

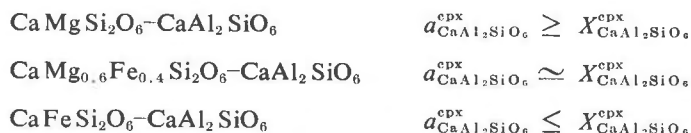
Mixing properties of tschermakitic clinopyroxenes

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Abstract

The relationship between clinopyroxene composition and $\text{CaAl}_2\text{SiO}_6$ activity has been determined for clinopyroxenes crystallized in the systems $\text{CaMgSi}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$, $\text{CaFeSi}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$, and $\text{CaMg}_{0.6}\text{Fe}_{0.4}\text{Si}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$. The activity of $\text{CaAl}_2\text{SiO}_6$ component was fixed in the clinopyroxenes by performing experiments at known pressures and temperatures in the presence of excess anorthite and quartz. The following approximate relationships have been obtained:

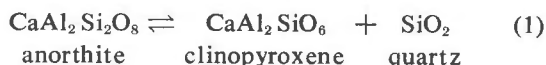


The activity-composition relationships imply Al–Si order in the tetrahedral site of clinopyroxene.

Introduction

A number of equilibria involving the tschermakitic ($\text{CaAl}_2\text{SiO}_6$) component of clinopyroxene are potentially useful for estimating the pressures of crystallization of appropriate mineral assemblages. Thermodynamic or experimental data on such equilibria cannot, however, be applied to rocks unless the mixing properties of multicomponent clinopyroxene solid solutions are known.

The object of this study has been to determine the relationship between activity ($a_{\text{CaAl}_2\text{SiO}_6}$) and mole fraction ($X_{\text{CaAl}_2\text{SiO}_6}$) of the calcium tschermak's component in two- and three-component clinopyroxene solutions as a preliminary to the determination of the properties of complex natural pyroxenes. The method adopted has been to crystallize starting compositions in the systems $\text{CaMgSi}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$, $\text{CaFeSi}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$, and $\text{Ca}(\text{Mg}_{0.6}\text{Fe}_{0.4})\text{Si}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$ to subsolidus assemblages of anorthite, quartz and clinopyroxene solid solution. If equilibrium is established at known temperature and pressure, the activity of $\text{CaAl}_2\text{SiO}_6$ component in the pyroxene solid solution is fixed by the reaction:



Analysis of product clinopyroxenes enables (given equilibrium) the relationship between composition and activity to be determined.

Experimental procedure

Experiments were performed in the pressure-temperature range 10–25 kbar and 900–1300°C using a 0.5" piston-cylinder apparatus. The run was initially brought to the desired temperature at a pressure of 5 kbar above the nominal run pressure. The pressure was then lowered and maintained at the required value during the run. Pressures were not corrected for possible friction effects and the pressure dependence of thermocouple (Pt–Pt₈₇Rh₁₃) emf has been neglected. Preliminary synthesis experiments were carried out using glass starting materials and variable run durations. Data points at 1100°C/15 kbar and 1300°/15 kbar were checked using crystalline starting materials (Table 1). For experiments in the system $\text{CaMgSi}_2\text{O}_6\text{--CaAl}_2\text{SiO}_6\text{--SiO}_2$, samples were run in unsealed Pt capsules. In the iron-bearing systems unsealed graphite capsules were used. The compositions of product clinopyroxenes were determined using an A.E.I. electron microscope-microanalyser (EMMA IV) with a Kevex solid state detector and the correction procedure described by Cliff and

