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ON THE SOLUBILITY OF ALBITE IN SUPERCRITICAL WATER IN THE RANGE 400 to 600°C and 750 to 3500 BARS

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ABSTRACT. The results of 64 determinations of the solubility of albite by a dynamic method are reported. The departures from equilibrium were experimentally evaluated. The solute, up to 0.3 percent by weight, is not isochemical with albite at any pressure or temperature in the range examined. The size and type of departures from isochemistry depend on pressure, temperature, and the rate of collection of the solutions. The solubility of albite in supercritical water can be quantitatively described by equations derived for non-ideal reaction mixtures. Qualitative calculations indicate that solutions may play an important petrologic role in regions surrounding dehydrating rock masses.

INTRODUCTION

A great many experimental systems of geologic interest contain one or more aqueous fluid phases. Experimental petrology however has generally concentrated on the solid phases, and relatively little is known about composition and properties of the coexisting aqueous solutions. The pioneering work of Morey and Hesselgesser (1951) and of Orville (1963) has shown that solutions in equilibrium with feldspars at elevated temperatures and pressures can produce important petrologic consequences. The present communication forms part of a systematic study of the solubility of the feldspars.

EXPERIMENTAL METHOD

Solubility was determined by a dynamic method similar to that of Morey and Hesselgesser (1951), utilizing two pressure vessels of Inconel X-750 with modified Bridgman seals and capacities of 80 and 120 milliliters respectively. The bomb, approximately 12 inches long, was placed in the central part of a 36 inch horizontal tube furnace whose temperature was adjusted by a recording controller connected to an iron-constantan thermocouple at the entrance to the bomb. A similar thermocouple at the exit of the bomb provided a check on the temperature, and reading of the two thermocouples did not differ by more than 3°C for any runs reported. Exploration at atmospheric pressure showed the interior of the bomb to be within 3°C of the temperature of the entrance thermocouple.

An air operated hydraulic pump, capable of maintaining 3500 bars pressure pumped distilled water through a 65 micron filter, into a heating tube, and thence into the bomb. Pressure, measured on a 12 inch Heise Bourdon gauge, fluctuated less than 25 bars during a run. The
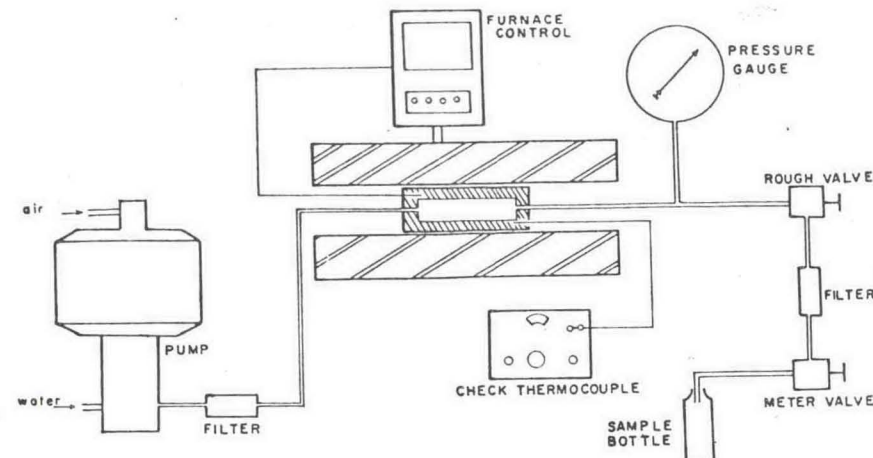
Fig. 1. Schematic diagram of the experimental apparatus.

solutions passed from the bomb into an 18 inch cooling tube, through a metering valve into polyethylene bottles. Approximately one liter was collected at rates varying from 40 to 60 milliliters per hour. A diagram of the apparatus is shown in figure 1.

Albite pegmatite from Amelia County Court House, Virginia, was used as experimental material so that the results could be compared with previous work on the same material by Morey and Hesselgesser (1951). The raw material, procured from Ward's, was crushed, and the fraction passing a four mesh screen and retained on an eight mesh screen used for experiment. Prior to a run the material was washed successively with dilute HCl and distilled water and handpicked to remove small amounts of white mica adhering to the cleavage fragments. A chemical analysis of the experimental material is given in table 1.

TABLE 1

Chemical analysis of experimental material

SiO_2	68.0
Al_2O_3	19.8
Fe_2O_3	0.09
CaO	0.22
MgO	0.04
Na_2O	11.42
K_2O	0.32
H_2O	0.03
	99.9

Analysts: G. R. Lachance, J. L. Bouvier

Assuming that all the magnesium and iron are in the An molecule the analysis computes to feldspar of composition $Ab_{97.5} An_{1.1} Or_{1.4}$.

ANALYTICAL METHODS

The experimental solutions were analyzed for silica, alumina, soda, potash, lime, iron, organic matter, and pH. Gravimetric analysis by the method of double evaporation was used to determine silica (Kolthoff

and Santell, 1952, p. 387) and yielded reproducible results. The molybdate method of determination which is easier and more rapid (Am. Soc. Testing Materials, Pub. 148D, 1959, p. 278) gave much lower and erratic values, even after digestion of the sample Na_2CO_3. When the sample was digested overnight in NaOH, the molybdate method gave results in fair agreement with gravimetric results.

Gravimetric analysis for alumina gave reliable and reproducible results but required large amounts of time and sample. Titration with EDTA was used in the later stages of the reported experiments and gave comparable results.

