Molal volumes of synthetic paragonite–muscovite micas

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Abstract

Molal volume data are presented for single-phase Na-rich and K-rich (Na,K) $Al_2(AlSi_3O_{10})(OH)_2$ micas synthesized at 2, 4, and 8 kbar pressure. Micas synthesized at 2 and 4 kbar pressure are $1M$ polytypes; but at 8 kbar pressure $1M$ micas crystallized at low temperatures, and with increased temperature, $1M$–$2M_1$ mixtures and finally just $2M_1$ polytypes were obtained. X-ray powder-diffraction data were used in the refinement of unit-cell parameters for each mica, and molal volumes calculated from refined unit-cell volumes suggest that: (1) for an Na-rich or K-rich mica of specified composition, the molal volume of the $2M_1$ polytype is slightly smaller than that of the $1M$ polytype; (2) change in molal volume with X_{mu} (dV/dX_{mu}) is significantly larger for Na-rich micas than for K-rich micas; (3) dV/dX_{mu} for Na-rich micas is essentially constant and the same for both $1M$ and $2M_1$ polytypes, and similarly, dV/dX_{mu} for K-rich micas is essentially constant and the same for both $1M$ and $2M_1$ polytypes; and (4) there is a small, approximately linear decrease in the molal volumes of $1M$ micas (of given composition) with increased synthesis pressure. Furthermore, although there is significant scatter in the molal volume data, least-squares fit polynomial equations calculated from these data suggest small, positive excess volumes for synthetic $(Na,K)Al_2(AlSi_3O_{10})(OH)_2$ micas over the entire compositional range.

Cubic least-squares fit polynomial equations calculated from the 2, 4, and 8 kbar molal volume data have been used to derive W_{V1} ($= W_{V,pa}$) and W_{V2} ($= W_{V,mu}$) Margules parameters for $(Na,K)Al_2(AlSi_3O_{10})(OH)_2$ micas. These W_V values are significantly different from W_V's for paragonite–muscovite micas listed in previous studies. Analysis of the available molal volume data for paragonite–muscovite micas suggests that relatively small inaccuracies in these data can have a significant effect on not only W_V values, but also thermodynamic or phase-equilibrium calculations based upon equations of state which contain these W_V values.

Introduction

There are few molal volume data for synthetic and natural paragonite–muscovite micas. The paucity of data for the synthetic micas has been due in part to the lack of an accurate method for determining compositions of Pa–Mu micas, and to uncertainties regarding the extent of crystalline solution in the $NaAl_2(AlSi_3O_{10})(OH)_2$–$KAl_2(AlSi_3O_{10})(OH)_2$ system.[2] However, results of several recent investiga-

tions (Eugster *et al.*, 1972; Blencoe, 1973; Blencoe and Luth, 1973) have alleviated these difficulties to a large extent.

This communication presents molal volume data and calculated excess molal volumes for single-phase Pa–Mu micas synthesized at 2, 4, and 8 kbar pressure. Possible sources of discrepancies between the results of this and previous investigations will be described. Application of Pa–Mu molal volume equations in calculating W_V Margules parameters for Pa–Mu micas also will be discussed.

Previous investigations

Eugster *et al.* (1972) were the first to obtain molal volume data for Pa–Mu crystalline solutions, and they presented the following least-squares fit polynomial equation relating molal volume to mica composition [Eugster *et al.*, 1972, equation (7)]:

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[2] "Pa–Mu" will be used as an abbreviation for "synthetic $(Na,K)Al_2(AlSi_3O_{10})(OH)_2$" to designate binary micas of the $NaAl_2(AlSi_3O_{10})(OH)_2$–$KAl_2(AlSi_3O_{10})(OH)_2$ system. The adjectives "paragonitic," "muscovitic," and "paragonite–muscovite" will be used to refer to either synthetic or natural Na–K micas, and the abbreviations "pa" and "mu" will refer to the components $NaAl_2(AlSi_3O_{10})(OH)_2$ and $KAl_2(AlSi_3O_{10})(OH)_2$, respectively, in a system or crystalline solution.

$$V(\text{cal/bar-gfw}) = 3.14333(40) + 0.22729(60)X_{mu}$$
$$+ 0.08220(500)X_{pa}X_{mu}^2$$
$$+ 0.12590(1100)X_{mu}X_{pa}^2 \qquad (1)$$

where numbers in parentheses are coefficient *e.s.d.*'s (*e.g.,* 3.14333(40) = 3.14333 ± 0.00040), and the *e.s.d.* of the dependent variable, V, is 0.0043 cal/bar-gfw. This equation indicates positive excess volumes of mixing for 1*M* Pa–Mu crystalline solutions over the entire compositional range (Eugster *et al.,* 1972, Fig. 3). Citing the reservations of Eugster *et al.* regarding the quality of the data used to calculate equation (1), Chatterjee and Froese (1975) presented an alternative molal volume equation based upon data (Chatterjee and Froese, 1975, Table 3) for the synthetic $2M_1$ end-members (Chatterjee, 1974; Chatterjee and Johannes, 1974) and natural $2M_1$ paragonite–muscovite micas (Burnham and Radoslovich, 1964; Zen *et al.,* 1964; Güven, 1971; Rothbauer, 1971). This least-squares fit equation [Chatterjee and Froese, 1975, equation (11)],

$$V(\text{cal/bar-gfw}) = 3.15374(159) + 0.10351(2382)X_{mu}$$
$$+ 0.37709(5606)X_{mu}^2 - 0.26804(3507)X_{mu}^3 \qquad (2)$$

(V *e.s.d.* = 0.00187 cal/bar-gfw), indicates negative excess volumes of mixing in the range $0.00 < X_{mu} \le 0.40$ and positive excess volumes for crystalline solutions more K-rich than $Pa_{0.60}Mu_{0.40}$ (Chatterjee and Froese, 1975, Fig. 2).[3] Thus, there are significant differences between Pa–Mu excess volumes calculated from equations (1) and (2) (Fig. 3), particularly for paragonitic micas.

Experimental methods

Solid starting materials with compositions at 5 mole percent intervals (a total of 21 compositions) along the $Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2$–$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2$ join were prepared, using a coprecipitated gel technique slightly modified from Luth and Ingamells (1965) (however, only those solid starting materials with compositions within 20 mole percent of the end members of this join were used to obtain the molal volume data presented in this report). The gels were made by combining appropriate quantities of standardized $NaNO_3$–H_2O, KNO_3–H_2O, and Al $(NO_3)_3$–H_2O solutions and ammonia-stabilized Ludox [E. I. du Pont de Nemours & Co. (Inc.)], and each mixture was stirred continuously during the gelling process to insure homogeneity. The gelatinous materials were then dried, denitrified, and fired at 800°C for 4 hours, and examination of the resultant solids by petrographic microscope and X-ray diffraction methods indicated that no crystalline materials were present. The solids were ground in ethanol to an average grain size of less than 5 μm in a micronizing mill (McCrone Research Associates Ltd.), refired at 700°C, and stored in a desiccator when not in use.

The solid starting materials were dried at 120°C under vacuum for a minimum of 15 minutes before being loaded into 2 mm (O.D.) gold capsules containing weighed amounts (generally 6–8 weight percent) of freshly boiled, distilled, and deionized water. After loading, the capsules were sealed, weighed, and heated to 120°C under vacuum for at least 30 minutes. The capsules were reweighed to confirm that leakage had not occurred, and then reheated to and maintained at 120°C for several hours to one day to insure that water was evenly distributed within each capsule.

Most of the synthesis experiments were conducted in externally-heated cold-seal pressure vessels (Tuttle, 1949; Luth and Tuttle, 1963), but 8 kbar experiments above 700°C were performed in an internally-heated vessel modified after the design of Yoder (1950). Stellite 25 "low-pressure" externally-heated vessels (2 kbar experiments) were oriented vertically with the closure-nut assembly up (orientation 1 of Boettcher and Kerrick, 1971, Fig. 2), while René 41 "high-pressure" externally-heated vessels (4 and 8 kbar experiments) were oriented vertically with the closure-nut assembly down (orientation 2 of Boettcher and Kerrick, 1971, Fig. 2). Pressure media were water in 2 kbar experiments and argon in 4 and 8 kbar experiments. Pressure measurements for 2 kbar experiments were made using gauges calibrated against a Heise gauge, while pressures of 4 and 8 kbar experiments were monitored using manganin cells and a modified Carey-Foster bridge (Harwood Engineering Company, Inc.). Pressure variations were less than ± 2 percent, and the accuracy of pressure measurements is estimated to be ± 3 percent. Temperatures of externally-heated experiments were measured by bare-wire chromel–alumel thermocouples calibrated by delayed thermal analysis, using the one atm melting points of NaCl (800.4 ± 0.5°C), and eutectic mixtures of KCl + Na_2SO_4 (517.1 ± 1.0°C) and NaCl + Na_2SO_4 (627.0 ± 0.5°C) (Roberts, 1924). Temper-

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[3] The correct coefficient for the second term in equation (2) is 0.10351 as listed and not 0.01351 as given by Chatterjee and Froese (1975). The V *e.s.d.* and coefficient *e.s.d.*'s for this equation were calculated by the writer. Excess volumes calculated from equation (2) are similar to those calculated from a paragonite–muscovite unit-cell volume equation presented by Fujii (1966, p. 115).

atures of internally-heated experiments were measured using inconel-sheathed Pt/Pt-10%Rh thermocouples calibrated against the melting points of NaCl and gold (1062.5 ± 0.5°C at one atm according to Akella and Kennedy, 1971). Temperature ranges (Table 1) are believed to be accurate to ± 5°C in the 4 and 8 kbar externally-heated experiments and ± 10°C in the internally-heated experiments. However, filler rods were not used in the 2 kbar externally-heated experiments, so temperature ranges at this pressure may be in error by as much as ± 15°C. Experiment durations were 28 days for 2 kbar experiments and 13.5–15.0 days for 4 and 8 kbar experiments, with the exception of 8 kbar experiments above 700°C, which lasted 7–8 days. After the conclusion of an experiment all capsules were checked for leakage, and capsules in which leakage was established or suspected were discarded immediately.

