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Al-Si ORDER-DISORDER AND CELL PARAMETERS IN CALCIC PLAGIOCLASES

RIASSUNTO. — I parametri delle celle dei plagioclasi permettono di distinguere una serie di « alta » ed una di « bassa temperatura » anche nell'intervallo An_{70}-An_{100}, a condizione che i termini di alta siano equilibrati a temperature prossime alla $T_{solidus}$. Di particolare interesse si è dimostrato il diagramma γ/composizione in cui le due curve di alta e di bassa si intersecano per una composizione di circa An_{80}. Per spiegare questo comportamento sono stati analizzati i dati relativi a strutture di plagioclasi di alta e di bassa e ne sono state tratte le seguenti conclusioni:

1) le variazioni di γ indotte dal trattamento termico trovano piena spiegazione nel grado d'ordine Al-Si;
2) un lieve ma significativo grado d'ordine è presente nei plagioclasi di alta, ad eccezione che nell'intervallo An_0-An_{20}.

Il contributo differenziale dei legami Ca/Na-O sugli ossigeni dei diversi tetraedri offre un'interpretazione cristallochimica del grado d'ordine presente nei plagioclasi equilibrati ad altissima temperatura.

ABSTRACT. — Unit-cell parameters of plagioclases allow to distinguish a « high » and a « low temperature » series in the range An_{70}-An_{100}, on condition that the high samples be equilibrated at temperatures near the $T_{solidus}$. Particular concern is taken in the plot γ versus An content, that shows the high and the low curves to intersect at about An_{80}. In order to explain this behaviour, the structural data of high and low plagioclases are analyzed and the following conclusions are drawn:

1) the variations of γ induced by thermal treatment are explained in terms of Al-Si order degree;
2) a significant amount of order is present in the high plagioclases, with the exception the sodic portion (An_0-An_{20}).

The different amount of the Ca/Na-O bond strengths on the oxygen atoms of the different tetrahedra offers a crystal chemical interpretation of the order degree present in plagioclases equilibrated at very high temperature.

It is well known that unit-cell dimensions in plagioclases are controlled by the Al-Si configuration and therefore by the structural state, that in turn depends upon the thermal history of the plagioclase. γ and γ-related parameters in particular are highly correlated to the structural state, i.e. to the Al-Si order degree. This correlation has been exhaustively interpreted (RIBBE et al., 1970; KROLL, 1971; BRUNO & FACCHINELLI, 1974b). Therefore in a plot γ versus An content is possible to distinguish a series of « high » (disordered) and a series of « low » (ordered) plagioclases. Of

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course intermediate structural states can exist. The distinction between the two series however is not possible in the whole range of composition of plagioclases; indeed it is very strong for albite but decreases with increasing An content and disappears at a composition around An_{70}. In the range An_{70}-An_{100} neither thermal treatments nor very peculiar geological environments (lavas or blocks ejected from volcanoes) could give plagioclase specimens with unit cell dimensions distinguishable from the « low » isochemical terms (LAVES & GOLDSMITH, 1954; RIBBE & MEGAW, 1962). It has been commonly accepted, on the basis of the above observations, that in this range two thermal series are impossible to be distinguished by means of the cell parameters.

Recently, significant modifications of the cell dimensions could be induced in an anorthite specimen by means of a thermal treatment near the melting point followed by a quenching (BRUNO & FACCHINELLI, 1974 a). Similar results have been observed by LAVES & GOLDSMITH (1955) and by KROLL (1971) in the products of a short devetrification at 1430° C of a glass of anorthitic composition, but the « anomalous » anorthite had been considered metastable by these authors. The results of BRUNO & FACCHINELLI (1974 a), on the contrary, as the starting material was a natural anorthite, allow to reject the hypothesis of metastability and probably reflect a structural state in equilibrium at very high temperature. The refinement of the structure of the above quoted quenched anorthite has been carried out (BRUNO et al., 1976; CHIARI et al., 1978) and the results have shown an Al-Si configuration not strictly controlled by the « Loewenstein rule » (LOEWENSTEIN, 1954), that is a non perfect Al-Si alternation. This Al-Si configuration can explain the observed unit-cell dimensions.

