The crystal structure of non-stoichiometric Eu-anorthite: an explanation of the Eu-positive anomaly

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Abstract

Synthetic Eu-anorthite of the alkali feldspar structure type has been refined to $R_w = 4.7\%$ using 3-D counter diffractometer data and full-matrix least-squares methods. The chemical composition of the feldspar is $Eu_{0.92}Al_{1.76}Si_{2.24}O_8$, based on both occupancy refinement of the Eu atom site and estimation of the Al/Si distribution calculated from the mean T–O bond length. The unit cell parameters are $a = 8.373(1)$, $b = 12.959(1)$, $c = 7.124(1)$ Å, and $\beta = 115.51(1)°$ and the symmetry is enhanced to $C2/m$. Mean bond lengths are $T(1)$–O = 1.677 Å, $T(2)$–O = 1.668 Å, and Eu–O = 2.721 Å. The average Al/Si distribution over the $T(1)$ and $T(2)$ sites calculated from the mean T–O bond length is in fairly good agreement with an estimate of the Al content from the bond strength calculation; the Al partition is calculated as $t_1 = 0.47$ and $t_2 = 0.41$ respectively. Summing the bond strengths of these Eu and partially disordered Al/Si cations approximates to electrostatic neutrality for the anion content of the feldspar structure, indicating that this synthetic Eu feldspar can be non-stoichiometric, signifying vacancies on the alkali cation site.

Plagioclase and melilite generally show a positive Eu anomaly. A fair insight into the driving force of this anomaly can be afforded by the crystallo-chemical affinities of Eu^{2+} and Eu^{3+} cations to the crystal structures of their host minerals; (1) ioinic radius, (2) electrostatic charge balance and (3) tolerance for non-stoichiometry of the crystal structure.

KEYWORDS: feldspars, anorthite, europium anomaly, non-stoichiometry.

Introduction

KNOWLEDGE of the behaviour of Eu in minerals at high temperatures and pressures is essential to an understanding of deep crustal, upper mantle and meteorite petrology. There are two valence states in the Eu atom–Eu^{2+} and Eu^{3+}. The geochemical coherence of Eu and Sr is widely recognized in minerals (Henderson, 1983); particularly, under reducing conditions, Eu in the divalent state tends to act like Sr^{2+} and has a greater preference for the larger cation site in plagioclase (Smith, 1983). A similar behaviour for Eu in the melilite structure has been recognized; syntheses of gehlenite-type phases have been made for $Sr_2Al_2SiO_7$ (Kimata, 1984) and $Eu_2Al_2SiO_7$ (Kimata, unpublished). Moreover, the trivalent Eu cation also is able to occupy the crystal structures of feldspar and melilite (Bettermann and Liebau, 1976; Ismatov and Gulyamov, 1976), which may help to explain the positive Eu anomaly in silicate minerals.

This paper presents a crystal structure refinement made on the non-stoichiometric Eu feldspar with the chemical composition of $Eu_{0.92}Al_{1.76}Si_{2.24}O_8$. Comments are also made on the significance of non-stoichiometric feldspars in explaining the positive Eu anomaly.

Experimental

The single crystal Eu-anorthite used in this investigation was first studied by Iwasaki and Kimizuka (1978). It was synthesized from a melt with the silica-excess composition; SiO_2:Al_2O_3:Eu_2O_3 = 5:2:1. The basis of the feldspar structure is a framework of linked tetrahedral SiO_4 and AlO_4 groups; consequently defects in the tetrahedral sites result in a failure to form the feldspar structure (Smith, 1983). However if the Al/Si molar ratio of the growing crystal is equivalent to that of the starting material, the resultant feldspar will be of the structure formula; $Eu_{0.89}\square_{0.11}Al_{1.78}Si_{2.22}O_8$. Unfortunately, electron

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microprobe analyses could not be performed on this synthetic sample, because Eu could not be determined, due to the absence of a suitable standard. Thus the chemical composition of the bulk crystals was deduced from the wet chemical technique of ICPA (Inductively Coupled Plasma Analysis, with a Jarrel–Ash Model 975). The chemical formula was determined as $Eu_{0.84}\square_{0.16}Al_{1.747}Si_{2.253}O_8$, which indicates that there are some detectable vacancies in the Eu site.