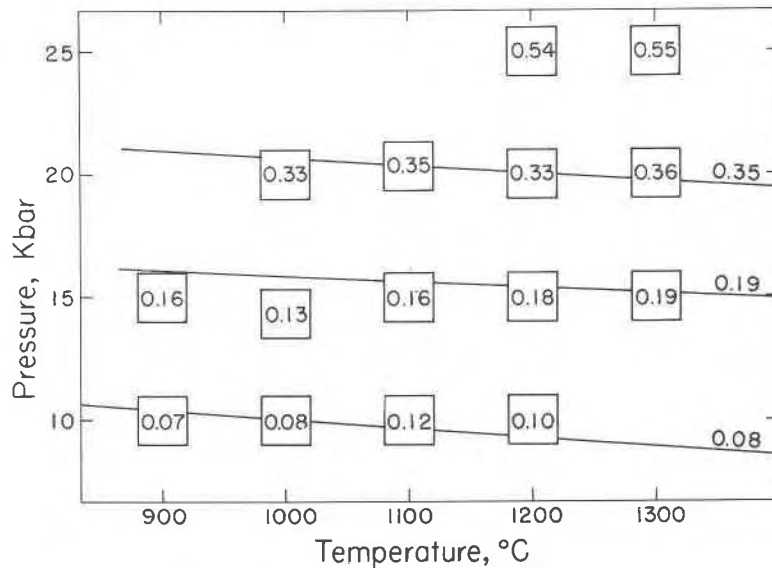


FIG. 1. The mole fraction of $\text{CaAl}_2\text{SiO}_6$ component in $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ solid solutions coexisting with anorthite and quartz at different temperatures and pressures. Lines labelled 0.08, 0.19, 0.35 represent approximate isopleths.

Lorimer (1975); between 15 and 20 analyses were performed on each specimen. Analyses are less precise than those obtained with a conventional microprobe but this disadvantage is compensated by greatly increased resolution (1000 Å approximately). The quality of individual analyses was checked by comparison with the "ideal" clinopyroxene stoichiometry.

Analyses deviating from the expected stoichiometry by more than 3 percent were discarded. At low pressures and low $X_{\text{CaAl}_2\text{SiO}_6}$, this procedure resulted in the rejection of a small proportion (10% approximately) of clinopyroxene analyses; but at $X_{\text{CaAl}_2\text{SiO}_6}$ greater than 0.3, the number of non-stoichiometric analyses was found to increase markedly. The observed deviation at high $X_{\text{CaAl}_2\text{SiO}_6}$ is towards excess SiO_2 and is believed to represent a real deviation from stoichiometry (*c.f.* Kushiro, 1969).

TABLE 1. Results of experiments

T°C	P kbar	Time (hrs)	Starting material	$X_{\text{CaAl}_2\text{SiO}_6}^{\text{cpx}*}$
900	10.0	16	glass	0.24
900	10.0	138	glass	0.07
1100	10.0	22.5	glass	0.12
1100	10.0	1.5	glass	-0.25
1200	10.0	3	glass	0.16
1200	10.0	6	glass	0.10
1100	14.6	15.5	glass	0.14
1100	15.0	26.5	glass	0.16
1100	15.0	22	An,Cpx,Qz†	0.15
1300	15.0	1.5	glass	0.18
1300	15.0	1.75	An,Cpx,Qz†	0.18

*Each composition represents the average of those analyses (about 15 per specimen) which fulfill the conditions of pyroxene stoichiometry (see text). One standard deviation for $X_{\text{CaAl}_2\text{SiO}_6}$ is generally in the range 5 to 10 percent relative.

†A mixture of solid phases crystallized at 1 atm from a glass of composition $(\text{CaMgSi}_2\text{O}_6)_{0.25}(\text{CaAl}_2\text{Si}_2\text{O}_8)_{0.6}(\text{SiO}_2)_{0.15}$ in which the clinopyroxene contains less than 0.05 mol fraction $\text{CaAl}_2\text{SiO}_6$ component.

Results

The compositions of clinopyroxenes synthesized from $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ - SiO_2 glasses together with anorthite and quartz are shown in Figure 1 in terms of mole fraction of $\text{CaAl}_2\text{SiO}_6$ component. Standard deviations are generally in the range 5 to 10 percent relative. Synthesis runs in this system tend to produce clinopyroxenes richer in $\text{CaAl}_2\text{SiO}_6$ than the equilibrium pyroxenes. The glass initially devitrifies to form an aluminous clinopyroxene, anorthite, and quartz. With time, the pyroxene reacts with quartz to produce more anorthite and a clinopyroxene poorer in alumina. This sequence has been established at several run temperatures (Table 1) and is consistent with other synthesis experiments involving clinopyroxenes (*e.g.* Mori and Green, 1975). At 1100°C and 15 kbar the equilibrium composition appears to be reached in synthesis experiments of about 15 hours duration. The composition of pyroxene obtained

from such a run agrees closely with that obtained from a crystalline anorthite-clinopyroxene (alumina-poor)-quartz assemblage in 22 hours. At 1300°C and 15 kbar glass and crystalline starting materials produce pyroxenes of similar compositions in runs of 1 to 2 hours duration. All the high temperature data shown in Figure 1 were obtained for experiments of 1 1/2 hour duration at 1300°C, 6 hour duration at 1200°C, and greater than 15 hour duration at 1100°C. Bracketing of equilibrium compositions using crystalline starting materials has not yet been possible at temperatures lower than 1100°C, so that 900° and 1000° results must be considered tentative at present. (Detailed run data will be presented at a later date.)

