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EFFECT OF OXYGEN FUGACITY ON FASSAITIC PYROXENE

by

Kosuke Onuma

(with 9 text-figures)

Abstract

Stability of fassaitic pyroxene in the system $CaMgSi_2O_6$-$CaFeAlSiO_6$-$CaAl_2SiO_6$-$CaTiAl_2O_6$ is discussed on the basis of published data. In the system $CaMgSi_2O_6$-$CaFeAlSiO_6$ the stability field of clinopyroxene decreases with an increase in $CaFeAlSiO_6$ content and a decrease in oxygen fugacity at constant temperature. The stability field of clinopyroxene in the system $CaMgSi_2O_6$-$CaAlFeSiO_6$-$CaAl_2SiO_6$ is strongly influenced by oxygen fugacity at low and high pressure and decreases with respect to $CaFeAlSiO_6$ component. Titanium content of the clinopyroxene does not seem to be affected by the change of oxygen fugacity when magnetite is stable. These data are probably useful in evaluating the condition under which natural fassaitic pyroxenes are formed.

Introduction

The clinopyroxenes in undersaturated alkalic rocks and also in some metamorphic rocks are rich in CaO, Al_2O_3, Fe_2O_3, and TiO_2, and most of them plot on the wollastonite-rich region beyond the diopside-hedenbergite join in the pyroxene quadrilateral. The main components of such pyroxenes are $CaMgSi_2O_6$(Di), $CaFeSi_2O_6$(Hd), $CaTiAl_2O_6$ (Ti-pyroxene component, Tp), $CaAl_2SiO_6$ (Ca-Tschermak's component, CaTs), $CaFe^{3+}AlSiO_6$ (ferri-aluminum Tschermak's component, FATs), $NaFe^{3+}Si_2O_6$(Ac), and $Mg_2Si_2O_6$(En) (Onuma and Yagi, 1971). According to Deer et al. (1978), the name fassaite is used to Al (Fe^{3+})-rich clinopyroxenes in which most of the M2 positions are occupied by Ca, and the introduction of the trivariant cations into M1 is compensated almost entirely by the replacement of Si by Al in tetrahedral site. From this view point the clinopyroxenes containing $CaFe^{3+}AlSiO_6$ and $CaAl_2SiO_6$ components are fassaitic pyroxene or fassaite. Onuma and Yagi (1975) and Onuma et al. (1981) emphasized the significance of the system Di-CaTs-FATs-Tp for understanding the crystallization of pyroxene in alkali rocks.

Since these pyroxenes contain $CaFe^{3+}AlSiO_6$ and $CaFe^{2+}Si_2O_6$, their composition and evolutionary trend must be significantly affected by the variation of oxygen fugacity of the magma from which the pyroxenes crystallize. Therefore, for evaluating the effect of oxygen fugacity on the fassaitic pyroxenes, the author has been engaged in the experimental study on the systems involving FATs component with co-workers. In this paper are reviewed the results of the experimental studies at controlled oxygen fugacity in our laboratory.

Effect of Oxygen Fugacity on Stability of Fassaite

The FATs component, which is regarded as a main component of Fe^{3+}-rich fassaite, is a stable compound with clinopyroxene structure C2/c at 1 atm in air below 1250°C (Hijikata, 1968; Huckenholz et al., 1974), and there is a complete series of solid solution between