Single-crystal precession photographs of the Eu-feldspar confirmed the space group *C*2/*m*, common to other monoclinic feldspars. Only '*a*' (*h* + *k* even, *l* even or odd)-type reflections were observed in the photographs and (*h* + *k* odd, *l* even or odd)-types ones were not detected. The generator used was a rotaflex Rigaku RU–200 with Mo–*Kα* radiation (50 kV, 160 mA).

A single crystal showing sharp optical extinction was selected for the intensity measurement and mounted on a Rigaku automated four-circle diffractometer, with a rotaflex RU–200 generator equipped with a Mo-target X-ray cap and highly oriented graphite crystal monochromator mounted with equatorial geometry. A scintillation counter was used to collect the X-ray diffraction data and the diffractometer was controlled by a Panafacom U-100 computer. Least-squares refinement of 15 reflections collected on the diffractometer produced the monoclinically constrained cell dimensions. All relevant crystal data are presented in Table 1.

Table 1. Crystallographic data for Eu-anorthite

formula	$Eu_{0.92}Al_{1.76}Si_{2.24}O_8$
molar wt.	378.20
symmetry	monoclinic
S. G.	C2/m
a (Å)	8.373(2)
b (Å)	12.959(1)
c (Å)	7.124(1)
β (°)	115.51(1)
Volume (Å^3)	679.6(1)
Z	4
Crystal size (mm)	0.05 sphere
$D_{cal.}$ (g.cm^{-3})	3.696
F(000)	704.8
μ(MoKα)	91.40
No. of non euivalent reflections	2600
R	4.7
wR	4.9

A set of intensity data was collected in the θ–$2\theta\omega$ scan mode. Three standard reflections were monitored every 50 measurements to check for stability and constancy of crystal alignment. A total of 2274 relections was measured out to a maximum 2θ of 90°. The data were corrected for background, Lorentz and polarization effects. The crystal was then remoulded to the shape of a sphere, and the absorption correction made by the ACACA program (Wuensch and Prewitt, 1965). Structure factors with $F_{obs} < 3\sigma F$ were not considered, leaving a data set of 2069 observations. These data were reduced to structure factors in the conventional manner.

Refinement

Full matrix, least-squares refinement was carried out using the program RFINE (Finger and Prince, 1975). Scattering curves for neutral atoms were taken from Doyle and Turner (1968). Corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography (1974, pp. 99, 149). Refinement was initiated using the positional parameters of Grundy and Ito (1974) with 8-coordinated sites presumed to be fully occupied by Eu, with the tetrahedral sites by $\frac{1}{2}$Al and $\frac{1}{2}$Si and with isotropic temperature factors of 1.0 for Eu, $\frac{1}{2}$(Al + Si) and O respectively. Refinement of the positional parameters and isotropic temperature factors converged with a conventional *R*-factor. Next, anisotropic temperature factors were introduced into the *R*-convergence process. The final refinement, including all coordinates, anisotropic temperature factors and Eu site population without constraining the total chemistry, rapidly converged to produce a model with $R = 0.047$ ($R_w = 0.053$). A difference synthesis ensures that no significant features have been missed. Positional parameters, temperature factors, and interatomic distances and angles are listed in Tables 2–5.

Discussion

The crystal structure of Eu-anorthite is illustrated in Fig. 1. This synthetic europium feldspar, belonging to a group of monoclinic *C*2/*m* feldspars with $c = 7$ Å, is crystallo-chemically analogous to a defect strontium feldspar, synthetic $Sr_{0.84}Na_{0.03}\square_{0.13}Al_{1.7}Si_{2.3}O_8$ analysed by Grundy and Ito (1974). The Al content of each tetrahedral site was calculated from the mean *T*–O bond length using the equations of Jones (1968), Ribbe and Gibbs (1969), and Kroll and Ribbe (1983). Moreover, a further estimate of the Al content may be obtained from the bond strength calculation (Brown, 1981). As shown in Table 6, the

Table 2. Site population, atomic coordinates and isotropic temperature factors.

