[AMERICAN JOURNAL OF SCIENCE, VOL. 251, JULY 1953, PP. 481-504]

American Journal of Science

JULY 1953

PETROLOGICAL CALCULATIONS IN METASOMATIC PROCESSES

ARIE POLDERVAART

ABSTRACT. Petrological calculations in metasomatic processes are critically reviewed. The six analyses of the Stavanger metamorphic series of Norway are used as examples in different methods of calculation. The application of the so-called law of equal volume to all cases of metasomatic changes in composition is questioned. A new method is suggested in which the number of $(Si,Al)O_4$ tetrahedra is assumed to remain constant. In terms of mineralogy and petrology this is believed to have more meaning than the assumption of constant volume.

INTRODUCTION

METASOMATISM has been defined by Lindgren (1933, p. 91) as "the process of practically simultaneous . . . solution and deposition by which a new mineral of partly or wholly differing . . . composition may grow in the body of an old mineral or mineral aggregate." It follows that metasomatic processes take place in the presence of a fluid phase—water—which acts as a solvent. The amount of pore fluid present in metasomatism is believed to vary, from the small fraction represented by "the intergranular film" to ten per cent or more of the total volume. Lindgren also distinguishes between (1) metasomatic changes proceeding in free crystals or loose aggregates where the force of crystallization can easily overcome the retaining pressure, and (2) metasomatic changes proceeding in rigid rocks where the new mineral makes room for itself by solution of the host mineral. In the first case there is a relatively large amount of pore fluid and metasomatism is accompanied by volume changes, while in the second case the amount of pore fluid is very small and the volume remains constant. The so-called law of equal volume has become the basis for all petrological calculations of metasomatic changes in bulk composition, even when there is

good reason to believe that changes in volume did occur during the process. Such calculations are especially important in determining compositional changes in metamorphism and granitization, i.e., for rocks which consist predominantly of silicates.

In this paper the various methods of calculation are reviewed particularly as applied to silicate rocks. Silicates possess a special type of structure in which (Si, Al)O_4 tetrahedra act as fundamental building blocks. Different structures and hence different minerals result from a different arrangement of these blocks and the occupation of the interstitial spaces by different cations. Thus it is suggested that a more realistic approach to the problem is obtained by assuming that during metasomatism of silicate rocks the number of (Si, Al)O_4 tetrahedra remains approximately constant.

The classic metamorphic series of the Stavanger region of Norway (Goldschmidt, 1920) is used throughout as example, also because this series has been quoted repeatedly in the recent literature (Reynolds, 1946; Chao, 1951; Joplin, 1952). Table 1 gives the original data. These have been recalculated to 100 per cent after subtraction of certain constituents listed in table 2,[1] while the specific gravity values have also been corrected. H_2O^- has been subtracted, but H_2O^+ is retained in the recalculated analyses, the assumption being that H_2O^+ represents water chemically bound in the rockforming minerals. There is good reason to believe that this is not true (Faber, 1941), but probably the error in thus regarding H_2O^+ is less than that introduced in recalculating the analyses on an anhydrous basis. This emphasizes the great need for a chemical method whereby H_2O which enters into the composition of rockforming minerals can be accurately determined and distinguished from absorbed water. The results are given in table 3, and these data are used throughout in the following calculations.

CALCULATIONS BASED ON CONSTANT VOLUME

In the most generally used method of calculating changes in composition during metasomatism the analyses are recal-

[1] Subtraction of these constituents is of course not essential, but this has been done to give a more uniform and simplified statement of the six analyses.

TABLE 1

The Stavanger Metamorphic Series; Original Data

	1	2	3	4	5	6
SiO_2	58.32	57.29	60.62	62.40	64.35	64.70
TiO_2	.98	.97	.80	.81	.70	.59
Al_2O_3	20.00	20.60	18.50	16.27	16.54	15.45
Fe_2O_3	2.01	2.40	1.32	1.44	2.24	1.36
FeO	4.98	5.48	5.65	5.78	3.92	4.18
MnO	.22	.41	.07	.35	.14	.05
MgO	1.85	1.76	2.42	2.19	2.04	1.48
CaO	.66	.37	1.66	2.07	2.04	2.92
BaO	.10	.10	....	.07	.11	.10
Na_2O	1.26	1.40	1.81	2.28	2.00	3.09
K_2O	4.49	4.30	4.02	3.16	3.82	3.46
H_2O^+	4.05	4.00	2.92	2.25	1.73	1.82
H_2O^-	.05	.05	.17	.16	.12	.15
P_2O_5	.15	.14	.08	.16	.17	.19
CO_2	.43	.05	....	.52	.13	.85
C	.36	.81	....	.10	....	....
S	.06	.11	.05	.04	....	.05
Cr_2O_3	.02	....	....	....	....	....
V_2O_3	.03	....	....	....	....	....
	100.02	100.24	100.09	100.05	100.05	100.44
Sp. gr.	2.798	2.862	2.838	2.814	2.812	2.777

1. Quartz-muscovite-chlorite phyllite.
2. Quartz-muscovite-chlorite-garnet phyllite.
3. Quartz-muscovite-biotite-garnet phyllite.
4. Quartz-muscovite-biotite-garnet schist.
5. Quartz-muscovite-biotite-garnet mica-schist.
6. Albite porphyroblast schist.