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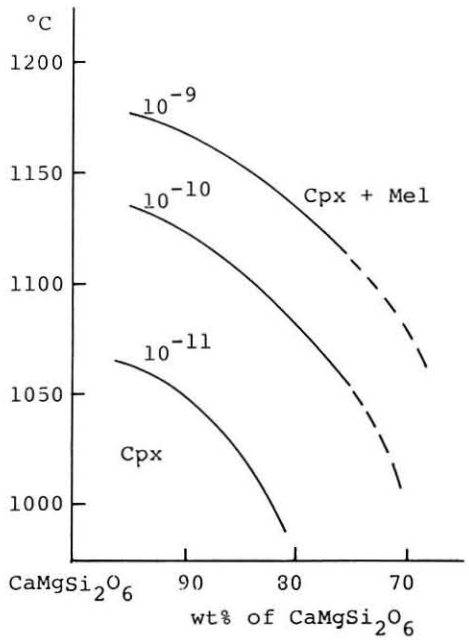
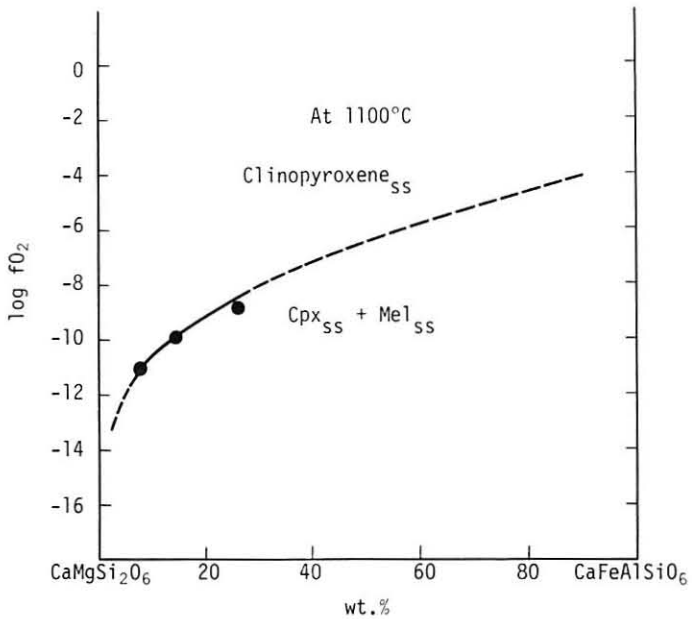
diopside and FATs under this condition (Hijikata & Onuma, 1969). Oba and Onuma (1978) made an experiment on this system with varying oxygen fugacity to clarify the effect of oxygen fugacity on the stability of Fe^{3+}-rich fassaite, and found that the stability field of pyroxene is restricted at low fO_2. Text-fig. 1 shows the change of clinopyroxene one-phase



Text-fig. 1 Pyroxene one-phase field in the Di-FATs system at low fO_2. From data of Oba and Onuma (1978).



Text-fig. 2 Stability field of the Di-FATs pyroxene for fO_2 at 1100°C. From data of Oba and Onuma (1978).

field with a change in fO_2. The one-phase field decreases with increasing temperature at constant fO_2 and decreases considerably with decreasing fO_2 at constant temperature as also shown in Text-fig. 2; 27 wt% at 10^{-9} and 14 wt% at 10^{-10} at 1100°C and 8 wt% at 10^{-11}, 1050°C. Two-phase field of Cpx + Mel is present to the higher temperature and lower fO_2 side of one-phase field. As demonstrated in Text-fig. 3, the pyroxene one-phase field is stable at least above the fO_2 defined by MW buffer, while the assemblage Cpx + Mel is present in the field where Wu is stabilized. Therefore, the melilite may contain $Ca_2Fe^{2+}Si_2O_7$ component as expected from the equation, $CaMgSi_2O_6 + CaFe^{3+}AlSiO_6 = Ca_2Fe^{2+}Si_2O_7 + MgSiO_3 + 1/2Al_2O_3 + 3/4O_2$, and clinopyroxene would become to contain Mg-Tschermak's component. At low fO_2 clinopyroxene becomes hedenbergitic due to the presence of Fe^{2+}. In the Di-poor portion the following reactions may take place and spinel is present.

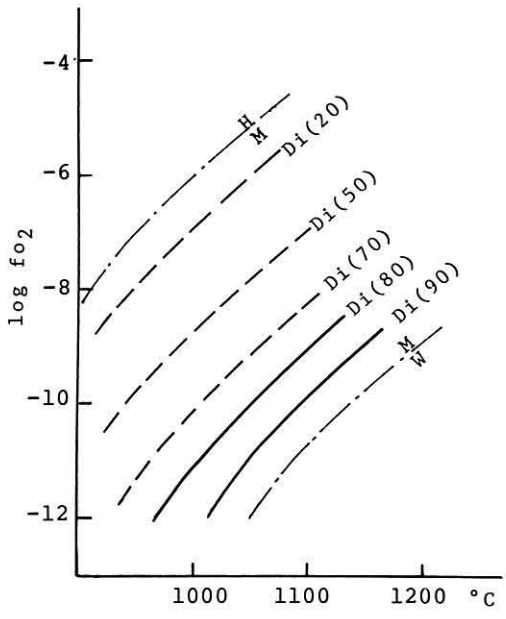
$$2CaMgSi_2O_6 + 6CaFe^{3+}AlSiO_6 = 4Ca_2Fe^{2+}Si_2O_7 + MgSiO_3 + Fe^{2+}SiO_3 + Al_2O_3 + MgAl_2O_4 + FeAl_2O_4 + 3/2O_2$$