Site	Population	x	y	z	B
Eu	0.92	.26935(3)	0	.13114(4)	1.575
Al1	See Table 6	.00508(11)	.17674(6)	.22466(15)	1.066
Al2	See Table 6	.68983(11)	.11664(7)	.34260(14)	0.980
OA1	1.0	0	.13110(27)	0	1.409
OA2	1.0	.59262(39)	0	.28742(58)	1.327
OB	1.0	.81856(35)	.12704(21)	.21942(48)	1.925
OC	1.0	.01577(33)	.30427(19)	.24947(46)	1.793
OD	1.0	.19207(32)	.12259(20)	.40145(41)	1.606

Table 3. Anisotropic temperature factors.

Site	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Eu	.00289(3)	.00277(1)	.01141(6)	0	.00130(3)	0
Al1	.00333(10)	.00137(4)	.00785(17)	-.000417(5)	.00122(11)	-.00004(6)
Al2	.00321(10)	.00136(4)	.00674(17)	.00020(5)	.00120(11)	-.00013(6)
OA1	.00567(40)	.00225(15)	.00755(61)	0	.00198(40)	0
OA2	.00374(34)	.00117(12)	.01312(75)	0	.00250(42)	0
OB	.00748(36)	.00227(12)	.01403(63)	-.00091(17)	.00339(39)	.00003(22)
OC	.00554(30)	.00224(11)	.01490(61)	-.00054(15)	.00343(36)	.00097(22)
OD	.00556(30)	.00262(12)	.00916(49)	-.00007(15)	.00176(31)	.00032(19)

Table 4. Bond multiplicities and interatomic distances (Å).

T(1) tetrahedron

T(1) - OA1	1	1.690(2)A
T(1) - OB	1	1.675(3)
T(1) - OC	1	1.660(3)
T(1) - OD	1	1.683(2)
Mean T(1) - O		1.677

T(2) tetrahedron

T(2) - OA2	1	1.681(2)
T(2) - OB	1	1.663(4)
T(2) - OC	1	1.668(3)
T(2) - OD	1	1.660(3)
Mean T(2) - O		1.668

Eu polyhedron

Eu - OA1	2	2.652(2)A
Eu - OA2	1	2.443(3)
Eu - OB	2	2.843(5)
Eu - OC	2	3.147(3)
Eu - OD	2	2.779(3)
Mean of 7 Eu - O		2.721
Mean of 9 Eu - O		2.816

T(1) tetrahedron		T(2) tetrahedron	
OA1 - OB	2.608(4)	OA2 - OB	2.704(5)
OA1 - OC	2.830(4)	OA2 - OC	2.602(3)
OA1 - OD	2.611(3)	OA2 - OD	2.692(3)
OB - OC	2.783(4)	OB - OC	2.781(5)
OB - OD	2.824(4)	OB - OD	2.741(5)
OC - OD	2.742(3)	OC - OD	2.798(3)
Mean O - O	2.733	Mean O - O	2.720

Table 5. Tetrahedral interatomic angles (°).

T(1) tetrahedron		T(2) tetrahedron		T - O - T	
OA1-T(1)-OB	101.6(1)	OA2-T(2)-OB	107.9(2)	T(1)-OA1-T(1)	139.0(2)
OA1- -OC	115.3(2)	OA2- -OC	102.0(1)	T(2)-OA2-T(2)	128.1(2)
OA1- -OD	101.5(1)	OA2- -OD	107.3(2)	T(1)-OB-T(2)	146.1(2)
OB - -OC	113.1(2)	OB - -OC	113.2(2)	T(1)-OC-T(2)	130.7(2)
OB - -OD	114.5(2)	OB - -OD	111.2(1)	T(1)-OD-T(2)	139.8(2)
OC - -OD	110.2(1)	OC - -OD	114.4(2)		
				Mean T-O-T	136.7
Mean O-T(1)-O	109.4	Mean O-T(2)-O	109.3		

Table 6. Occupancies of T(1) and T(2) tetrahedra

Reference	T(1)		T(2)	
	Al	Si	Al	Si
1.	0.473	0.527	0.414	0.586
2.	0.467	0.533	0.410	0.590
3.	0.474	0.526	0.407	0.593
4.*	0.487	0.513	0.400	0.600

