

THE ROLE OF Ti^{4+} IN THE CRYSTAL STRUCTURE OF PYROXENE ISOMORPHOUS SERIES: DIOPSIDE $(CaMgSi_2O_6) - CaTiAl_2O_6$

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The crystal structure of a model-system clinopyroxene of approximate 72 mole % diopside-28 mole % $CaTiAl_2O_6$ solid solution was refined. The space group is $C2/c$, cell parameters $a = 9.781(5)$, $b = 8.856(4)$, $c = 5.331(3) \cdot 10^{-10}$ m, $\beta = 106.06(5)^\circ$. The problem of Ti^{4+} location was solved by the least-squares refinement and difference Fourier syntheses to an R-value 6.1%. The Ti^{4+} presumably occupy the M1 site but a small part of Ti^{4+} is placed in the tetrahedrally coordinated positions. These results are confirmed by the increase of T-O2 interatomic distance. With respect to crystallisation of east basalt products, TiO_2 is not suitable as a nucleation admixture because of its "solubility" in clinopyroxenes.

INTRODUCTION

Possibility or impossibility of isomorphous replacement $IVSi^{4+} \rightarrow IVTi^{4+}$ in silicates have been frequently discussed in literature. As a result from these works, the tetrahedrally coordinated titanium in silicates has been found [1], [2] but at the same time its presence is considered to be improbable [3]. In the studies dealing with crystal structure refinements of synthetic diopside containing 2.13 wt. % of Ti and diopside (Di in the following) — titanotschermakite ($CaTiAl_2O_6$; TiTsch) solid solution respectively, Schröpfer [4], [5] stated the possibility of titanium to be in clinopyroxenes tetrahedrally coordinated. His conclusions were made on the basis of refined site occupancy factors.

In an effort to find the influence of TiO_2 admixture upon the crystallisation of east basalt products and to verify Schröpfer's conclusions, another crystal structure refinement of a member Di-TiTsch solid solution was carried out.

EXPERIMENTAL

Starting material suitable for X-ray work was kindly supplied by Dr. J. Voldán, CSc. (State Glass Research Institute, Hradec Králové). It was prepared from the stoichiometric mixture of TiO_2 , SiO_2 , $Al(OH)_3$, $CaCO_3$ and dolomite, supposing theoretical chemical composition 70 mole % Di — 30 mole % TiTsch. Electron microprobe analysis gave the chemical composition slightly different from the theoretical one: 36.26 % SiO_2 , 9.44 % TiO_2 , 25.39 % CaO, 12.40 % MgO and 16.03 % Al_2O_3 (total sum of oxides 99.52 wt. %).

Unit cell dimensions were obtained by least-squares refinement on the basis of silicon-calibrated powder diffraction data. The refined values are $a = 9.781(5)$, $b = 8.856(4)$, $c = 5.331(3) \cdot 10^{-10}$ m, $\beta = 106.06(5)^\circ$.

* Roman numerals indicate the coordination number of a cation.

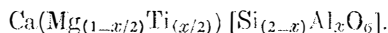
Systematic absences of hkl -type reflections for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ obtained from Weissenberg photographs indicated space group $C2/c$ or Cc . Refinement of the structure confirmed the centrosymmetric $C2/c$ space group, common for the majority of clinopyroxene structures.

The intensity data were collected from an irregular, prismatic-like crystal fragment of dimensions approximately $0.5 \times 0.16 \times 0.125$ mm, in a Weissenberg geometry semiautomatic diffractometer STOE using monochromatised (graphite monochromator) Mo radiation and the ω -scan technique. The 2798 independent reflections (up $2\theta = 100^\circ$) of hkl and $\bar{h}kl$ type were obtained (332 reflections with "zero" intensities). All data were corrected for absorption ($\mu = 34.14 \text{ cm}^{-1}$) and Lorentz-polarisation factor. Absorption correction was carried out using the modified version of Burnham's program GNABS [6] taking into account the crystal shape approximated for this purpose by 6 faces. Unobserved reflections were assigned the intensity values equal to $I_{\min}/3$ [7], where $I_{\min}$ is the minimum observable intensity for a reflection.