pyroxene spinel

$$3CaFe^{3+}AlSiO_6 = Ca_2Fe^{2+}Si_2O_7 + CaSiO_3 + 3/2FeAl_2O_4 + 1/6Fe_3O_4$$

pyroxene spenel

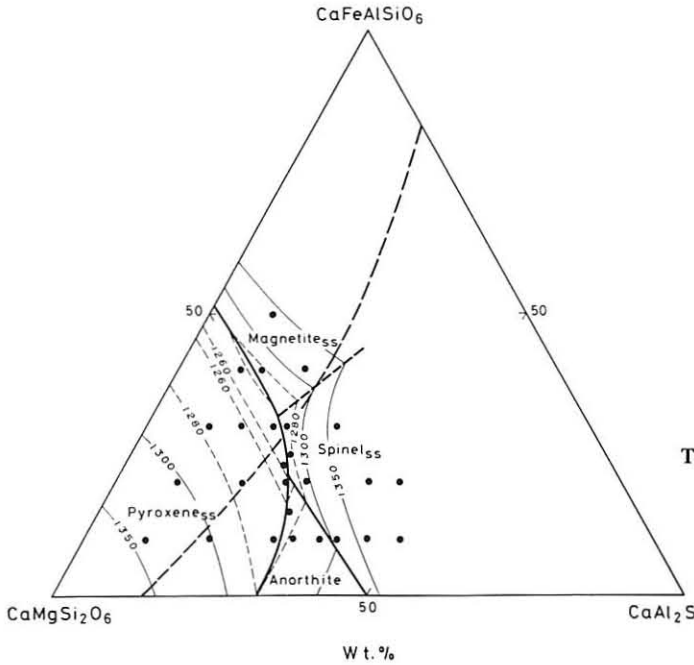
Thus, $CaFe^{2+}Si_2O_6$ component is expected in the clinopyroxene of the magnetite stability field. Text-fig. 3 shows the stability of clinopyroxenes with various compositions in the Di-FATs system over temperature and fO_2. The clinopyroxene poorer in Di than 70 wt% is not stable at the temperature and fO_2 ranges studied, and therefore the broken lines are drawn tentatively. Text-fig. 3 indicates that the stability field of clinopyroxene for temperature and fO_2 decreases with an increase in the FATs content of clinopyroxene.



Text-fig. 3 Stability of the Di-FATs pyroxene for fO_2 and temperature. The pyroxene is stable above curves.

The stability of FATs-pyroxene at high pressure has been studied by Ohashi and Hariya (1975 a, b). The FATs-pyroxene is stable up to about 43 kbar and 1300°C under the condition where hematite is stabilized, and above this pressure and temperature decomposes into garnet + oxide as suggested by Hijikata and Onuma (1969). On the other hand, the stability field of this pyroxene decreases with decreasing fO_2, and the clinopyroxene decomposes into Cpx + Gar + Sp at least 6 kbar at the fO_2 defined by $Fe_2O_3 - Fe_2O_4$ and $MnO - Mn_3O_4$ buffers. The observations mentioned above indicate that there is a complete series of solid solution between Di and FATs from 1 atm to 45 kbar under the condition where hematite is stabilized, and that the stability of fassaitic pyroxene of Di-FATs system is more sensitive for change of fO_2 than pressure.