Soda and potash were determined by flame photometer after tenfold dilution of the sample. Analysis failed to detect calcium in any
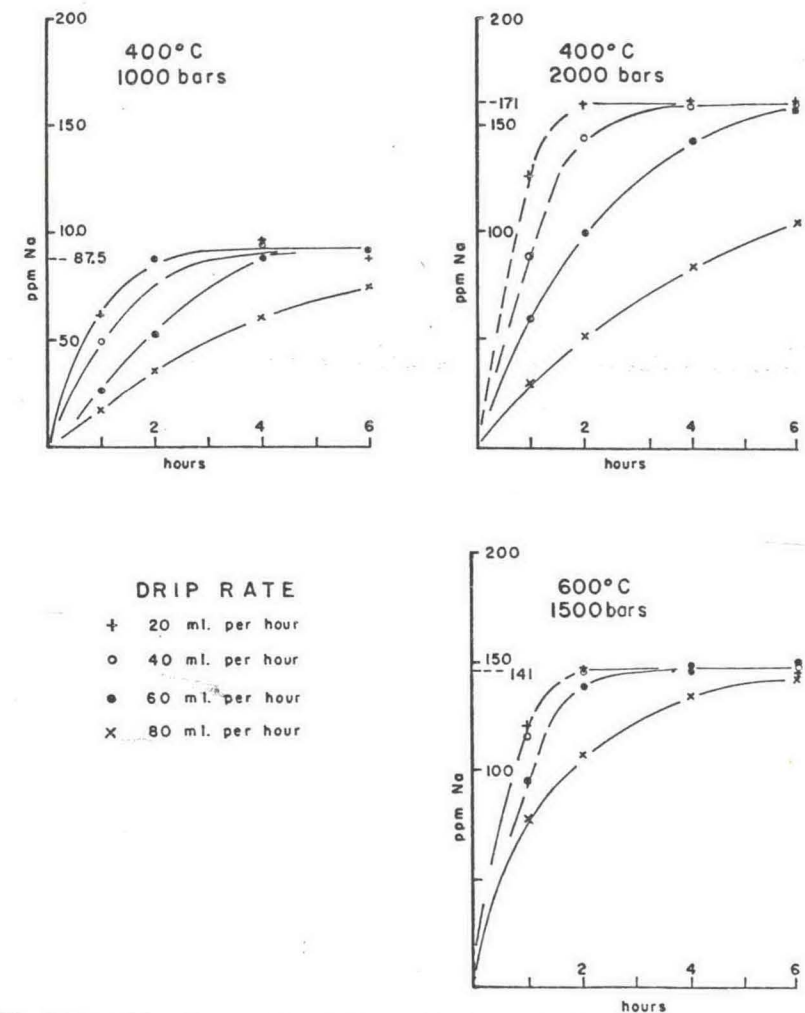
Fig. 2. Rate of attainment of a steady state by albite solutions. Na content in ppm.

TABLE 2

Sodium content of solutions collected at various flow rates

Run No.	T (°C)	P (bars)	Flow rate ml/per hr	Hrs of run when sample collected	Na ppm
A-1	1000	400	20	0-1	62
				1-2	86
				2-4	96
				4-6	84
A-2			40	0-1	50
				1-2	87
				1-4	93
				4-6	91
A-3			60	0-1	27
				1-2	53
				2-4	87
				4-6	89
A-4			80	0-1	18
				1-2	36
				2-4	62
				4-6	76
A-5	2000	400	20	0-1	126
				1-2	161
				2-4	163
				4-6	162
A-6			40	0-1	90
				1-2	145
				2-4	161
				4-6	160
A-7	2000	400	60	0-1	62
				1-2	102
				2-4	144
				4-6	159
A-8			80	0-1	30
				1-2	52
				2-4	84
				4-6	105
A-9	1500	600	20	0-1	120
				1-2	148
				2-9	146
				4-6	144
A-10			40	0-1	116
				1-2	143
				2-9	146
				4-6	147
A-12			60	0-1	96
				1-2	139
				2-4	150
				4-6	151
A-13			80	0-1	79
				1-2	108
				2-4	137
				4-6	142

of the samples. Iron appeared sporadically in concentrations up to 0.12 ppm, presumably as a result of corrosion of the pressure vessel. Organic matter was not detected in any samples, indicating that lubricating material from the pump does not contaminate the pumped fluid to any detectable extent. pH was measured periodically during a run on 5 milliliters of sample collected directly from the sampling tube. After the first hour of a run, the pH rarely changed by more than 0.05.

EXPERIMENTAL RESULTS

The results of experiments designed to test the rate at which a steady state is reached are tabulated in table 2 and shown graphically in figure 2. The charge was brought to temperature in about 20 to 30 minutes, then pumped up to pressure, and collection of the sample begun at the rate indicated. Every hour the collected sample was analyzed for soda content. The results show that at collection rates of less than 60 milliliters per hour a steady state is reached in a few hours. In the absence of flow, the system would probably reach a steady state in less than 2 hours at both 400° and 600°C. The influence of pressure on this time appears to be slight.

These results suggested the following procedure which was adopted for the solubility runs. The charge of approximately 120 grams was brought to temperature and pressure and held there overnight under static conditions. Sample collection was then commenced at a rate of 50
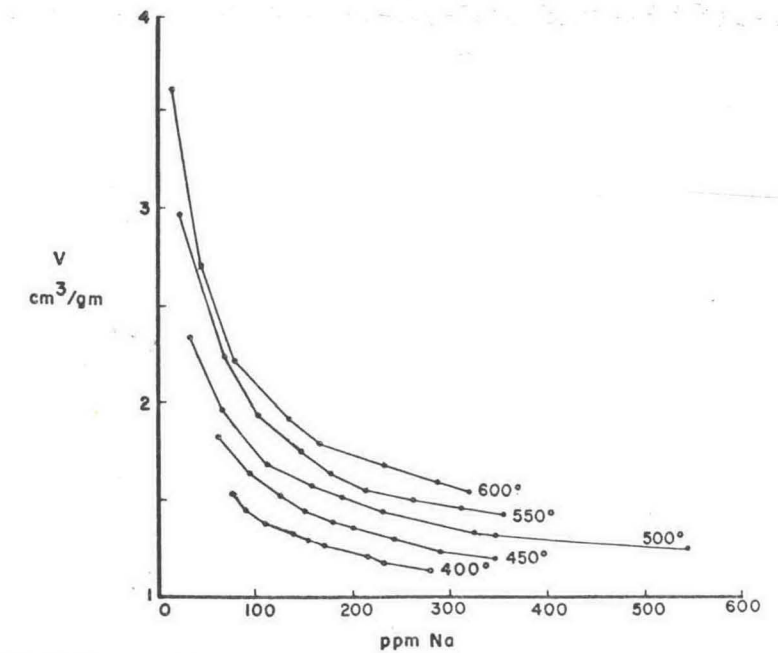
Fig. 3. Content of sodium in albite solutions at various temperatures and pressures. V is specific volume of water in cubic centimeters per gram.

milliliters per hour. Various imperfections in the valves caused the actual rate to vary from 40 to 60 milliliters per hour. Run A41 used as a starting fluid 5 liters of solution collected at 600°/2000 bars. The fact that the analysis of run A41 agrees with that of run A42, which used distilled water as a starting fluid, suggests that equilibrium is closely approached by the steady state achieved during the runs.