Examination of experimental products

Experimental products were examined mainly by X-ray powder diffractometry using a Nonius Guinier-de Wolff focussing camera and a fine-focus copper anode tube. CuKα radiation was employed, and film-exposure durations were normally 24 hours. Spinel (a = 8.0833A at 25°C), described by Luth and Querol-Suñé (1970), was added to all experimental samples to serve as an internal standard. Films were read using an optical comparitor (Grant Instrument Company) which measured to 0.001 mm (0.0005°2θ), and almost all measurements were reproducible to ± 0.01 mm (0.005°2θ). Measured reflection positions are believed to be accurate to ± 0.010°2θ, with the exception of the 001 diffraction maxima of 1M Pa–Mu micas, which are considered to be accurate to ± 0.015°2θ. X-ray diffraction patterns and examinations of the charges by petrographic microscope indicated that a single mica and a small amount of corundum were the only phases present in each charge.[4] Criteria for establishing that a charge contained a single mica rather than a Pa–Mu pair were: (1) detection of a single d_{003} (1M) [or d_{006} (2M_1)] reflection in the d-spacing range (≈3.202–3.361A) of this reflection for Pa–Mu micas (in most instances two of these reflections, one for each mica, were detected when a charge contained two Pa–Mu micas); and (2) the d_{003} (1M) [or d_{006} (2M_1)] value was external to the d-spacing range for this reflection delimited by Pa–Mu solvus-pairs synthesized at or

near the same pressure and temperature (Blencoe, 1973; Blencoe and Luth, 1973). The second criterion was applied because diffraction maxima of 1M micas frequently were diffuse, so detection of small amounts of these micas was difficult. If an experimental product satisfied the two conditions just cited, then the mica in the sample was assumed to possess an Na/K ratio identical to that of the solid starting material from which it was synthesized.[5] This assumption ignores such possibilities as H_3O^+ substitution for K^+ in muscovitic micas and other forms of incongruent solution of alkalies in the coexisting H_2O-rich fluid phase.

Mathematical and computer methods

Unit-cell volumes for Pa–Mu micas synthesized in this study were obtained from refinements calculated by the FORTRAN IV least-squares computer program of Appleman and Evans (1973). The principal input data for each cell refinement were: (1) estimated unit-cell parameters, considering the composition and polytype of the mica, obtained from linear interpolations of cell-parameter data for synthetic 1M and 2M_1 muscovite (Yoder and Eugster, 1955) and paragonite (Chatterjee, 1970); and (2) fixed-index reflections (in °2θ) which were assigned unit weight. Diffraction maxima of very low intensity and/or poor "quality" were excluded from the input data. The number of reflections accepted by the program ranged from 9 to 21 (approximately 15 on the average) for 1M micas, and 13 to 36 (approximately 20 on the average) for 2M_1 micas (results of the unit-cell refinements will be described in greater detail in a subsequent publication).

Molal volumes for the micas in cal/bar-gfw were calculated from the unit-cell volumes in cm³ using the relation

$$V(\text{cal/bar-gfw}) = V(\text{cm}^3)N_0/(41.84Z) \qquad (3)$$

where N_0 = Avogadro's Number, 0.602252 × 10²⁴ formula units per mole, and $Z = 2(1M)$ or $4(2M_1)$

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[4] Small amounts of corundum were present in the solid starting materials owing to contamination by the corundum grinding elements of the micronizing mill used to comminute the solids.

[5] Accuracies of Na/K ratios of solid starting materials were checked qualitatively and indirectly by crystallizing each of these materials in the presence of a small amount of H_2O at 2 kbar pressure and ≈755°C. A crystalline phase assemblage consisting of a single alkali feldspar and corundum was obtained for each bulk composition, and $d_{\overline{2}01}$ (A) values for the alkali feldspars were measured using X-ray methods described previously. These $d_{\overline{2}01}$ data indicate an essentially linear variation of $d_{\overline{2}01}$ with X_{or}, and a determinative curve based upon the 21 data points (Blencoe, in preparation) is nearly identical to the $d_{\overline{2}01}$ versus X_{or} determinative curve for synthetic high albite–sanidine feldspars presented by Orville (1967, Fig. 9).

Table 1. Experimental and molal volume data for synthetic $(Na,K)Al_2(AlSi_3O_{10})(OH)_2$ micas

Left half

$X_{mu}^@$	Capsule No.	T (°C)	Polyt.@@	$V^{\#}$ (cal/bar-gfw)	$V^{ex\#\#}$
a) 2 Kilobars					
0.00	55	404 ± 2	1M	3.17499(677)	0.0
0.00	184	441 ± 3	1M	3.17226(417)	0.0
0.00	170	482 ± 2	1M	3.17399(353)	0.0
0.00	29	519 ± 8	1M	3.18341(166)	0.0
0.00	214	554 ± 3	1M	3.18507(151)	0.0
				3.17794 ± 0.00586	
0.05	54	404 ± 2	1M	3.19241(497)	–
0.05	183	441 ± 3	1M	3.18924(439)	0.00560
0.05	169	482 ± 2	1M	3.19169(432)	0.00648
0.05	31	519 ± 8	1M	3.19183(209)	-0.00218
0.05	213	554 ± 3	1M	3.19730(295)	0.00158
				3.19249 ± 0.00295	
0.95	50	404 ± 2	1M	3.40552(813)	–
0.95	238	441 ± 2	1M	3.39335(626)	0.00476
0.95	165	482 ± 2	1M	3.38947(446)	0.00230
0.95	30	519 ± 8	1M	3.38774(482)	0.00283
0.95	209	554 ± 3	1M	3.38913(230)	0.00173
0.95	158	584 ± 4	1M	3.39364(180)	–
0.95	39	619 ± 2	1M	3.38968(230)	–
0.95	432	642 ± 4	1M	3.38702(439)	–
				3.39001 ± 0.00257	
1.00	49	404 ± 2	1M	3.42473(281)	0.0
1.00	178	441 ± 3	1M	3.39997(295)	0.0
1.00	164	482 ± 2	1M	3.39839(475)	0.0
1.00	28	519 ± 8	1M	3.39551(554)	0.0
1.00	208	554 ± 3	1M	3.39810(367)	0.0
1.00	157	584 ± 4	1M	3.39753(302)	0.0
1.00	37	619 ± 2	1M	3.39832(266)	0.0
1.00	438	642 ± 4	1M	3.39026(468)	0.0
				3.39687 ± 0.00320	
b) 4 Kilobars					
0.00	638	400 ± 4	1M	3.17636(813)	0.0
0.00	1181	430 ± 3	1M	3.16981(763)	0.0
0.00	1178	460 ± 3	1M	3.17355(396)	0.0
0.00	649	491 ± 3	1M	3.16916(396)	0.0
0.00	678	520 ± 3	1M	3.16880(475)	0.0
0.00	575	552 ± 3	1M	3.17118(504)	0.0
0.00	568	580 ± 4	1M	3.17665(374)	0.0
0.00	836	596 ± 3	1M	3.16557(828)	0.0
				3.17138 ± 0.00388	
0.05	989	400 ± 3	1M	3.17989(972)	-0.00664
0.05	1180	430 ± 3	1M	3.18478(907)	0.00410
0.05	1177	460 ± 3	1M	3.17859(964)	-0.00548
0.05	759	490 ± 3	1M	3.17665(381)	-0.00326
0.05	1321	520 ± 3	1M	3.18255(381)	0.00275
0.05	574	552 ± 3	1M	3.18788(439)	0.00591
0.05	660	580 ± 3	1M	3.19054(489)	0.00360
				3.18298 ± 0.00506	
0.90	999	550 ± 3	1M	3.37673(554)	0.01129
0.90	567	580 ± 4	1M	3.37507(353)	0.01317
0.90	1454	610 ± 3	1M	3.36629(396)	–
0.90	545	640 ± 3	1M	3.37155(202)	–
				3.37241 ± 0.00462	
0.95	749	401 ± 4	1M	3.37558(784)	0.00600
0.95	1319	430 ± 3	1M	3.37860(482)	0.00230
0.95	1149	460 ± 3	1M	3.38090(677)	0.00750
0.95	755	490 ± 3	1M	3.38443(374)	0.01117
0.95	1006	520 ± 3	1M	3.38975(425)	0.01194
0.95	573	552 ± 3	1M	3.37500(475)	-0.00123
0.95	566	580 ± 4	1M	3.37874(353)	0.00655
0.95	559	611 ± 3	1M	3.37558(461)	–
0.95	544	640 ± 3	1M	3.37846(238)	–
0.95	1230	670 ± 4	1M	3.37716(533)	–
				3.37942 ± 0.00460	