1. Ribbe and Gibbs (1969)
2. Jones (1968)
3. Kroll and Ribbe (1983)
1. - 3. Calculations from mean T-O distance.
4. Calculations from bond-strength (Brown, 1981).
*Total bond-strength of Eu site is 1.862, which corresponds to Eu atomic number, 0.931.

agreement is fairly good, affording conclusive evidence that Al and Si cations merge into two tetrahedral sites during the crystallization process. Furthermore, a quantitative examination of the Eu atom was obtained by an electrostatic occupancy refinement made following Brown's method (1981). Summation of the bond strength in the *M*-site gives 1.862, which corresponds to a content of 0.931 Eu. This is almost identical to the Eu atom occupancy (0.92) obtained by the final refinement. There is a slight difference between the amount of Eu determined by wet chemical analysis and that obtained by the occupancy refinement. This is thought to be due to the difference in chemical composition between the single and bulk crystals. As noted above, the bulk crystals are shown to be poorer in Eu than the refined crystals, whereas the contents of Al and Si atoms in these two structural formulae are in agreement with each other. The refined structural formula is then electrostatically balanced within the limits of the standard deviation. Natural and synthetic non-stoichiometric anorthites $Ca_{1-z}Al_{2-2z}Si_{2+2z}O_8$ ($Z \leqslant 0.15$) have been reviewed (Smith, 1983). It is reasonable to conclude that this Eu-anorthite is of a non-stoichiometric type, having Eu defects and a partially disordered Al/Si distribution.

The equivalent isotropic temperature factors of the tetrahedral sites (Table 2) are reasonably close to those in high albite with a disordered Al/Si state (Ribbe *et al.*, 1969). This effect can be ascribed in part to the Al/Si disorder in both the *T*(1) and *T*(2) sites of the present Eu-feldspar. The direction of greatest expansion of the thermal ellipsoid axis for the Eu cation in this monoclinic Eu-feldspar almost coincides with the crystallographic *c*-axis (Table 7), regardless of symmetry, which is inconsistent with that direction for *M* cations in stoichiometric monoclinic alkali feldspars (Smith, 1974). As found in a defect Sr-feldspar (Grundy and Ito, 1974), the greatest expansion of the thermal ellipsoid *c*-axis in the alkali cation is characteristic of a non-stoichiometric monoclinic alkali feldspar.

Table 8 shows *T*–O distances and tetrahedral distortion in feldspars of the monoclinic $c = 7$ Å type. In all these feldspars Al and Si are found to be partially disordered over the tetrahedral sites. As pointed out by Smith (1974), Rb-feldspar has the lowest distortion of all feldspars. This table shows that the distortion tends to be greater for Al- than Si- bearing tetrahedra and to be greater for *T*(1) than *T*(2) tetrahedra, and highlighting the fact that the present Eu-anorthite has the greatest distortion. Defects on the *M*-site in two non-stoichiometric Sr- and Eu-feldspars proved to be one of factors increasing the tetrahedral distortion.

The present Eu-anorthite, which is apparently a solid solution of the 'excess silica', $\square Si_4O_8$, is similar to several crystalline solution types. Knowledge of the Eu content suggests the following Eu^{3+}-bearing solid solution; $0.20Eu^{3+}_{2/3}\square_{1/3}Al_2Si_2O_8 + 0.8Eu^{2+}Al_2Si_2O_8 = Eu^{2+}_{0.80}Eu^{3+}_{0.13}\square_{0.07}Al_2Si_2O_8 = Eu_{0.93}\square_{0.07}Al_2Si_2O_8$; this is substantially different from the present Eu-anorthite in its Al/Si ratio. This negates the existence of Eu^{3+} cations in this sample. Introduction of the stoichiometric $EuAl_2Si_2O_8$ end-member is hereafter approximately referred to one typical solid solution; $0.92EuAl_2Si_2O_8 + 0.40SiO_2$. As noticed

