

## Variations in the chemical compositions and lattice dimensions of (Ba,K,Na)-feldspars from Otjosondu, Namibia and their significance

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### Abstract

X-ray and chemical studies of twenty samples of (Ba,K,Na)-feldspars from Otjosondu, Namibia reveal that they can be divided into the following three groups: (1) Cn(Ba Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>)-poor, Ab-rich ones containing unmixed albite phases (2) Cn-rich varieties showing occasional unmixed celsian phases (3) those with Cn contents intermediate between those of the first two groups. The compositions of the unmixed phases in the second group of specimens, determined with the electron microprobe, are Cn<sub>54</sub>Or<sub>34</sub>Ab<sub>12</sub> and Cn<sub>95</sub>Or<sub>5</sub>. Almost all contain considerable amounts of Fe<sup>3+</sup> (up to 10 atomic %), which probably replaces Al<sup>3+</sup>. As a result, their lattice dimensions are slightly larger than those of other (Ba,K)-feldspars reported previously.

In order to estimate the influence of the Na<sup>+</sup>-ion on the lattice constants of (Ba,K,Na)-feldspars, all of the specimens were ion-exchanged in KCl-melt. The lattice parameters were corrected for the presence of Fe<sup>3+</sup> and Na<sup>+</sup> and then correlated with volumes or Cn contents in order to determine their variations with respect to chemical composition and structural state.

It was observed that the cell edges of (Ba,K)-feldspars behave similarly to those of the plagioclases; however, the magnitudes of the changes involved are different in the two groups. This, in turn, can be attributed to differences in their respective chemical composition and to certain structural features of feldspars in general.

### Introduction

Natural and synthetic feldspars, particularly the alkali feldspars and plagioclases, have been the subject of careful and intensive study during the last thirty years. Results of these studies have revealed that the physical properties and structures of all feldspar mixed crystals depend upon the order/disorder of the (Si,Al) atoms and unmixing into different phases. However, both of these phenomena were found, in turn, to depend upon the composition and structure of the end members involved. For example, the similarity of the end members of the alkali feldspars with respect to both these features leads to simpler ordering schemes and exsolution textures compared to those of plagioclase feldspars. The latter exhibit very fine exsolution lamellae and complicated superstructures. Intergrowths of Ba-poor and Ba-rich feldspars (Viswanathan, 1978) in a few specimens from Otjosondu, Namibia, suggest that the barium feldspars are probably so influenced by these two phenomena

that exsolution textures coarser than those found in the basic plagioclases appear. Hence, the aim of this paper is to study the variations in the chemical composition and structural state of (Ba,K,Na)-feldspars from Otjosondu in order to determine their effect on the lattice parameters and, if possible, to determine the exact composition of the unmixed phases in the specimens showing exsolution. It is hoped that such investigations may also contribute to the understanding of the complicated subsolidus relations in the plagioclase feldspars, which are chemically similar to the (Ba,K)-feldspars because of the coupled substitution of Na (or K) + Si by Ca (or Ba) + Al. Preliminary results of this study were presented by Viswanathan and Brandt (1978).

All the investigated specimens from Otjosondu occur in the metamorphosed manganese deposits which were described by De Villiers (1952) and Roper (1956). According to Katz (1978) the barium feldspars are found mainly in banded and massive manganese ores, which also contain yellow garnets or pyroxene. The feldspar crystals occur mostly in

pockets of irregular sizes. The crystals are usually large, some of them reaching a few millimeters or even centimeters. Ba-feldspars with compositions  $Cn_{10}$  ( $Cn$  refers to  $BaAl_2Si_2O_8$ ) and  $Cn_{94}$  were first reported by De Villiers (1951). Later Vermaas (1953) described two specimens with the compositions  $Cn_{50}$  and  $Cn_{55}$ .

Gay and Roy (1968) investigated both synthetic and partially ordered natural Ba-feldspars from different localities. They correlated the lattice parameters with  $Cn$  content and established the following trends:

(1) The volume of Ba-feldspars increases with increasing  $Cn$  content. The lattice dimension  $a$  shows a substantial increase.

(2) The angle  $\beta$  decreases almost linearly with increasing  $Cn$  content.

(3) The  $c$ -dimension decreases with disorder for a given composition.

(4) The synthetic high temperature (Ba,K)-feldspars form a continuous solid solution series. But for the natural, partially ordered ones they postulated two miscibility gaps—one in the  $Cn$ -poor region ( $Cn_0$ – $Cn_{30}$ ) to account for the observed complex diffraction effects in single crystal photographs and the other one in the  $Cn$ -rich region ( $Cn_{60}$ – $Cn_{80}$ ) on the basis of a compositional gap in the natural specimens.

The figures in Gay and Roy's paper show clearly the above mentioned trends but the exact positions of the limiting lines are uncertain because of the limited number of available specimens, and because of the considerable scatter of the plotted data. The latter can be attributed to the following reasons: (1) Only partial chemical analyses were available for many specimens. Moreover, the influence of  $Na^+$  and  $Fe^{3+}$  on the lattice constants could not be estimated. (2) Some of the specimens were zoned so that an exact correlation between the composition and the lattice constants might not have been possible.

None of these difficulties arose in this work because the Otjosondu specimens were predominantly homogeneous, and complete chemical analyses could be carried out. In addition, Na-free specimens could be produced by ion-exchange methods. Two unzoned specimens, one from Jakobsberg, Sweden, and one from Yugoslavia, were also included in this study. Dr. Gay kindly supplied ten samples from his collection. The lattice constants of these samples were redetermined (Table 1), however, the amounts were not enough for complete chemical analyses.

## Experimental

Guinier-Jagodzinski powder patterns of all the specimens were made using  $CuK\alpha_1$ -radiation, and the lattice constants were refined using a slightly modified version of C. W. Burnham's LCLSQ program (Table 1). For monoclinic feldspars about 40–50 lines were used for refinement and for the triclinic ones more than 65 lines were used. Precession photographs were made of many specimens whose powder patterns contained additional reflections indicating the presence of more than one Ba-feldspar phase.

The chemical compositions of individual crystals were determined with an electron microprobe. Composition was determined at five different points on each crystal and an average was taken. The elements determined were Ba, K, Na, Al, Fe, and Si. No attempt was made to determine trace elements such as Sr, Rb, *etc.* As a preliminary study indicated only minor amounts of calcium (<0.02 mol.%), it was also ignored during calculation of the formula; all the iron present was assumed to be  $Fe^{3+}$  (Table 2).