Right half

X_{mu}	Capsule No.	T (°C)	Polyt.	V (cal/bar-gfw)	V^{ex}
c) 4 Kilobars (cont'd)					
1.00	748	401 ± 4	1M	3.37975(410)	0.0
1.00	1155	430 ± 3	1M	3.38716(648)	0.0
1.00	1148	460 ± 3	1M	3.38393(590)	0.0
1.00	646	491 ± 3	1M	3.38400(626)	0.0
1.00	675	520 ± 3	1M	3.38882(569)	0.0
1.00	572	552 ± 3	1M	3.38702(489)	0.0
1.00	565	580 ± 4	1M	3.38249(403)	0.0
1.00	450	610 ± 4	1M	3.38824(266)	0.0
1.00	446	640 ± 4	1M	3.38385(338)	0.0
1.00	579	671 ± 3	1M	3.38846(173)	0.0
1.00	1237	699 ± 3	1M	3.38184(417)	0.0
				3.38505 ± 0.00305	
c) 8 Kilobars					
0.00	258	401 ± 4	1M	3.16787(525)	0.0
0.00	722	431 ± 3	1M	3.16837(633)	0.0
0.00	479	460 ± 3	1M	3.16535(576)	0.0
0.00	191	490 ± 3	1M	3.16564(518)	0.0
0.00	354	520 ± 4	1M	3.16341(497)	0.0
0.00	347	550 ± 3	1M	3.16607(482)	0.0
0.00	815	594 ± 4	$1M > 2M_1$	3.16657(446)	0.0
				3.16618 ± 0.00166	
0.00	333	581 ± 4	$1M < 2M_1$	3.15657(122)	0.0
0.00	319	611 ± 4	$2M_1$	3.15153(79)	0.0
0.00	822	625 ± 3	$2M_1$	3.15585(317)	0.0
0.00	312	641 ± 3	$2M_1$	3.16002(187)	0.0
0.00	829	655 ± 4	$2M_1$	3.15599(130)	0.0
0.00	340	670 ± 4	$2M_1$	3.16146(194)	0.0
				3.15690 ± 0.00350	
0.05	257	401 ± 4	1M	3.18435(353)	0.00539
0.05	396	430 ± 4	1M	3.17334(799)	-0.00537
0.05	478	460 ± 3	1M	3.16967(684)	-0.00624
0.05	325	490 ± 3	1M	3.17125(633)	-0.00532
0.05	504	520 ± 3	1M	3.16765(525)	-0.00692
0.05	511	550 ± 3	1M	3.17463(547)	-0.00173
0.05	518	580 ± 3	1M	3.16794(504)	–
				3.17269 ± 0.00576	
0.05	814	594 ± 4	$1M < 2M_1$	3.16391(439)	–
0.05	525	610 ± 3	$1M < 2M_1$	3.16665(101)	–
0.05	821	625 ± 3	$1M < 2M_1$	3.17024(187)	–
0.05	532	641 ± 3	$2M_1$	3.16413(65)	–
0.05	828	655 ± 4	$2M_1$	3.16492(122)	–
0.05	588	671 ± 3	$2M_1$	3.17154(202)	0.00004
				3.16690 ± 0.00326	
0.10	375	521 ± 4	$1M > 2M_1$	3.19263(590)	0.00689
0.10	389	551 ± 3	$1M > 2M_1$	3.18500(633)	-0.00166
				3.18882 ± 0.00540	
0.10	382	582 ± 4	$1M < 2M_1$	3.18356(259)	–
0.10	368	611 ± 4	$1M < 2M_1$	3.17881(158)	–
0.10	820	625 ± 3	$2M_1$	3.17859(252)	–
0.10	207	641 ± 3	$2M_1$	3.17838(108)	–
0.10	827	655 ± 4	$2M_1$	3.17730(137)	–
0.10	200	668 ± 3	$2M_1$	3.17931(86)	-0.00223
				3.17932 ± 0.00218	
0.15	819	625 ± 3	$1M < 2M_1$	3.19140(324)	–
0.15	206	641 ± 3	$2M_1$	3.19637(122)	–
0.15	826	655 ± 4	$2M_1$	3.19313(115)	–
0.15	199	668 ± 3	$2M_1$	3.19918(122)	0.00760
				3.19502 ± 0.00345	
0.20	198	668 ± 3	$2M_1$	3.21551(101)	0.01389
0.80	195	668 ± 3	$2M_1$	3.33707(151)	0.01497

Table 1, continued

X_{mu}	Capsule No.	T (°C)	Polyt.	V (cal/bar-gfw)	V^{ex}	X_{mu}	Capsule No.	T (°C)	Polyt.	V (cal/bar-gfw)	V^{ex}
				c) 8 Kilobars (cont'd)						**c) 8 Kilobars (cont'd)**	
0.85	313	611 ± 4	$2M_1$	3.34247(108)	–	0.95	587	671 ± 3	$1M < 2M_1$	3.35758(151)	0.00536
0.85	306	641 ± 3	$2M_1$	3.34038(144)	–	0.95	172	702 ± 2	$2M_1$	3.35816(130)	–
0.85	334	670 ± 4	$2M_1$	3.34427(180)	0.01213	0.95	1098	725 ± 8	$2M_1$	3.35794(158)	–
0.85	593	701 ± 3	$2M_1$	3.34103(94)	–					3.35789 ± 0.00029	
				3.34204 ± 0.00173							
						1.00	252	401 ± 4	1M	3.38961(928)	0.0
0.90	185	490 ± 3	1M	3.37507(828)	0.01259	1.00	390	430 ± 4	1M	3.37500(677)	0.0
0.90	369	521 ± 4	1M	3.36708(914)	0.00268	1.00	474	460 ± 3	1M	3.37651(677)	0.0
0.90	383	551 ± 3	1M	3.37428(525)	0.02296	1.00	190	490 ± 3	1M	3.38436(655)	0.0
0.90	376	582 ± 4	$1M > 2M_1$	3.37140(684)	–	1.00	373	521 ± 4	1M	3.38673(1274)	0.0
				3.37196 ± 0.00361		1.00	387	551 ± 3	1M	3.37191(410)	0.0
						1.00	380	582 ± 4	1M	3.38774(1130)	0.0
0.90	201	641 ± 3	$1M < 2M_1$	3.35399(238)	–	1.00	366	611 ± 4	1M	3.39091(497)	0.0
0.90	194	668 ± 3	$2M_1$	3.35147(151)	0.00929					3.38285 ± 0.00730	
0.90	136	698 ± 4	$2M_1$	3.34592(122)	–						
				3.35046 ± 0.00413		1.00	586	671 ± 3	$1M < 2M_1$	3.36226(137)	0.0
						1.00	171	702 ± 2	$2M_1$	3.36780(115)	0.0
0.95	253	401 ± 4	1M	3.37781(763)	-0.00072	1.00	1097	725 ± 5	$2M_1$	3.36744(288)	0.0
0.95	391	430 ± 4	1M	3.37378(698)	0.00911	1.00	1363	750 ± 8	$2M_1$	3.36672(58)	0.0
0.95	475	460 ± 3	1M	3.37968(842)	0.01372	1.00	1430	775 ± 10	$2M_1$	3.36435(72)	0.0
0.95	320	490 ± 3	1M	3.37997(309)	0.00655					3.36571 ± 0.00235	
0.95	502	520 ± 3	1M	3.36939(633)	-0.00618						
0.95	509	550 ± 3	1M	3.36975(684)	0.00813						
0.95	516	580 ± 3	1M	3.37788(353)	–						
0.95	523	610 ± 3	1M	3.37054(569)	–						
				3.37485 ± 0.00452							

[@]Definitions of symbols:

    X_{mu} = mole fraction $KAl_2(AlSi_3O_{10})(OH)_2$ V = molal volume in cal/bar-gfw

    T = experimental temperature range in degrees Celsius V^{ex} = excess molal volume in cal/bar-gfw

    Polyt. = polytype

[@@]The "greater than" (>) and "less than" (<) symbols refer to estimates (from X-ray diffraction patterns) of $1M/2M_1$ ratios of more than 3:1 and less than 1:3, respectively, in samples (charges) which contained both polytypes.

[#]Numbers in parentheses are molal volume e.s.d.'s from unit cell refinements, and each refers to the last decimal places of a molal volume value. Hence, 3.17499(677) cal/bar-gfw indicates an e.s.d. of 0.00677 cal/bar-gfw. Blank lines separate the molal volume values into short individual columns of data for micas of identical composition, polytype and pressure of synthesis. Numbers immediately below the horizontal solid line at the bottom of an individual column of data are the mean and e.s.d. for the molal volumes in that column. These means and e.s.d.'s are illustrated in Figure 1 where arrows point to the mean value of each set of data and short horizontal lines show the e.s.d. Molal volumes of the 1M $Pa_{0.05}Mu_{0.95}$ and $Pa_{0.00}Mu_{1.00}$ micas synthesized at 2 kbar and 404°C are believed to be outliers (see text), so these values were disregarded in the calculations of the means and e.s.d.'s for the columns of data which include these values.

[##]Excess molal volumes for Pa-Mu crystalline solutions synthesized at a given pressure and temperature were calculated from the molal volumes of the $Pa_{1.00}Mu_{0.00}$ and $Pa_{0.00}Mu_{1.00}$ micas of identical structure (polytype) crystallized at the same pressure and temperature (see text for details). Consequently, excess volumes for micas crystallized at temperatures above the upper thermal stability of end-member paragonite at a given pressure could not be calculated by this method. Excess volumes for 1M micas synthesized at 2 kbar and 404°C were not computed because, as noted previously, the molal volume of the 1M $Pa_{0.00}Mu_{1.00}$ mica crystallized at this pressure and temperature is believed to be an outlier.

formula units per unit cell. Molal volumes calculated from equation (3) and *e.s.d.*'s for the molal volumes are listed in Table 1, and examination of these data reveals that *e.s.d.*'s for $2M_1$ micas are generally smaller than those for $1M$ micas. This can be attrib-

uted to the larger number and better "quality" of reflections in the diffraction patterns of most of the $2M_1$ polytypes.