Runs A70 and A73 are duplicate runs conducted on different days on different charges. They suggest that analytical results for a given temperature and pressure are reproducible within about 10 percent of the amount present for soda and alumina and about 5 percent for silica.

The results of 44 experimental runs are tabulated in table 3 and figures 3, 4, and 5. Two results of Morey and Hesselgesser (1951), which fall in the range of the present experiments, are also tabulated and agree with the newer runs within experimental error.

The solutions are clear and colorless and display remarkable stability at room temperature if kept sealed. Sample A50 has been analyzed at intervals of about two months for more than 2 years and still yields results in agreement with the original analysis, although it contains 2415 ppm silica and 532 ppm alumina. The solutions are moderately to strongly alkaline when fresh, but the pH slowly declines with age to values between 7 and 8. Titration curves of the solutions with 0.01 normal HCl show a slight break at pH 8.3, suggesting the presence of silicate ion. Lowering the pH of the solutions below about 4.0 causes rapid precipitation of alumina and silica.
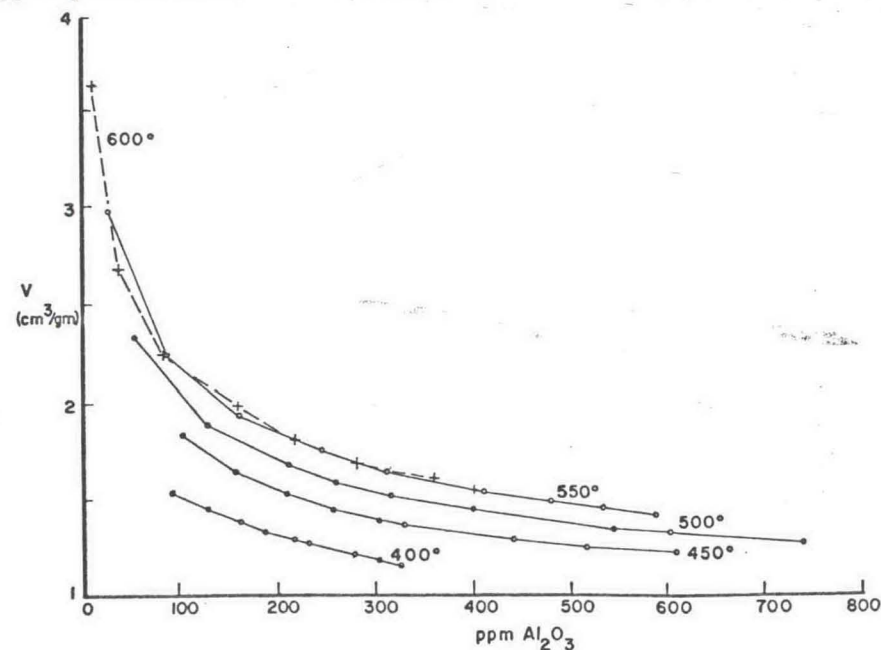
Fig. 4. Content of alumina in albite solutions at various temperatures and pressures.
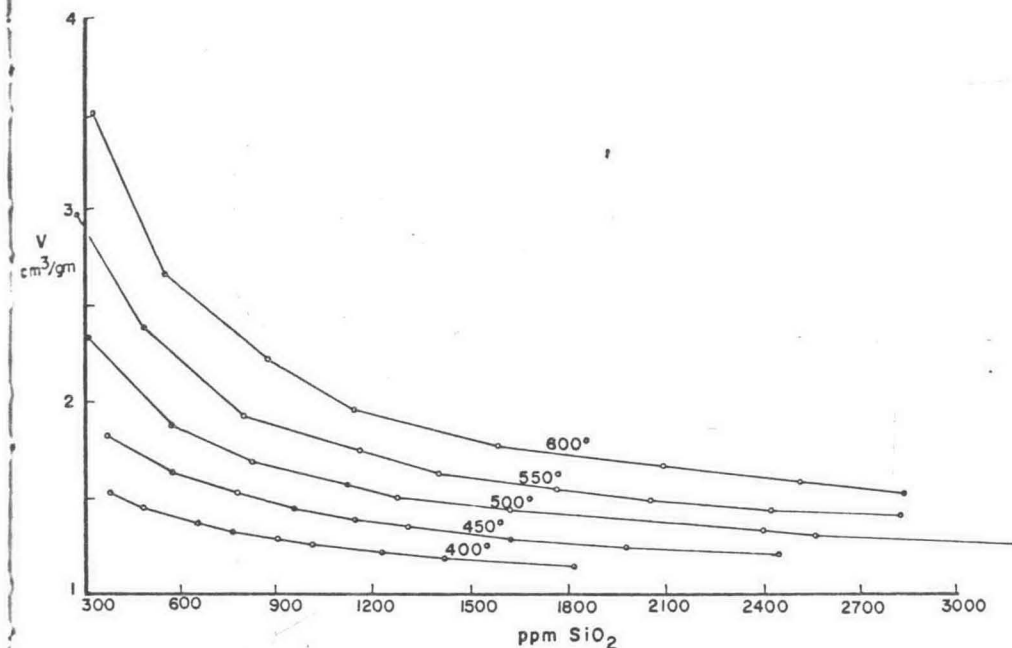
Fig. 5. Content of silica in albite solutions at various temperatures and pressures.

At the end of a run, the charge was always found to be partly reduced to an extremely fine powder. Routine X-ray powder diffraction patterns of this material only yield a pattern for albite. The non-stoichiometry of the solutions implies that the composition of the solid residue must depart from that of albite. However the total amount of material dissolved during a run is only 4 to 5 grams of the original charge of 120 grams, and the changes produced in the residue evidently either remain within the compositional range of albite or produce different phases in amounts so small as not to be detected. In runs A37 and A60, which suffered partial valve failures, much larger amounts of the charge were dissolved. Small amounts of a porcelain-like deposit on some fragments of the residue yielded an X-ray pattern of nepheline.