In order to eliminate the effect of sodium on the volume and the lattice constants, all the specimens were ion-exchanged in KCl-melt at 900°C. Just as in the plagioclase feldspars (Viswanathan, 1971a), a finer fraction had to be used in the case of Ba-rich specimens in order to obtain an almost complete exchange of sodium by potassium. The lattice parameters of the ion-exchanged specimens are given in Table 3.

All attempts to exchange the potassium in Ba-feldspars by sodium in NaCl-melt proved futile. Hence K-free (Na,Ba)-feldspars could not be produced by this method.

## Results

In this section we consider the characteristic chemical features of the (Ba,K,Na)-feldspars from Otjosondu. The compositions of the 20 specimens (Table 2) are plotted in a ternary  $Cn$ – $Ab$ – $Or$  diagram (Fig. 1). These specimens can be divided into three types:

(1)  $Cn$ -rich specimens with compositions  $Cn_{46-55}Or_{33-43}Ab_{11-13}$ . These show small amounts of probably unmixed, almost pure celsian as seen in Guinier-Jagodzinski powder patterns. It is interesting to note that one of them (Specimen No. 16, Table 1 and 2) is triclinic.

(2)  $Cn$ -poor,  $Ab$ -rich ternary feldspars with the composition  $Cn_{9-21}Or_{55-71}Ab_{12-35}$ . These contain varying amounts of unmixed albite.

Table 1. Lattice constants of natural (Ba,K,Na)-feldspars

Specimen No.	<u>a</u>	<u>b</u>	<u>c</u>	$\alpha$	$\beta$	$\gamma$	V
1	8.540(3)	12.998(3)	14.396(3)	90.00	115.95(2)	90.00	1437.0(9)*
2	8.509(2)	13.008(2)	14.400(3)	90.00	115.94(1)	90.00	1433.3(6)
3	8.514(2)	13.010(3)	14.404(4)	90.00	115.93(2)	90.00	1434.8(9)
4	8.552(2)	13.022(3)	14.411(4)	90.00	115.86(2)	90.00	1444.2(9)
5	8.518(2)	13.025(3)	14.412(4)	90.00	115.91(2)	90.00	1437.8(9)
6	8.516(1)	13.023(2)	14.412(2)	90.00	115.90(1)	90.00	1437.8(5)
7	8.564(2)	13.019(2)	14.407(4)	90.00	115.87(1)	90.00	1445.3(1)
8	8.524(2)	13.023(2)	14.414(4)	90.00	115.89(1)	90.00	1439.5(8)
9	8.542(1)	13.036(2)	14.410(3)	90.00	115.81(1)	90.00	1444.5(6)
10	8.546(2)	13.041(3)	14.421(4)	90.00	115.82(2)	90.00	1446.9(9)
11	8.547(2)	13.046(3)	14.426(4)	90.00	115.82(2)	90.00	1448.0(9)
12	8.547(2)	13.046(2)	14.411(3)	90.00	115.73(2)	90.00	1447.6(7)
13	8.555(2)	13.051(2)	14.419(4)	90.00	115.78(2)	90.00	1449.7(8)
14	8.575(2)	13.055(2)	14.425(3)	90.00	115.65(1)	90.00	1455.7(6)
15	8.576(2)	13.054(2)	14.422(3)	90.00	115.62(1)	90.00	1455.7(7)
16	8.575(2)	13.053(2)	14.422(3)	90.02(2)	115.66(1)	89.93(1)	1455.0(7)
17	8.582(2)	13.058(2)	14.420(3)	90.00	115.67(2)	90.00	1456.4(7)
18	8.575(2)	13.056(2)	14.430(3)	90.00	115.62(1)	90.00	1456.7(8)
19	8.570(2)	13.052(2)	14.423(3)	90.00	115.66(1)	90.00	1454.2(7)
20	8.578(2)	13.057(2)	14.431(4)	90.00	115.64(2)	90.00	1457.1(8)
21	8.544(2)	13.030(2)	14.391(4)	90.00	115.68(2)	90.00	1443.8(8)
22	8.634(1)	13.049(2)	14.412(2)	90.00	115.14(1)	90.00	1470.1(5)
23	8.555(2)	13.002(2)	14.397(4)	90.00(2)	115.92(2)	89.90(2)	1440.2(9)
24	8.535(2)	12.995(2)	14.403(3)	90.00	115.94(1)	89.95**	1436.6(7)
25	8.576(2)	13.022(2)	14.405(3)	90.04(2)	115.81(1)	89.83(1)	1448.2(8)
26	8.593(1)	13.038(2)	14.409(3)	90.00	115.70(1)	90.00	1454.6(6)
27	8.547(2)	13.029(2)	14.395(3)	90.00	115.76(1)	90.00	1443.7(7)
28	8.562(2)	13.037(3)	14.403(4)	90.00	115.73(2)	90.00	1448.3(9)
29	8.555(2)	13.037(2)	14.395(3)	90.00	115.68(1)	90.00	1447.0(6)
30	8.631(1)	13.048(1)	14.409(2)	90.00	115.15(1)	90.00	1469.0(4)
31	8.640(1)	13.043(1)	14.404(2)	90.00	115.16(1)	90.00	1469.2(5)
32	8.636(1)	13.047(1)	14.408(2)	90.00	115.15(1)	90.00	1469.5(4)

Notes on sources; 1 to 20 from Otjosondu; 21 from Yugoslavia; 22 from Jakobsberg, Sweden; 23 to 32 specimens of Gay and Roy (1968), the lattice constants of which were determined by the authors. The numbers given by Gay and Roy are: (23)g11156, (24)g21009, (25)g11130, (26) F. 54, (27)B.M. 84765, (28)B.M. 31990, (29)195867, (30)STR/5/15, (31)100978, (32)B.M.1958,284.

\*Estimated standard errors are in brackets and refer to the last decimal place.

\*\* $\alpha$  and  $\gamma$  are estimated based on the width of the lines (e.g.  $\bar{3}32$ ,  $\bar{4}24$ ,  $\bar{3}50$ ,  $\bar{4}62$ ,  $\bar{2}80$ ), which tend to split in triclinic varieties.

(3) Specimens with intermediate compositions, which show neither unmixed albite nor celsian.