Least-squares fit equations for the molal volume data are presented in Table 2. These equations were

Table 2. Polynomial equations for molal volumes of synthetic $(Na,K)Al_2(AlSi_3O_{10})(OH)_2$ micas

Cryst. sol., polyt.	P (kbar)	n[@]	A[@@]	B	C	D	e.s.d.[#] (cal/bar-gfw)	f.e.v.[##]
a) Equations of the form $V(cal/bar-gfw) = A + BX_{mu} + CP(kb/10) + DT(°C/1000)$								
Pa,1M[*]	2,4,8	41	3.18168 (0.00631)	0.22756 (0.02606)	-0.02400 (0.00311)	0.00212 (0.01257)	0.00483	0.761
Mu,1M	2,4,8	59	3.27452 (0.02120)	0.12721 (0.02036)	-0.01972 (0.00306)	-0.00935 (0.00926)	0.00534	0.637
b) Equations of the form $V(cal/bar-gfw) = A + BX_{mu} + CP(kb/10)$								
Pa,1M	2,4,8	41	3.18269 (0.00177)	0.22772 (0.02571)	-0.02396 (0.00306)	– –	0.00477	0.761
Mu,1M	2,4,8	59	3.26685 (0.01980)	0.12959 (0.02023)	-0.01900 (0.00297)	– –	0.00535	0.630
c)[**] Equations of the form $V(cal/bar-gfw) = A + BX_{mu} + CX^2_{mu} + DX^3_{mu}$								
Pa-Mu,1M	2	24	3.17794 (0.00165)	0.29423 (0.05179)	-0.06395 (0.11210)	-0.01135 (0.06810)	0.00370	0.999
Pa-Mu,1M	4	40	3.17139 (0.00145)	0.22789 (0.04704)	0.07926 (0.09910)	-0.09344 (0.05607)	0.00410	0.998
Pa-Mu,1M	8	36	3.16522 (0.00193)	0.18043 (0.04664)	0.19677 (0.10174)	-0.16043 (0.06187)	0.00533	0.998
Pa-Mu,2M$_1$	8	39	3.15513 (0.00118)	0.26723 (0.01684)	-0.03931 (0.03876)	-0.01783 (0.02538)	0.00332	0.999

[@] Number of data points.

[@@] Numbers in parentheses are e.s.d.'s of the coefficients.

[#] Estimated standard deviation (Deming, 1943).

[##] Fraction of explained variance, or R^2 (Draper and Smith, 1966, p. 26). These values are dimensionless and they vary between 0.0 and 1.0.

[*] Data used to calculate this equation and subsequent equations are listed in Table 1. Enough significant figures are provided to prevent serious round-off errors in calculations. The number of figures is not related to the precision or accuracy of the data listed in Table 1. Mutual paragonite-muscovite crystalline solution is very limited at 2-8 kbar pressure, so data could be obtained only over narrow compositional ranges near the end-member compositions (see Figure 1). Statistical (regression) analysis of the data indicate that the 2 kbar, 404°C $Pa_{0.00}Mu_{1.00}$ and $Pa_{0.05}Mu_{0.95}$ data points are outliers, so these data were excluded in calculations of the equations given in this table.

[**] W_V Margules parameters calculated from the equations in this section, and W_V's for Pa-Mu micas listed in previous studies are as follows (see text for explanation):

Equation	$W_{V1} = W_{V,pa}$	$W_{V2} = W_{V,mu}$
1M, 2 kbar	0.0867	0.0753
1M, 4 kbar	0.1076	0.0142
1M, 8 kbar	0.1241	-0.0363
2M$_1$, 8 kbar	0.0750	0.0571
(1) (Eugster et al., 1972)	0.0822	0.1259
Blencoe and Luth (1973)	-0.034	-0.077
(2) (Chatterjee and Froese, 1975)	0.1590	-0.1090

calculated using a FORTRAN IV "step-up" stepwise multiple-regression computer program written by the author, which employs the Efroymson algorithm of stepwise acceptance (and rejection) of regression variables (Efroymson, 1960; Draper and Smith, 1966). Statistical evaluations of each equation were made, using the following at each step in the regression calculations:

(1) *e.s.d.* of the dependent variable (V)

(2) *e.s.d.*'s of the regression coefficients

(3) fraction of explained variance (Draper and Smith, 1966, p. 26)

(4) plots of residuals versus (a) "normal scores,"[6] (b) calculated molal volumes (fitted values as opposed to "observed" values), and (c) "primary" independent variables (X_{mu}, P, and T), all "drawn" by the FORTRAN IV subroutine RECPLT (Blencoe, 1975, 1976).

Examination of residuals is an important part of regression analysis, because outliers ("bad" data points) can have a significant effect on the coefficients and statistics of least-squares fit equations. In this study, outliers were detected using the various plots listed above and methods described by Daniel and Wood (1971, p. 27–32). Residuals are normally distributed about zero for a "good" least-squares fit equation, so a plot of residuals versus "normal scores" (a cumulative distribution diagram) can be used to study the numerical disposition of residuals and to detect outliers. An "abnormal" residual on this diagram will plot away from an approximately straight line drawn through points representing normally distributed residuals, and this aberrant residual may be the product of an outlier which should be deleted from the data. However, it should be established that aberrant residuals are not attributable to curvature in the data at or near the limiting values of the dependent and independent variables, or to a systematic variation of variance with these variables. These circumstances indicate that the equation does not represent the data adequately, so another least-

squares fit equation containing additional or different terms should be calculated.

This procedure for detecting outliers was followed in calculating preliminary least-squares fit equations for the molal volume data in Table 1, and cumulative distribution diagrams for these equations indicated "abnormal" residuals for the molal volumes of the $1M$ $Pa_{0.00}Mu_{1.00}$ and $Pa_{0.05}Mu_{0.95}$ micas synthesized at 2 kbar and 404°C. These molal volumes are at the low-pressure and low-temperature boundaries of the data in Table 1, so the possibility of curvature in the data near these boundaries must be considered. However, Figure 1 illustrates that these molal volumes are anomalously large when compared with molal volumes of other micas of the same composition synthesized at the same pressure. Furthermore, available data on the crystal chemistry, phase equilibria, and thermodynamics of muscovitic micas provide no obvious explanation for a sharp increase in the molal volumes of these micas at temperatures near 400°C at 2 kbar pressure. Hence, the two anomalous molal volumes are probably outliers, and they were deleted from the data used to calculate the equations given in Table 2. Figure 1 also illustrates that the molal volume of the $1M$ $Pa_{0.95}Mu_{0.05}$ mica synthesized at 8 kbar and 401°C is anomalously large, but the cumulative distribution diagrams for the preliminary equations indicated that this molal volume is not an outlier. Consequently, this value was retained in calculations of the equations listed in Table 2.[7]

Results

Compositions, synthesis temperatures, polytypic structures, molal volumes and excess molal volumes for the single-phase Pa-Mu micas synthesized at 2, 4, and 8 kbar pressure are listed in Table 1. Compositional ranges over which single-phase micas could be crystallized were limited mainly by the compositions of the solid starting materials used in this study (compositions were at 5 mole percent intervals along the $Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 - K_2O \cdot 3Al_2O_3 \cdot 6SiO_2$ join) and by the extensive miscibility gap (solvus) of the system (Blencoe and Luth, 1973). Temperature ranges over

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[6] "Normal scores" are values which approximate a normal (Gaussian) distribution. If a set of numbers (*e.g.*, residuals) has a normal distribution, and if these numbers are in either ascending or descending order by magnitude, then points representing the numbers will lie along an approximately straight line on a linear-scale rectangular diagram when they are plotted against an equal number of normal scores calculated from the equation

$$4.91 \, [p^{0.14} - (1 - p)^{0.14}]$$

(Joiner and Rosenblatt, 1971) where, for each normal score,

$$p = \frac{\text{sequence number of the corresponding data point} - 0.375}{\text{total number of data points} + 0.25}$$