The above results have lead the authors to analyze more in detail the modifications of the cell parameters of plagioclases in the calcic portion. Further results (FACCHINELLI & BRUNO, 1977) have shown that in the range An_{70}-An_{100} a high temperature series, distinct by the low one, can be identified by means of the cell parameters only if specimens heated at temperature near the melting point are considered. Thermal treatments at lower temperature, even if very high in absolute (e.g. 1430° C for the term An_{100}), are not able to induce variations in the Al-Si distribution and therefore in the unit-cell dimensions. This last observation is in agreement with the non-occurence in nature of « high » calcic plagioclases with unit-cells different from the « low » ones.

Aim of this work is to determine the variations of the unit-cells of the « high » plagioclases in the range An_{50}-An_{100} and to give a structural explanation of the observed variations.

Unit-cell parameters

Unit-cells of plagioclases from different sources, partly original and partly offered from the literature, have been used to define the variations of unit-cell dimensions in plagioclases An_{50}-An_{100}. Two calcic plagioclases from basic granulites of Ivrea-

TABLE 1

Chemical compositions in wt.% of oxydes and in number of atoms on the basis of 8 oxygens

	A	B	C	D
CaO	18.90	18.42	17.38	17.42
Na_2O	.92	.97	1.63	1.59
K_2O	.03	.05	.03	.03
FeO	.13	.15	.01	.06
MgO	-	-	-	-
Al_2O_3	35.24	34.53	34.36	33.79
SiO_2	45.13	44.10	46.00	46.11
Total	100.34	98.22	99.41	99.00
Ca	.932	.928	.862	.867
Na	.082	.089	.145	.143
K	.002	.003	.002	.003
Fe	.005	.006	.007	.002
Al	1.911	1.914	1.873	1.850
Si	2.077	2.074	2.127	2.142

A and C: untreated; B and D: treated. Analyst: G. VEZZALINI.

-Verbano Zone (Western Italian Alps) have been selected. Crystals have picked at the microscope and some of them have been heated for 16-18 hours at a temperature of about 30° C below the $T_{solidus}$. Chemical analyses have been carried out both on the treated and on the untreated crystals; the results are given in table 1. The analyses were carried out in the wavelength-dispersive mode on a fully automated ARL-SEMQ instrument operated at 15 kV, 0.15 μA beam current and a defocused beam (spot size ≃ 50 μm). Under these conditions no appreciable loss of Na counts was detected during three successive analyses on the same specimen point. Counting times were 2, 20, 2 s for high background, peak and low background respectively. On-line data reduction was based on the

TABLE 2

Unit-cell parameters of low plagioclases

An	Or	a	b	c	α	β	γ	V	Tr[110]	Tr[1$\bar{1}$0]	Sources
100	-	8.173(1)	12.869(1)	14.165(1)	93.113(6)	115.913(6)	91.261(6)	1337.7	15.092	15.396	Wainwright & Starkey (1971)
98	.3	8.173(1)	12.869(2)	14.165(2)	93.11(2)	115.91(1)	91.26(1)	1337.7	15.092	15.396	Bruno et al. (1976)
93.1		8.179	12.873	14.180	93.21	115.97	91.11	1338.6	15.117	15.385	Bambauer et al. (1967)
92	.1	8.177(1)	12.869(2)	14.174(3)	93.25(3)	115.95(2)	91.05(1)	1337.5	15.120	15.373	This work
86	.2	8.181(1)	12.875(2)	14.191(3)	93.32(3)	116.03(2)	90.94(1)	1339.4	15.141	15.367	"
80	.2	8.179	12.868	14.186	93.34	116.08	90.80	1337.4	15.151	15.343	Bambauer et al. (1967)
77	.3	8.180	12.869	14.192	93.38	116.13	90.63	1337.6	15.173	15.324	" "
73.1	.6	8.181	12.870	14.198	93.41	116.10	90.55	1339.0	15.184	15.316	" "
69	.7	8.179	12.869	14.204	93.49	116.16	90.36	1338.4	15.204	15.291	" "
59.8	.2	8.173	12.862	14.214	93.56	116.19	89.98	1337.6	15.241	15.237	" "
53.8	1.0	8.173	12.855	14.220	93.58	116.23	89.79	1337.0	15.256	15.210	" "

An, Or in mol.%; *a, b, c,* Tr[110], Tr[1$\bar{1}$0] in Å; α, β, γ in degrees; V in Å^3.