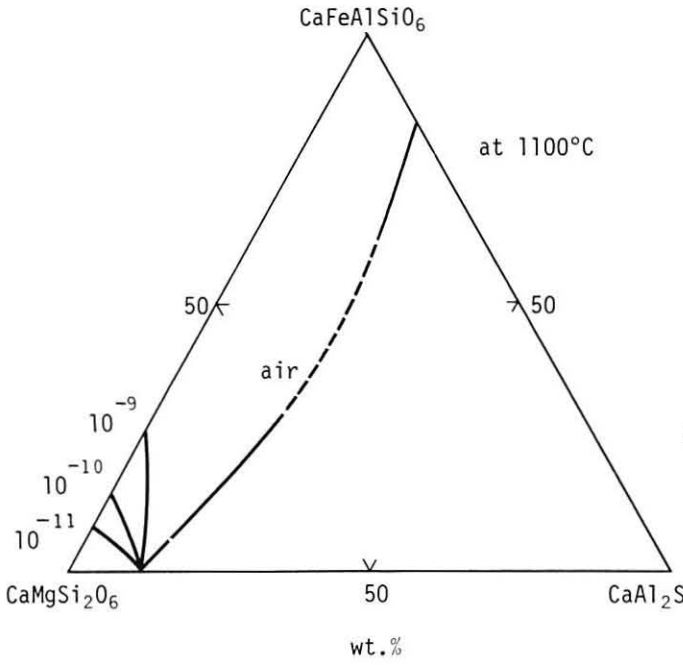
The phase relation in the system Di-FATs-CaTs at 1 atm in air was studied by Onuma and Yagi (1975) and Onuma et al. (1981). The phase relation at liquidus is shown in Text-fig. 4. Clinopyroxene, anorthite, spinel, and magnetite are present as primary phase. In the liquidus diagram there are two points showing four-phase assemblage; one at 1250°C, shows the liquid coexisting with Cpx + An + Sp and the other, at 1270°C, the liquid coexisting with Cpx + Mt + Sp. These points, however, are neither eutectic nor piercing points because of the nature of the six-component system at liquidus temperature. At subsolidus temperatures there are present one-phase fieled of pyroxene, Cpx + An + Mel, and Cpx + An + Mel + Sp, and the limit of one-phase field of pyroxene is shown with a heavy broken line in Text-fig. 4.



Text-fig. 4 Liquidus diagram of the Di-FATs-CaTs system in air at 1 atm (Onuma et al., 1981). Broken line shows the limit of pyroxene one-phase field at subsolidus.

An experimental study for the Di-CaTs system at 1 atm has made by Schairer and Yoder (1970), who demonstrated that the clinopyroxene one-phase field attains 12 wt% CaTs at about 1250°C. The substitution of CaTs in diopside, according to Clark et al. (1962), is favored by high pressure. The lowest stability of CaTs was found by Hays (1966) and Hijikata and Yagi (1967) to be located at about 11 kbar and 1100°C. Below this temperature and pressure the clinopyroxene breaks down into Cpx + An + Sp. Hijikata (1973) determined the P-T stability of clinopyroxene in the Di-CaTs system and demonstrated that the lowest stability of $Di_{50}CaTs_{50}$ and $Di_{25}CaTs_{75}$ is 5.8 kbar, 975°C and 8.8 kbar, 1010°C, respectively. These data show that the stability field of clinopyroxene increase with increasing pressure.

On the basis of the data stated above, we can estimate the stability field of fassaitic pyroxene over pressure and fO_2 in the Di-CaTs-FATs system. The stability field is strongly influenced by fO_2 at low and high pressure and decrease with respect to the FATs component with decreasing fO_2 as shown in Text-fig. 5. The clinopyroxene is stable in the



Text-fig. 5 Estimated stability field of the pyroxene for fO_2 in the Di-FATs-CaTs system. Pyroxene is stable in the region to the left of the curve. (Onuma et al., 1981).

region to the left of the curve. There exists only small clinopyroxene one-phase field at 10^{-11} atm. The stability field of pyroxene, however, expands from the Di-FATs line toward the CaTs apex, indicating that mostly the CaTs component is affected by the change of pressure.

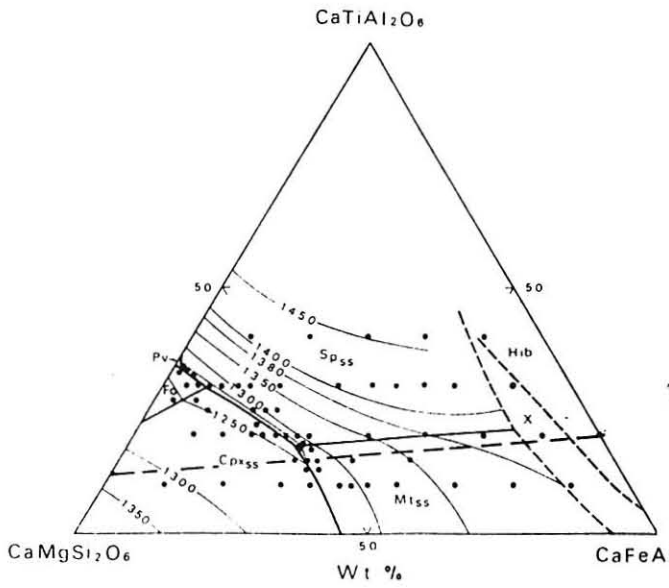
Although the earlier works (Oba and Onuma, 1978; Schairer and Yoder, 1970; Hays, 1966; Hijikata and Yagi, 1967) did not give the chemical compositions of the pyroxenes, since the composition of pyroxene in the Di-FATs-CaTs system (Onuma et al., 1981) and