In none of the runs does the dissolved material have the same composition as the starting material. This phenomenon was noted by Morey and Hesselgesser (1951) in both albite and orthoclase. They suggested that stoichiometric solutions would be obtained at temperatures and pressures only slightly higher than those used by them. The present results show that departures from stoichiometry are pronounced at all temperatures and pressures in the range examined. These departures are shown graphically in figure 6. If stoichiometry were preserved, the ratio $SiO_2/Al_2O_3 = 3.47$ and $SiO_2/Na = 7.83$, where all quantities are expressed in ppm. Figure 6 shows that $SiO_2/Al_2O_3 > 3.47$ for all the experimental runs, while SiO_2/No varies markedly on both sides of 7.83. Particularly spectacular deviations resulted from unintentional experi-

TABLE 3A

Solubility of albite in supercritical water

Run No.	T (°C)	P (k bars)	SiO$_2$ ppm	Al$_2$O$_3$ ppm	Na ppm	K ppm	pH	Run No.	T (°C)	P (k bars)	SiO$_2$ ppm	Al$_2$O$_3$ ppm	Na ppm	K ppm	pH
A-14	400	0.75	369	90	79	0.3	9.79	A-43	550	0.75	272	27	23	1.8	9.46
15		1.00	490	127	89	0.5	9.84	44		1.00	505	87	67	2.2	9.74
16		1.25	651	160	112	0.7	9.94	45		1.25	795	160	102	2.6	9.93
17		1.50	778	185	140	1.1	10.05	46		1.50	1150	243	148	2.9	10.06
18		1.75	880	215	152	1.5	10.07	47		1.75	1403	310	178	3.7	10.13
19		2.00	1017	230	170	1.6	10.12	48		2.00	1760	410	214	4.2	10.22
26		2.50	1223	279	218	2.0	10.23	49		2.25	2080	479	263	4.9	10.31
27		3.00	1407	304	231	2.2	10.25	50		2.50	2415	532	310	5.1	10.35
28		3.50	1805	324	280	3.1	10.36	51		2.75	2790	587	355	5.3	10.46
A-20	450	0.75	375	103	62	0.5	9.75								
21		1.00	572	155	94	0.8	9.85	A-58	600	0.75	291	11	15	3.4	9.07
22		1.25	778	207	125	1.2	9.98	42		1.00	550	36	40	3.6	9.50
23		1.50	945	256	150	1.5	10.06	59		1.25	827	85	77	4.1	9.79
24		1.75	1135	301	177	1.7	10.13	69		1.50	1140	159	134	5.0	10.00
25		2.00	1300	328	200	1.8	10.20	61		1.75	1590	217	165	5.3	10.08
29		2.50	1617	440	241	2.4	10.27	40		2.00	2065	281	230	5.3	10.25
30		3.00	1967	515	290	2.6	10.38	63		2.25	2401	357	286	5.9	10.37
31		3.50	2440	606	346	2.9	10.43	64		2.50	2760	400	319	6.6	10.40
A-32	500	0.75	310	53	33	1.0	9.49	A-70	500	2.00	1541	418	215	4.8	10.23
33		1.00	574	126	76	1.2	9.78	71	500	2.00	1550	406	231	5.1	10.27
34		1.25	821	210	111	1.7	9.94	72	500	2.00	1565	412	216	6.1	10.26
38		1.50	1110	259	157	1.8	10.07	73	500	2.00	1557	399	233	5.3	10.24
39		1.75	1260	313	189	3.8	10.16	41	600	1.00	518	37	36	2.9	9.52
40		2.00	1605	397	230	6.5	10.25	66	400	1.00	481	124	89	0.6	9.81
54		2.75	2393	545	325	6.9	10.38	67	400	1.50	727	183	124	1.0	10.00
55		3.00	2550	600	346	7.3	10.43	68	400	2.00	993	216	161	1.4	10.09
56		3.50	3201	738	545	7.6	10.63	*	500	1.00	544	135	88		
								*	500	2.00	1591	436	221		

* Results of Morey and Hesselgesser, 1951.

TABLE 3B

Solubility of albite in supercritical water under non-equilibrium conditions

| Run No.	T (°C)	P (k bars)	SiO$_2$ ppm	Al$_2$O$_3$ ppm	Na ppm	K ppm	pH	Drip rate** (ml/hour)
A-35	500	1.50	2820	93	51	—	8.1	200
36	500	1.50	2076	141	83	0.8	8.3	120
37	600	2.00	4236	97	99	1.1	8.4	130
52	500	2.25	4007	151	149	1.4	8.3	160
53	500	2.50	6900	27	17	—	7.6	170
57	600	0.75	467	17	13	—	7.1	250
60	500	1.50	1567	186	137	1.5	8.9	95
62	600	2.00	4675	197	176	3.6	9.0	110
65	600	2.00	2576	251	209	5.3	9.6	80
69	400	2.50	2011	229	190	—	8.8	220

** Estimated from volume of solution collected divided by length of run.
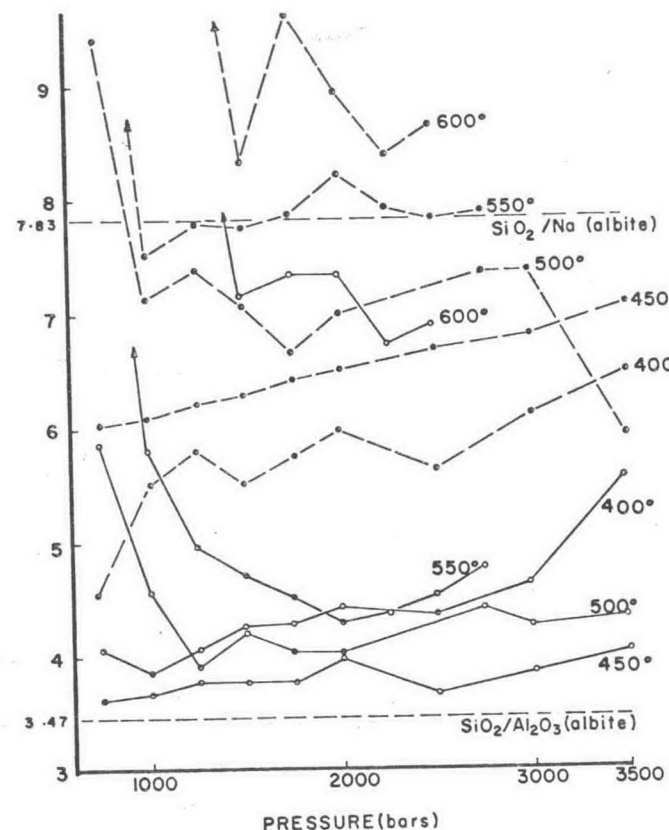
Fig. 6. Plot of SiO_2/Na ratios and SiO_2/Al_2O_3 ratios in albite solutions, where all quantities are expressed in ppm. Dashed lines: SiO_2/Na; solid lines: SiO_2/Al_2O_3.

mental runs in which partial valve failures allowed the collection rate to exceed 100 milliliters per hour. The results, quoted on table 3B show that the soda and alumina contents are greatly depressed, as might be expected, but that the silica content is markedly enhanced. Examination of the temperature and pressure records of these runs indicates that, after an initial sharp fluctuation, temperatures and pressures were maintained near the quoted values, though fluctuations were much larger than those in the runs believed to approach equilibrium.