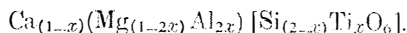
Refinement of the structure

From the crystallochemical point of view, three following models of the structure were possible:

1. With isomorphous replacement in the M1 site $\text{Mg}^{2+} \rightarrow \text{Ti}^{4+}$ and in the T site $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$ characterised by the crystallochemical formula unit

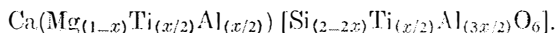


2. Isomorphous replacement in the M1 site $\text{Mg}^{2+} \rightarrow \text{Al}^{3+}$ and $\text{Si}^{4+} \rightarrow \text{Ti}^{4+}$ in the site T with corresponding crystallochemical formula unit



This model was improbable because of vacancy in the M2 site (impossible in clinopyroxene structures) and restriction of miscibility Di-TiTsSch to 25 mole % of TiTsSch which is in contradiction with previous work [8].

3. Intermediate model with both $\text{Mg}^{2+} \rightarrow \text{Ti}^{4+}$, Al^{3+} substitutions in the M1 site and $\text{Si}^{4+} \rightarrow \text{Al}^{3+}$, Ti^{4+} in the T site (ratio $^{\text{VI}}\text{Al}/^{\text{VI}}\text{Al} = 3$ and $^{\text{VI}}\text{Al}/^{\text{VI}}\text{Ti} = 1$) as proposed by Schröpfer [5]. Crystallochemical formula unit of this model has the form



Refinement of the structure was carried out using the full-matrix least-squares program ORFLS [9]. The atomic scattering factors were those of Cromer and Waber [10] for neutral atoms. The weighting scheme was defined as $w = 1/\sigma$ (σ values established on the basis of the counting statistics [6]). No restrictions of "zero" intensities have been made.

Refinement has been initialised on the basis of Schröpfer's [5] atomic coordinates and anisotropic temperature factors. Occupancy factors (for one formula unit) were set for the third model as follows from the microprobe analysis:

site M1 $a_{\text{Mg}} = 0.656$	site T $a_{\text{Si}} = 1.368$
$a_{\text{Al}} = 0.172$	$a_{\text{Al}} = 0.554$
$a_{\text{Ti}} = 0.172$	$a_{\text{Ti}} = 0.090$

according to the Schröpfer proposed proportions of $^{\text{VI}}\text{Al}$ and $^{\text{VI}}\text{Ti}$ (1 : 1) in the site M1. Starting from R-factor 19.6 % with the whole data collection after several cycles

of atomic coordinates and anisotropic temperature factor refinement*), R-factor dropped rapidly to 12.6 %. No occupancy factor refinement has been made at this stage. On this level of R-factor the second model of the structure has been excluded (based on no significant changes of a_{Ca}). Opening of a_i and calculation of difference Fourier syntheses (program FFSYNT [11]) were on this level of precision useless. Results of weighting scheme inspection showed the increase of R-values due to diffractions lying in the region of $\sin\theta/\lambda$ over 0.772 ($2\theta \sim 60^\circ$). Into this region falls the majority of weak and „zero“ diffractions. Consequently, the rejection of data for the range mentioned above resulted in a decrease of the R-factor to 6.4 %. We would like to note that because of similarity of scattering factor curves for Ti, Si and Ti, Mg respectively, reflections lying into region with $\sin\theta/\lambda$ greater than 0.6 are not useful for a_i verification or refinement. Final atomic coordinates are listed in Table I.

Table I

Final atomic coordinates compared with values for pure diopside [14] (2nd line). Standard deviations in parentheses, nomenclature of positions according to [13]

	x	y	z
M2	0.00000	0.90597(20)	0.25000
	0.00000	0.90823(9)	0.25000
M1	0.00000	0.30596(9)	0.25000
	0.00000	0.30154(5)	0.25000
TA1	0.28752(11)	0.09328(12)	0.22551(19)
	0.28623(5)	0.09331(5)	0.22928(9)
O1A1	0.11194(21)	0.08699(13)	0.13572(37)
	0.1156(1)	0.0873(1)	0.1422(2)
O2A1	0.36298(24)	0.25668(26)	0.31968(39)
	0.3611(1)	0.2500(1)	0.3180(3)
O3A1	0.35301(21)	0.01958(24)	— 0.00829(38)
	0.3505(1)	0.0176(1)	— 0.0047(2)

Difference $F_o - F_c$ Fourier syntheses computed on $R = 6.4\%$ clearly showed a deficit of electrons in the T site, e.g. confirmed the presence of tetrahedrally coordinated titanium. Further refinement of anisotropic temperature factors (positions treated as occupied by one atom with scattering curves proportional to atomic fractions in the site) minimised the residue to 6.1 % (5.9 % for „non zero“ diffractions) connected with disappearance of local minimum in the site T. Final values of β_{ij} are listed in Table II. List of observed and calculated structure factors can be obtained upon request from the author.