TABLE 2

Material Subtracted in Recalculating Analyses

	1	2	3	4	5	6
FeS_2	.13	.21	.11	.08	..	.11
$CaCO_3$	.93	.11	..	1.18	.30	1.93
H_2O^-	.05	.05	.17	.16	.12	.15
C	.36	.81	..	.10	..	..
Cr_2O_3	.02	..	..	..	..	..
V_2O_3	.03	..	..	..	..	..
	1.52	1.18	.28	1.52	.42	2.19

TABLE 3

Recalculated Analyses

	1	2	3	4	5	6
SiO_2	59.21	57.85	60.74	63.34	64.59	65.86
TiO_2	.99	.98	.80	.82	.70	.60
Al_2O_3	20.31	20.81	18.54	16.51	16.60	15.73
Fe_2O_3	2.04	2.42	1.32	1.46	2.25	1.38
FeO	4.99	5.41	5.60	5.83	3.93	4.19
MnO	.22	.41	.07	.36	.14	.05
MgO	1.88	1.78	2.42	2.22	2.05	1.51
CaO	.16	.31	1.66	1.43	1.88	1.87
BaO	.10	.10	....	.07	.11	.10
Na_2O	1.28	1.41	1.81	2.31	2.01	3.15
K_2O	4.56	4.34	4.03	3.21	3.83	3.52
H_2O^+	4.11	4.04	2.93	2.28	1.74	1.85
P_2O_5	.15	.14	.08	.16	.17	.19
	100.00	100.00	100.00	100.00	100.00	100.00
Sp. gr.	2.756	2.828	2.830	2.771	2.800	2.716

culated to represent compositions of 100 cc. rock.[2] The data are then compared with one another to determine additions and subtractions of material. Table 4 lists the results as applied to the Stavanger metamorphic series, while additions and subtractions between successive pairs of members of the series are given in table 5. It may be seen that no single constituent varies in the same manner throughout the series, but that any constituent may show gains in one or more pairs of rocks and losses in the next paired analyses.

Additions and subtractions are sometimes represented in percentages (Reynolds, 1943), and this has been done on an anhydrous basis in table 6. In the writer's opinion such representations are of little use and add no further information to the problem. Speculations regarding the composition of the pore fluid during the various metamorphic intensities can be drawn as well from table 5 as from table 6. Comparisons of the data of table 6 with compositions of magmas are probably unjustified and misleading. The time element is completely dis-

[2] In this method, and in others described later, sp. gr. data of rocks are used. It is doubtful whether the sp. gr. of a rock is generally determined with the same care and precision as is expended on its chemical analysis. A plea is here made for greater accuracy in the determination of this important physical constant of rocks.

TABLE 4

Compositions of 100 cc. Rock

	1	2	3	4	5	6
SiO_2	163.18	163.60	171.89	175.52	180.85	178.88
TiO_2	2.73	2.77	2.26	2.27	1.96	1.63
Al_2O_3	55.97	58.85	52.47	45.75	46.48	42.72
Fe_2O_3	5.62	6.84	3.74	4.05	6.30	3.75
FeO	13.75	15.30	15.85	16.15	11.00	11.38
MnO	.61	1.16	.20	1.00	.39	.14
MgO	5.18	5.03	6.85	6.15	5.74	4.10
CaO	.44	.88	4.70	3.96	5.26	5.08
BaO	.28	.28	....	.19	.31	.27
Na_2O	3.53	3.99	5.12	6.40	5.63	8.56
K_2O	12.57	12.27	11.40	8.89	10.72	9.56
H_2O^+	11.33	11.43	8.29	6.32	4.87	5.02
P_2O_5	.41	.40	.23	.44	.48	.52
	275.60	282.80	283.00	277.09	279.99	271.61

TABLE 5

Additions and Subtractions*

	1-2		2-3		3-4		4-5		5-6	
	+	−	+	−	+	−	+	−	+	−
SiO_2	.42	..	8.29	....	3.63	....	5.33	...	...	1.97
TiO_2	.04	..	....	.51	.01	....	....	.31	...	.33
Al_2O_3	2.88	..	....	6.38	...	6.72	.73	...	...	3.76
Fe_2O_3	1.22	..	....	3.10	.31	....	2.25	...	...	2.55
FeO	1.55	..	.55	....	.30	....	....	5.15	.38	....
MnO	.55	..	....	.96	.80	....	....	.61	...	.25
MgO	...	.15	1.82	....	...	.70	....	.41	...	1.64
CaO	.44	..	3.82	....	...	.74	1.30	...	...	.18
BaO	...	..	....	.28	.19	....	.12	...	...	.04
Na_2O	.46	..	1.13	....	1.28	....	....	.77	2.93	....
K_2O	...	.30	....	.87	...	2.51	1.83	...	...	1.16
H_2O^+	.10	..	....	3.14	...	1.97	....	1.45	.15	....
P_2O_5	...	.01	....	.17	.21	....	.04	...	.04	....
	7.66	.46	15.61	15.41	6.73	12.64	11.60	8.70	3.50	11.88
Less H_2O^+	7.56	.46	15.61	12.27	6.73	10.67	11.60	7.25	3.35	11.88

*(+) and (−) symbols at top of columns indicate respectively additions and subtractions.

regarded in these speculations. Subtraction of, e.g., 5 per cent MgO does not mean that the resulting solution contained 5 per cent MgO, but that probably very dilute solutions in time removed 5 per cent MgO from the rock. Only the final results are observed in terms of rocks, and not in terms of pore fluids.

TABLE 6

Additions and Subtractions in Percentages
(on a Dry Basis)

	1-2		2-3		3-4		4-5		5-6	
	+	−	+	−	+	−	+	−	+	−
SiO_2	5.56	.....	53.11	.....	53.93	.....	45.95	.....	.....	16.58
TiO_2	.53	.....	.....	4.16	.15	.....	.....	4.28	.....	2.78
Al_2O_3	38.10	.....	.....	52.00	.....	62.98	6.29	.....	.....	31.66
Fe_2O_3	16.14	.....	.....	25.26	4.61	.....	19.40	.....	.....	21.46
FeO	20.49	.....	3.52	.....	4.46	.....	.....	71.03	11.34	.....
MnO	7.28	.....	.....	7.82	11.89	.....	.....	8.41	.....	2.10
MgO	.....	32.61	11.66	.....	.....	6.56	.....	5.66	.....	13.80
CaO	5.82	.....	24.47	.....	.....	6.94	11.21	.....	.....	1.52
BaO	.....	.....	.....	2.28	2.82	.....	1.03	.....	.....	.34
Na_2O	6.08	.....	7.24	.....	19.02	.....	.....	10.62	87.47	.....
K_2O	.....	65.22	.....	7.09	.....	23.52	15.78	.....	.....	9.76
P_2O_5	.....	2.17	.....	1.39	3.12	.....	.34	.....	1.19	.....
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Joplin (1952) uses a slightly different method of calculation in which the rock exhibiting the lowest metamorphic grade is taken as standard and the percentages of the other analyses are multiplied with a factor reflecting the percentage increase or decrease in specific gravity as compared with that of the standard sample. The results of these calculations are listed in table 7. The present writer considers that there is no advantage in this manner of calculation instead of the more generally used method described above. The results of the calculations are ratio numbers and therefore less precise information is obtained by this method.