DISCUSSION OF RESULTS

The absence of Ca in the solutions confirms the qualitative work of Euler and Hellner (1958) who found sodium to be preferentially leached from plagioclase by supercritical steam. The soda to potash ratio on the other hand is always less in the solutions than that in the starting material. It varies from 60 in the starting material down to 30 in some of the solutions. Additional work in progress by the author shows that in solutions derived from mixtures of soda and potash feldpars this ratio

always tends toward a fixed value of the order of one determined by the temperature and pressure, regardless of the proportions of soda and potash feldspar. The low values of potash in these solutions probably indicate complete leaching of potash from the starting material.

The enhancement of silica in solutions collected under non-equilibrium conditions cannot be explained by any theory of solution known to the author. Together with the solubility equations derived below, it seems to indicate that the feldspar lattice breaks down in the presence of water, and various parts react with water at different speeds.

The most notable features of the equilibrium solubility of albite in this range are (1) the non-stoichiometric composition of the solutions, (2) the difference in behavior of silica, soda, and alumina, and (3) the remarkable stability of highly supersaturated solutions at room temperature and pressure. These phenomena can be explained by a theory of solution in dense reacting fluids developed by Franck (1956). Assume the solute, designated by the subscript 1, to form complexes. Formation of such complexes can be represented schematically by

$$1 + n\,2 = 12_n \qquad (1)$$

where n may have values from zero up to m, the maximum association number. If the solute dissolves non-stoichiometrically, it can be represented by two or more "species" chosen to represent the bulk chemical composition of the solute and the non-stoichiometric behavior of the solution. It will be shown below that the chemically analyzed components may be used as species, no matter what the actual composition of the complexes may be. The composition of the complexes is not elucidated by this treatment. Using the virial equation of state, the chemical potential μ for a species in a reaction mixture is, to terms linear in the mole volume V,

$$\mu 1/RT = -\ln F_i + \ln x_i/V + \sum_j 2x_j\,(B_{ij}/V) \qquad (2)$$

(Fowler and Guggenheim, 1938, chap. 8), where F_i is the volume independent part of the potential, x_i the mole fraction of species i in the mixture, and B_{ij} the second virial coefficient. At equilibrium, for the reaction of equation (1)

$$n\,\mu_2 + \mu_1 = \mu_{12_n} \qquad (3)$$

Now if the solution is very dilute $x_2 \sim 1$ and $V \sim V_2$. Substituting (2) into (3) and setting $x_2 = 1$,

$$\ln\,(x_{12_n}/x_1) = \ln\,(F_{12_n}/F_1 F_2{}^n) - n \ln V_2 + (2/V_2)\,(B_{1,2} + nB_{2,2} - B_{12_n,2})$$
$$(4)$$

where interactions between solute species are assumed negligible because of the diluteness of the solutions.

Assuming that the association of each of the n molecules of 2 with 1 is accompanied by the same change in enthalpy and entropy,

$$\ln\,(F_{12_n}/F_1 F_2{}^n) = (n/RT)\,(H_{21} - T\,S_{21}) \qquad (5)$$

where H_{21} and S_{21} are respectively the change of enthalpy and entropy

per molecule. This equation assumes that the associated solvent molecules do not strongly influence one another and have but slight influence on the properties of the central molecule.

The terms of the last bracket of equation (4) are all independent of pressure and temperature and may be collected

$$(2/V_2)\ (B_{1,2} + nB_{2,2} - B_{1_2_n,2}) = s_n/V_2 \tag{6}$$

The mole fraction x_1 of unassociated solute molecules in the solution is due to the vapor pressure of the solid under the given temperature and pressure. This is approximately given by (Zwikker, 1954, p. 168).

$$\ln P^{\circ\prime} = k - E/RT \tag{7}$$

where k is a constant, and E the molar heat of evaporation. E has a pressure dependence, but in view of the low compressibilities of solids, this will be small. Franck (1956, eq 15) suggests it should be of the form

$$E = E_o + PV_f \tag{8}$$

where E_o is the value of E at zero pressure, P the pressure, and V_f the mole volume of the solid, assumed to be constant.

Now the number of molecules per unit volume of unassociated 1 is, at low P° where $V_1 = RT/P^\circ$,

$$q_1 = N^\circ/V_1 = (N^\circ/RT)\ (\exp\ \{k - (E_o + PV_f/RT)\}) \tag{9}$$

where N° is Avagadro's number. Noting that the number of molecules of 2 per unit volume is N°/V_2,

$$x_1 = q_1/q_1 + q_2 =$$

$$q_1/q_2 = V_2/V_1 = (V_2/RT\ (\exp\ \{k - (E_o + PV_f/RT)\}) \tag{10}$$

Substituting equations (5), (6), and (10) in equation (4) gives

$$\ln x_{1_2_n} = (k - nS_{21}/R) + s_n/V_2 - (n-1)\ \ln V_2 - \ln RT$$
$$- (nH_{21} + E_o + PV_f)/RT \tag{11}$$

Assuming that the bulk of 1 is present as the associated complex 1_2_n, $x_{1_2_n}$ may be identified with the analytically determined mole fraction of 1. Collecting constant terms in equation (11), the solubility of 1 under these conditions should obey an equation of the form

$$\log X_1 = (a + bP)/RT + c/V_2 + d\ \log V_2 + e\ \log T + f \tag{12}$$

where X_1 is the analytically determined mole fraction of 1, and a,b,c, d,e,f are constants. This equation assumes that (a) the solubility of species 1 in solvent 2 is slight, (b) species 1 forms only one quantitatively important complex with solvent 2, and (c) the volume dependence of the free energy of complexing can be represented by terms linear in the volume, and (d) complex formation leaves the electronic configuration of the participating molecules unchanged, with the possible exception of slight changes in the configuration of the most loosely bound electrons. Equation (12) differs from that of Franck (1956) in that an explicit dependence of solubility on pressure, temperature, and mole volume is given, the log solubility depends on both $1/V$ and log V, and the dependence of log solubility on $1/T$ is not linear.