*) Because of statistically occupied positions the dependent parameters have been constrained using the subprograms RESETX and RESETB of the OR FLS least-squares program. On this level of refinement the M1 and T positions have been treated formally as three atoms.

Table II

Coefficients of the anisotropic temperature factor*). Standard deviations in parentheses, nomenclature of positions according to [13]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M2	0.0017(1)	0.0017(1)	0.0051(3)	—	0.0003(2)	—
M1	0.0004(1)	0.0015(2)	0.0034(5)	—	0.0004(2)	—
TA1	0.0002(1)	0.0011(1)	0.0043(3)	0.0001(1)	0.0008(2)	—0.0003(2)
O1A1	0.0009(3)	0.0022(4)	0.0063(9)	0.0002(2)	0.0009(5)	—0.0003(5)
O2A1	0.0023(3)	0.0028(4)	0.0061(9)	0.0002(2)	0.0016(5)	—0.0001(5)
O3A1	0.0009(3)	0.0031(4)	0.0086(10)	0.0001(3)	0.0002(5)	—0.0019(5)

*) anisotropic temperature factor defined as $\exp \left\{ - \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij} \right\}$

Discussion of interatomic distances

Interatomic distances were computed using the OR FFE program [12] and are listed with corresponding bond angles in Table III. Nomenclature of equivalent positions (Fig. 1) is that, proposed in [13]. For all interatomic distances the standard deviations are considerably higher than for those, published for pure diopside [14]. It is due to the positional uncertainty of statistically occupied positions and consequently of uncertainty of oxygen coordinates.

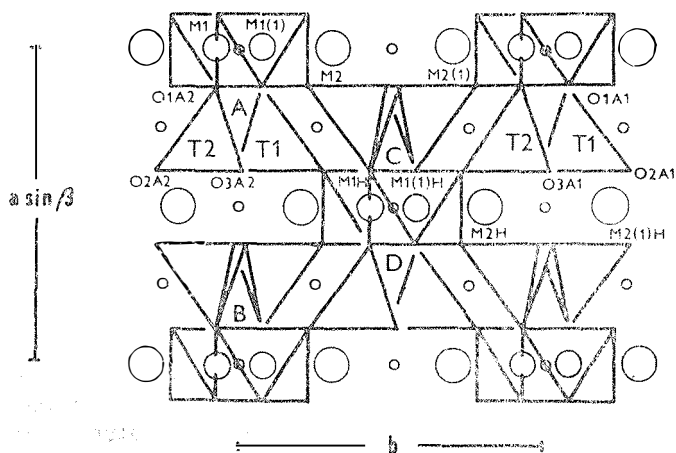


Fig. 1. Nomenclature of equivalent positions in clinopyroxene structures according to [13].

Octahedron M1. There are no great differences between interatomic distances in our sample and those of diopside. Because of similar ionic radii of $\text{V}^{\text{I}}\text{Mg}^{2+}$ (0.72) and $\text{V}^{\text{I}}\text{Ti}^{4+}$ (0.605)* the interatomic distances M1—O are unaffected by the $\text{Mg} \rightarrow \text{Ti}$

*) Ionic radii taken from the work of Shannon and Prewitt [15], values in 10^{-10} m.