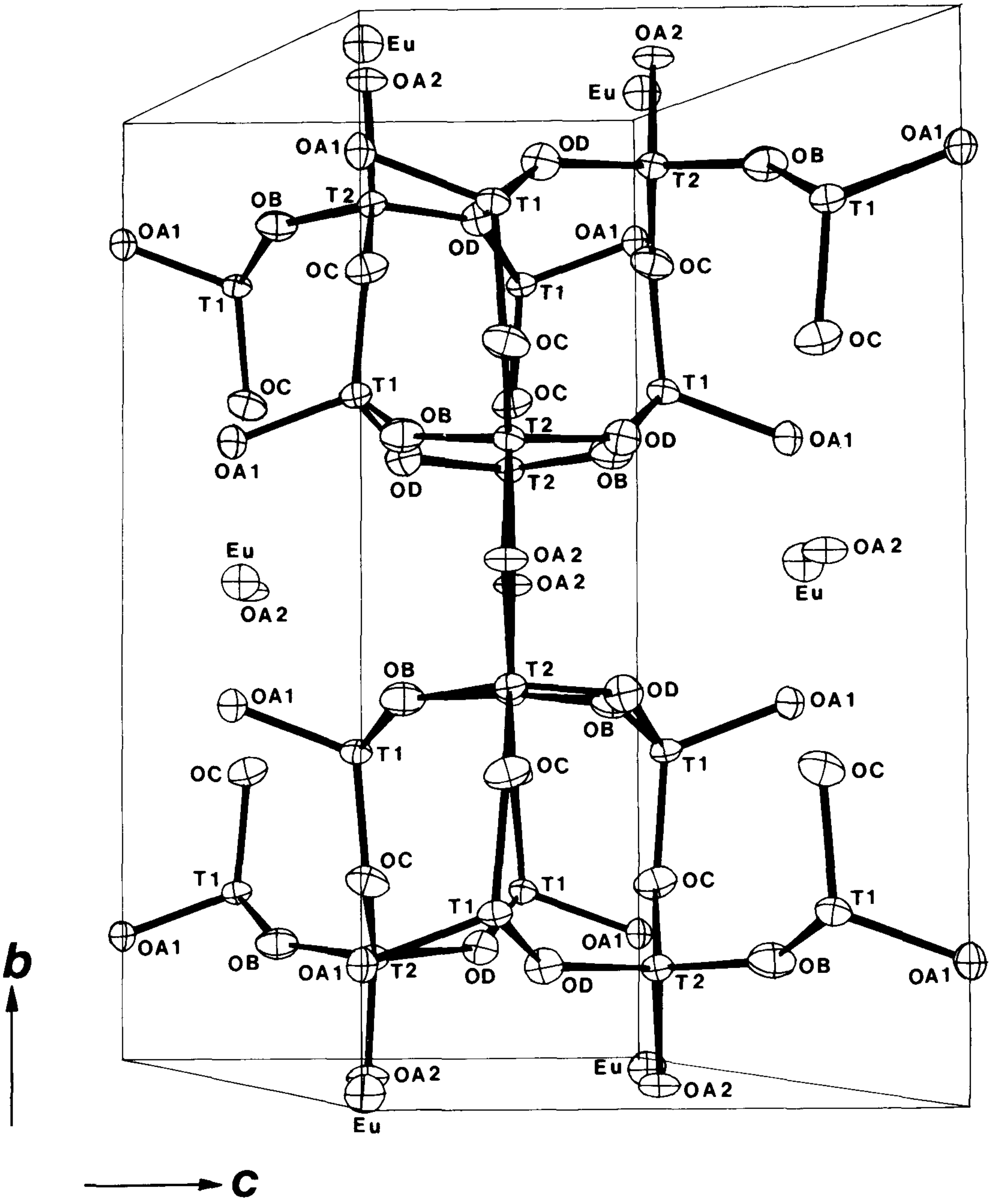

FIG. 1. A projection of the Eu-feldspar structure onto (100) showing the probability ellipsoids of thermal vibration. Tetrahedral bond directions associated with the framework are represented as solid lines; the bonding of Eu to the framework is not shown.

by Zoltai and Buerger (1959) and quantified by Megaw (1970), consistent with the idea of silica solid solution is the fact that the aluminosilicate feldspar framework structure is polytypic to the structure of coesite, one of the high-pressure polymorphs of SiO_2. The present Eu-anorthite is iden-

Table 7. Magnitudes (Å) and orientation of thermal ellipsoids (°).