[7] Scatter in the molal volume data for $1M$ micas synthesized in this study can be attributed mainly to poor crystallinity of these micas. Measurable reflections in the X-ray diffraction patterns of $1M$ micas were frequently diffuse and/or asymmetric, and it is likely that there are significant errors in the 2θ values for some of these reflections. Such errors would have an adverse effect on the accuracy of: (1) refined unit-cell volumes obtained from the computer program of Appleman and Evans (1973); and consequently, (2) the molal volumes calculated from the unit-cell volumes using equation (3).
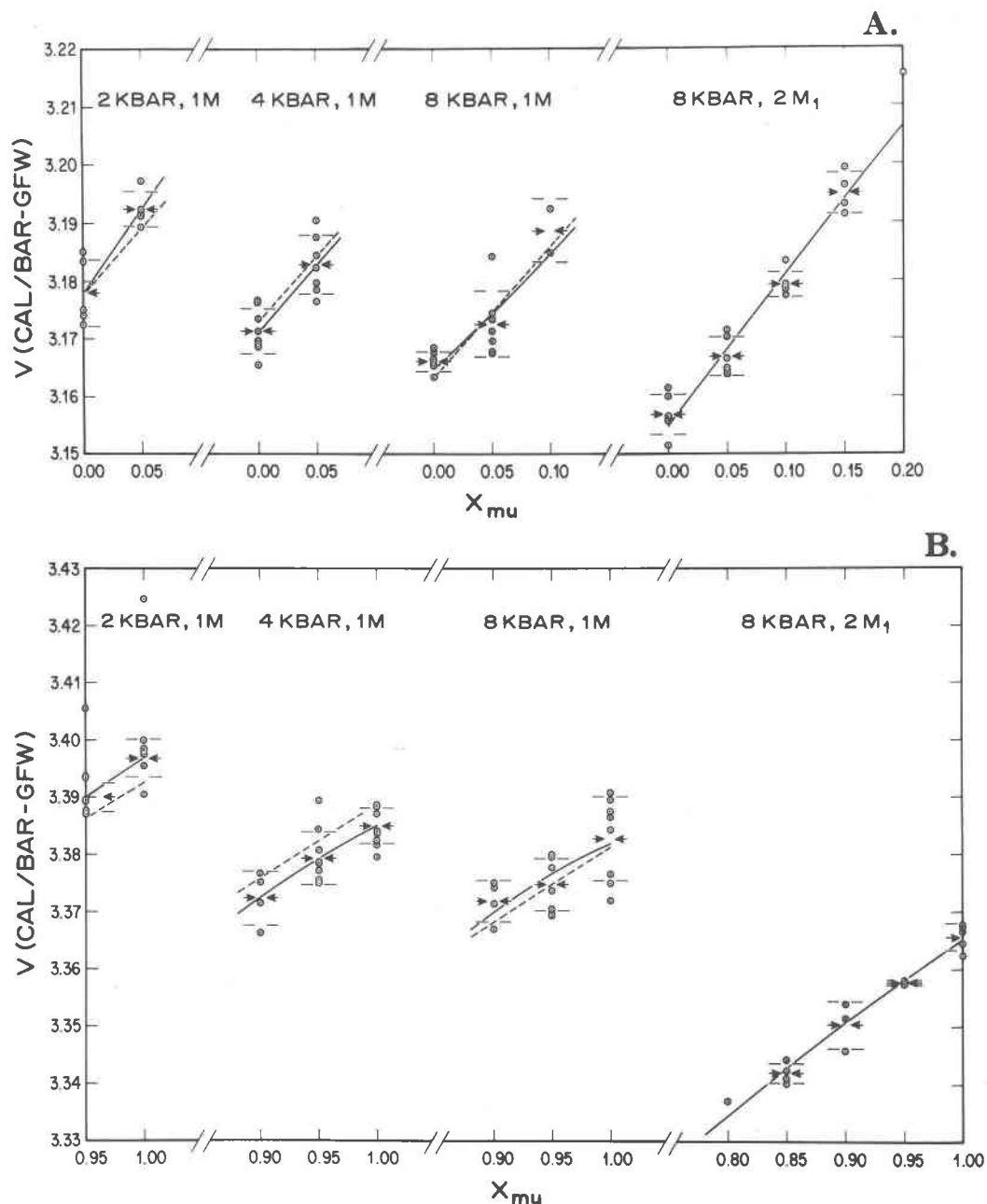
Fig. 1. Molal volume data and calculated molal volumes (cal/bar-gfw) for $1M$ and $2M_1$: A. paragonitic micas, and B. muscovitic micas synthesized at 2, 4, and 8 kbar pressure plotted against mole fraction $KAl_2(AlSi_3O_{10})(OH)_2$ (X_{mu}) in the micas. Molal volume data illustrated in this figure are listed in Table 1. Solid curves denote molal volumes calculated from the isobaric cubic equations listed in Table 2, section c, and straight dashed lines designate molal volumes calculated from the polybaric equations listed in Table 2, section b. Opposed arrows point to the mean value of a set of molal volume data, and short horizontal lines show the $e.s.d.$ (see Table 1).

which successful synthesis experiments could be conducted were restricted by: (1) crystallization of clay minerals at "low" temperatures (below 400°C), and (2) the upper thermal stabilities of the micas at "high" temperatures.

Micas synthesized at 2 and 4 kbar pressure are $1M$ polytypes. In the 8 kbar experiments, micas synthesized at low temperatures are $1M$, and with increased temperature, $1M$–$2M_1$ mixtures and finally just $2M_1$ polytypes were obtained. Only a small number of

diffraction maxima could be measured accurately for charges which contained the $1M$ and $2M_1$ polytypes in approximately equal proportions, mainly due to interferences and weak intensities of the reflections. Several of the cell refinements for these charges (for both the $1M$ and $2M_1$ structures) yielded somewhat aberrant molal volumes, so all molal volume data for samples with estimated $1M/2M_1$ ratios between $1:3$ and $3:1$ have been deleted from Table 1.

Molal volume data listed in Table 1 are plotted in Figure 1 according to mica composition, polytype, and pressure of synthesis. Important general characteristics of the data are evident from this figure and from the coefficients and statistics of least-squares fit polybaric equations for the molal volumes of the $1M$ Na-rich and K-rich micas (Table 2, sections a and b). Specifically, molal volume data illustrated in Figure 1 indicate that:

(1) For an Na-rich or K-rich mica of specified composition, the molal volume of the $2M_1$ polytype is slightly smaller than that of the $1M$ polytype. Differences between the molal volumes of the two polytypes are apparently somewhat larger for K-rich micas (≈ 0.02 cal/bar-gfw) than for Na-rich micas (≈ 0.01 cal/bar-gfw).

(2) Change in molal volume with X_{mu} (dV/dX_{mu}) is significantly larger for Na-rich micas than for K-rich micas.

(3) dV/dX_{mu} for Na-rich micas is essentially constant and the same for both $1M$ and $2M_1$ polytypes, and similarly, dV/dX_{mu} for K-rich micas is essentially constant and the same for both $1M$ and $2M_1$ polytypes.

Because the molal volume data indicate that dV/dX_{mu} for Na-rich micas is significantly larger than that for K-rich micas, molal volumes for $1M$ micas were subdivided into two groups—molal volumes for Na-rich micas and K-rich micas, and least-squares fit equations for each polybaric data set were calculated with X_{mu}, P, and T as independent variables (Table 2, section a). Coefficient $e.s.d.$'s for these equations indicate that the coefficients of the temperature terms are insignificant statistically, so a second set of equations was calculated with just X_{mu} and P as independent variables (Table 2, section b). The dependent variable (V) $e.s.d.$'s for this set of equations are essentially the same as those for the equations which included temperature as an independent variable, so the exclusion of T terms in the polybaric equations is considered to be justified. Coefficient $e.s.d.$'s of the X_{mu}–P equations are small, and plots of residuals versus (1) fitted molal volumes, (2) X_{mu},

and (3) P for each equation indicate no obvious systematic relationship between variance and values for these variables. Therefore, regression analysis indicates that: (1) the molal volume data for $1M$ Na-rich and K-rich micas do not justify polybaric equations more complex than those listed in Table 2, section b; and (2) there is a small, approximately linear decrease in the molal volumes of $1M$ micas (of given composition) with increased synthesis pressure.

In addition to the polybaric molal volume equations (one equation for each of the two single-phase fields), isobaric least-squares fit molal volume equations have been calculated for the 2, 4, and 8 kbar $1M$ micas and the 8 kbar $2M_1$ micas, using molal volume data from both single-phase fields at each of these pressures (Table 2, section c). These cubic equations were calculated for comparison with equation (1) for synthetic $1M$ micas (Eugster *et al.*, 1972) and equation (2) for synthetic and natural $2M_1$ micas (Chatterjee and Froese, 1975). Curves illustrating the relationship between molal volume and X_{mu} according to each of these equations are shown in Figure 2.

Excess molal volumes for Pa–Mu crystalline solutions have been calculated using the molal volume data listed in Table 1, equations (1) and (2), and the equations given in sections b and c of Table 2. Excess volumes listed in Table 1 were calculated using the relation

$$V^{ex}(\text{cal/bar-gfw}) = V - (X_{pa}V_{pa} + X_{mu}V_{mu}) \quad (4)$$

Data used to calculate each V^{ex} value were the composition (X_{pa} and X_{mu}) and molal volume (V) of the mica, and the molal volumes (V_{pa} and V_{mu}) for the $Pa_{1.00}Mu_{0.00}$ and $Pa_{0.00}Mu_{1.00}$ micas of identical structural type (polytype) crystallized at the same pressure and temperature (consequently, this method could not be used to calculate excess volumes for micas crystallized at temperatures above the upper thermal stability of end-member paragonite at a given pressure). Excess volumes for micas of identical composition, polytype, and synthesis pressure are grouped together in Table 1, and many of these sets of data contain both positive and negative excess volumes, or excess volumes of the same sign but significantly different magnitudes. This variability can be attributed largely to errors in the molal volume data, which are apparently of the same magnitude as the excess volumes.

To discern trends in the values of the excess volumes in Table 1 which are obscured by scatter in the data, and to utilize all the molal volume data in this table and not just those data obtained at temper-
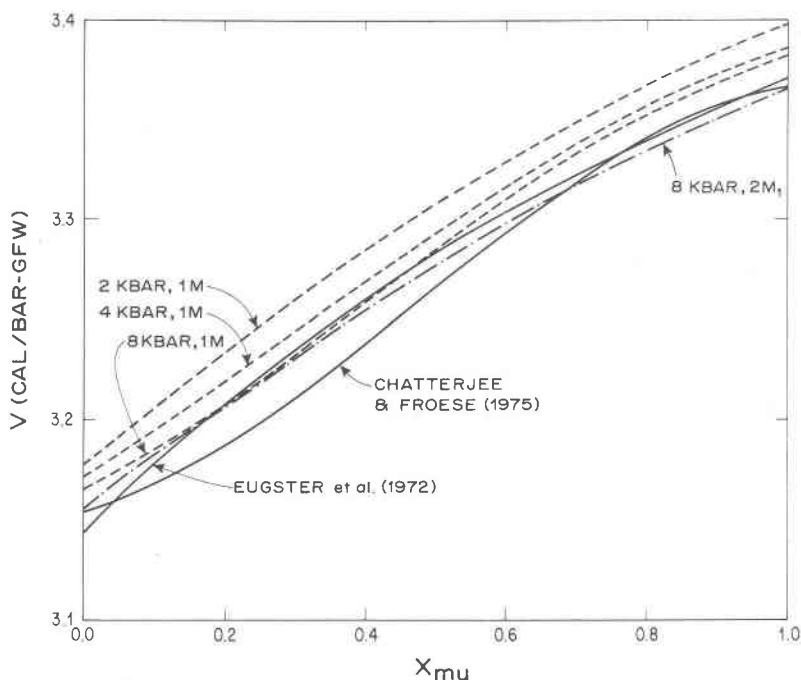
Fig. 2. Molal volumes (cal/bar-gfw) for Pa–Mu micas calculated from equations (1), (2), and the equations in Table 2, section c, plotted against mole fraction $KAl_2(AlSi_3O_{10})(OH)_2$ (X_{mu}) in the micas. Solid curves are for equations (1) (Eugster *et al.*, 1972) and (2) (Chatterjee and Froese, 1975), dashed curves denote molal volumes calculated from the isobaric cubic equations for 1M micas crystallized at 2, 4, and 8 kbar pressure, and the dash-dot curve designates molal volumes calculated from the isobaric cubic equation for $2M_1$ micas synthesized at 8 kbar pressure.