Table III

Bond lengths [10^{-10} m] and bond angles [$^{\circ}$]. Standard deviations in parentheses, nomenclature of positions according to [13]

bond length		bond angle	
Octahedron M1			
M1O-1A1, B1	2.124(4)	O1A2-O1B2	176.6(1)
O-1A2, B2	2.079(23)	(2)O1A1-O2D1	169.4(1)
O-2C1, D1	1.993(4)	O1A1-O1B1	81.9(2)
mean of 6	2.065	O2C1-O2D1	96.4(2)
O1A1-O1B1	2.784(11)	(2)O1A1-O2C1	91.4(2)
O2C1-O2D1	2.972(9)	(2)O1A1-O1A2	95.2(2)
(2)O1A1-O2C1	2.947(5)	(2)O1A1-O1B2	82.5(2)
(2)O1A1-O1A2	3.081(3)	(2)O1A2-O2C1	90.4(3)
(2)O1A1-O2C1	2.866(5)	(2)O1A2-O2D1	91.8(3)
(2)O1A2-O2D1	2.855(10)	T-O1A1-M1	121.3(2)
(2)O1A1-O1B2	2.903(13)	T-O1A2-M1	120.9(5)
mean of 12	2.922	T-O2C1-M1	144.6(1)
M1-M1(1)	3.142(8)		
M1-TA1	3.300(2)		
M1-TA2	3.225(20)		
Tetrahedron T			
T-O1	1.652(6)	O1-T-O2	117.5(2)
T-O2	1.645(4)	O1-T-O3A1	110.4(4)
mean, non brg.	1.649	O1-T-O3A2	109.9(4)
T-O3A1	1.686(6)	O2-T-O3A1	109.9(2)
T-O3A2	1.707(6)	O2-T-O3A2	103.5(4)
mean, brg.	1.697	O3A1-T-O3A2	104.8(1)
mean of 4	1.673	mean of 6	109.3
O1-O2	2.818(9)	T-O3-O4	135.4(2)
O1-O3A1	2.741(7)	O3A2-O3A1-O3A2	165.1(3)
O1-O3A2	2.751(15)		
O2-O3A1	2.726(5)		
O2-O3A2	2.633(5)		
O3A1-O3A2	2.688(2)		
mean of 6	2.726		
T-TA2	3.139(3)		
Polyhedron M2			
M2-O1A1, O1B1	2.393(4)	O1A1-O1B1	71.1(2)
-O2C2, O2D2	2.381(12)	O2C2-O2D2	145.8(1)
-O3C1, O3D1	2.547(8)	O3C1-O3D1	85.5(4)
-O3C2, O3D2	2.637(13)	O3C2-O3D2	109.9(3)
mean of 6	2.440	O1A1-O2C2	83.1(2)
mean of 8	2.499	O1A1-O3C1	120.9(2)
O3C1-O3D1	3.394(22)	O2C2-O3C1	64.5(3)
(2)O1A1-O2D2	2.904(16)	O2C2-O3C2	112.9(2)
(2)O1A1-O3C2	3.596(5)	O3C1-O3C2	63.7(2)
(2)O2C2-O3C1	2.633(5)	O1A1-O2D2	67.4(2)
(2)O2C2-O3D2	3.411(8)	O1A1-O3D1	134.3(1)
(2)O3C1-O3C2	2.688(2)	O1A1-O3D2	159.9(1)
(2)O3C1-O3D2	2.875(6)	O2C2-O3D2	84.7(2)
		O3C1-O3D2	66.8(1)
		O2C2-O3D1	141.3(2)

(2)-multiplicity of bond length and bond angle respectively, brg: — bridging

substitution. Taking into account the linear relationship of Al-content in this position versus mean bond length $M1-O$ [14] the proportions of $VIAl^{3+}$ estimated from the structure refinement and interpolated between mean diopside (2.077*) and jadeite (1.928, [15]) $M1-O$ distance are in good agreement.

Polyhedron $M2$. $M2-O$ distances for both diopside and our sample are very similar and mean $M2-O$ distances are identical within the standard deviation limit.

Tetrahedron T . The most affected coordination body by the substitution $Si \rightarrow Al$, Ti is the TO_4 tetrahedron. All $T-O$ distances are — relative to pure diopside — higher, but significantly increased (greater than three times of its standard deviation) $T-O2$ distance only. Clark et al. [14] have pointed out a linear relationship between the length of $T-O2$ distance and Al^{3+} content in the T site. Results of interpolation between $T-O2$ distances reported for diopside — 1.585 (100 % of Si in T site), fassaite — 1.629 (25 % Al , 75 % Si ; [16]) and tschermakite — 1.665 [17] indicated for our sample (1.645) the occupancy of T position by 37.5 % of Al and 62.5 % of Si . As follows from the microprobe analysis the Si content in the T site is 68 %. Supposing the rest to be occupied by Al only, the theoretical $T-O2$ distance should be 1.635. Consequently, the increasing of $T-O2$ distance to 1.645 must be due to a cation with ionic radius greater than those for $IVSi^{4+}$ and $IVAl^{3+}$. In our case only the titanium is the suitable cation with the corresponding ionic radius.