A third method has been seldom used (e.g., Ellis, 1947), probably because it requires more involved calculations and hence is more time-consuming. However, the use of a calculating machine largely alleviates the tediousness of the various computations. The atomic proportions are first calculated (table

TABLE 7

Equivalent Sp. Gr. Calculations

	1	2	3	4	5	6
SiO_2	59.21	59.36	62.37	63.68	65.62	64.91
TiO_2	.99	1.01	.82	.82	.71	.59
Al_2O_3	20.31	21.35	19.04	16.60	16.87	15.50
Fe_2O_3	2.04	2.48	1.36	1.47	2.29	1.36
FeO	4.99	5.55	5.75	5.86	3.99	4.13
MnO	.22	.42	.07	.36	.14	.05
MgO	1.88	1.83	2.49	2.23	2.08	1.4[illegible]
CaO	.16	.32	1.70	1.44	1.91	1.8[illegible]
BaO	.10	.10	.....	.07	.11	.10
Na_2O	1.28	1.45	1.86	2.32	2.04	3.10
K_2O	4.56	4.45	4.14	3.23	3.89	3.4[illegible]
H_2O^+	4.11	4.15	3.01	2.29	1.77	1.8[illegible]
P_2O_5	.15	.14	.08	.16	.17	.19
	100.00	102.61	102.69	100.53	101.59	98.55

8). H_2O^+ is reckoned as $2(OH)^{-1}$, the additional O being subtracted from the total oxygen proportion.[3] A conversion factor X is next found by dividing the specific gravity of the rock by $166.04\left(\frac{100}{\text{Avogadro number}}\right)$.[4] Multiplying the atomic proportions with the conversion factor finally gives the number of different atoms in 1 cc. of rock (table 10). The number of atoms added and subtracted in comparing rock pairs is given in table 11. Weights may be obtained from these figures by multiplying with the weight of the respective atoms. The sum of the weights of atoms should, of course, equal the specific gravity of the rock.

[3] The procedure followed here is slightly different from that normally used, in that H_2O^+ is reckoned as $2OH^{-1}$ and newer and more accurate physical constants are employed.

[4] Avogadro number and atomic weights from Handbook of Chemistry and Physics, 33rd ed., 1951-1952; ionic radii from Ahrens (1952).

TABLE 8

Atomic Proportions

	1	2	3	4	5	6
Si	.9858	.9632	1.0113	1.0546	1.0754	1.0966
Ti	.0125	.0123	.0100	.0103	.0088	.0075
Al	.3984	.4082	.3638	.3240	.3256	.3086
Fe^{+3}	.0256	.0304	.0166	.0182	.0282	.0172
Fe^{+2}	.0694	.0753	.0779	.0811	.0547	.0583
Mn	.0032	.0058	.0010	.0051	.0020	.0007
Mg	.0466	.0441	.0600	.0551	.0508	.0375
Ca	.0029	.0055	.0296	.0255	.0335	.0333
Ba	.0007	.0007	....	.0005	.0007	.0007
Na	.0412	.0454	.0584	.0746	.0648	.1016
K	.0968	.0922	.0856	.0682	.0814	.0748
OH^{-1}	.4568	.4488	.3256	.2534	.1934	.2056
P	.0022	.0020	.0012	.0022	.0024	.0026
O^{-2}	2.8299	2.8141	2.8567	2.8873	2.9199	2.9221
Less O for OH	2.6015	2.5897	2.6939	2.7606	2.8232	2.8193

TABLE 9

Physical Constants

Avogadro number: 6.0228×10^{23}

Element	Ion. rad. (Å)	Ion. vol. 4.19 r^3	At. wt.	Wt. 1 atom (gms)
Si^{+4}	0.42	0.31	28.06	46.60×10^{-24}
Ti^{+4}	0.68	1.32	47.90	79.55
Al^{+3}	0.51	0.56	26.97	44.80
Fe^{+3}	0.64	1.10	55.85	92.76
Fe^{+2}	0.74	1.70	55.85	92.76
Mn^{+2}	0.80	2.15	54.93	91.21
Mg^{+2}	0.66	1.20	24.32	40.39
Ca^{+2}	0.99	4.07	40.08	66.56
Ba^{+2}	1.34	10.08	137.36	228.10
Na^{+1}	0.97	3.82	22.997	38.18
K^{+1}	1.33	9.86	39.096	64.94
OH^{-1}	1.40	11.48	17.008	28.24
P^{+5}	0.35	0.18	30.98	51.44
O^{-2}	1.40	11.48	16.000	26.57

TABLE 10

Number of Atoms in 1 cc. Rock

	1	2	3	4	5	6
X	1.66×10^{22}	1.70×10^{22}	1.70×10^{22}	1.67×10^{22}	1.69×10^{22}	1.64×10^{22}
N_o	4.316×10^{22}	4.410×10^{22}	4.590×10^{22}	4.605×10^{22}	4.760×10^{22}	4.610×10^{22}
N_{si}	1.635	1.640	1.723	1.759	1.813	1.793
N_{ti}	.021	.021	.017	.017	.015	.012
N_{al}	.661	.695	.620	.540	.549	.505
$N_{fe^{+3}}$	.042	.052	.028	.030	.048	.028
$N_{fe^{+2}}$	.115	.128	.133	.135	.092	.095
N_{mn}	.005	.010	.002	.009	.003	.001
N_{mg}	.077	.075	.102	.092	.086	.061
N_{ca}	.005	.009	.050	.043	.056	.054
N_{ba}	.001	.001	...	.001	.001	.001
N_{na}	.068	.077	.100	.124	.109	.166
N_k	.161	.157	.146	.114	.137	.122
N_{oh}	.758	.764	.555	.423	.326	.336
N_p	.004	.003	.002	.004	.004	.004
	7.869	8.042	8.068	7.896	7.999	7.788