Atom	r.m.s. displacement	Angle with the a-axis	Angle with the b-axis	Angle with the c-axis
Eu	0.09138(2)	26.85(1)	90	88.66(1)
	0.15365(1)	90	180	90
	0.16694(2)	116.85(1)	90	1.34(1)
T(1)	0.0912(1)	41.5(5)	59.56(6)	86.4(8)
	0.1127(4)	69(1)	148.4(7)	79(2)
	0.1396(3)	124.0(2)	82(2)	12(2)
T(2)	0.09397(9)	35.9(6)	107.7(2)	84.0(6)
	0.1076(6)	97(1)	158(1)	106(2)
	0.1297(5)	125.0(2)	103(3)	17(2)
OA1	0.12104(2)	61.56(6)	90	53.95(6)
	0.13841(1)	90	180	90
	0.14048(2)	28.56(6)	90	144.07(6)
OA2	0.099771(8)	90	90	90
	0.10325(3)	159.48(2)	90	85.01(1)
	0.17270(3)	110.52(2)	90	4.99(1)
OB	0.1253(5)	55.2(5)	37.0(7)	94(3)
	0.1565(10)	126(1)	56(3)	106(3)
	0.1815(12)	125.2(6)	77(4)	17(4)
OC	0.1154(13)	38(2)	53(2)	104(2)
	0.1400(12)	119(2)	44(4)	103(1)
	0.1876(17)	111.89(8)	70(3)	20(2)
OD	0.1224(1)	46.6(8)	92(3)	69.0(7)
	0.1456(26)	115(5)	146(5)	60(4)
	0.1576(25)	126(3)	56(5)	38(4)

Table 8. T-O distance (Å) and distortion of tetrahedra in several C2/m feldspars.

feldspars	T(1)		T(2)		References
	T-O	σ*	T-O	σ*	
Rb-feldspar	1.635	2.40	1.632	2.05	Gasperin (1971)
High sanidine	1.645	3.01	1.640	2.60	Ribbe (1963)
Low sanidine	1.656	2.90	1.628	2.68	Colville and Ribbe (1968)
Sr-anorthite	1.670	5.536	1.657	3.993	Grundy and Ito (1974)
Eu-anorthite	1.677	6.303	1.668	4.576	This study

* Distortion defined by Robinson et al. (1971).

tified as the solid solution between feldspar and minor amounts of coesite. The mechanism of these crystalline solutions can be accounted for by the charge coupled substitution; $Eu^{2+} + 2Al^{3+} = \square + 2Si^{4+}$, and so we may safely say that the vacant cation sites are present in the silica-rich domain of this feldspar. In spite of non-stoichiometry, furthermore, neutrality to the electrostatic valence is generally realized in natural feldspars (Smith, 1983). The present study of Eu-feldspar indicates that the reducing environment at a high temperature can yield the non-stoichiometric feldspar and that a persilicic parental melt is prerequisite to the genesis of Si-rich non-stoichiometric feldspar.

Factors affecting an Eu-positive anomaly

The causes of the variations in *REE* distributions in minerals have been debated for a number of years. Semenov (1957, 1958) suggested that the crystal structure of the mineral plays the predominant role in admitting particular *REE* ions. On the other hand Neumann *et al.* (1966) have shown that both processes operate and give the factors controlling the *REE* distributions in minerals as (*a*) the availability of elements of suitable ionic radius, and (*b*) the appropriate bonding forces, charge, and optimum ionic radius for the given structural position. Eu appears to be the only rare earth element that will reduce to the divalent state in nature, and the feldspar structure is postulated to be such that Eu^{2+} is readily accepted, resulting in excess Eu in the mineral relative to the *REE* of adjacent atomic number and a disruption of the straightforward pattern of *REE* fractionation in igneous rocks in which it occurs (Henderson, 1983). This excess state is called a positive Eu-anomaly. Feldspars and melilites invariably reveal a pronounced positive europium anomaly (Nagasawa *et al.*, 1977).