Equation (12) is in a form suitable for regression analysis. The data in table 3 have been fitted to equation (12) by regression analysis using

TABLE 4A

Solubility of albite in supercritical water calculated from solubility equations: silica

T (°A)	P (k bars)	V cm³/gm	−log X (calc)	ppm SiO₂ (calc)	ppm SiO₂ (observed)	T (°A)	P (k bars)	V cm³/gm	−log X (calc)	ppm SiO₂ (calc)	ppm SiO₂ (observed)
673	0.75	1.534	3.937	387	369	773	1.75	1.502	3.410	1297	1260
	1.00	1.444	3.829	467	485		2.00	1.444	3.333	1547	1605
	1.25	1.382	3.739	607	651		2.75	1.333	3.162	2293	2393
	1.50	1.333	3.663	723	752		3.00	1.305	3.112	2543	2550
	1.75	1.295	3.597	843	880		3.50	1.256	3.017	3203	3201
	2.00	1.264	3.539	963	1003	823	0.75	2.989	4.081	277	272
	2.50	1.213	3.435	1223	1223		1.00	2.248	3.798	530	481
	3.00	1.178	3.349	1493	1407		1.25	1.932	3.609	820	795
	3.50	1.146	3.267	1803	1805		1.50	1.751	3.469	1130	1150
723	0.75	1.827	3.952	373	375		1.75	1.632	3.355	1473	1390
	1.00	1.631	3.782	550	572		2.00	1.549	3.264	1813	1760
	1.25	1.518	3.656	737	778		2.25	1.493	3.197	2120	2040
	1.50	1.447	3.565	907	945		2.50	1.445	3.131	2463	2412
	1.75	1.396	3.491	1080	1135		2.75	1.407	3.074	2813	2815
	2.00	1.354	3.429	1240	1300	873	0.75	3.618	4.059	291	300
	2.50	1.291	3.319	1600	1617		1.00	2.669	3.807	520	550
	3.00	1.243	3.224	1990	1967		1.25	2.220	3.601	837	867
	3.50	1.202	3.136	2437	2440		1.50	1.953	3.451	1180	1140
773	0.75	2.335	4.036	307	310		1.75	1.787	3.323	1583	1577
	1.00	1.896	3.781	550	574		2.00	1.676	3.224	1990	2082
	1.25	1.694	3.615	810	821		2.25	1.596	3.140	2413	2501
	1.50	1.576	3.497	1060	1110		2.50	1.535	3.070	2837	2827

Solubility equation

$$\log X\ SiO_2 = \frac{2.478}{V} + \frac{30.089P - 2400.6}{T} - 2.0199$$

TABLE 4B

Solubility of albite in supercritical water calculated from solubility equation: alumina

T (°A)	P (k bars)	V cm³/gm	−log X (calc)	ppm Al₂O₃ (calc)	ppm Al₂O₃ (observed)	T (°A)	P (k bars)	V cm³/gm	−log X (calc)	ppm Al₂O₃ (calc)	ppm Al₂O₃ (observed)
673	0.75	1.534	4.774	95	90	773	1.75	1.502	4.214	349	313
	1.00	1.444	4.659	124	127		2.00	1.444	4.131	418	397
	1.25	1.382	4.583	148	160		2.75	1.333	3.987	584	545
	1.50	1.333	4.516	172	185		3.00	1.305	3.953	628	600
	1.75	1.295	4.460	196	215		3.50	1.256	3.880	748	738
	2.00	1.264	4.418	216	230						
	2.50	1.213	4.341	258	279	823	0.75	2.989	5.378	24	27
	3.00	1.178	4.286	293	304		1.00	2.248	4.857	79	87
	3.50	1.146	4.236	329	324		1.25	1.932	4.577	150	160
							1.50	1.751	4.394	229	243
723	0.75	1.827	4.762	98	103		1.75	1.632	4.267	307	310
	1.00	1.631	4.556	157	155		2.00	1.549	4.171	382	410
	1.25	1.518	4.420	215	207		2.25	1.493	4.103	447	479
	1.50	1.447	4.330	275	256		2.50	1.445	4.043	512	532
	1.75	1.396	4.267	305	301		2.75	1.407	3.992	577	587
	2.00	1.354	4.212	347	328						
	2.50	1.291	4.123	427	440	873	0.75	3.618	5.719	11	11
	3.00	1.243	4.054	501	515		1.00	2.669	5.159	39	36
	3.50	1.202	3.991	579	606		1.25	2.220	4.822	85	85
							1.50	1.953	4.585	147	159
773	0.75	2.335	5.032	53	53		1.75	1.787	4.419	216	217
	1.00	1.896	4.638	130	126		2.00	1.676	4.304	281	281
	1.25	1.694	4.431	210	210		2.25	1.596	4.212	347	357
	1.50	1.576	4.300	284	259		2.50	1.535	4.140	410	400

Solubility equation

$$\log X\ Al_2O_3 = 157.15\ \frac{17160}{T} - 4.081 \log T - 4.241 \log V$$

TABLE 4C

Solubility of albite in supercritical water calculated from solubility equations: soda

T (°A)	P (k bars)	V cm³/gm	−log X (calc)	ppm Na (calc)	ppm Na (observed)	T (°A)	P (k bars)	V cm³/gm	−log X (calc)	ppm Na (calc)	ppm Na (observed)
673	0.75	1.534	4.659	79	79	773	1.75	1.502	4.259	190	189
	1.00	1.444	4.544	98	89		2.00	1.440	4.178	229	230
	1.25	1.382	4.463	118	112		2.75	1.333	4.025	325	325
	1.50	1.333	4.392	140	140		3.00	1.305	3.988	353	346
	1.75	1.295	4.330	160	152		3.50	1.256	3.808	537	545
	2.00	1.264	4.285	178	170						
	2.50	1.213	4.200	217	218	823	0.75	2.989	5.228	21	23
	3.00	1.178	4.137	251	231		1.00	2.248	4.802	59	67
	3.50	1.146	4.078	287	280		1.25	1.932	4.556	96	102
							1.50	1.751	4.387	144	148
723	0.75	1.827	4.778	57	62		1.75	1.632	4.263	188	178
	1.00	1.631	4.580	90	94		2.00	1.549	4.167	235	214
	1.25	1.518	4.446	123	125		2.25	1.493	4.102	273	263
	1.50	1.447	4.355	152	150		2.50	1.445	4.038	315	310
	1.75	1.396	4.287	178	177		2.75	1.407	3.986	355	355
	2.00	1.354	4.229	203	200						
	2.50	1.291	4.135	253	241	873	0.75	3.618	5.363	15	15
	3.00	1.243	4.058	301	290		1.00	2.669	4.932	40	40
	3.50	1.202	3.987	355	346		1.25	2.220	4.652	77	77
							1.50	1.953	4.443	124	134
773	0.75	2.355	5.015	33	33		1.75	1.787	4.291	176	165
	1.00	1.896	4.673	73	76		2.00	1.676	4.168	234	230
	1.25	1.694	4.478	113	111		2.25	1.596	4.091	279	286
	1.50	1.576	4.349	154	157		2.50	1.535	4.020	329	319