TABLE 11

Additions and Subtractions

(All Numbers x 10^{22})

	1-2		2-3		3-4		4-5		5-6	
	+	−	+	−	+	−	+	−	+	−
O	.094	...	.180	...	.015	...	.155	...	...	.150
Si	.005	...	.083	...	.036	...	.054	...	...	.020
Ti	...	...	...	.004	...	...	...	.002	...	.003
Al	.034	...	...	.075	...	.080	.009	...	...	.044
Fe^{+3}	.010	...	...	.024	.002	...	.018	...	...	.020
Fe^{+2}	.013	...	.005	...	.002	...	...	.043	.003	...
Mn	.005	...	...	.008	.007	...	...	.006	...	.002
Mg	...	.002	.027	...	...	.010	...	.006	...	.025
Ca	.004	...	.041	...	...	.007	.013	...	...	.002
Ba	...	...	...	.001	.001	...	...	...	...	...
Na	.009	...	.023	...	.024	...	...	.015	.057	...
K	...	.004	...	.011	...	.032	.023	...	...	.015
OH	.006	...	...	.209	...	.132	...	.097	.010	...
P	...	.001	...	.001	.002	...	...	...	...	...
	.180	.007	.359	.333	.089	.261	.272	.169	.070	.281
Vals.	.011	.013	.141	.138	.174	.174	.036	.036	.053	.057

In table 12 the ion volumes have been listed, as obtained by multiplying the number of atoms with the corresponding ionic volume (table 9). Summation of the ion volumes gives a measure of the packing of the rock comparable with the packing index concept $\left(\frac{\text{ion volume x } 10}{\text{volume rock}}\right)$ introduced by Fairbairn (1943). When comparing packing percentages with packing indices given by Fairbairn, it should be noted that different values are used for ionic volumes. This is especially significant in the case of oxygen (11.48 as against 9.64 cubic Å). Again no regular trend can be discerned in the packing variation of the six rocks.

TABLE 12

Ion Volumes in 1 cc. Rock

	1	2	3	4	5	6
V_o	.495 cc	.506 cc	.527 cc	.529 cc	.546 cc	.529 cc
V_{si}	.005	.005	.005	.006	.006	.006
V_{ti}	.000	.000	.000	.000	.000	.000
V_{al}	.004	.004	.004	.003	.003	.003
$V_{fe^{+3}}$	.001	.001	.000	.000	.001	.000
$V_{fe^{+2}}$	.002	.002	.002	.002	.002	.002
V_{mn}	.000	.000	.000	.000	.000	.000
V_{mg}	.001	.001	.001	.001	.001	.001
V_{ca}	.000	.000	.002	.002	.002	.002
V_{ba}	.000	.000	.000	.000	.000	.000
V_{na}	.003	.003	.004	.005	.004	.006
V_k	.016	.016	.014	.011	.014	.012
V_{oh}	.087	.088	.064	.049	.037	.039
V_p	.000	.000	.000	.000	.000	.000
	.614 cc	.626 cc	.623 cc	.608 cc	.616 cc	.600 cc
Packing (%)	61.4	62.6	62.3	60.8	61.6	60.0

CALCULATIONS BASED ON A "UNIT CELL" OF 160 O ATOMS

Barth (1948) introduced a new method of calculation based on no less than three premises: (1) that in metasomatic processes the volume remains constant, (2) that the number of oxygen atoms also remains constant, and (3) that rocks generally contain 100 cations to 160 oxygen atoms. Thus the analyses are recalculated to a unit cell of 160 O atoms, for which Barth uses the total available oxygen. The results of these calculations for the six Stavanger rocks are shown in table 13, while pairs of rocks are compared in table 14.

TABLE 13

Analyses Recalculated to 160 O Unit Cell

	1	2	3	4	5	6
Si	51.57	50.72	53.59	55.98	57.04	58.00
Ti	.65	.65	.53	.55	.47	.40
Al	20.84	21.49	19.28	17.20	17.27	16.32
Fe^{+3}	1.34	1.60	.88	.97	1.50	.91
Fe^{+2}	3.63	3.97	4.13	4.31	2.90	3.08
Mn	.17	.31	.05	.27	.11	.04
Mg	2.44	2.32	3.18	2.93	2.69	1.98
Ca	.15	.29	1.57	1.35	1.78	1.76
Ba	.04	.04	.....	.03	.04	.04
Na	2.16	2.39	3.09	3.96	3.44	5.37
K	5.06	4.86	4.54	3.62	4.32	3.96
H	23.90	23.63	17.25	13.45	10.26	10.88
P	.12	.11	.06	.12	.13	.14
	112.07	112.38	108.15	104.74	101.95	102.74

As shown in the last table, the total charge of the ions added roughly equals that of the subtracted ions; thus electrostatic equilibrium is maintained during metasomatism. The same approximate balance of valences may be observed in the addition and subtraction of atoms when comparing their numbers in 1 cc. rock (table 11). Comparison of tables 5, 11, and 14 shows discrepancies in the addition or subtraction of Si^{+4} and H^{+1}.

TABLE 14

Additions and Subtractions

	1-2		2-3		3-4		4-5		5-6	
	+	−	+	−	+	−	+	−	+	−
Si	...	.85	2.87	...	2.39	...	1.06	...	.96	...
Ti	...	...	...	.12	.02	...	...	.08	...	.07
Al	.65	...	...	2.21	...	2.08	.07	...	...	.95
Fe^{+3}	.26	...	...	.72	.09	...	.53	...	...	.59
Fe^{+2}	.34	...	.16	...	.22	...	...	1.41	.18	...
Mn	.14	...	...	.26	.18	...	...	.16	...	.07
Mg	...	.12	.86	...	...	.25	...	.24	...	.71
Ca	.14	...	1.28	...	...	.22	.43	...	...	.02
Ba	...	...	...	.04	.03	...	.01	...	...	...
Na	.23	...	.70	...	.87	...	...	.52	1.93	...
K	...	.20	...	.32	...	.92	.70	...	...	.36
H	...	.27	...	6.38	...	3.80	...	3.19	.62	...
P	...	.01	...	.05	.06	...	.01	...	.01	...
	1.76	1.45	5.87	10.10	3.86	5.27	2.81	5.60	3.70	2.77
Vals.	4.20	4.16	16.78	16.82	11.94	11.90	7.67	7.65	6.80	6.86

Inspection of table 10 shows that Barth's second premise is not correct when taken in conjunction with the first; constant volume does not necessarily mean a constant number of oxygen atoms. On these and other grounds the Barth method of calculation has been criticized severely by Rosenqvist (1949) and Brajnikov (1949).

