a local modified version of the ORFFE program of (BUSING, MARTIN and LEVY, 1964)]. The bond distances and the bond angles in soda melilite (Table 4) do not include any corrections for the thermal movements of the atoms.

4. Discussion

This study confirms that the compound $\text{CaNaAlSi}_2\text{O}_7$, synthesized at 10 kbar does possess the melilite structure. In the structure analysis of gehlenite crystal it was discussed (LOUISNATHAN, 1970) that T_1 in the melilite structure has the properties of a tetrahedron in a framework aluminosilicate. The $T_1\text{—O}(3)$ distance in soda melilite is $1.762 \pm 0.003 \text{ \AA}$, which compares nicely with the Al—O distance of $1.75 \pm 0.01 \text{ \AA}$ for framework aluminosilicates given by SMITH and BAILEY (1963). The site-occupancy of the T_1 site, obtained as a least-squares parameter is 0.245 ± 0.003 which compares well with the ideal value of 0.250. Thus both the $T_1\text{—O}$ distance and the site-occupancy of the T_1 site indicate that T_1 in soda melilite is occupied by $\text{Al}_{1.0}$.

The mean $T_3\text{—O}$ distance in soda melilite is $1.622 \pm 0.003 \text{ \AA}$, which compares well with the mean Si—O distance of $1.618 \pm 0.003 \text{ \AA}$, observed in hardystonite, the Zn melilite (LOUISNATHAN, 1969). The site-occupancy of 0.455 ± 0.003 obtained as a least-squares parameter deviates only marginally from the ideal value of 0.5. The variation of the individual Si—O distances can be explained on the basis of π -bonding theory as for hardystonite (LOUISNATHAN, 1969).

As in other melilites the 8-coordination site in soda melilite shows four short M—O bonds and four long ones. Since the ionic radii of Ca^{+2} (0.99 Å) and Na^{+1} (0.97 Å) are nearly equal the mean M—O distances in the various melilites should vary only very marginally, which is what is observed. The site-occupancy (0.497 ± 0.003) obtained from the least-squares refinement compares well with the ideal value of 0.50.

EDGAR (1965) investigated the systems gehlenite—soda melilite and åkermanite—soda melilite finding that in both systems the cell parameters plot linearly with the composition. His results can be explained by ideal mixing of Ca and Na in the 8-coordination sites in the gehlenite—soda melilite system; and by ideal mixing of Mg and Al in the the T_1 tetrahedral sites in the åkermanite—soda melilite system. In both systems there are no substitutions in the T_3 site which is occupied only by Si.

5. Acknowledgements

I thank Professor J. V. SMITH whose critical discussions have helped in the making of this paper, and Professor H. S. YODER for providing the sample. The financial support for this work came from NSF-GA 1658 research grant administered to Professor J. V. SMITH.

References

- W. R. BUSING, K. O. MARTIN and H. A. LEVY (1962), ORFLS, a FORTRAN crystallographic least squares program. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- (1964), ORFFE, a FORTRAN crystallographic functions and error program. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- OLAV H. J. CHRISTIE (1961*a*), On sub-solidus relations of silicates. I. The lower breakdown temperature of the åkermanite-gehlenite mixed crystal series at moderate water pressure. *Norsk Geol. Tidsskr.* **41**, 255–269.
- (1961*b*), On sub-solidus relations of silicates. II. Preliminary note on the chemistry of melilites. *Norsk Geol. Tidsskr.* **42**, 1–29.
- OLAV H. J. CHRISTIE (1962), On sub-solidus relations of silicates. IV. The systems åkermanite-sodium gehlenite and gehlenite-sodium gehlenite. *Norsk Geol. Tidsskr.* **42**, 31–44.
- A. D. EDGAR (1965), Lattice parameters of melilite solid solutions and a reconnaissance of phase relations in the system $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite)— $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (åkermanite)— $\text{NaCaAlSi}_2\text{O}_7$ (soda melilite) at 1000 kg/cm² water vapor pressure. *Canadian Journ. Earth Sci.* **2**, 596–621.
- W. G. HAMILTON (1964), *Statistics in physical science*. New York, The Ronald Press Company.

- S. J. LOUISNATHAN (1969), The refinement of the crystal structure of hardy-
stonite $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. *Z. Kristallogr.* **130**, 427–437.
- S. J. LOUISNATHAN (1970), Refinement of the crystal structure of a natural
gehlenite, $\text{Ca}_2\text{Al}(\text{Al},\text{Si})_2\text{O}_7$. [Submitted to *Canadian Mineral.*]
- J. F. SCHAIRER, H. S. YODER and C. D. TILLEY (1965), Behavior of melilites in
the join gehlenite-soda-melilite-åkermanite. *Carnegie Inst. Wash. Yearbook*,
64, 95.
- J. V. SMITH (1953), Reexamination of the crystal structure of melilite. *Amer.*
Mineral. **38**, 643–661.
- J. V. SMITH and S. W. BAILEY (1963), Second review of Al–O and Si–O
tetrahedral distances. *Acta Crystallogr.* **16**, 801–811.
- H. S. YODER (1964), Soda melilite. *Carnegie Inst. Wash. Yearbook* **63**, 86.