atures below the upper thermal stability of end-member paragonite at a given pressure, the equations in Table 2, sections b and c, have been used to obtain the molal volume values needed to calculate excess volumes according to equation (4). Figure 3 illustrates the relationship between V^{ex} and X_{mu} according to the equations in Table 2, section c, and equations (1) and (2). Each curve in this figure indicates similar positive excess volumes for K-rich micas. However, excess volumes for Na-rich micas range from positive, according to equation (1) (Eugster *et al.*, 1972) and the equations presented in this study, to negative according to equation (2) (Chatterjee and Froese, 1975). The equation for 1M micas synthesized at 8 kbar pressure in this study indicates slightly negative excess volumes in the range $0.0 < X_{mu} \leq 0.2$, but this is of questionable significance because the magnitudes of these excess volumes ($-0.002 \leq V^{ex}(cal/bar-gfw) < 0.0$) are smaller than the *e.s.d.* of molal volumes calculated from the equation (0.00533 cal/bar-gfw). Excess volumes calculated from the 1M polybaric equations in section b of Table 2 are similar to those for the 4 kbar 1M isobaric equation, and plots of these values versus X_{mu} would form straight

lines emanating from 0.0 cal/bar-gfw at $X_{mu} = 0.0$ and $X_{mu} = 1.0$ in Figure 3. Thus, at $X_{mu} = 0.2$, excess volumes calculated from these polybaric equations and equation (4) are 0.00260, 0.00240, and 0.00200 cal/bar-gfw at 2, 4, and 8 kbar pressure, respectively, while at $X_{mu} = 0.8$ these excess volumes are 0.01703, 0.01723, and 0.01763 cal/bar-gfw at 2, 4, and 8 kbar pressure, respectively. Therefore, although there is significant scatter in the molal volume data presented in this study, it is apparent from Figure 3 and the equations in section b of Table 2 that these data indicate small positive excess volumes for Pa–Mu micas over the entire compositional range.

Partial molal volumes for Pa–Mu crystalline solutions can be calculated using the relations

$$\bar{V}_{pa} = V - X_{mu} \frac{dV}{dX_{mu}} \qquad (5a)$$

and

$$\bar{V}_{mu} = V + X_{pa} \frac{dV}{dX_{mu}} \qquad (5b)$$

in which V and dV/dX_{mu} are calculated from a Pa–Mu molal volume equation. Figure 1 indicates that
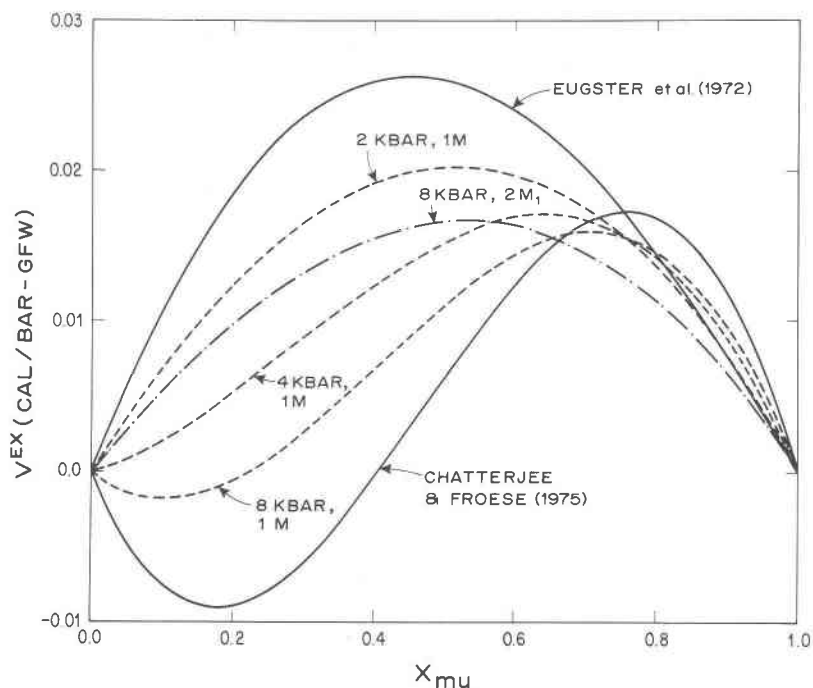
Fig. 3. Excess molal volumes (cal/bar-gfw) for Pa–Mu micas calculated from equations (1), (2), and the equations in Table 2, section c, plotted against mole fraction $KAl_2(AlSi_3O_{10})(OH)_2$ (X_{mu}) in the micas. Labelling of curves (solid, dashed and dash-dot) is in accordance with labelling described in the legend for Fig. 2.

dV/dX_{mu} is essentially constant in the two single-phase regions of the $NaAl_2(AlSi_3O_{10})(OH)_2$–$KAl_2(AlSi_3O_{10})(OH)_2$ system between 2 and 8 kbar pressure, so from equations (5) it is evident that $\bar{V}_{pa}$ in Na-rich micas is approximately equal to V_{pa}, and $\bar{V}_{mu}$ in K-rich micas is approximately equal to V_{mu} [$\bar{V}_{pa}$ in Na-rich micas is exactly equal to V_{pa}, and $\bar{V}_{mu}$ in K-rich micas is exactly equal to V_{mu}, if the equations in Table 2, section b are used to obtain V and dV/dX_{mu} for equations (5)]. On the other hand, the different dV/dX_{mu} for paragonitic and muscovitic micas indicate that $\bar{V}_{mu}$ in Na-rich micas is slightly larger than V_{mu}, and $\bar{V}_{pa}$ in K-rich micas is significantly larger than V_{pa}.

Discussion

As discussed previously, the data in Table 1 indicate that molal volumes of $1M$ Pa–Mu micas decrease with increased synthesis pressure. The effect of synthesis pressure on unit-cell parameters of several different micas has been described previously by Crowley and Roy (1960), and for $1M$ muscovite they suggested that contraction of the unit cell with increased synthesis pressure can be attributed to tetrahedral Al–Si ordering accompanied by collapse of silica tetrahedra into the vacant octahedral site. The

$1M$ Pa–Mu molal volume data listed in Table 1 are not inconsistent with this hypothesis, but molal volume data alone do not provide a definitive test. Furthermore, $2M_1$ Pa–Mu polytypes crystallized in this investigation were obtained only in 8 kbar experiments, so it is uncertain that synthesis pressure has any effect on the molal volumes of these micas.[8] Therefore, while the data of this study indicate that molal volumes of $1M$ Pa–Mu micas decrease with increased synthesis pressure, the cause(s) and implications of this phenomenon are poorly understood.

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[8] Data presented by Chatterjee (1974, Table 2) indicate that the molal volume of synthetic $2M_1$ end-member paragonite may decrease very slightly with increased synthesis pressure. However, while his data are very precise they are far too few in number (3) to be conclusive, and molal data for $2M_1$ end-member paragonite synthesized in this study are too scattered for meaningful comparison with Chatterjee's data. Molal volume data for $2M_1$ end-member muscovite synthesized at various pressures also is scanty and inconclusive, and the writer is unaware of molal volume data for synthetic $2M_1$ paragonite-muscovite crystalline solutions other than those presented here. Apart from the question of whether molal volumes of $2M_1$ Pa–Mu micas decrease with increased synthesis pressure, and in contrast to the conclusions drawn by Crowley and Roy (1960) for synthetic $1M$ muscovite, Chatterjee and Johannes (1974, p. 111) argue that refinements of the crystal structure of natural $2M_1$ muscovites and theoretical considerations both indicate that there is no tetrahedral Al–Si ordering in these micas.

Curves illustrated in Figure 2 indicate major disparities between the molal volume data of Eugster *et al.* (1972), Chatterjee and Froese (1975), and this study. These disparities are much larger than the *e.s.d.*'s of molal volumes calculated from equations (1) and (2) (see "Previous investigations") and the isobaric cubic equations of this study (Table 2, section c). However, differences between the curves are considered to be only semi-quantitative for two principal reasons:

(1) The positions of the curves probably are meaningful only in the compositional ranges near the end members. This is so because: (a) the curves are based upon data that were obtained largely or entirely in the compositional ranges $0.0 \leq X_{mu} \leq 0.15$ and $0.85 \leq X_{mu} \leq 1.00$; and (b) Pa–Mu micas with compositions in the range $0.30 \leq X_{mu} \leq 0.60$ are unstable, except perhaps at pressures and temperatures above 8 kbar and 685°C.

(2) Coefficient *e.s.d.*'s for the cubic molal volume equations of this study (Table 2, section c) suggest that three of these four equations contain at least one more term than the data justify, and the fourth equation (for 8 kbar $1M$ micas) has rather large *e.s.d.*'s for the coefficients of both the quadratic and cubic terms. Therefore, the molal volume data of this study have been "overfit" in the calculation of these cubic equations.