Goldschmidt (1928) has emphasized the role of oxygen in rocks; the lithosphere is essentially an "oxysphere." Bragg (1937, p. 31) states that "oxygen is the prominent union in most minerals. It is so large that the packing together of the ions in the structures is mainly a packing of oxygen ions, with the metallic cations in the interstices." Read (1948, p. 180) suggests that in metasomatic processes such as metamorphism and granitization "the large oxygen atoms of the silicate lattice remain more or less in position whilst the small migrating atoms drift through." It is on these authoritative statements that Barth bases his assertion that the volume of a rock is essentially the volume of the oxygen atoms in the rock, and that therefore constant volume means a constant number of oxygen atoms. This argument ignores the fact that a considerable proportion of any mineral or rock consists of empty space, and that due to different ionic packing, the proportion of empty space is likely to vary from one mineral to another, or from one rock to another.

The present writer, while recognizing the predominant role played by oxygen in silicate structures, is not convinced that oxygen remains at a constant level during metasomatism. The large size of the oxygen ion does not provide a valid argument, because the potash ion is nearly as large and yet potash apparently migrates with great ease. In the rearrangement of the $(Si, Al)O_4$ tetrahedra, resulting in the formation of new minerals, oxygen is liberated or introduced, presumably combining in or produced from OH^{-1} ions present in the ubiquitous aqueous fluid phase. Much mineralogical evidence points toward the high stability of the $(Si, Al)O_4$ tetrahedral structure and the high energy barrier to be overcome in destroying this structure. Apparently even in magmas SiO_4 tetrahedra are present. It appears therefore more logical to assume that the $(Si, Al)O_4$ building blocks of the silicate structure are merely rearranged to a different pattern and remain at an approximately constant

number in metasomatism, than that the number of oxygen atoms remains constant.

An illustration of this view is provided by the coronas developed in metamorphosed rocks consisting of magnesian olivine and calcic plagioclase only. Magnesian orthopyroxene generally occurs as the first rim around olivine crystals and is formed at the expense of that mineral. The orthodox equation for the reaction is

$$(Mg,Fe)_2SiO_4 + SiO_2 \rightarrow 2\ (Mg,Fe)SiO_3.$$

The source of the silica required for this reaction is a mystery in the present case. Shand (1945) has also expressed dissatisfaction with current equations explaining the formation of coronas. In the opinion of the present writer the formation of orthopyroxene from olivine results in this case from a rearrangement of the independent tetrahedra sharing no oxygen in olivine, to a pattern consisting of chains of tetrahedra, each sharing two oxygen atoms, in orthopyroxene. Together with this rearrangement of the fundamental building blocks Mg^{+2} and O^{-2} migrated outwards, the oxygen combining in OH^{-1} ions. SiO_4 tetrahedra were neither added nor subtracted in the process. If this is written at all in the form of a chemical equation, some such representation as the following would seem to be preferable to the orthodox equation

$$(Mg,Fe)_2SiO_4 + H_2O \rightarrow (Mg,Fe)SiO_3 + (Mg,Fe)^{+2} + 2OH^{-1}.$$

CONSTANT VOLUME IN METAMORPHISM AND GRANITIZATION

The law of equal volume has dominated petrological thought concerning metasomatic processes for a considerable length of time. It is based on such observations as the perfect preservation of fossils in metamorphic minerals (Bucher, 1953) and the pseudomorphous replacement of one mineral by another, both without sign of cracks or open spaces to indicate volume changes. A good case can therefore be made for constant volume relations in detail, but it remains uncertain whether its extension to rocks showing evidence of regional metamorphism and granitization is fully justified.

Acceptance of constant volume relations has led to acceptance of external rather than internal forces to explain the

intricate foldings so commonly observed in metamorphic terrains. Thus the remarkable thinning of highly metamorphosed pelitic beds is attributed to tight squeezing, and the up-doming of migmatized sediments is ascribed to the upward pressures of ascending magmas which remain hidden from direct observation. Whatever changes in volume did occur were the consequence of externally applied tension or compression, rather than the result of recrystallization and changes in composition within the rocks themselves. The logical conclusion is that regional metamorphism is the outcome of orogenesis by such external forces, rather than that the foldings observed in plutonic terrains result from metamorphism, an interesting viewpoint advanced by Read (1952).

Not all authorities have thus widely applied the law of equal volume. Van Hise (1904) assumed that metamorphism is normally attended by volume changes which can be calculated by the application of Lepsius' volume law (mol. vol. $= \frac{\text{mol. weight}}{\text{sp. gr.}}$). Irving (1911, pp. 664-665) argued that replacement is frequently accompanied by a decrease in volume, as shown by vugs in the new rock, but significantly states: "It is . . . impossible to calculate this change exactly from analyses, unless some one element has persisted unchanged in the process . . . which does not often happen. Whatever the theoretically calculated change, the observed facts show that in nearly all siliceous replacements and in the greater number of metallic replacements, there has been an appreciable and often marked decrease in the volume of the rock." More recently Eskola (1948) suggested that granitization of sediments causes an increase in volume whereby the rocks are arched up in mantled gneiss domes. Perrin (1950) employed the calculation methods of Brajnikov (1949) and Barth (1948) in an attempt to determine volume changes resulting from granitization processes, using analyses given by Grout (1937) and Anderson (1937) as examples. Those favoring volume changes in metamorphic and granitization metasomatism are distinctly in the minority today, and are by no means agreed that a volume increase or decrease is the outcome of such processes.