also in the Di-CaTs system (Yang, 1975) varies beyond the one-phase field, the stability limit does not necessarily mean the solubility limit of the FATs and CaTs components in pyroxene. Nevertheless, it is expected that pressure and fO_2 give arise the same effect on the composition of solid solution as on the stability limit. It is therefore concluded that FATs content of fassaitic pyroxene is influenced by fO_2 and is independent of pressure, while CaTs content is effected by pressure.

Ti-Fassaite

The phase relation in the Di-FATs-Tp system at 1 atm in air was determined by Akasaka and Onuma (1979). A liquidus diagram is shown in Text-fig. 6. Clinopyroxene, forsterite, perovskite, magnetite, spinel, and hibonite are present. An unknown phase was encountered. It was first found by Hijikata and Onuma (1969) in the Di-FATs system and named "phase X". Although there are four points showing a four-phase assemblage, these points are again neither eutectic nor piercing points, because the system belongs to the seven-component system Fe-O-CaO-MaO-Al_2O_3-TiO_2-SiO_2 at liquidus temperature.

In the 10 wt% Tp section, a complete series of solid solution of pyroxene is present at subsolidus temperatures. In the portion more than 10% Tp, the pyroxene one-phase field is no more stable, and perovskite or Pv + Mel + An appears in addition to the pyroxene solid solution. The limit of pyroxene one-phase field is shown as broken line in Text-fig. 6.



Text-fig. 6 Liquidus diagram of the Di-FATs-Tp system in air at 1 atm (Akasaka and Onuma, 1979). Broken line shows the limit of pyroxene one-phase field.

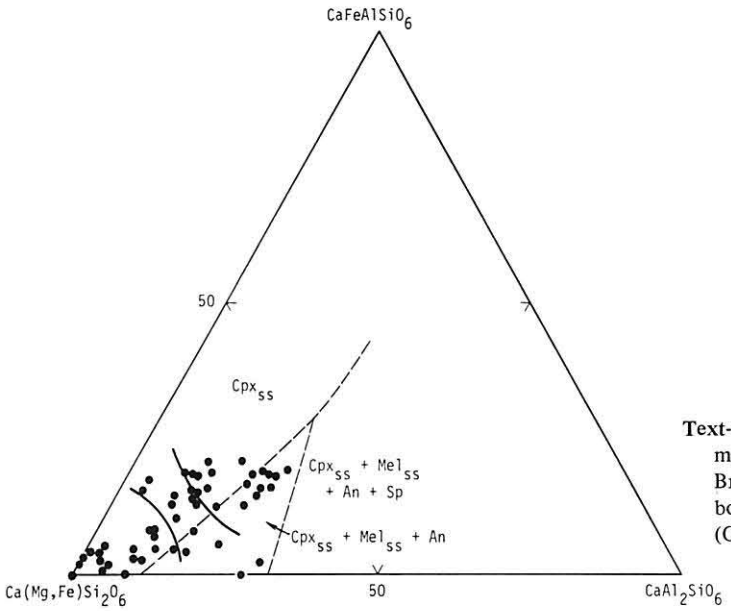
Akasaka (1981) made an experimental study on this system at 10^{-11} atm fO_2. No one-phase field of clinopyroxene was observed, and the fields of Cpx + Mel, Cpx + Mel + Sp, and Cpx + Mel + Sp + An were present instead at subsolidus temperatures in the compositions with 10% Tp. Akasaka (1981) analysed the clinopyroxenes and the melilite by Mössbauer spectra method as well as microprobe, and demonstrate that the clinopyroxenes

contain 9 wt% $CaFe^{2+}Si_2O_6$ as well as FATs component, supporting the estimated reaction of Oba and Onuma (1978). The melilite was also confirmed to contain at least 35.5 wt% $Ca_2Fe^{3+}Si_2O_7$. He also showed that Ti content of the clinopyroxene is not too much affected by the change of fO_2 and the clinopyroxenes crystallizing from the compositions with 10 wt% Tp also contain about 10 wt% Tp (3.4 wt% TiO_2).