ZIEBOLD & OGILVIE (1964) method by the use of ALBEE & RAY (1970) correction factors. Synthetic plagioclase glasses and natural microcline were used as standards for Si, Al, Ca, Na and K; natural olivine for Fe and Mg.

X-ray powder spectra of both treated and untreated specimens have been obtained with a Guiner-De Wolff camera, using the CuKα radiation and an internal standard.

Unit-cell parameters have been refined by least-squares. Data concerning 9 plagioclases chemically analyzed and assumed to be of low thermal state have been also chosen from literature. Crystallographic parameters, chemical composition and sources of low plagioclases are given in table 2 .As far as the « high » series is concerned, both synthetic materials (KROLL, 1971) and natural heated samples (KROLL, 1978; BRUNO et al., 1976) have been used. Nature of starting materials, compositions, conditions of thermal treatment and sources are given in table 3; unit-cell dimensions in table 4. α and γ show the most marked and interesting variations in function of thermal state and therefore these angular parameters and the Tr [110] (1), a parameter strongly related to γ (KROLL, 1971), have been plotted versus An content (figg. 1, 2, 3). From inspection of these figures two distinct trends of the « high » and « low » series are well identifiable in the whole range taken in consideration even if the best fit curves are only tentative ones. These results are in agreement with the curves proposed by FACCHINELLI & BRUNO, 1977. The two curves, markedly separate at composition around An_{50}, converge and then intersect with increasing An content. Therefore in the calcic portion of the diagram the two curves are separate again but the relationships between thermal state and modifications of the crystallographic parameters are inverse with respect to the sodic portion. The point of intersection can only approximately be placed around An_{80} because of the uncertainty

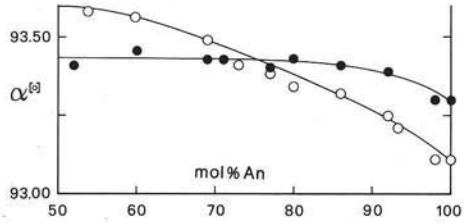

Fig. 1. — γ plotted versus composition. O: low terms; ●: high terms.

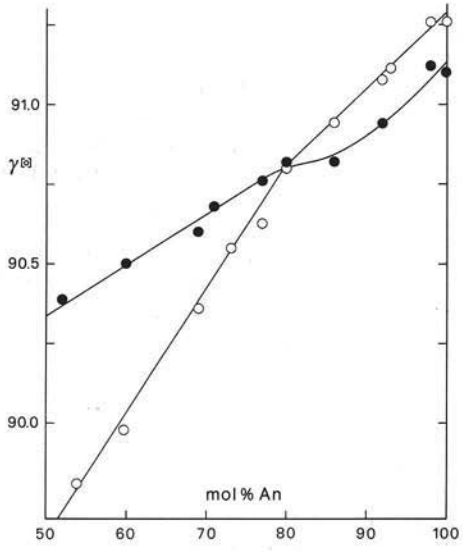

Fig. 2. — α plotted versus composition. Symbols as in fig. 1.

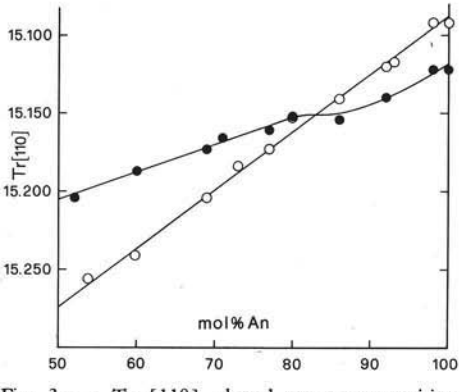

Fig. 3. — Tr [110] plotted versus composition. Symbols as in fig. 1.

(1) $\mathrm{Tr}\ [110] = \sqrt{a^2 + b^2 + 2\ ab\ cos\gamma}$

in the position of the curves and their similar slopes, in particular in the α plot. As predictable, the Tr [110] plot is closely analogous to the γ plot.

To sum up, in the range An_{70}-An_{100} « high » and « low » series can be distinguished but on condition that high plagioclases be equilibrated at temperatures near the $T_{solidus}$.