The volume of a rock really incorporates several variable components, the most significant of which are: (1) the ion

volumes, (2) the theoretical empty space resulting from ideal packing of the ions in different minerals, (3) the disorder empty space, and (4) the pore space which also includes the minute capillary and sub-capillary openings normally not measured in porosity determinations. Metasomatism resulting from regional metamorphism means essentially the invasion of a rock by an active, aqueous fluid of low viscosity, consequent to a rise in temperature level. This fluid must gain access to every part of the rock, hence it is reasonable to suppose that a large number of openings were available in the rock at the time of replacement. Many of these minute cracks probably were healed at a later stage in a similar fashion as the cracks in quartz from Washington (D. C.) were healed, leaving trails of fluid inclusions as only evidence of their erstwhile existence (Tuttle, 1949). Metasomatism probably is attended by an initial increase in both pore space and disorder empty space, which may be augmented by an increase, or offset by a decrease in ion volume and theoretical empty space. The assumption that throughout the process increases of some of the volume components are always exactly balanced by decreases in the other components, so that the bulk volume remains the same, is scarcely to be credited.

It appears impossible to calculate with accuracy the actual change in volume which might occur upon the metasomatic transformation of any given rock. On the basis of constant oxygen or constant number of $(Si,Al)O_4$ tetrahedra we may calculate apparent volume changes, but the results are representative of only two of the four volume components, and completely ignore volume changes resulting from differences in disorder empty space and pore space. It is also likely that during lengthy processes such as metamorphism, metasomatism, or granitization, there are several changes in volume which may in part counteract one another. Field studies may indicate such changes in volume, and the present writer attaches much greater significance to properly presented field evidence of volume changes than to hypothetical volume changes calculated, by whatever method, from chemical analyses. However, rigid adherence to the law of equal volume inevitably results in translation of the field evidence in terms of externally applied forces. Even when an unbiased attitude is preserved, field relations may yield apparently conflicting results. For instance, an initial decrease

in volume may be followed by a later increase in volume, or vice versa, during the same metamorphic cycle. Yet the writer believes that the problem of volume changes during metamorphism is probably attacked best by detailed studies of field relations. Evidence from orogenic belts of alternating periods of compression and tension might perhaps be interpreted as due to volume changes resulting from metamorphism and granitization.

CALCULATIONS BASED ON A CONSTANT NUMBER OF (SI,AL)O_4 TETRAHEDRA

Modern mineralogical and petrological theory evokes a picture in which changes in composition of rocks and changes of one mineral to another are the result of a rearrangement in the configuration of the fundamental building blocks of (Si,Al)O_4 tetrahedra, accompanied by removal, substitution, or introduction of the interstitial cations. The most probable conclusion is that in these changes the number of (Si,Al)O_4 tetrahedra remains the same, although there may be partial substitution of Si^{+4} by Al^{+3} in the tetrahedra. The problem is therefore to find a method which allows for the calculation of the approximate number of tetrahedra in a rock. If the mode and chemical analyses of the constituent minerals are available in addition to the chemical analysis of the rock, Si^{+4}-Al^{+3} substitution and the number of (Si,Al)O_4 tetrahedra can be calculated with accuracy. In the absence of chemical analyses of the constituent minerals, the geologic literature can be consulted for reliable mineral analyses from comparable rocks, in order to determine Si^{+4}-Al^{+3} substitution. If, as in the present case, the modes of the rocks are also lacking, a less accurate method of calculation must be used. In the C.I.P.W. calculation of the norm, the alkalies and calc-alkalies, after allotment for certain minor constituents, are used up in the formation of feldspars, the excess alumina, if any, being assumed to exist as corundum. A similar procedure is followed in table 15, based on the atomic proportions listed in table 8. Part of the Ca is allotted for apatite in the ratio P : Ca = 2 : 3, while the remaining (Ca+Ba) is allotted for anorthite in the ratio (Ca+Ba) : Al = 1 : 2. The combined alkalies are allotted for albite and orthoclase in the ratio (Na+K) : Al = 1 : 1. Aluminum used for feldspar is assumed to represent the total aluminum substituting for silicon in tetrahedral posi-

TABLE 15

Calculation of $(Si,Al)O_4$ Tetrahedra Number

	1	2	3	4	5	6
Ca	.0029	.0055	.0296	.0255	.0335	.0333
P	.0022	.0020	.0012	.0022	.0024	.0026
Ca for Ap.	.0029	.0030	.0018	.0033	.0036	.0039
Rest Ca	.0000	.0025	.0278	.0222	.0299	.0294
Ba	.0007	.0007	.0000	.0005	.0007	.0007
Al for An.	.0014	.0064	.0556	.0454	.0612	.0602
Na	.0412	.0454	.0584	.0746	.0648	.1016
K	.0968	.0922	.0856	.0682	.0814	.0748
Al for Ab.+Or.	.1380	.1376	.1440	.1428	.1462	.1764
Al repl. Si	.1394	.1440	.1996	.1882	.2074	.2366
Si	.9858	.9632	1.0113	1.0546	1.0754	1.0966
Proportion $(Si,Al)O_4$	1.1252	1.1072	1.2109	1.2428	1.2828	1.3332
Factor X	1.66×10^{22}	1.70×10^{22}	1.70×10^{22}	1.67×10^{22}	1.69×10^{22}	1.64×10^{22}
Number of $(Si,Al)O_4$ in 1 cc ..	1.867×10^{22}	1.886×10^{22}	2.063×10^{22}	2.073×10^{22}	2.180×10^{22}	2.180×10^{22}

TABLE 16

Number of Atoms to Constant $(Si,Al)O_4$ Tetrahedra Number
2.180×10^{22}

	1	2	3	4	5	6
N_o	5.040×10^{22}	5.098×10^{22}	4.849×10^{22}	4.842×10^{22}	4.760×10^{22}	4.610×10^{22}
N_{si}	1.909	1.896	1.820	1.850	1.813	1.793
N_{ti}	.025	.024	.018	.018	.015	.012
N_{al}	.772 { .271 / .501	.803 { .284 / .519	.655 { .360 / .295	.568 { .330 / .238	.549 { .367 / .182	.505 { .387 / .118
$N_{fe^{+3}}$	.049	.060	.030	.032	.048	.028
$N_{fe^{+2}}$	.134	.148	.141	.142	.092	.095
N_{mn}	.006	.012	.002	.009	.003	.001
N_{mg}	.090	.087	.108	.097	.086	.061
N_{ca}	.006	.010	.053	.045	.056	.054
N_{ba}	.001	.001	....	.001	.001	.001
N_{na}	.079	.089	.106	.130	.109	.166
N_k	.188	.181	.154	.120	.137	.122
N_{oh}	.885	.883	.586	.445	.326	.336
N_p	.005	.003	.002	.004	.004	.004
	9.189×10^{22}	9.295×10^{22}	———	———	———	———
	———	———	8.524×10^{22}	8.303×10^{22}	7.999×10^{22}	7.788×10^{22}