Thus the first two types appear to limit the compositional variations of the Otjosondu (Ba,K,Na)-feldspars with respect to the celsian and albite end members.

Another interesting feature is that all these specimens contain considerable amounts of  $\text{Fe}^{3+}$  (0.05–0.13, Table 2). It increases with celsian content reaching a maximum value (0.17) in an unmixed celsian phase. Thus, the incorporation of  $\text{Fe}^{3+}$  in these specimens appears to depend upon the amount of aluminium present in the structure. On the other hand, the albite content decreases with Cn content. Though this trend is expected because of the tendency of albite to unmix from (Ba,K,Na)-

feldspars, it is noteworthy that even Ba-rich feldspars (type 1) contain as much as 10–12 mol% Ab in solid solution. Naturally-occurring Ca-rich plagioclases do not contain more than 4–5% Or molecule (Corlett and Eberhard, 1967).

The ion-exchange experiments also revealed that (Ba,K)-feldspars behave differently from (Ca,Na)-feldspars. It is known that  $\text{Na}^+$  in plagioclase can be exchanged with  $\text{K}^+$  and that the latter in the exchanged plagioclases can be reexchanged with  $\text{Na}^+$  (Viswanathan, 1972). In the (Ba,K,Na)-feldspars it was possible to replace the small  $\text{Na}^+$ -ion with the larger  $\text{K}^+$ -ion, but an exchange of  $\text{K}^+$ -ion by  $\text{Na}^+$ -ion could not be achieved either in the natural ternary Ba-feldspars or in the K-exchanged Ba-feldspars. All attempts to exchange  $\text{K}^+$  by  $\text{Na}^+$

Table 2. Chemical formulas of (Ba,K,Na)-feldspars, determined by microprobe analysis and calculated on the basis of eight oxygen atoms

Sp. No.	Ba	K	Na	Fe <sup>3+</sup>	Al	Si
1	0.091	0.545	0.349	0.027	0.998	2.963
2	0.139	0.616	0.235	0.056	1.078	2.867
3	0.143	0.615	0.234	0.059	1.104	2.844
4	0.171	0.632	0.213	0.087	1.143	2.781
5	0.189	0.569	0.213	0.051	1.132	2.822
6	0.190	0.590	0.220	0.050	1.130	2.820
7	0.202	0.711	0.122	0.010	1.203	2.781
8	0.205	0.581	0.204	0.088	1.127	2.790
9	0.299	0.484	0.210	0.096	1.099	2.781
10	0.302	0.489	0.200	0.088	1.192	2.717
11	0.308	0.513	0.207	0.091	1.183	2.711
12	0.338	0.441	0.201	0.061	1.231	2.701
13	0.393	0.448	0.165	0.088	1.300	2.610
14	0.469	0.405	0.135	0.110	1.339	2.546
15	0.471	0.427	0.105	0.081	1.376	2.539
16	0.497	0.388	0.133	0.109	1.362	2.517
17	0.516	0.353	0.129	0.123	1.401	2.484
18	0.541	0.356	0.127	0.129	1.376	2.480
19	0.546	0.345	0.120	0.135	1.389	2.468
20	0.546	0.335	0.123	0.130	1.389	2.473
21	0.397	0.466	0.137	0.0	1.411	2.592
22	0.95	0.05	n.d.	n.d.	n.d.	n.d.

n.d....not determined. See Table 1 for sources.

always lead to the destruction of Ba-feldspars and formation of sodalite. This appears to indicate that the K-equivalents of partially-ordered plagioclases can exist metastably, but the Na-equivalents of (Ba,K)-feldspars cannot.

One of the main aims of this investigation was to determine the exact composition of the unmixed phases, especially the Ba-poor phase. The end member compositions given by Viswanathan (1978) were derived from the lattice constants, which are affected by the presence of minor amounts of Na<sup>+</sup> and Fe<sup>3+</sup> as shown later. On the basis of this study of Cn-rich feldspars, the following observations were made:

(1) Powder patterns of all but one Cn-rich specimen show the presence of minor amounts of the unmixed celsian phase (about 5% as estimated by the intensities of the powder lines). Precession photographs of single crystals chosen from these specimens rarely showed the celsian phase. It is therefore concluded that the unmixing is coarse, and the unmixed celsian is not homogeneously distributed throughout the specimens. In all the precession photographs in which both phases were seen, the orientation relationship was the same as that observed by Viswanathan (1978), namely, the *a*\*-axes of the unmixed phases are split, whereas the *b*\* and *c*\* coincide.

The one specimen which showed larger amounts of celsian in powder patterns and which showed more frequently both unmixed phases in the precession patterns had an approximate bulk composition of Cn<sub>71</sub>Or<sub>27</sub>Ab<sub>2</sub> (Viswanathan, 1978).

Table 3. Lattice parameters of ion-exchanged (Ba,K)-feldspars

Specimen No.	a	b	c	β	V
1	8.607(2)	13.013(2)	14.411(4)	115.96(2)	1451.2(9)*
2	8.607(2)	13.026(2)	14.419(3)	115.91(2)	1454.4(7)
3	8.609(1)	13.022(2)	14.421(3)	115.91(1)	1454.2(6)
4	8.614(2)	13.034(2)	14.425(4)	115.85(2)	1457.6(8)
5	8.609(2)	13.028(3)	14.416(3)	115.86(2)	1455.0(8)
6	8.607(2)	13.029(3)	14.418(4)	115.85(2)	1455.0(9)
7	8.600(2)	13.017(2)	14.405(4)	115.83(2)	1451.3(8)
8	8.608(1)	13.033(1)	14.419(2)	115.84(1)	1455.9(9)
9	8.601(2)	13.039(3)	14.414(3)	115.75(2)	1456.1(8)
10	8.612(2)	13.047(3)	14.424(4)	115.74(2)	1460.0(9)
11	8.607(2)	13.043(3)	14.420(4)	115.73(2)	1458.3(9)
12	8.613(2)	13.047(3)	14.405(4)	115.83(2)	1460.7(9)
13	8.611(1)	13.048(2)	14.417(2)	115.67(1)	1459.9(5)
14	8.619(1)	13.061(1)	14.423(2)	115.60(1)	1464.3(4)
15	8.617(1)	13.059(2)	14.425(2)	115.59(1)	1464.1(5)
16	8.615(2)	13.060(2)	14.426(3)	115.59(1)	1463.7(6)**
17	8.619(2)	13.065(2)	14.430(3)	115.59(2)	1465.4(7)
18	8.616(1)	13.061(2)	14.426(3)	115.60(1)	1464.1(6)
19	8.616(2)	13.061(2)	14.427(3)	115.60(1)	1464.1(7)
20	8.614(2)	13.057(2)	14.424(4)	115.59(2)	1463.2(8)
21	8.600(2)	13.038(2)	14.403(3)	115.73(1)	1454.9(7)
22***	-	-	-	-	-

\*Estimated standard errors are in brackets and refer to the last decimal place.