TABLE 3

Composition An	Or	Starting materials	Thermal treatment T°C	t(h)	Sources
100	-	glass	1525	.08	Kroll (1971)
98	.2	nat.	1530	.50	Bruno et al. (1976)
92	.3	nat.	1480	16	This work
86	.2	nat.	1450	18	"
80	-	glass	1410	360	Kroll (1971)
77	-	glass	1390	360	"
71	-	glass	1360	360	"
69	.2	nat.	1365	1008	Kroll (1978)
60	-	glass	1300	360	Kroll (1971)
52	2.5	nat.	1255	696	Kroll (1978)

Al-Si order-disorder

Among the results given in the last paragraph, the variation of γ is particularly interesting because of its aboved emphasized structural meaning. The observed variations of this angular parameter put the question of wich are the structural modifications induced by the thermal treatment in plagioclases of composition ranging from An_{80} to An_{100}. By extrapolating the relationships between γ and structural state valid in alkali feldspars and sodic plagioclases, one should infer, paradoxically, that a thermal treatment induces an increase of the Al-Si order degree, inasmuch as γ decreases. The problem can be directly approached by analyzing the data on the structures of high and low plagioclases available in literature. In table 5 are listed 1) the average T-O bond lengths of individual tetrahedra (2); 2) the ΔAl of each structure, calculated as $\Delta Al = t_1(0) - 1/3\ [t_1(m) + t_2(0) + t_2(m)]$ (RIBBE, 1972, 1975). The last parameter

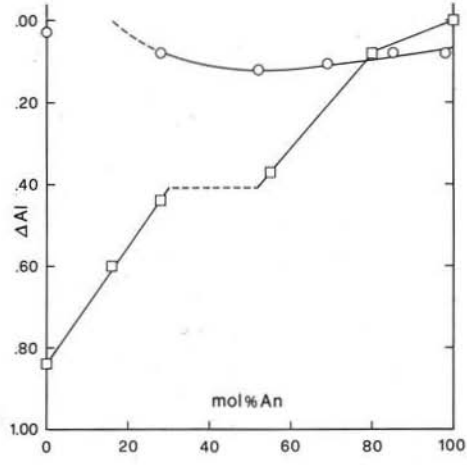

Fig. 4. — Δ Al plotted versus composition. □: low terms; O high terms.

(2) In 14 Å plagioclases 16 independent tetrahedral sites exist. In order to make possible the comparison with 7 Å plagioclase, the 4 sites related by the pseudo-symmetry vectors [1/2, 1/2, 0] and [0, 0, 1/2] have been averaged so to obtain 4 independent sites.

TABLE 4
Unit-cell parameters of high plagioclases

An	Or	a	b	c	α	β	γ	V	Tr[110]	Tr[1$\bar{1}$0]	Sources
100	-	8.186	12.874	14.175	93.30	115.73	91.10	1341.8	15.122	15.388	Kroll (1971)
98	.2	8.186(1)	12.876(2)	14.182(2)	93.30(2)	115.79(1)	91.12(1)	1342.2	15.122	15.392	Bruno et al. (1976)
92	.3	8.180(1)	12.875(2)	14.178(2)	93.39(2)	115.84(2)	90.94(1)	1340.2	15.140	15.367	This work
86	.2	8.184(2)	12.872(3)	14.183(3)	93.41(3)	115.91(3)	90.82(1)	1340.2	15.154	15.352	"
80	-	8.181	12.871	14.186	93.43	115.86	90.82	1340.7	15.152	15.349	Kroll (1971)
77	-	8.178	12.875	14.188	93.40	115.91	90.76	1339.6	15.161	15.344	"
71	-	8.174	12.872	14.190	93.43	115.95	90.68	1338.8	15.166	15.330	"
69	.2	8.1748(6)	12.8687(7)	14.1928(10)	93.428(5)	115.986(4)	90.602(5)		15.173	15.318	Kroll (1978)
60	-	8.172	12.872	14.196	93.46	116.03	90.50	1338.2	15.187	15.307	Kroll (1971)
52	2.5	8.1739(7)	12.8752(9)	14.2064(14)	93.407(7)	116.133(5)	90.394(6)		15.204	15.297	Kroll (1978)

Units as in table 2.