TABLE 17

Additions and Subtractions
(All Numbers x 10^{22})

	1-2		2-3		3-4		4-5		5-6	
	+	−	+	−	+	−	+	−	+	−
O	.058	...	...	.249	...	.007	...	.082	...	.150
Si	...	.013	...	.076	.030	...	...	.037	...	.020
Ti	...	.001	...	.006	...	...	...	.003	...	.003
Al	.013	...	.076	...	...	.030	.037	...	.020	...
	.018	...	...	.224	...	.057	...	.056	...	.064
Fe^{+3}	.011	...	...	.030	.002	...	.016	...	...	.020
Fe^{+2}	.014	...	...	.007	.001	...	...	.050	.003	...
Mn	.006	...	...	.010	.007	...	...	.006	...	.002
Mg	...	.003	.021	...	...	.011	...	.011	...	.025
Ca	.004	...	.043	...	...	.008	.011	...	...	.002
Ba	...	...	...	.001	.001	...	...	...	...	...
Na	.010	...	.017	...	.024	...	...	.021	.057	...
K	...	.007	...	.027	...	.034	.017	...	...	.015
OH	...	.002	...	.297	...	.141	...	.119	.010	...
P	...	.002	...	.001	.002	...	...	...	...	...
	.134	.028	.081	.852	.067	.288	.044	.348	.070	.281
Vals.	.068	.077	.145	.135	.178	.178	.087	.089	.053	.057

tion, the remaining aluminum being interstitial to the tetrahedra. Thus the proportion of $(Si,Al)O_4$ tetrahedra is represented by the atomic proportion of total Si plus Al used in feldspar. From this proportion the number of tetrahedra in 1 cc. of rock is found by multiplying with the conversion factor X (table 10). Table 16 lists the number of atoms, assuming a constant number of $(Si,Al)O_4$ tetrahedra of 2.180×10^{22}, the number found for the highest grade of the series.[5] Table 17 shows additions and subtractions of atoms obtained by comparing pairs of rocks of table 16. As may be expected, table 17 differs materially from table 11. Weights may again be calculated from the number of atoms listed in table 17, by multiplying with the weight of the corresponding atom (table 9).

Several significant features of the changes of composition in the six rocks can be deduced from table 16. First, it is clear that there is a general tendency toward decrease in oxygen; total oxygen, oxygen not bound in OH^{-1}, as well as oxygen bound in OH^{-1}. This means that in this rock series there is an increase in the number of oxygen atoms shared between $(Si,Al)O_4$ tetrahedra. Second, the number of silicon atoms decreases in the rock series, in spite of the number of $(Si,Al)O_4$ tetrahedra being kept constant, and in spite of the fact that the percentage silica of the original analyses shows a marked increase. The decrease in silicon at constant number of tetrahedra is explained by the progressive increase in Si^{+4}-Al^{+3} substitution. There is a progressive decrease in total aluminum, compounded of an increase in the number of Al atoms substituting for Si in the tetrahedral structure, and a decrease in the number of Al atoms in 6-coordination. Third, the number of cations interstitial to the $(Si,Al)O_4$ tetrahedra shows a progressive decrease in the rock series. The fact that there is a progressive decrease in both total oxygen and in the number of interstitial cations explains why there should be an increase in the percentage of silica in the original analyses, although the number of silicon atoms decreases. The rocks have been relatively enriched in silica, yet silicon atoms were not added but *removed* in the process.

We may recalculate the analyses also to a hypothetical unit cell consisting of a certain number of $(Si,Al)O_4$ tetrahedra.

[5] It is purely a matter of choice to which number of $(Si, Al)O_4$ tetrahedra the data are recalculated.

This considerably simplifies the computations, but the results are again qualitative rather than quantitative, and may even be misleading. Barth (1948) used a similar procedure in his assumption of constant number of oxygen atoms, and chose a unit cell of 160 O atoms, with the further assumption that rocks generally contain 100 cations to 160 O atoms. It is easily calculated from table 10 that in the present case the number of oxygen atoms per 100 cations varies from 142 for analysis 2, to 157 for analysis 5. A unit cell of a certain number of $(Si,Al)O_4$ tetrahedra would be entirely artificial and would have no constant relation to the number of included cations or oxygen atoms. Hence the present writer cannot recommend such a procedure.

In replacement ore bodies $(Si,Al)O_4$ tetrahedra have evidently been removed. Similarly, in weathering the tetrahedral building blocks of silicates may be partly broken down and removed. However, these processes are perhaps not the same as the metasomatic changes in chemical compositions of rocks which accompany metamorphism and granitization. Weathering proceeds at lower energy levels than apply to metamorphism and granitization. Moreover, rock-reconstitutions in metamorphism are usually effected in response to a gradually rising energy level, while replacement ore bodies are believed to have been formed in an environment of slowly diminishing temperatures. The assumption of a constant number of $(Si,Al)O_4$ tetrahedra clearly cannot be applied to *all* metasomatic processes, but it is thought to be valid when restricted to metamorphism, granitization, and similar replacements of silicates by other silicates in the absence of actual melting.

Metamorphism and granitization are here regarded as essentially the result of increasing temperatures. This is attended by an initial rapid increase in pore spaces, affording passages for invading, active fluids, the media of replacement. Changes of volume necessarily occur as the outcome of increase in pore space and disorder empty space, recrystallization, and ionic substitution, addition, or subtraction, but such changes can only be predicted qualitatively from field relations, and probably vary even during the different stages of the process. Volume changes result in the deformation of the rocks, rendered plastic by the existing higher temperatures and permeation by the aqueous fluids. Thus, the intricate foldings often observed in

metamorphic terrains are believed to be, at least in part, the outcome of these volume changes which in turn result from the rise in temperature. This last factor initiates metamorphism and granite formation.