Solubility equation

$$\log X\ Na_2O = \frac{1.324}{V} - 2.275 \log V - \frac{1884.7}{T} - 2.300$$

Fortran computer program FLUFF. Examination of various stages of the regression procedure revealed that the first three stages of regression calculation accounted for virtually all the variation, the last two stages accounting for only 0.3 to 0.7 percent. Furthermore the regression coefficients for the two least significant variables had t values less than 2.5, showing that they were not significant. The analysis was therefore terminated after three stages. The results are displayed in table 4. Values for V_2 were taken from the tables of Kennedy (1950) and Sharp (1962).

Experimental concentration data for SiO_2 in albite solutions can be fitted with an error of less than 2 percent in the logarithm (about 5 percent in the solubility), whereas data for soda and alumina can be fitted with an error of less than 3 percent in the logarithm (about 7 percent in the solubility). These errors approach or are within the analytical errors.

All three chemical species give markedly different types of solubility equations. The solubility of SiO_2 depends on P/T, $1/T$, and $1/V$ in that order of importance, while that of Al depends on $\log V$, $1/T$, and $\log T$, and that of Na on $\log V$, $1/T$, and $1/V$. The experimental data show that solutions of albite in supercritical water are non-stoichiometric under the experimental conditions; extrapolation of the data by means of the derived equations suggests that stoichiometric solution cannot be achieved at any temperature or pressure.

In order to check the applicability of equation 12 to solubility data for other materials of geological interest, the data of Weill and Fyfe (1964) were analyzed by the technique outlined above. The results are tabulated in table 5. The data could be fitted to equation 12 with a maximum error in the logarithm of about 0.7 percent. The variation was found to depend almost entirely on $\log V$ and $1/T$ with a very weak (0.3 percent of variation) dependence of $1/V$. Jasmund (1952) deduced a similar equation from other data on the solubility of quartz. The considerably better fit of the equation to the data for quartz reflects the better data for quartz solubility than for albite solubility. It would be desirable to obtain data on the solubility of feldspars by the same method used for quartz (weight loss of individual plates). However this technique is applicable only if the solid dissolves stoichiometrically, a condition not obeyed by feldspars.

The composition of the solute differs from that of albite in all parts of the pressure-temperature range studied. The experimental results show the SiO_2/Al_2O_3 ratio to be in excess of that in albite (3.47) for all parts of the P-T range (fig. 6), although the computed solubility equations shows a small p-T region centered about 450°C and 1500 bars where SiO_2/Al_2O_3 is predicted to be less than 3.47. The ratio SiO_2/Na is 7.83 in albite. In the solutions it varies from 4.57 to 19, in general increasing with temperature. Na is present in excess of the amount required for albite at temperatures below 550°C, whereas at temperatures higher than 550°C the amount present is markedly less than required to form albite. From these data it is clear that systematic motions of

TABLE 5

Solubility of quartz in supercritical water compared to computed solubility equation (Data after Weill and Fyfe, 1964)

T (°C)	P (k bars)	V	-log X (calc)	Wt % SiO₂ (calc)	Wt % SiO₂ (observed)
400	1.00	1.444	3.289	0.171	0.170
	1.25	1.382	3.238	0.192	0.185
	1.50	1.333	3.193	0.213	0.208
	1.75	1.295	3.173	0.223	0.232
	2.00	1.264	3.151	0.235	0.248
	2.25	1.239	3.122	0.251	0.258
	2.50	1.213	3.111	0.257	0.268
	2.75	1.197	3.093	0.268	0.274
	3.00	1.178	3.080	0.277	0.276
	3.25	1.162	3.067	0.285	0.281
	4.00	1.118	3.033	0.308	0.290
450	1.00	1.631	3.191	0.215	0.216
	1.25	1.518	3.109	0.259	0.260
	1.50	1.447	3.062	0.289	0.281
	1.75	1.396	3.026	0.313	0.315
	2.00	1.354	2.992	0.339	0.331
	2.25	1.322	2.966	0.359	0.356
	2.50	1.291	2.939	0.383	0.376
	2.75	1.266	2.922	0.399	0.396
	3.00	1.243	2.899	0.419	0.421
	3.50	1.202	2.874	0.466	0.453
	4.00	1.168	2.855	0.467	0.495
500	1.00	1.896	3.134	0.245	0.240
	1.50	1.576	2.957	0.367	0.372
	2.00	1.444	2.870	0.449	0.456
	2.50	1.364	2.809	0.516	0.505
	3.00	1.305	2.768	0.570	0.568
	3.50	1.256	2.735	0.613	0.612
	4.00	1.214	2.698	0.689	0.668
550	1.00	2.248	3.116	0.255	0.260
	1.50	1.751	2.884	0.437	0.448
	2.00	1.549	2.769	0.566	0.569
	2.50	1.445	2.707	0.553	0.656
	3.00	1.374	2.651	0.743	0.740
	4.00	1.266	2.570	0.895	0.879
625	1.00	2.893	3.086	0.273	0.271 (avg of 5)

Solubility equation

$$\log X \, SiO_2 = \frac{-2142.2}{T(°A)} - 1.296 \log V + \frac{0.614}{V} + 0.047$$

solutions in contact with albite will produce chemical differentiation. Whether or not such differentiation is significant depends on the volume of solutions and scales of transport involved.