\*\*Calculated monoclinic ignoring the small splitting of a few lines.

\*\*\*Not exchanged.

(2) It was not possible to observe the unmixed phases microscopically. Attempts to locate the unmixed celsian with the electron microprobe in the specimens with minor amounts of celsian proved futile. Hence only the composition of the Ba-poor phase could be determined on these specimens, which was found to be Cn<sub>54</sub>Or<sub>34</sub>Ab<sub>12</sub> (average of five values).

(3) Only in the specimens containing larger amounts of celsian could two types of unmixing (Fig. 2 and 3) be observed. In Figure 2 a photomicrograph made with BaK $\alpha$  radiation shows three regions: (a) A darker region containing only a Cn-poor phase with a composition of about 50–52% Cn, 36–35% Or, 14–13% Ab (Fe<sup>3+</sup> almost nil). (b) A

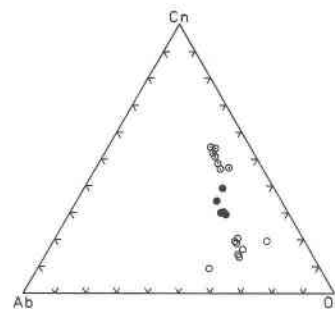


Fig. 1. Variations in the chemical composition of the (Ba,K,Na)-feldspars from Otjosondu, Namibia. ○: Cn-rich specimens; ○: Cn-poor specimens; ●: Specimens with intermediate compositions.

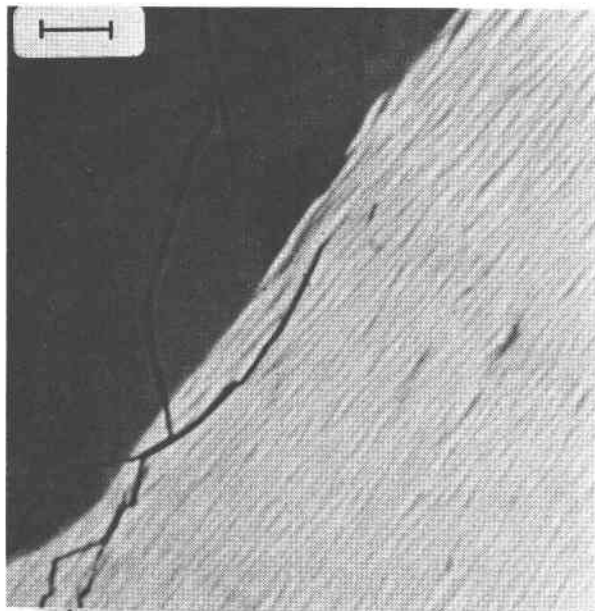


Fig. 2. X-ray (BaK $\alpha$ ) area scan showing the coarse unmixing in a barium feldspar from Otjosondu (see text). Scale bar = 17  $\mu$ .

bright transitional region very near the sharp boundary containing dark lamellae of apparently Cn-poor phase, whose composition could not be determined exactly because the lamellae were narrower than the electron beam. However, the average Cn content increased abruptly at the sharp boundary. (c) As the distance from the boundary increases, there exists a region (not shown in the figure) where the dark lamellae completely disappear and the Cn content reaches a maximum value of about 95% (Ab almost nil, Fe<sup>3+</sup> = 0.17). This coarser unmixing can be compared with a finer one (Fig. 3), in which Cn-rich and Cn-poor (dark) regions are traversed by a system of fine lamellae, which terminate abruptly in the lower Ba-rich region.

In view of the identical orientation relations between the Cn-poor and Cn-rich phase in all the specimens, and considering the similar compositions of the specimens showing small amounts of unmixed celsian, it is concluded that the compositions of the unmixed phases must be about Cn<sub>52-54</sub>Or<sub>35-36</sub>Ab<sub>13-12</sub> and Cn<sub>95-100</sub>Or<sub>5-0</sub>.

Having considered the variations in the chemical compositions, let us now consider their effects on lattice parameters. In order to determine the changes in the various lattice parameters with increasing Cn content in the binary system BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-KAlSi<sub>3</sub>O<sub>8</sub>, either (Ba,K)-feldspars with different (Ba/K)-ratios and structural states must be

synthesized or all the Ab-component which is invariably present in the natural (Ba,K)-feldspars must be ion-exchanged. Because ordered (Ba,K)-feldspars have not been synthesized so far, the second method was used to produce ordered or partially ordered specimens. As the ion-exchanged feldspars from Otjosondu represent only a limited compositional range, a few specimens of Gay and Roy (1968) have also been used. Because the chemical analyses given by them were not always complete, it was necessary to find an indirect method to estimate the amount of sodium in the specimens and to determine which are sodium-free.

A diagram (Fig. 4) using a plot of *a* against cell volume was chosen for this purpose, as both are considerably affected by the exchange of Na<sup>+</sup> by K<sup>+</sup>. All Na-free (Ba,K)-feldspars should fall on the curve joining pure sanidine (or microcline), synthetic (Ba,K)-feldspars of Gay and Roy (1968) and pure celsian. Those containing Na should lie below the curve. The ion-exchanged Otjosondu feldspars plotted very slightly above this curve, thereby showing slightly larger values for *a*. This could be attributed to the presence of larger Fe<sup>3+</sup> ion in the structure, which is assumed to be in tetrahedral coordination.