TABLE 5

H I G H

	An_0(1)	An_{28}(2)	An_{52}(2)	An_{69}(2)	An_{85}(3)	An_{98}(4)
$T_1(0)$	1.646	1.662	1.675	1.679	1.687	1.690
$T_1(m)$	1.641	1.649	1.656	1.663	1.676	1.675
$T_2(0)$	1.641	1.649	1.658	1.663	1.676	1.683
$T_2(m)$	1.642	1.649	1.656	1.662	1.673	1.677
ΔAl	.03	.09	.12	.11	.08	.08

L O W

	An_0(5)	An_{16}(6)	An_{28}(6)	An_{55}(7)	An_{80}(8)	An_{100}(9)
$T_1(0)$	1.740	1.718	1.700	1.70	1.684	1.683
$T_1(m)$	1.609	1.622	1.637	1.65	1.670	1.680
$T_2(0)$	1.614	1.629	1.638	1.64	1.667	1.679
$T_2(m)$	1.615	1.630	1.639	1.65	1.675	1.680
ΔAl	.84	.60	.41	.35	.09	.02

1) PREWITT et al. (1976); 2) KROLL (1978); 3) FACCHINELLI et al. (1979); 4) BRUNO et al. (1976); 5) WAINWRIGHT & STARKEY (1968); 6) PHILLIPS et al. (1971); 7) TOMAN & FRUEH (1973); 8) FLEET et al. (1976); 9) WAINWRIGHT & STARKEY (1971).

is a measure of the Al concentration in $T_1(0)$ sites, therefore a measure of the Al-Si order degree. The ΔAl values are plotted versus An content in fig. 4, wich displays two curves clearly analogous to the γ curves. From inspection of this figure the following conclusions can be drawn:

1) thermal treatment increases the Al-Si order degree in the range An_{80}-An_{100}, decreases it in the range An_0An_{80};
2) at a composition about An_{80} the order degree is not affected by thermal treatment;
3) in the whole range of composition, with the possible exception of the portion An_0-An_{20}, the high plagioclases never reaches the perfect disorder (ΔAl = 0.00).

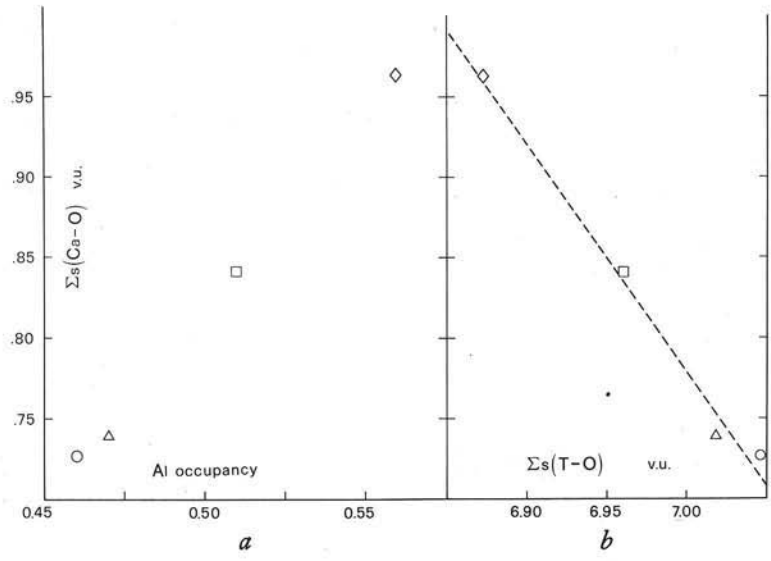

Fig. 5. — Ca-O bond strength sums on the oxygens of tetrahedra plotted versus Al occupancies (*a*) and versus T-O bond strength sums (*b*) in the structured of a quenched anorthite. ◇: $T_1(0)$; □: $T_2(0)$; △: $T_2(m)$; ○ $T_1(m)$.