The reported experiments give no direct information about the species in solution. It may be inferred from the pH that the sodium is dominantly in ionic form. The long term stability of the solutions suggests that silica and alumina must be bound up in reasonably stable hydrated complexes. The present treatment does not exclude the possibility that two or even all three of the components of albite may be present in each of the complexes. If this is the case, at least three complexes must be present to explain the varying behavior of silica, alumina, and soda. Assuming that each of these complexes obeys the assumptions made in the present treatment, the thermodynamic analysis presented above would be valid as far as equation (11), with the proviso that each complex contains one or more of the analyzed components. Now the number of moles of the analyzed component is related to the number of moles of the complex by

$$q_k = g \ q_{12_n} \tag{13}$$

where q_k is the number of moles of analyzed component k in complex 12_n, and g is a constant. Equation (12) can now be rewritten as

$$\ln x_{12_n} = f(P,V,T) \cong \ln (q_{12_n} /q_2) = \ln(q_k/gq_2) = \ln x_k - \ln g \tag{14}$$

In other words, equation (12) can be modified by the addition of a constant only, to give the mole fraction of the analyzed component. The total amount of the analyzed component is easily found by summing equation (14) over all complexes containing the component k

$$\ln X_k = \Sigma_i (f_i (P,V,T,) + \ln g_i) \tag{15}$$

This equation is identical in form to equation (12). The form of the solubility equations is therefore independent of the choice of analyzed components; conversely the solubility equations can give no direct information on the species in solution.

POSSIBLE GEOLOGIC SIGNIFICANCE OF ALBITE SOLUBILITY

The maximum measured amount of albite components present in solution of albite reported approximates 2 percent by weight. Considering that the water content of rocks under plutonic conditions rarely exceeds 10 weight percent, the significance of solution processes appears negligible. A model calculation however shows this simple conclusion to be deceptive.

Consider a dehydrating cylinder of radius R, which might be a crystallizing pluton or a body of rocks undergoing progressive metamorphism. Let w be the weight of water per unit volume expelled during the process. Then the total amount of water expelled by a right slice across the cylinder of thickness dz is

$$m_t = \pi R^2 dz \ w \tag{16}$$

Now consider a cylindrical surface concentric to the dehydrating cylinder but of radius r (greater than R). Consider a segment of this surface subtending angle $d\theta$ and of height dz. Then if the water from the dehydrating cylinder migrates radically outward, the weight of water passing through the element of surface is

$$m = (\pi wR^2 dz \ d\theta)/2\pi \tag{17}$$

Now the weight of material per unit area of a thin cylindrical shell of radius r and thickness dr is

$$m_s = Dr \ d\theta \ dz \ dr \tag{18}$$

where D is the density. Therefore the ratio of the weight of water passing through the layer to the weight of material in the layer is

$$B = m/m_s = wR^2/2rD \ dr \tag{19}$$

B is inversely dependent on dr, hence for thin layers the weight of water passing through will be large compared to the weight of rock in the layer. Consider a layer 1 cm thick. Substituting into equation 19, some geologically reasonable values, $W = 0.1$ gms/cc, $R = 1$ km (10^5), $r = 10$ km (10^6), and $D = 2.7$ gms/cc, yields $B = 185$. That is, a cylindrical body 1 km in radius, expelling 0.1 gms/cc of water, will cause, at a distance of 9 km from its margin, a total flux of water 185 times the weight of rock locally present, assuming that none of the expelled water is trapped in the rocks immediately surrounding the pluton.

Of course it is a matter of observation that this latter assumption is not true. Aureoles of hydrous minerals either in the body of the rock or along fractures commonly surround plutonic masses. We might therefore replace (16) by the more realistic assumption that the amount of water transported falls off exponentially with distance from the margin of the dehydrating cylinder.

$$m_t = awR^2 \ dz \ \exp \ (-r/R) \tag{16A}$$

The constant a can be evaluated by noting that (16A) must equal (16) at r = R, giving $a = \pi e$. Substituting (16A) in (17) yields in place of equation (19)

$$B = (wR^2/2Drdr) \ \exp \ (-r/R + 1) \tag{19A}$$

Using the same values as before, we find that a weight of water 0.02 times the weight of rock passes through a surface 9 km from the margin of the pluton and at a distance of 3.5 km from the margin of pluton $B \sim 33$. Even allowing for the escape of volatiles it seems clear that metamorphic or intrusive processes of dehydration will produce large fluxes of water through volumes many times the size of the dehydrating body. The influence of solutions must be far greater than their small amount and low concentration would suggest.

Three important cases suggest themselves: (1) solutions escape suddenly and rapidly from a dehydrating body, (2) solutions escape slowly and uniformly under conditions where the SiO_2/Na ratio exceeds the stoichiometric ratio in albite, (3) solutions escape slowly and uniformly with SiO_2/Na ratio less than that in albite.

The first possibility seems quite plausible for shallow intrusions that fracture their roofs. The experimental results suggest that solutions that rush off under disequilibrium conditions of this kind will be highly enriched in silica. Conversely the rocks from which the solutions are derived will be desilicated. A probable example of the operation of this process has been discovered in the Belleoram adamellite stock, Newfoundland (Ermanovics, Edgar, and Currie, 1967). The adamellite intrudes impervious, unfractured shales and slates without notable marginal effects. Where it intrudes permeable, fractured conglomerate, a highly desilicated, syenitic phase is developed with an imperceptible gradation from the intrusive into the conglomerate. Solubility experiments on the adamellite showed that under disequilibrium conditions, silica solubility was highly enhanced, just as it is in albite. This suggests that rapid loss of volatiles into the fractured, permeable conglomerate desilicated the solidified borders of the intrusion. At a distance of 2 km from the intrusive, a girdle of quartz veins is found that can be plausibly identified with the silica lost from the intrusive.

Under deeper-seated conditions, a much slower, more uniform motion of solutions may be expected. The arguments advanced above show that at the lower end of the P/T range covered, the solutions will be relatively soda and alumina rich. If the vein component in igneous and metamorphic complexes is identified with material deposited from solutions, this reasoning suggests that veins in low grade rocks should be comparatively Na rich and quartz poor, while at higher grades they should contain free quartz. Conversely the (depleted) host rocks should be relatively rich in silica at low grades and become relatively richer in alkalies at higher grades. To a first approximation this is an accurate description of many metamorphic complexes.

In the absence of data on potash and lime feldspars and on mixtures of feldspars and quartz, these conclusions are highly tentative. However preliminary work on the solubility of natural rocks (Ermanovics, Edgar, and Currie, 1967) and work in progress on the solubility of other feldspars suggest that these conclusions are qualitatively correct.

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