As the data of Otjosondu feldspars cannot be used further without correcting for the effects of Fe<sup>3+</sup> two independent methods were considered to estimate them. The first one was to determine the effects in synthetic feldspars containing Fe<sup>3+</sup>. A

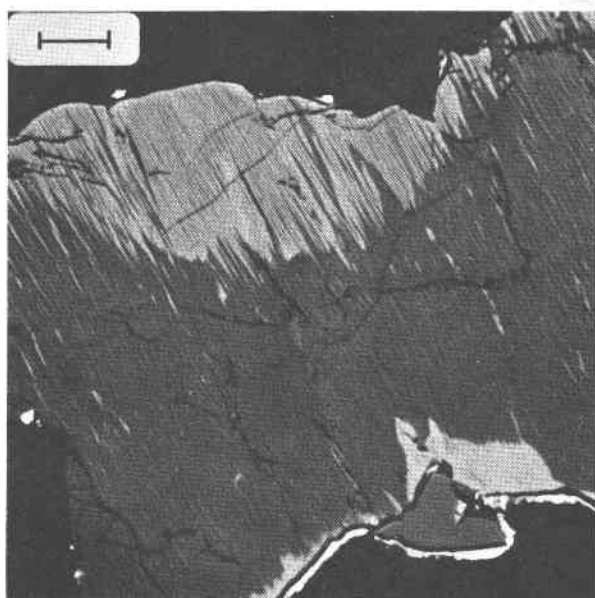


Fig. 3. X-ray (BaK $\alpha$ ) area scan showing the finer unmixing (see text). Scale bar = 17  $\mu$ .

comparison of the volume of  $\text{KAlSi}_3\text{O}_8$  with that of  $\text{KFeSi}_3\text{O}_8$  (type HS or LM; Smith, 1974, p. 219) reveals that the replacement of Al by  $\text{Fe}^{3+}$  results in an increase in volume by about  $50\text{\AA}^3$  (considering the  $14\text{\AA}$ -cell). Again, the volume of  $\text{BaAlFeSi}_2\text{O}_8$  ( $V = 1515.1\text{\AA}^3$ ,  $a = 8.713\text{\AA}$ ,  $b = 13.169\text{\AA}$ ,  $c = 14.573\text{\AA}$ ,  $\beta = 115.04$ ; Pentinghaus, 1981, personal communication) is larger than that of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (Smith, 1974, p. 219) thereby suggesting that the replacement of one Al by one  $\text{Fe}^{3+}$  in the formula of celsian increases the volume by  $45\text{\AA}^3$ . If a linear influence is assumed, a replacement of 0.1 Al by 0.1  $\text{Fe}^{3+}$  should cause an expansion in volume by about  $4.5\text{\AA}^3$  in all (Ba,K)-feldspars.

The second approach is based on the reasonable assumption that the cell volumes of ordered and disordered (Ba,K)-feldspars must be nearly equal because the volumes of high sanidine and low microcline are nearly equal. Hence the discrepancies in the volumes of the ion-exchanged natural specimens can be determined by comparing them with those of synthetic specimens with same Cn contents (Fig. 5). By plotting the differences ( $\Delta V$ ) against the observed  $\text{Fe}^{3+}$  content a slightly smaller value of  $3.5\text{\AA}^3$  for the replacement of 0.1 Al by 0.1  $\text{Fe}^{3+}$  was obtained for the Otjosondu specimens. Using this observed value the volumes of the samples in this study were corrected.

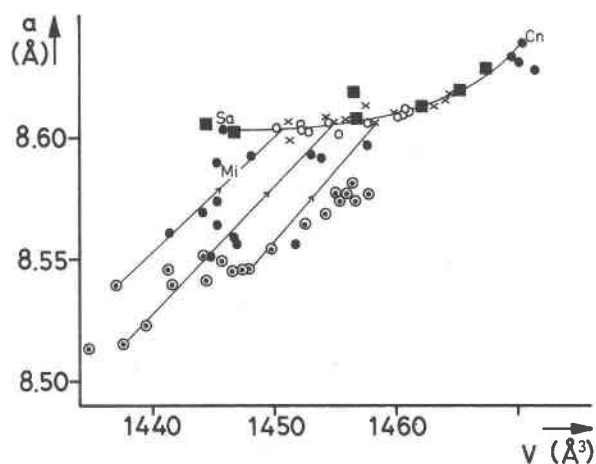


Fig. 4. The  $a$  cell dimension of (Ba,K,Na)-feldspars vs. volume.  $\times$ : (Ba,K)-equivalents of (Ba,K,Na)-feldspars produced by ion-exchange of specimens from Figure 1;  $\circ$ : Ion-exchanged specimens corrected for their  $\text{Fe}^{3+}$  content;  $\bullet$ : Natural feldspars of Gay and Roy (1968);  $\blacksquare$ : Synthetic feldspars of Gay and Roy (1968);  $\circ$ : Natural (Ba,K,Na)-feldspars from Otjosondu, Namibia; Cn: celsian, Sa: sanidine, Mi: microcline. The straight lines join ion-exchanged specimens and thus show the effect of ion-exchange.

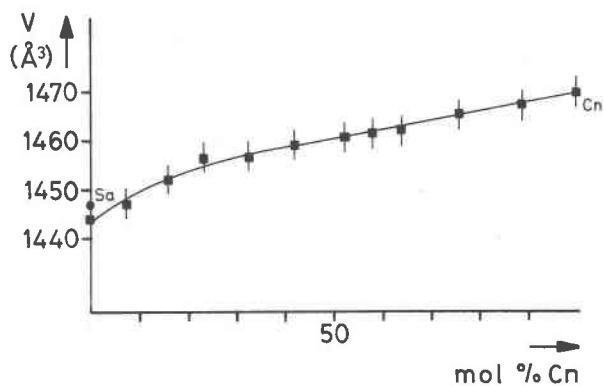


Fig. 5. Variation of unit cell volume of a synthetic (Ba,K)-feldspar with Cn content (data from Gay and Roy, 1968).

The next problem was to determine the effects of  $\text{Fe}^{3+}$  on different lattice dimensions. A comparison of the data of the synthetic specimens shows that the increase of  $4.5\text{\AA}^3$  in volume is accompanied by an increase of about  $0.008\text{\AA}$  in  $a$ ,  $0.011\text{\AA}$  in  $b$ ,  $0.020\text{\AA}$  in  $c$  and a negligible change in  $\beta$ . As a corresponding replacement causes a smaller expansion ( $3.5\text{\AA}^3$ ) in Otjosondu specimens a proportional increase in the different lattice parameters ( $\Delta a = 0.006$ ,  $\Delta b = 0.008$ ,  $\Delta c = 0.016$ ) was assumed to be due to the incorporation of  $\text{Fe}^{3+}$ .