Discussion

The activity of CaAl₂SiO₆ component in clinopyroxene solid solution coexisting with anorthite and quartz was calculated from the reversal of reaction (1) by Hariya and Kennedy (1968) at 1400°C and 30.8 kbar. This result was extrapolated to lower temperatures and pressures using the high-temperature entropy and 298 K/1 bar volume data of Robie and Waldbaum (1968). Activities at pressures below the metastably extrapolated equilibrium boundary were calculated from:

$$RT \ln a_{CaAl_2SiO_6}^{cpx} = (Po - Pr) \Delta V_{298/1}^{\circ} \quad (2)$$

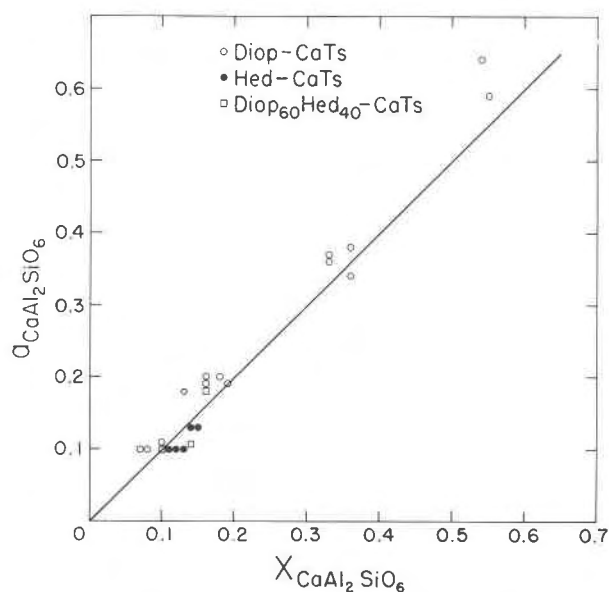


FIG. 2. $a_{CaAl_2SiO_6}^{cpx}$ plotted against $X_{CaAl_2SiO_6}^{cpx}$ for clinopyroxene solid solutions of different Mg/Fe ratio (see text). Diagonal line corresponds to activity equal to mole fraction.

where $\Delta V_{298/1}^{\circ} = 0.349$ cal/bar, Po = equilibrium pressure for pure phases at the temperature of interest, and Pr = run pressure.

Assuming an uncertainty of ± 0.5 kbar in the run pressures employed during this study and ± 0.5 kbar in those of Hariya and Kennedy, the uncertainty in activity is 10 percent relative. This conservative uncertainty estimate ignores the unresolved inconsistency between Hariya and Kennedy's data and those of Hays (1966) on CaAl₂SiO₆ clinopyroxene stability. Activities will be known with more certainty when the position of reaction (1) has been established using identical run procedures to those employed during this study.

The relationship between activity and composition for CaAl₂SiO₆ component in clinopyroxene (CaMgSi₂O₆-CaAl₂SiO₆) solid solutions is shown in Figure 2 together with synthesis data for the two iron-bearing systems. It may be seen from this diagram that $a_{CaAl_2SiO_6}^{cpx}$ is an extremely simple function of clinopyroxene composition:

$$CaMgSi_2O_6-CaAl_2SiO_6 \quad a_{CaAl_2SiO_6}^{cpx} \geq X_{CaAl_2SiO_6}^{cpx}$$

$$CaMg_{0.6}Fe_{0.4}Si_2O_6-CaAl_2SiO_6 \quad a_{CaAl_2SiO_6}^{cpx} = X_{CaAl_2SiO_6}^{cpx}$$

$$CaFeSi_2O_6-CaAl_2SiO_6 \quad a_{CaAl_2SiO_6}^{cpx} \leq X_{CaAl_2SiO_6}^{cpx}$$

Similar relationships for Mg₂Si₂O₆-MgAl₂SiO₆ and Mg₂Si₂O₆-Fe₂Si₂O₆-MgAl₂SiO₆ solid solutions were observed by Wood and Banno (1973) and Wood (1974).