These reservations notwithstanding, qualitative differences between the curves in Figure 2 are believed to be real and significant. Differences between the curves for $1M$ micas synthesized at 2, 4, and 8 kbar pressure in this study can be attributed mainly to decreases in the molal volumes of $1M$ micas with increased synthesis pressure. However, the positions of these curves and the equations in Table 2, section b, suggest that the effect of synthesis pressure will be negligible over small pressure ranges (less than 500 bars or so), and this indicates that the significant discrepancies between the 2.07 kbar $1M$ molal volume curve of Eugster *et al.* (1972) and the 2 kbar $1M$ curve of this study cannot be attributed to the very slight difference in synthesis pressure. As noted previously, the molal volume data plotted in Figure 1 imply that the $2M_1$ structure is slightly more dense than the $1M$ structure, and this largely explains the differences between the 8 kbar $1M$ and $2M_1$ curves of this study. However, it is apparent that discrepancies between the $1M$ curve of Eugster *et al.* (1972) and the $2M_1$ curve of Chatterjee and Froese (1975) are not readily explained by differences between the densities of the two polytypes. The two curves for $2M_1$ micas

(this study, and Chatterjee and Froese, 1975) give essentially the same values at $X_{mu} = 0.0$ and $X_{mu} = 1.0$, and they are in fairly good agreement for K-rich micas, but the curve of Chatterjee and Froese indicates considerably smaller molal volumes for Pa–Mu micas with compositions in the range $0.05 \leq X_{mu} \leq 0.50$. Both curves give essentially the same values at $X_{mu} = 0.0$ and $X_{mu} = 1.0$, because two of the seven molal volume values that Chatterjee and Froese used to calculate equation (2) were: (1) the molal volume of synthetic $2M_1$ end-member paragonite (3.1545 ± 0.0012 cal/bar-gfw) given by Chatterjee (1974), and (2) the molal volume of synthetic $2M_1$ end-member muscovite (3.3654 ± 0.0007 cal/bar-gfw) presented by Chatterjee and Johannes (1974), and these values are in excellent agreement with the molal volume data for these micas given in this study (Table 1 and Fig. 1). The other (five) values that Chatterjee and Froese used were molal volumes for natural paragonite–muscovite crystalline solutions, so disparities between the two $2M_1$ curves can be attributed almost entirely to inconsistencies between these data and the molal volume data for $2M_1$ Pa–Mu crystalline solutions presented in this paper.

The appreciable discrepancies between the molal volume data of Eugster *et. al.* (1972), Chatterjee and Froese (1975), and this study indicate significant inaccuracies in the data of at least two of the three investigations. Molal volumes calculated by Eugster *et al.* may be inaccurate because only part of their data were obtained from unit-cell refinements, the rest having been calculated "indirectly" using d_{001} values and a least-squares fit polynomial equation for the product of the a and b unit-cell parameters obtained from refinements [Eugster *et al.,* 1972, equation (5)]. Molal volume data for natural paragonite–muscovite micas that Chatterjee and Froese used may be inaccurate because these micas contain various amounts of "minor impurities" (Chatterjee and Froese, 1975, Table 3), and the molal volume of each of these micas may be measurably different from the molal volume of a $2M_1$ Pa–Mu mica with the same Na/K ratio. There also is considerable scatter in the $1M$ Pa–Mu molal volume data of the present investigation which can be attributed principally to poor crystallinity of these micas.

This analysis of available molal volume data for Pa–Mu micas suggests that there are many uncertainties involved in calculating excess molal volumes from these data. Data of this study indicate that molal volumes of $1M$ Pa–Mu micas decrease with increased synthesis pressure, and the 2, 4, and 8 kbar

isobaric equations in Table 2, section c, give modestly different calculated V^{ex} vs. X_{mu} curves (Fig. 3). Therefore, it is possible but unlikely that excess volumes of $1M$ paragonitic micas change significantly with pressure. It also is uncertain whether V^{ex} vs. X_{mu} curves for $1M$ and $2M_1$ Pa–Mu micas should be nearly identical, although this seems likely (the previously described, slightly different densities of the two polytypes indicate but do not require slightly different V^{ex} vs. X_{mu} curves for $1M$ and $2M_1$ Pa–Mu micas). Furthermore, curves illustrated in Figure 3 indicate that excess volumes of paragonite–muscovite micas are small (less than $\pm$ 0.03 cal/bar-gfw), so accuracies of calculated Pa–Mu excess volumes can be affected significantly by "minor" errors in the molal volume data used to calculate the excess volumes. In view of these difficulties it is somewhat surprising that there are only slight differences between the excess volume curves for the $1M$ and $2M_1$ Pa–Mu micas crystallized in this study.

Thermodynamic and petrologic applications

In several previous investigations, molal volume data for paragonite–muscovite micas have been used in accordance with the two-parameter Margules solution model to calculate various phase relations involving these micas; for example, P–T–X limits for coexistence of Pa–Mu pairs, and Pa–Mu phase relations in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–Al_2O_3–SiO_2–H_2O (Eugster et al., 1972; Chatterjee and Froese, 1975). In these investigations molal volume data were used to calculate W_{V1} and W_{V2} coefficients of pressure terms for the Margules equations

$$W_{G1} = W_{G,pa} = W_{E1} - W_{S1}T + W_{V1}P \quad (6a)$$

and

$$W_{G2} = W_{G,mu} = W_{E2} - W_{S2}T + W_{V2}P \quad (6b)$$

As described by Waldbaum and Thompson (1968, p. 2001–2002), the W_V coefficients for equations (6) can be derived by using molal volume data to calculate a cubic equation of the form

$$V(\text{cal/bar-gfw}) = A + BX_2 + CX_2^2 + DX_2^3 \quad (7)$$

such as equation (2) in which $X_{mu} = X_2$, and subsequently calculating W_{V1} and W_{V2} from equation (7) using the relations

$$W_{V1} = -(C + 2D) \quad (8a)$$

and

$$W_{V2} = -(C + D) \quad (8b)$$

[Waldbaum and Thompson, 1968, equations (11a)]. Eugster et al. (1972) and Chatterjee and Froese (1975) employed this method for deriving W_V values, because the 2.07 kbar Pa–Mu two-phase data of Eugster et al. and equations (87a) and (87b) of Thompson (1967) were sufficient to derive W_E and W_S coefficients for equations (6), but W_V values cannot be calculated from two-phase data obtained at just one pressure, and solvus data at pressures other than 2.07 kbar were unavailable to them. As discussed by Eugster et al. (1972), Thompson (1974), and Chatterjee and Froese (1975), the principal petrologic applications of calculated Pa–Mu phase relations are to medium-grade and high-grade Ca-deficient pelitic schists for estimation of (1) final equilibration temperatures of paragonite–muscovite pairs, and (2) P–T stabilities of paragonite–muscovite crystalline solutions.

Three important implicit assumptions are associated with the calculation of W_V values from equations (7) and (8), incorporation of these values into equations (6), and subsequent employment of equations (6) to compute excess properties or phase relations for binary crystalline solutions. These assumptions are:

(1) Molal volume data for the crystalline solutions are very accurate, and consequently, there can be only small errors in the C and D coefficients of equation (7) and in the W_V's calculated from these coefficients.

(2) W_V values are constants, that is, excess volumes of the crystalline solutions are not a function of pressure and/or temperature.

(3) Nonideality of the crystalline solutions can be represented accurately by the two-parameter Margules solution model, that is, by the excess properties (not just V^{ex}) calculated using equations (6) and/or appropriate derivatives of these equations.
Subsequent discussion examines the first two assumptions as they apply to paragonite–muscovite molal volume data.

Considering the sets of data on molal volumes of paragonite–muscovite crystalline solutions presented to date, it is uncertain that the first assumption holds for any of these data. W_V values for Pa–Mu micas are listed in the last footnote to Table 2, and this listing shows significant differences between the four pairs of W_V's calculated from the molal volume data of this study and the pairs of W_V's presented by Eugster et al. (1972) and Chatterjee and Froese (1975). Therefore, as discussed previously, there must be significant inaccuracies in the molal volume data of at least

two of the three investigations. Figure 3 illustrates that excess volumes calculated from equations (1) and (2) are the most different, and W_V values derived from these equations are: equation (1), $W_{V1} = 0.0822$, $W_{V2} = 0.1259$; and equation (2), $W_{V1} = 0.1590$, $W_{V2} = -0.1090$. W_V values calculated from equation (1), along with W_E and W_S coefficients derived from the 2.07 kbar Pa–Mu two-phase data of Eugster *et al.* (1972), yield the following polybaric, polythermal Margules mixing-parameter equations:

$$W_{G1}(\text{cal/gfw}) = W_{G,\text{pa}}$$

$$= 3082.1 + 0.1698T(\text{K}) + 0.0822P(\text{bars}) \quad (10a)$$

and

$$W_{G2}(\text{cal/gfw}) = W_{G,\text{mu}}$$

$$= 4163.9 + 0.3954T(\text{K}) + 0.1259P(\text{bars}) \quad (10b)$$

Chatterjee and Froese (1975) modified equations (10) in accordance with the W_V values calculated from equation (2) to obtain

$$W_{G1}(\text{cal/gfw}) = W_{G,\text{pa}}$$

$$= 2923.1 + 0.1698T(\text{K}) + 0.1590P(\text{bars}) \quad (11a)$$

and

$$W_{G2}(\text{cal/gfw}) = W_{G,\text{mu}}$$

$$= 4650.1 + 0.3954T(\text{K}) - 0.1090P(\text{bars}) \quad (11b)$$

The writer used equations (10) and (11) and the methods of Luth and Fenn (1973) to calculate the following compositions for Pa–Mu pairs at 8 kbar pressure and 670°C: from equations (10), $Pa_{0.923}Mu_{0.077}–Pa_{0.198}Mu_{0.802}$; and from equations (11), $Pa_{0.772}Mu_{0.228}–Pa_{0.203}Mu_{0.797}$. Therefore, 8 kbar Pa–Mu solvi calculated from equations (10) and (11) are significantly different, and this difference is directly attributable to the different W_V values in the two pairs of equations. This demonstrates that inaccuracies in molal volume data can be manifest not only in the W_V values for Pa–Mu micas calculated from an equation of the form of (7), but also in Pa–Mu excess properties or phase relations calculated from equations of state which contain these W_V values.