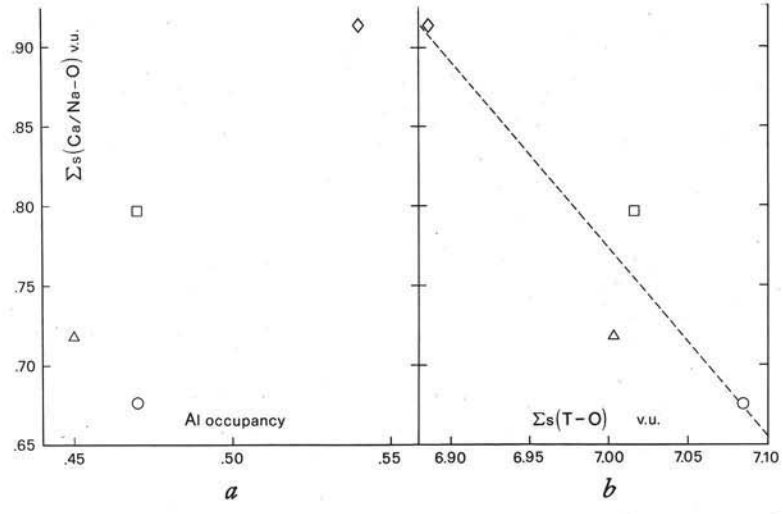

Fig. 6. — Ca/Na-O bond strength sums on the oxygens of tetrahedra plotted versus Al occupansies (*a*) and versus T-O bond strength sums (*b*) in the structure of a quenched bytownite. Symbols as in fig. 5.

To throw light on the apparent contradiction of point 1) it is necessary to consider that in the low anorthite structure the Al-Si configuration is controlled by the Löwenstein rule, which imposes a perfect Al-Si alternation and is incompatible with an Al segregation in $T_1(0)$ sites. It follows that $\Delta Al = 0$, but in this case it is not indicative of a perfect disorder, rather of an ordering scheme different

from the albite scheme. Thermal treatment induces a certain degree of Al-Si diffusion that destroys the perfect alternation and allows an Al segregation in $T_1(0)$ sites ($\Delta Al = 0.08$). The forces driving this segregation will be discussed in the next paragraphs. The same behaviour as in anorthite is observable in the range An_{80}-An_{100}, where the structure is dominated by the anorthite scheme. In the range An_0-An_{80}, with the possible exception of the albitic portion, the thermal treatment leaves a residual amount of order, the extent of which ($\Delta Al \simeq 0.1$) is approximately the same as observed in the high calcic plagioclases.

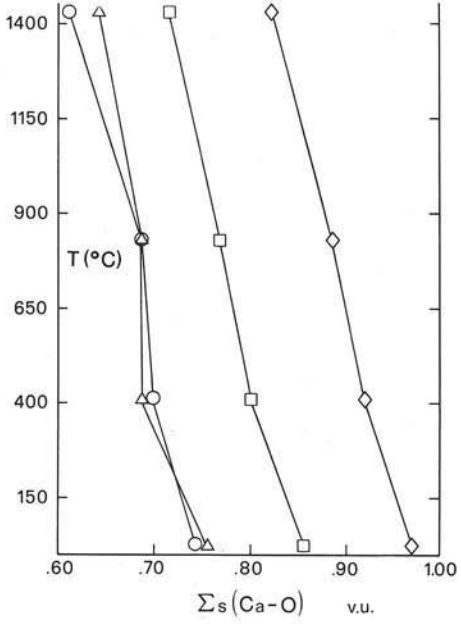

Fig. 7. — Ca-O bond strength sums on the oxygens of tetrahedra plotted versus temperature in the structure of anortite. Symbols as in fig. 5.

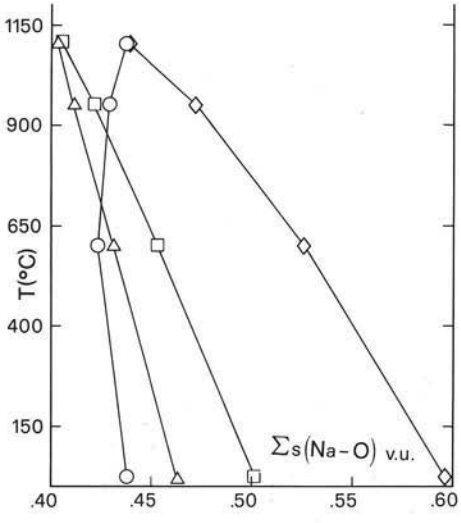

Fig. 8. — Na-O bond strength sums on the oxygens of tetrahedra plotted versus temperature in the structure of high albite. Symbols as in fig. 5.