After the correction, the Otjosondu specimens plotted (Fig. 4) slightly under the curve for Na-free varieties in accordance with the fact that they are partially ordered. As there was little An-molecule in any specimens, it could be safely ignored in all these considerations.

Figure 4 shows the following features:

(1) An exchange of Na by K produces larger changes in  $a$  and cell volume than the coupled substitution of (Ba+Al) by (K+Si). Hence this diagram can be used to estimate the Ab content of (Ba,K,Na)-feldspars.

(2) In Ba-poor (Ba,K)-feldspars  $a$  changes only slightly with increasing Cn content, but more rapidly in Ba-rich varieties.

(3)  $\text{Fe}^{3+}$ -free (Ba,K)-feldspars fall on or near the curve joining celsian and sanidine. As microcline plots near sanidine, the effect of ordering of (Al,Si) atoms can be considered negligible, especially in Cn-rich varieties.

(4) If specimens plot above the curve joining Sa and Cn, they are likely to contain considerable amounts ( $>0.05$  atomic%) of  $\text{Fe}^{3+}$  in tetrahedral coordination. Thus, Ab content and  $\text{Fe}^{3+}$  content show opposite effects.

Gay and Roy (1968) suggested that a diagram correlating  $\beta$  with Cn content is most suitable to determine the Cn in (Ba,K)-feldspars. This is illustrated in Figure 6 where  $\beta$  is plotted against cell volume. It is noteworthy that the exchange of K by Na considerably decreases the volume, but only slightly increases  $\beta$ . As microcline is also plotted, it can be inferred that the ordering of Si/Al atoms has a negligible effect on  $\beta$ . Hence  $\beta$ -values of natural barium feldspars containing small amounts of Ab-component and possessing different degrees of order can still be used to determine the approximate Cn content. A suitable diagram correlating  $\beta$  with celsian content can be drawn using Figures 5 and 6. Figure 6 clearly shows the expansion in cell volumes caused by the additional  $\text{Fe}^{3+}$ , which increases with increasing Cn content in the K-exchanged Otjosondu feldspars.

The variation of the  $b$ -dimension with Cn content of almost Na-free (Ba,K)-feldspars is shown in Figure 7. As the synthetic sanidine of Gay and Roy (1968) possesses a smaller  $b$ -value than the high sanidine, it must be assumed that the former is partially ordered. The K-rich ion-exchanged Otjosondu specimens show (after correction for  $\text{Fe}^{3+}$ -content) even smaller values, thereby indicating that they are more ordered. It can be seen that there is only a small change in the  $b$ -dimension of the disordered (Ba,K)-feldspar series, high sanidine to celsian.

In order to study the variation of  $b$  in partially ordered natural (Ba,K)-feldspars, a few specimens of Gay and Roy (1968) (Cn > 35 mol%) were also included in Figure 7. Though a few of them may contain small amounts of Ab in solid solution, ion

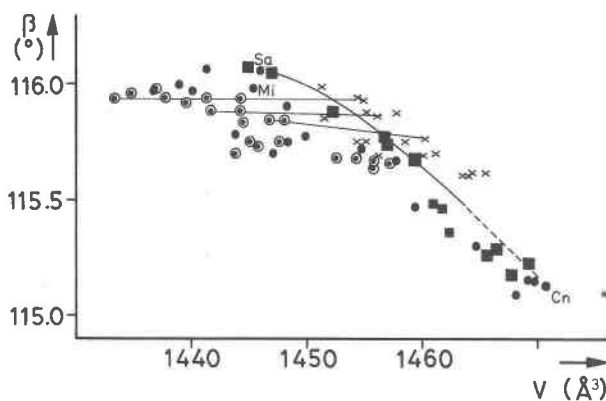


Fig. 6. Lattice angle  $\beta$  of (Ba,K,Na)-feldspars plotted against volume. \*: Data point of unmixed celsian (Viswanathan, 1978). See Figure 4 for other symbols. The straight lines join ion-exchanged specimens.

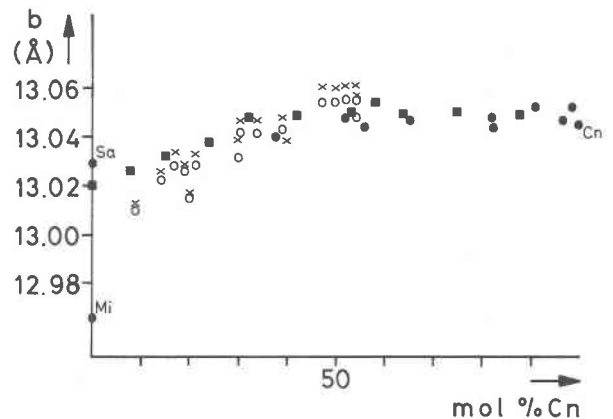


Fig. 7. Variation of  $b$  of (Ba,K)-feldspars with Cn content (mol%). See Figure 4 for explanation of symbols.

exchange experiments have shown that 10 mol% Ab decreases  $b$  only insignificantly in such Cn-rich specimens (about  $0.006\text{\AA}$ ). The partially ordered natural (Ba,K)-feldspars show a rapid increase in  $b$  for K-rich compositions until about Cn<sub>35</sub> and then almost no change occurs. Viswanathan (1971b, 1972) and Ribbe (1975) made a similar observation in low plagioclases and arrived at the conclusion that the rapid increase in  $b$ -parameter of natural plagioclases from An<sub>0</sub> to approximately An<sub>30-35</sub> must be attributed to the disordering of Al,Si atoms, which accompanies increasing calcium content. The similarity in the nature of variation of  $b$  is also reflected in the magnitudes. The difference in the  $b$  value of albite (low) and anorthite (Smith, 1974, p. 219) is  $0.088\text{\AA}$ , whereas that between microcline (low) and celsian is  $0.080\text{\AA}$ . A discussion of the behavior of  $b$  is presented later.