CONCLUSIONS

Crystal structure refinement of a member $Di-Ti$ solid solution confirmed the Schröpfer's [5] hypothesis of the presence of tetrahedrally coordinated titanium with final occupancy factors for $M1$ and T positions (standard deviations given in parentheses):

site $M1$	$a_{Mg} = 0.656(4)$	site T	$a_{Si} = 1.368(4)$
	$a_{Al} = 0.172(6)$		$a_{Al} = 0.554(6)$
	$a_{Ti} = 0.172(3)$		$a_{Ti} = 0.090(7)$

The presence of tetrahedrally coordinated titanium is confirmed by difference Fourier syntheses and changes of $T-O2$ distance related to other end-member clinopyroxenes. With respect to crystallisation of east basalt products, TiO_2 is not suitable as a nucleation admixture because of its "solubility" in clinopyroxenes.

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*) Values in 10^{-10} m.

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POSTAVENIE Ti^{4+} V KRYŠTÁLOVEJ ŠTRUKTÚRE IZOMORFNÉHO RADU DIOPSID $(\text{CaMgSi}_2\text{O}_6) - \text{CaTiAl}_2\text{O}_6$

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Röntgenovou štruktúrnou analýzou pyroxénového izomorfneho radu diopsid — $\text{CaTiAl}_2\text{O}_6$ (priestorová grupa C2/c , $a = 9.781(5)$, $b = 8.856(4)$, $c = 5.331(3) \cdot 10^{-10}$ m, $\beta = 106.06(5)^\circ$; 4 vzorové jednotky v základnej bunke) sa zistilo, že Ti^{4+} — ako je to u silikátových štruktúr bežné — prednostne obsadzuje pozíciu M1 v koordinácii 6. Jeho časť sa však podieľa i na obsadzovaní tetraédricky koordinovaných pozícií, izomorfne v nich nahrádzajúc Si^{4+} . Uvedený izomorfny rad predstavoval modelový systém pri overovaní procesu nukleácie čadičovej taveniny pomocou TiO_2 . Výsledky práce ukázali, že TiO_2 tvorí tuhý roztok s pyroxénmi, tvoriacich podstatnú časť čadičových výrobkov a preto sa nehodí ako nukleačné činidlo.

•obr. 1. Nomenklatura ekvivalentných pozícií v kryštálových štruktúrach monoklinických pyroxénov podľa [13].

ПОЗИЦИЯ Ti^{4+} В КРИСТАЛЛИЧЕСКОЙ СТРУКТУРЕ ИЗОМОРФНОГО РЯДА ДИОПСИД $(\text{CaMgSi}_2\text{O}_6) - \text{CaTiAl}_2\text{O}_6$

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На основании рентгеновского структурного анализа пироксенового изоморфного ряда диопсид — $\text{CaTiAl}_2\text{O}_6$ (пространственная группа C2/c , $a = 9.781$ [5], $b = 8.856$ [4], $c = 5.331$ [3] $\cdot 10^{-10}$ м, $\beta = 106.06$ [5]°; 4 молекул в элементарной ячейке) было установлено, что Ti^{4+} — как это бывает у силикатных структур — прежде всего занимает позицию M1 в координации 6. Однако его часть занимает даже тетраэдрически координированные позиции, изоморфно замещая в них Si^{4+} . Приводимый изоморфный ряд представляет собой модельную систему при проверке процесса образования зародышей базальтовой расплава помощью TiO_2 . Полученные результаты показывают, что TiO_2 образует твердый раствор с пироксенами, составляющими существенную часть базальтных изделий и поэтому оказывается непригодной для применения в качестве нуклеационного реактива.

Рис. 1. Номенклатура эквивалентных позиций в кристаллических структурах моноклинических пироксенов согласно [13].