The activity-composition relationships for tschermakitic clinopyroxenes which have been obtained in this study bear an interesting relationship to pyroxene crystal structure. If mixing in multi-component clinopyroxenes is of charge-balanced CaAl₂SiO₆, CaMgSi₂O₆, and CaFeSi₂O₆ "molecules" with complete Al-Si order, then $a_{CaAl_2SiO_6}$ should be related to $X_{CaAl_2SiO_6}$ in the following way:

$$a_{CaAl_2SiO_6} = X_{CaAl_2SiO_6} \gamma_{CaAl_2SiO_6} \quad (3)$$

As may be seen from Table 2 this "ordered" model

TABLE 2. Activity coefficients $\gamma_{CaAl_2SiO_6}$ for CaMgSi₂O₆-CaAl₂SiO₆ solid solutions

$X_{CaAl_2SiO_6}$	γ -Disordered	γ -Local chargebalance	γ -Ordered
0.07	10.6	3.1	1.43
0.16	4.0	2.3	1.19
0.33	2.0	1.6	1.12
0.55	1.35	1.26	1.07
Excess enthalpy of mixing at $X_{Cats} = 0.5$	≈ 1.5 Kcals	≈ 0.75 Kcals	≈ 0.02 Kcals

produces γ 's close to 1.0 and excess enthalpy of mixing close to zero. Okamura *et al.* (1974) have found from crystallographic studies, however, that Al and Si atoms are completely disordered in pure $\text{CaAl}_2\text{SiO}_6$ clinopyroxene. If, as seems likely, this result also applies to $\text{CaAl}_2\text{SiO}_6$ -bearing solid solutions, the activity of $\text{CaAl}_2\text{SiO}_6$ component should be given by:

$$a_{\text{CaAl}_2\text{SiO}_6} = X_{\text{CaAl}_2\text{SiO}_6}^2 (2 - X_{\text{CaAl}_2\text{SiO}_6}) \gamma_{\text{CaAl}_2\text{SiO}_6} \quad (4)$$

If Al and Si atoms are indeed disordered over the entire clinopyroxene structure, activity coefficients (γ) are very much greater than 1.0 and excess enthalpies of mixing are quite large (Table 2). The close correspondence of $X_{\text{CaAl}_2\text{SiO}_6}$ and $a_{\text{CaAl}_2\text{SiO}_6}$ suggests, however, that Al and Si atoms are to some extent ordered in the clinopyroxene structure, although ordered in such a way as to be undetectable by X-ray methods. One possible mechanism (designated "local charge-balance" in Table 2) is the coupling of each octahedral Al substituted in $\text{CaMgSi}_2\text{O}_6$ to an Al in one of the six nearest neighbor tetrahedral positions with complete Al-Si disorder over these six positions. This type of substitution would produce apparent Al-Si disorder (from X-rays), but activity-composition relationships fairly close to those obtained for complete Al-Si order. The actual mechanism of solid solution in tschermakitic clinopyroxene would be

greatly elucidated by calorimetric measurement of enthalpies of mixing.

Acknowledgment

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References

- CLIFF G. AND G. W. LORIMER (1975) The quantitative analysis of thin specimens. *J. Microscopy*, **103**, 203-207.
- HARIYA, Y. AND G. C. KENNEDY (1968) Equilibrium study of anorthite under high pressure and high temperature. *Am. J. Sci.* **59**, 549-557.
- HAYS, J. F. (1966) Lime-alumina-silica. *Carnegie Inst. Wash. Year Book*, **65**, 234-239.
- KUSHIRO, I. (1969) Clinopyroxene solid solutions formed by reactions between diopside and plagioclase at high pressures. *Mineral. Soc. Am. Spec. Pap.* **2**, 179-191.
- MORI, T. AND D. H. GREEN (1975) Pyroxenes in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ at high pressure. *Earth Planet. Sci. Lett.* **26**, 277-286.
- OKAMURA, F. P., S. GHOSE AND H. OHASHI (1974) Structure and crystal chemistry of calcium Tschermak's pyroxene, $\text{CaAl}_2\text{SiO}_6$. *Am. Mineral.* **59**, 549-577.
- ROBIE, R. A. AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U. S. Geol. Surv. Bull.* **1259**, 256 pp.
- WOOD, B. J. (1974) The solubility of alumina in orthopyroxene coexisting with garnet. *Contrib. Mineral. Petrol.* **46**, 1-15.
- AND S. BANNO (1973) Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contrib. Mineral. Petrol.* **42**, 109-124.