The best parameter to determine the difference in the structural states of  $\text{Fe}^{3+}$ -free (Ba,K)-feldspars is  $c$  (Fig. 8) because it is more sensitive to changes in the structural states of specimens with Cn content greater than 30–40 mol%. The cell volume was chosen as the abscissa instead of Cn content because it is possible to consider all (Ba,K)-feldspars, with or without sodium. Thus the effect of ionic exchange on  $c$  and cell volume can be simultaneously shown. In Figure 8 the synthetic feldspars studied by Gay and Roy (1968), all their natural feldspars for which complete analyses are available, and all the natural and ion-exchanged feldspars from this study are plotted after correcting for the presence of  $\text{Fe}^{3+}$ .

The following observations can be made regarding this figure:

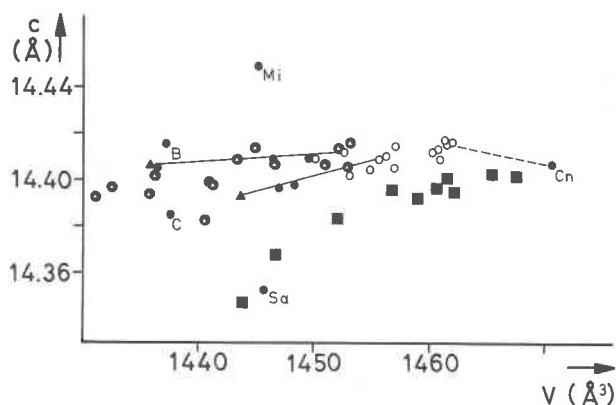


Fig. 8.  $c$ -dimension of (Ba,K,Na)-feldspars plotted against volume.  $\blacktriangle$ : (Ba,K,Na)-feldspars for which structure data are available;  $\bullet$ : Natural (Ba,K,Na)-feldspars from Otjosondu, corrected for their  $\text{Fe}^{3+}$ -content. See Figure 4 for explanation of other symbols; B, C: refers to sanidines, Spencer "B" and Spencer "C" (Colville and Ribbe, 1968); The dashed line connects unmixed barium feldspar phases (corrected for  $\text{Fe}^{3+}$ -content, see text). The continuous lines join ion-exchanged specimens.

(1) All the disordered synthetic specimens of Gay and Roy have the smallest  $c$ -values. For a specimen with a given cell volume the higher the order of (Si,Al)-atoms the larger is the  $c$  value. In making this conclusion the small changes in volume caused by ordering are ignored.

(2) The  $c$ -dimension of a disordered synthetic (Ba,K)-feldspar increases rapidly at Ba-poor compositions and only slightly at the Ba-rich compositions, a trend which is opposite to that of  $a$ .

(3) The fact that  $c$  of celsian is less than that of microcline clearly indicates that the increasing disorder of Si/Al-atoms (considering the  $7\text{\AA}$ -cell) which accompanies increasing Cn content has a diminishing effect on  $c$  as in plagioclases (Viswanathan, 1972). However, the magnitude of reduction is smaller than that in plagioclases. A discussion of the behaviour of  $c$  is presented later.

(4) That the  $c$ -parameter can be used to determine the Al/Si-distributions on (Ba,K,Na)-feldspars is demonstrated using the data of two barium feldspars whose structures have been refined (Viswanathan and Brandt, 1980; Viswanathan and Kielhorn, 1983). It is seen in Figure 8 that one of them, the Cn-poor variety, has a larger  $c$ -dimension, even after correcting for the presence of  $\text{Fe}^{3+}$ . The Cn-rich specimen, on the other hand, has a smaller  $c$ -parameter both before and after the exchange of Na. This suggests that it possesses a more disordered Al/Si-distribution, which is confirmed by the

structure determination. It should be possible to estimate the approximate Al/Si-distributions in the tetrahedral positions,  $T_1$  and  $T_2$ , if structure data of only a few more barium feldspars were available, and if curves joining (Ba,K)-feldspars having similar structural states (as defined by Viswanathan and Brandt, 1980) are drawn in this figure. For example, the Cn-rich specimen lies below the line (not shown in Fig. 8) joining the structurally similar Spencer "C" and the Cn-poor specimen (Viswanathan and Brandt, 1980), thereby suggesting that it should have less than 0.494 Al in  $T_1$  and more than 0.211 Al in  $T_2$ -positions, which is in agreement with the observed data.

(5) Many ternary (Ba,K,Na)-feldspars from Otjosondu lie outside the field Mi-Sa-Cn. This is due to the effect of the sodium in solid solution. It is noteworthy that ion-exchange causes all the specimens to move towards the line joining the plots of the Ba-poor and Ba-rich phases of the unmixed specimens (Viswanathan, 1978). This line can be assumed to represent the approximate boundary line for Fe-free, Na-free (Ba,K)-feldspars with maximum possible order, and thus it differs in position from that published earlier (Viswanathan and Brandt, 1980). Hence it can be concluded that many (Ba,K,Na)-feldspars from Otjosondu are relatively ordered. This should not be surprising because the very presence of a few unmixed specimens indicates that the  $P$ - $T$  conditions in Otjosondu were favorable for ordering. Another explanation is that the considerable amount of the Ab component present in these specimens must have accelerated the ordering and probably also the unmixing in them. The observation that albite or Ab-rich feldspars order faster than Or-rich ones seems to support this view. Probably both factors are important.

#### Discussion and conclusions

It is well known that the lattice parameters of feldspars are influenced differently by the size of the larger interstitial cations, the size of the tetrahedral cations and finally by Al/Si order-disorder. In the case of monoclinic (Ba,K)-feldspars the lattice angles,  $\alpha$  and  $\gamma$ , are constrained to be  $90.0^\circ$  and hence, only  $\beta$  varies with Cn content. It is not therefore possible to compare the variations in the lattice angles of triclinic plagioclases with those of monoclinic (Ba,K)-feldspars and to correlate them with compositional changes. Hence further discussion will be confined only to unit cell volumes and lattice dimensions and will include an interpretation



only of the *trends* and not the exact magnitudes of the changes in different lattice parameters.

First, we examine the volumes of the high-temperature disordered plagioclases and (Ba,K)-feldspars. Because the mean Ca–O bond in anorthite is 0.16 Å shorter than the mean Na–O bond in high albite, and the mean Al–O bond is 0.13 Å larger than the mean Si–O bond, the coupled substitution of Na + Si by Ca + Al should be compensating in its effect on volume. Thus the fact that the volumes of all high-temperature plagioclases are nearly equal can be understood. Similarly, as the mean Ba–O bond is only 0.05 Å shorter than the mean K–O bond, a larger difference in the volumes of sanidine and celsian should be observed. In the case of low plagioclases the volume is also affected considerably by the changes in the (Al,Si)–O framework accompanying Al/Si order, whereas in the (Ba,K)-feldspars the larger interstitial cations appear to permit only very small changes in the framework. Though the *a*-dimension shows only small changes in Ba-poor (Ba,K)-feldspars its behavior is, in general, similar to that of volume in both groups of minerals.