CONCLUSIONS

Doubts are expressed in this paper that either constant volume relations or a constant number of oxygen atoms invariably prevail in regional metamorphism and granitization. These assumptions form the basis of all current methods of calculating changes in bulk composition of rocks in their transformation from one metamorphic grade or phase of granitization to another. Instead, it is suggested that the number of $(Si,Al)O_4$ tetrahedra remains constant in these processes, which are further marked by partial substitution of Si^{+4} by Al^{+3}, rearrangement of the tetrahedral building blocks of silicate structures to different patterns, and substitution, introduction, or removal of the interstitial ions. A method is suggested whereby changes in bulk composition of rocks during these processes may be calculated. Volume changes which attended the transformation of the rocks may be calculated on the same basis, but the results are not believed to have much significance.

In the writer's view, metasomatic transformations of rocks as a result of regional metamorphism, are heralded by an increase in temperature and the soaking of the rocks by an active, aqueous fluid which permeates the rocks through passages opened at least partly in response to rising temperature. Changes in volume of the rocks may be responsible for their deformation, and in the case of granitized rocks, for their eventually assuming intrusive relations towards the associated rocks. Thus a great deal of the foldings exhibited by plutonic terrains may be the consequence of metamorphism and granitization, instead of their being the outcome of external forces which also resulted in metamorphism and granitization.

ACKNOWLEDGMENTS

The writer has benefited greatly from many discussions with his students and with geologists interested in the problems of regional metamorphism. Drs. Ch. H. Behre, W. H. Bucher, A. F. Buddington, H. H. Hess, and H. Kuno critically read the first draft and made many valuable suggestions. The views

expressed in this paper are entirely the writer's, but he is very appreciative of the kind interest shown and helpful comments made by these fellow geologists.

References

Ahrens, L. H., 1952. The use of ionization potentials. Part 1. Ionic radii of the elements: Geochim. Cosmochim. Acta, vol. 2, pp. 155-169.

Anderson, G. H., 1937. Granitization, albitization and related phenomena in the Inyo Range of California-Nevada: Geol. Soc. America Bull., vol. 48, pp. 1-74.

Barth, T. F. W., 1948. Oxygen in rocks: A basis for petrographic calculations: Jour. Geology, vol. 56, pp. 50-60.

Bragg, W. L., 1937. Atomic structure of minerals, Cornell University Press, Ithaca, N. Y.

Brajnikov, B., 1949. Les rapports numériques et volumiques de l'oxygêne dans les minéraux et les roches: Instituto de Tecnologia Industrial, Minas Gerais, Bol. 8.

Bucher, W. H., 1953. Fossils in metamorphic rocks: A review: Geol. Soc. America Bull., vol. 64, pp. 275-300.

Chao, E. C. T., 1951. Granitization and basification by diffusion: Norsk geol. tidsskr., vol. 29, pp. 84-107.

Ellis, J., 1947. The Marievale granophyre—a metamorphic rock: Geol. Soc. South Africa Trans., vol. 50, pp. 121-160.

Eskola, P. E., 1948. The problem of mantled gneiss domes: Geol. Soc. London Quart. Jour., vol. 104, pp. 461-476.

Faber, H., 1941. On the salt solutions in microscopic cavities in granites: Danmarks geol. Undersögelse, vol. 2, no. 67.

Fairbairn, H. W., 1943. Packing in ionic minerals: Geol. Soc. America Bull., vol. 54, pp. 1305-1374.

Goldschmidt, V. M., 1920. Die Injektionsmetamorphose im Stavanger-Gebiete. Geologisch-petrographische Studien im Hochgebirge des südlichen Norwegens. V: Norske vidensk.-akad. Skr., Mat.-Nat. Kl., no. 10.

———, 1928. Ueber die Raumerfüllung der Atome (Ionen) in Kristallen und über das Wesen der Lithosphäre: Neues Jahrb., Beilage-Band 57, Abt. A, pp. 1119-1130.

Grout, F. F., 1937. Criteria of inclusions in plutonic rocks: Geol. Soc. America Bull., vol. 48, pp. 1521-1572.

Irving, J. D., 1911. Replacement ore-bodies and the criteria for their recognition: Econ. Geology, vol. 6, pp. 527-561, 619-669.

Joplin, G. A., 1952. The granitization process and its limitations as exemplified in certain parts of New South Wales: Geol. Mag., vol. 89, pp. 25-38.

Lindgren, W., 1933. Mineral deposits, 4th ed., McGraw-Hill Book Company, New York.

Perrin, P., 1950. L'oxygêne en les calculs pétrographiques, une discussion: Jour. Geology, vol. 58, pp. 163-168.

Read, H. H., 1948. A commentary on place in plutonism: Geol. Soc. London Quart. Jour., vol. 104, pp. 155-205 (presidential address).

———, 1952. Metamorphism and granitization: Geol. Soc. South Africa Trans., vol. 54, suppl.

Reynolds, D. L., 1943. The south-western end of the Newry Igneous Complex. A contribution towards the petrogenesis of the granodiorites: Geol. Soc. London Quart. Jour., vol. 99, pp. 205-246.

———, 1946. The sequence of geochemical changes leading to granitization: Geol. Soc. London Quart. Jour., vol. 102, pp. 389-446.

Rosenqvist, I. Th., 1949. The distribution of oxygen in the lithosphere and oxygen in rocks; a basis for petrographic calculations. A discussion: Jour. Geology, vol. 57, pp. 420-423.

Shand, S. J., 1945. Coronas and coronites: Geol. Soc. America Bull., vol. 56, pp. 247-266.

Tuttle, O. F., 1949. Structural petrology of planes of liquid inclusions: Jour. Geology, vol. 57, pp. 331-356.

Van Hise, C. R., 1904. A treatise on metamorphism: U. S. Geol. Survey Mon., 47.

Department of Geology
Columbia University
New York, N. Y.