Previous investigators (Eugster *et al.*, 1972; Thompson, 1974; Chatterjee and Froese, 1975) have assigned constant values to the W_V's in equations of state for Pa–Mu micas. However, the molal volume data for $1M$ micas synthesized at 2, 4, and 8 kbar pressure in this study indicate that $W_{V1} (= W_{V,\text{pa}})$ increases and $W_{V2} (= W_{V,\text{mu}})$ decreases with increased

synthesis pressure (see last footnote to Table 2). If these systematic changes in W_V values for $1M$ Pa–Mu micas are valid, and if W_V's for $2M_1$ Pa–Mu micas are affected similarly by synthesis pressure, then assigning constant values to the W_V's in equations of state for Pa–Mu micas may produce significant errors in thermodynamic or phase-equilibrium calculations in which pressure is a variable. However, differences between the pairs of W_V values for the $1M$ micas are simply a reflection of differences between the C and D coefficients of the 2, 4, and 8 kbar isobaric molal volume equations for these micas listed in Table 2, section c, and the comparatively large *e.s.d.*'s for many of the coefficients (some are larger than the coefficients themselves) suggest that disparities between the W_V's can be attributed largely to scatter in the molal volume data.[9] Furthermore, $2M_1$ polytypes crystallized in this investigation were obtained only in 8 kbar experiments, so it also is uncertain that synthesis pressure has any effect on W_V's for these micas. The writer concludes that it remains to be demonstrated that W_V's for Pa–Mu micas are not essentially constant at pressures up to 8 kbar.

Another and perhaps more well-known procedure for obtaining W_V values involves the calculation of least-squares fit equations of the form of equations (6), using W_G values calculated from the compositions of binary solvus-pairs synthesized at two or more pressures and temperatures (Thompson and Waldbaum, 1969). This method has the advantage that it avoids the difficult problem of obtaining highly accurate molal volume data to derive W_V values, and it also may provide an opportunity to determine whether W_V's are constant or variable for the crystalline solutions. However, W_V values calculated from solvus data are affected by errors in the measured compositions of the phases in the solvus-pairs, and it has not been established just how sensitive such W_V values will be to "typical" compositional inaccuracies for the phases (*e.g.*, $\pm$ 2–3 mole percent). (Of course, accuracies of W_V values also are diminished if equilibrium is not achieved in the two-phase experiments.) The writer will present two-phase data for

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[9] It should be recognized that systematic decreases in the molal volumes of $1M$ micas with increased synthesis pressure (which the equations in Table 2, section b, suggest) do not require systematic changes in the W_V values for these micas. As shown by Waldbaum and Thompson (1968, Fig. 1), the W_V value for a component i ($W_{V,i}$) represents the difference between the partial molal volume of the component at infinite dilution ($\bar{V}_i^*$) and the molal volume of the pure component (V_i). Consequently, if $\bar{V}_i^*$ and V_i change by the same amount $W_{V,i}$ will remain constant.

Pa–Mu micas in a subsequent publication, and W_V values calculated from these data will be compared with W_V's calculated from molal volume data in that report. However, it should be noted here that Blencoe and Luth (1973) used two-phase data to derive tentative W_V's for Pa–Mu micas, and both of these W_V's are negative (see last footnote to Table 2). Negative values for both $W_{V,pa}$ and $W_{V,mu}$ imply negative excess volumes for Pa–Mu micas over the entire compositional range, and this is inconsistent with the molal volume data presented in this paper. This inconsistency indicates that the effect of inaccuracies in two-phase data on W_V values calculated from such data should be examined in detail.

Acknowledgments

References

Akella, J. and G. C. Kennedy (1971) Melting of gold, silver and copper—proposal for a new high-pressure calibration scale. *J. Geophys. Res., 76*, 4969–4977.

Appleman, D. E. and H. T. Evans, Jr. (1973) Job 9214: Indexing and least-squares refinement of powder diffraction data. *Natl. Tech. Inf. Serv., U.S. Dept. Commer.*, Springfield, Virginia, Document PB 216 188.

Blencoe, J. G. (1973) Least-squares linear regression equations for determining compositions of synthetic muscovite and paragonite crystalline solutions (abstr.). *Geol. Soc. Am. Abstr. with Programs, 5*, 553.

——— (1975) Rectangular plot subroutine (RECPLT). Contributed program, The Pennsylvania State University Computation Center. 16 p.

——— (1976) RECPLT and TRIPLT: FORTRAN printer-plotting routines for rectangular and triangular plots. *Computers & Geosciences, 2*, 171–194.

——— and W. C. Luth (1973) Muscovite–paragonite solvi at 2, 4 and 8 kb pressure (abstr.). *Geol. Soc. Am. Abstr. with Programs, 5*, 553–554.

Boettcher, A. L. and D. M. Kerrick (1971) Temperature calibration in cold-seal pressure vessels. In G. C. Ulmer, Ed., *Research*

Techniques for High Pressure and High Temperature, p. 179–193. Springer-Verlag, New York.

Burnham, C. W. and E. W. Radoslovich (1964) Crystal structures of coexisting muscovite and paragonite. *Carnegie Inst. Wash. Year Book, 63*, 232–236.

Chatterjee, N. D. (1970) Synthesis and upper stability of paragonite. *(Contrib. Mineral. Petrol., 27*, 244–257.

——— (1974) X-ray powder pattern and molar volume of synthetic $2M$-paragonite: a refinement. *Contrib. Mineral. Petrol., 43*, 25–28.

——— and W. Johannes (1974) Thermal stability and standard thermodynamic properties of synthetic $2M_1$-muscovite, $KAl_2[AlSi_3O_{10}(OH)_2]$. *Contrib. Mineral. Petrol., 48*, 89–114.

——— and E. Froese (1975) A thermodynamic study of the pseudobinary join muscovite–paragonite in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–Al_2O_3–SiO_2–H_2O. *Am. Mineral., 60*, 985–993.

Crowley, M. S. and R. Roy (1960) The effect of formation pressures on sheet structures—a possible case of Al–Si ordering. *Geochim. Cosmochim. Acta, 18*, 94–100.

Daniel, C. and F. S. Wood (1971) *Fitting Equations to Data.* John Wiley and Sons, New York.

Deming, W. E. (1943) *Statistical Adjustment of Data.* John Wiley and Sons, New York.

Draper, N. R. and H. Smith, Jr. (1966) *Applied Regression Analysis.* John Wiley and Sons, New York.

Efroymson, M. A. (1960) Multiple regression analysis. In A. Ralston and H. S. Wilf, Eds., *Mathematical Methods for Digital Computers*, p. 191–203. John Wiley and Sons, New York.

Eugster, H. P., A. L. Albee, A. E. Bence, J. B. Thompson, Jr., and D. R. Waldbaum (1972) The two-phase region and excess mixing properties of paragonite–muscovite crystalline solutions. *J. Petrol., 13*, 147–179.

Fujii, T. (1966) *Muscovite–Paragonite Equilibria.* Ph.D. Thesis, Harvard University, Cambridge, Massachusetts.

Güven, N. (1971) The crystal structures of $2M_1$ phengite and $2M_1$ muscovite. *Z. Kristallogr., 134*, 196–212.

Joiner, B. L. and J. R. Rosenblatt (1971) Some properties of the range in samples from Tukey's symmetric lambda distributions. *J. Am. Stat. Assoc., 66*, 394–399.

Luth, W. C. and O. F. Tuttle (1963) Externally heated cold-seal pressure vessels for use to 10,000 bars and 750°C. *Am. Mineral., 48*, 1401–1403.

——— and C. O. Ingamells (1965) Gel preparation of starting materials for hydrothermal experimentation. *Am. Mineral., 50*, 255–258.

——— and F. Querol-Suñé (1970) An alkali feldspar series. *Contrib. Mineral. Petrol., 25*, 25–40.

——— and P. M. Fenn (1973) Calculation of binary solvi with special reference to the sanidine-high albite solvus. *Am. Mineral., 58*, 1009–1015.

Orville, P. M. (1967) Unit-cell parameters of the microcline-low albite and the sanidine-high albite solid-solution series. *Am. Mineral., 52*, 55–86.

Roberts, H. S. (1924) Some new standard melting points at high temperatures. *Phys. Rev., 23*, 386–395.

Rothbauer, R. (1971) Untersuchung eines $2M_1$ Muskovits mit Neutronenstrahlen. *Neues Jahrb. Mineral. Monatsh.*, 143–154.

Thompson, A. B. (1974) Calculation of muscovite–paragonite–alkali feldspar phase relations. *Contrib. Mineral. Petrol., 44*, 173–194.

Thompson, J. B., Jr. (1967) Thermodynamic properties of simple

solutions. In P. H. Abelson, Ed., *Researches in Geochemistry*, Vol. 2, p. 340–361. John Wiley and Sons, New York.

—— and D. R. Waldbaum (1969) Mixing properties of sanidine crystalline solutions: III. Calculations based on two-phase data. *Am. Mineral., 54,* 811–838.

Tuttle, O. F. (1949) Two pressure vessels for silicate-water studies. *Bull. Geol. Soc. Am., 60,* 1727–1729.

Waldbaum, D. R. and J. B. Thompson, Jr. (1968) Mixing properties of sanidine crystalline solutions: II. Calculations based on volume data. *Am. Mineral., 53,* 2000–2017.

Yoder, H. S., Jr. (1950) High-low quartz inversion up to 10,000 bars. *Trans. Am. Geophys. Union, 31,* 827–835.

—— and H. P. Eugster (1955) Synthetic and natural muscovite. *Geochim. Cosmochim. Acta, 8,* 225–280.

Zen, E-an, M. Ross and P. Bearth (1964) Paragonite from Täsch Valley near Zermatt, Switzerland. *Am. Mineral., 49,* 183–190.