The other two lattice dimensions, *b* and *c*, are considerably influenced by the distribution of the Si,Al atoms, as in alkali feldspars (Wright and Stewart, 1968, Stewart and Ribbe, 1969). The *b*-dimensions of the high-temperature plagioclases are nearly equal, whereas those of the high-temperature (Ba,K)-feldspars increase slightly (about 0.015 Å) towards celsian. Though this trend is the same as that exhibited by the cell volume, the magnitude of the change in *b* is much smaller. Two different causes are probably responsible for this effect. First is the influence of the coupled substitution, which has a small resultant effect on *b* of (Ba,K)-feldspars. The second, probably a more important reason, appears to be the inability of a feldspar with a given (Al,Si)–O framework to expand in *b* direction beyond a certain value. This can be inferred if one compares the *b*-dimensions of high sanidine and high RbAlSi<sub>3</sub>O<sub>8</sub> (13.029 Å and 13.034 Å, respectively; Smith, 1974 p. 219) or those of low microcline and low RbAlSi<sub>3</sub>O<sub>8</sub> (12.996 Å and 12.964 Å, respectively; Smith, 1974 p. 219). It is observed that after *b* reaches a value of about 12.96 Å, it is more influenced by a change in the framework caused by ordering (or disordering) of Al/Si atoms than by replacement of existing interstitial cations by even larger ones. Perhaps this also explains the smaller changes noted in *b* (as compared to *c*) where tetrahedral Al<sup>3+</sup> is replaced by Fe<sup>3+</sup>.

The rapid increase in *b* in natural (Ba,K)-feldspars (and plagioclases) must be attributed to the increasing Al/Si disorder which accompanies increasing Cn content (An content). Hence the change in *b* can be considered as a measure of the accompanying order/disorder in Ba-poor feldspars. In both low plagioclases and (Ba,K)-feldspars, the *b*-dimension increases rapidly until about 30–40% (An or Cn, respectively) and then it remains constant. In both cases, a doubling of the cell must occur in the An-rich (or Cn-rich) members. Hence the distinct two-trend variation of *b* cannot be considered accidental. The explanation that *b* increases rapidly until 30–40% An in plagioclases because disordering takes place predominantly within the 7 Å-cell appears plausible and can be applied to (Ba,K)-feldspars. The inability of *b* to increase further in Cn-rich members can also be attributed to another type of disorder that takes place in them. Viswanathan (1971b, p. 41) suggested that this ordering involved the enrichment of Al in a tetrahedral position in one 7 Å-cell and a reduction of Al in the corresponding tetrahedral position in the adjacent cell—a process, which should ultimately produce an anorthite-like cell. This process need not necessarily take place between two adjacent cells. It may take place over regions containing a few cells as indicated by the superstructures in more calcic plagioclases.

The *c*-dimension of disordered plagioclase feldspars decreases with increasing anorthite content, whereas that of disordered (Ba,K)-feldspars increases with increasing Cn content. This behavior clearly reveals that the differences in the mean bond lengths of the interstitial cations and those in the mean bond lengths of the tetrahedral cations have larger effects on *c* than on *b*. This should not be surprising because substitution of K by Rb in Rb-feldspars (*c* = 7.250 Å in low RbAlSi<sub>3</sub>O<sub>8</sub>, 7.182 Å in high RbAlSi<sub>3</sub>O<sub>8</sub>; Smith, 1974, p. 219) causes *c* to expand much more than *b*, and because the variation in *c* in feldspars containing Fe<sup>3+</sup> is more sensitive to the size of the tetrahedral cation.

The reduction of *c* of high plagioclases must be attributed predominantly to influence of the smaller Ca–O bond whereas the increase in *c* of disordered (Ba,K)-feldspars must be due to the dominating influence of the larger Al–O bond. In examining the variation of *c* in natural, ordered or partially ordered feldspars, the influence of Al/Si distributions should also be considered. All three factors affect the *c*-parameter of low plagioclases in such a way that only an approximate linear relationship with

anorthite content is observed (Fig. 2, Bambauer *et al.*, 1967). The available data (Fig. 8) are inadequate to make similar statements regarding (Ba,K)-feldspars; we may, however, state that a two-trend variation, as shown by *b*, is not observed.

It is now recognized that Al/Si disorder is introduced in the feldspar structure either by heating a low albite (or low microcline) or by the coupled substitution of Na + Si by Ca + Al (or of K + Si by Ba + Al), and that such a disorder leads to an increase in *b* and a reduction in *c*. The difference in behavior of the *b*-*c* relationship may lie in the fact that alkali-feldspars do not show any doubling of the unit cell. As order/disorder in alkali-feldspars takes place only within the 7 Å unit cell, the second type of disorder never becomes important, and hence both lattice constants are subjected to the same type of disordering. Thus the influence of the second type of disorder appears to be different on the two lattice constants *b* and *c* of plagioclases. The influence on *b* is such that there is no further change in it. But *c*, which is more sensitive to the size of tetrahedral cation, shows a net resultant effect. Thus *c* appears to be more useful for determining the structural state of the whole plagioclase- or hyalophane-series, whereas *b* appears to be a more sensitive indicator in the range of 0 to 30–40% (An or Cn, respectively).

Before concluding, it is relevant to comment on the triclinic (Ba,K,Na)-feldspars. Gay's triclinic specimens have a Cn content less than 30 mol%, whereas those from Otjosondou possess as much as 49 mol%. This rather surprising observation suggests that the composition at which the change of symmetry occurs in natural barium feldspars should be at least 50 mol% Cn. If it can be assumed that the degree of triclinity shown by a (Ba,K,Na)-feldspar is a function of its chemical composition and structural state, and that the triclinity values of the barium feldspars with maximum possible order (as defined by Viswanathan and Brandt, 1980) increase with decreasing Cn content, then we conclude that the structural states of two specimens, Nos 16 and 25, Table 1, are nearest to the maximum order possible for their respective compositions as compared to others.

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