The present Eu-phase is a trace feldspar end-member. The feldspar tolerating significant amounts of a trivalent cation on the non-tetrahedral *M*-position was synthetically demonstrated as a lanthanum–calcium–sodium alumosilicate $La_xCa_{8-2x}Na_x[Al_{16}Si_{16}O_{64}]$ which is a stoichiometric type (Bettermann and Liebau, 1976). Inasmuch as the ionic radius of Eu^{3+}, 1.066 Å, is very similar to that of La^{3+}, 1.16 Å, (Shannon, 1976), this suggests that feldspars can be also acceptors of minor amounts of Eu^{3+}. The presence of Eu^{3+} yields a solid solution consisting of the component with a vacant site:

$$\begin{aligned} Eu_x^{2+}Eu^{3+}{}_{0.5-0.5x}\square_{0.5-0.5x}Al_{1.5-0.5x}Si_{2.5-0.5x}O_8 \\ = xEu_{1.0}^{2+}Al_{2.0}Si_{2.0}O_8 \\ + (1-x)Eu_{0.5}^{3+}\square_{0.5}Al_{1.5}Si_{2.5}O_8 (0 \leqslant x \leqslant 1). \end{aligned}$$

The latter end-member is however structurally unstable owing to an excess of *M*-site vacancies; therefore values of *x* close to 1 favour a stable Eu-bearing feldspar. A structural preference for the $Eu^{2+}Al_2Si_2O_8$ end-member is essential for a positive Eu anomaly in feldspar.

Recent work on the crystal structure of melilites has shown the importance of both local bond-valence requirements and their relationships to variation in bond length, suggesting that the same mechanism should exert stringent controls on cation ordering (Kimata, 1983). Its crystal chemistry suggests that it is another receptacle of europium in nature. In studying the site of the Eu^{3+} cation, pure $CaEuAl_3O_7$ with the melilite structure was synthesized (Ismatov and Gulyamov, 1976). Synthesis of this Eu^{3+}-aluminate melilite has been confirmed by Kimata (1986, unpublished). Part of Table 9 shows the bond strengths (Pauling, 1960) in this melilite-type compound. Furthermore, a melilite phase of $(Eu^{2+})_2Al_2SiO_7$ composition has been crystallized under an H_2-flow environment by solid-state reaction at 1400 °C for 48 hrs (Kimata, unpublished). This Eu^{2+}-melilite is tetragonal, a = 7.825(2), c = 5.237(2) Å, presenting a striking similarity to Sr-gehlenite $Sr_2Al_2SiO_7$ with parameters a = 7.820(1), c = 5.264(1) Å (Kimata, 1984). The analogous relationship between ionic radii of Sr and Eu (Shannon, 1976) highlights the fact that natural melilite can also accommodate divalent Eu cations. Therefore a phase with the melilite structure can crystallo-chemically admit both Eu^{2+} and Eu^{3+} cations.

Table 9. A bond strength (Po) in several mineral-type compounds.

1) The existing $CaEuAl_3O_7$ melilite

	Ca,Eu	T_1(Al)	T_2(Al)	Po
O(1)	2/8+3/8	3/4	3/4	2.125
O(2)	2/8+2x3/8		3/4	1.750
O(3)	2/8+3/8	3/4	3/4	2.125

2) The existing $NaYSiO_4$ olivine

	M1(Na)	M2(Y)	Si	Po
O(1)	2x1/6	3/6	4/4	1.833
O(2)	2x1/6	3/6	4/4	1.833
O(3)	1/6	2x3/6	4/4	2.167

3) The supposed pyroxenes with the larger trivalent M(2) cation and the smaller monovalent M(1) cation.

A. Clinopyroxene-type

	M1(I)	M2(III)	Si	Po
O(1)	2x1/6	3/8	4/4	1.708
O(2)	1/6	3/8	4/4	1.542
O(3)		2x3/8	2x4/4	2.750

B. Orthopyroxene-type

	M1(I)	M2(III)	SiA	SiB	Po
O1A	2x1/6	3/6	4/4		1.833
O1B	2x1/6	3/6		4/4	1.833
O2A	1/6	3/6	4/4		1.667
O2B	1/6	3/6		4/4	1.667
O3A		3/6	2x4/4		2.500
O3B		3/6	2x4/4		2.500

Non-stoichiometry in the melilite structure was first described in a sulphide compound $Ln_{10/3}Ga_6S_{14}$ (Lozac'h *et al.*, 1972). This phase exhibits a crystallographic tolerance of $\square_{1/3}$ vacancy in the eight-coordinated site. Recently in blastfurnace slags, melilite crystals over a wide range within the åkermanite–gehlenite series proved to be non-stoichiometric, there being a deficiency of Mg and/or Al relative to Si in the structure (Scott *et al.*, 1986). Non-stoichiometry does not seem to be uncommon in the melilite structure. Thus enhancement of a positive Eu-anomaly is inherent in melilite phases capable of accommodating Eu^{2+} and Eu^{3+} cations concurrently.