To sum up, the proposed curves of γ versus composition can be explained in terms of Al-Si configuration.

Crystalchemical discussion

The results given in the last paragraph open a question: why plagioclases equilibrated at extremely high temperature display a significant degree of Al concentration in $T_1(0)$ sites and not a fully disordered structure? A tentative answer, proposed and discussed in a previous paper concerning anorthite (Chiari et al., 1978), is that during the dynamic disorder occurring at high temperature the « lenght of stay » of Al and Si in the different T sites is controlled by different bond strength contributions from Ca/Na to the oxygen atoms of each tetrahedron. The higher

bond strength sum from non tetrahedral cations to the oxygens of the $T_1(0)$ tetrahedra favours the presence in these sites of a trivalent cation (Al) rather than a tetravalent one (Si). According to this model the ultimate cause of the Al-Si configuration is therefore the charge balance requirement. The quenching freezes the dynamic equilibrium and turns a time average into a space average. Relevant to this problem are the data on the structures of an anorthite quenched from 1530° C (Bruno et al., 1976; Chiari *et* al., 1978) and of a bytownite quenched from 1450° C (Facchinelli et al., 1979). The values of the bond strength sums of Ca/Na-O bonds for each tetrahedron, calculated with the bond length-bond strength curves proposed by Brown & Kang Kun Wu (1976), are plotted versus tetrahedral Al content for the two structure in fig. 5*a* and 6*a*. A good correlation is observed for anorthite and a rough one for bytownite. In order to check the charge balance of the two structures, however, it is necessary to take into account all the T-O bonds involving each tetrahedron, whereas the Al occupancies are directly related only to the T-O bonds from the T atoms inside the tetrahedra.

In fig. 5*b* and 6*b* the Ca/Na-O bond strength sum is plotted against the sum of all the T-O bond strengths on the oxygen of a tetrahedron. The correlations displayed by these figures show the atteinment of charge balance in the two structures; the comparison with fig. 5*a* and 6*a* shows that the Al occupancies play a significant role in the achievement of the balance. For a more detailed discussion see Facchinelli et al. (1979).

The above considerations have been inferred from data of structural investigations carried on at room temperature on quenched specimens. Nevertheless these structures are believed to reflect closely the high temperature situation not only as for Al-Si configuration, that can be changed only through very sluggish diffusive transformation, but also as for the Ca/Na-O contribution. The structures of anorthites refined on data collected at high temperature by Foit & Peacor (1973) and Czank (1973) demonstrate that no significant modification affects the environment of the non tetrahedral cation during the heating (see fig. 7). A different behaviour is displayed by the high albite: in this structure the unit-cell moves towards monoclinic symmetry and the Na environment undergoes drastical modifications with increasing temperature (Prewitt et al., 1976). When equilibrated at temperature above 1000° C, the unit-cell of albite exhibits a monoclinic metric. In these conditions the preferential contribution of Na-O bonds to the oxygens of $T_1(0)$ tetrahedra, which is the cause of the Al segregation in $T_1(0)$, is missing (see fig. 8). Consequently the ΔAl approaches the value of 0.00 within the limits of significance. Unfortunately structures of high plagioclases, of intermediate composition, refined with data collected at high temperature, are not available. It has been observed however, that the transition triclinic-monoclinic is possible only in the range An_0-An_{20} (Kroll, 1971). It is therefore justifiable to infer that only within these limits a perfect disorder can take place in high temperature plagioclases.

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E. Bruno, A. Facchinelli

Al-Si ORDER-DISORDER AND CELL PARAMETERS IN CALCIC PLAGIOCLASES

In the captions of Fig. 1 and 2, page 62, α and γ must be interchanged.

Rendiconti Società Italiana di Mineralogia e Petrologia, Vol. 35 (1979), fasc. 1, pagg. 217-225.

Riccardo Vannucci, Ambrogio Mazzucotelli, Sandro Meloni, Massimo Oddone

CLASTI ANDESITICI NEI CONGLOMERATI DELLA VAL D'AVETO CARATTERISTICHE CHIMICHE E CONSIDERAZIONI PETROGENETICHE

A pagina 226 è stata omessa la seguente parte finale della bibliografia:

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