It is known that olivine and pyroxene show no positive Eu-anomaly (Henderson, 1983). A key difference between the olivine and orthopyroxene structures is the valence balance for the oxygens. A structure field map for the A_2BX_4 structure constructed by Muller and Roy (1974) suggests that the octahedral *A* cations in the olivine structure type can range from monovalent to trivalent with radius values ranging from 0.53 Å (Al^{3+}) to 1.02 Å (Na^{+}) (Shannon, 1976). Inasmuch as the ionic radii of Eu^{2+} and Eu^{3+} cations are beyond this range, these cations cannot be accommodated by the olivine structure, although the fact that each oxygen is surrounded by one tetrahedral and three octahedral cations conforms to the formal valence balance in the Pauling sense (Table 9). The olivine-type compounds including trivalent cations have been exemplified by $LiLnSiO_4$ (*Ln* = Ho–Lu) and $NaYSiO_4$ (Paques-Ledent, 1976). Furthermore the mineral laihunite referring to a sample with composition close to $(Fe^{2+})_{0.5}\square_{0.5}(Fe^{3+})_{1.0}SiO_4$, is a non-stoichiometric type (Laihunite Research Group, 1976). Ionic radius is, therefore, now regarded as a major contribution to a negative Eu anomaly in olivine.

In the pyroxene-structure types there are two types of *M* sites, labelled *M*1 and *M*2. The *M*1 site accommodates divalent, trivalent, and tetravalent cations with ionic radii ranging from 0.53 Å (Al) to 0.83 Å (Mn), and the radii of cations that occupy the *M*2 site range from 0.72 Å (Mg^{VI}) to 1.16 Å (Na^{VIII}) (Brown, 1980). The ionic radius of Eu^{2+} is beyond the latter range. These characteristics of *M* sites throw some light upon the trend that the *M*2 site is always of the larger size than *M*1 (Cameron and Papike, 1982). For the presumed $NaEuSi_2O_6$ of the orthopyroxene type, geometrical constraints in the pyroxene structure leads to the distribution of Na in *M*1 site and Eu in *M*2, and the formal electrostatic balance is represented in Table 9. Remarkable underbonding of the O(2*A*) oxygens and overbonding of the O3 will prevent the presumed compounds from existing or being synthesized (Table 9). This unbalance limits the ability of Eu^{3+} to occupy the pyroxene structure.

Reliable information on non-stoichiometry of the pyroxene structure has resulted from the synthesis of clinopyroxenes in the system CaO–Al_2O_3–SiO_2 (Gasparik and Lindsley, 1980). From this, the composition of pyroxenes with vacancies can be extrapolated to the Ca-Eskola end-member $Ca_{0.5}\square_{0.5}AlSi_2O_6$ (McCormick, 1986), but because of the larger ionic radii of the substituting cations, incorporation of Eu^{2+} and Eu^{3+} cations into this phase is not possible. Therefore the pyroxene structure does not provide a favourable situation for a positive Eu anomaly.

Self-consistency is achieved for the positive Eu anomaly when the Eu^{2+} and Eu^{3+} cations match the particular site-potential in the crystal. The present Eu-anorthite is expected to be one of possible receptacles of europium in nature. Therefore it qualifies as a potential *REE* aluminiosilicate mantle phase present as a trace in feldspar end-members. In conclusion, only minerals capable of accommodating Eu^{2+} and Eu^{3+} at crystallographic sites simultaneously exhibit an Eu-positive anomaly. We suggest that the key factors which give rise to this anomaly are crystallo-chemical affinities of these cations to the occupying structure; (1) ionic radius, (2) electrostatic charge balance and (3) tolerance for non-stoichiometry of the crystal structure. Strict conformity with the three affinities is clearly a prerequisite for a positive Eu anomaly in a mineral. These factors may also be applicable to understanding Ce- and Yb-anomalies (Henderson, 1983).

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