Significance of the Di-CaTs-FATs-Tp System to the Natural Pyroxene

The significance of the Di-CaTs-FATs-Tp system to the Natural fassaitic pyroxene has been discussed by Akasaka and Onuma (1979), Onuma and Akasaka (1980), and Onuma et al. (1981). The main points in these discussion are briefly stated here.

Text-Fig. 7 shows the plots of metamorphic Ca-pyroxene from various localities in the

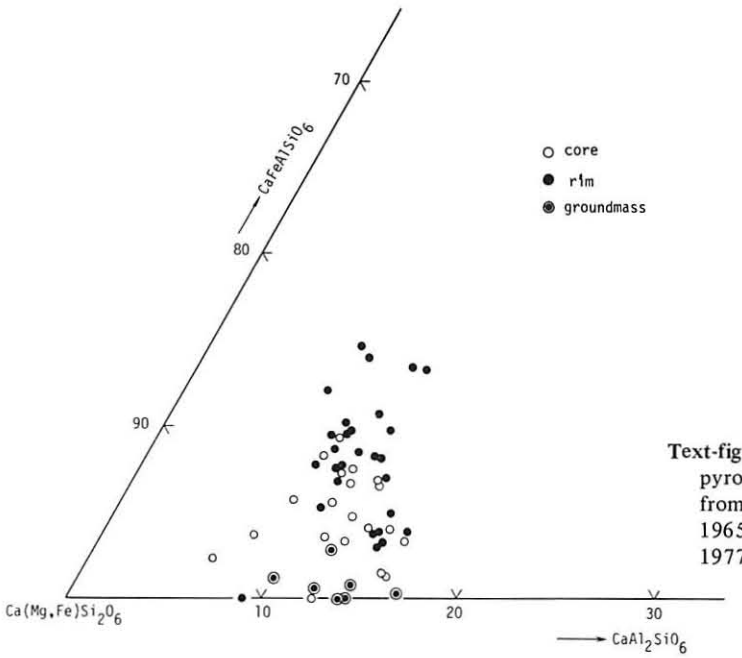


Text-fig. 7 Compositions of metamorphic Ca-pyroxenes. Broken lines show the phase boundaries at 1200°C, 1 atm. (Onuma et al., 1981).

Di-CaTs-FATs triangle. Most pyroxenes fall in the clinopyroxene stability field below 6 kbar at higher fO_2 where hematite or magnetite is stabilized, or at least in the field of Cpx + An + Mel, where the Al and Fe^{3+} contents of pyroxene vary continuously at 1 atm in air. This indicates that it is possible for metamorphosed fassaite to be formed even at low pressure (at least below 6 kbar and even at 1 atm) if fO_2 is high enough to stabilize hematite or magnetite. As stated before, pyroxenes contain a considerable amount of FATs at high pressure under the condition where hematite is stable. However, it is unlikely that magma undergoes such a high fO_2. If fO_2 is lowered, FATs-rich pyroxene becomes unstable and decomposes into CATs-rich pyroxene and some other phases at high pressure. The FATs-pyroxene decomposes into Cpx + Gar + Sp at 6 kbar, 1000°C at the fO_2 defined by

$MnO\text{-}Mn_2O_4$ buffer, where magnetite is stable (Ohashi and Hariya, 1975 b). According to Onuma and Hariya (unpublished data), a pyroxene having the composition of $Di_{70}FATs_{15}$-$CaTs_{15}$ decomposes into aluminous pyroxene, garnet, and spinel at 10 kbar, 1000°C under the same condition. Judging from the data of Oba and Onuma (1978), this pyroxene may stable under this condition at 1 atm. These experimental results and chemical compositions of natural fassaitic pyroxenes suggest that the volcanic rocks including fassaitic pyroxene, such as melilitite, nephelinite, basanite, etc., formed at rather lower pressure (less than 10 kbar), if fO_2 is lower than that defined by $MnO\text{-}Mn_3O_4$ buffer, where magnetite is stable.

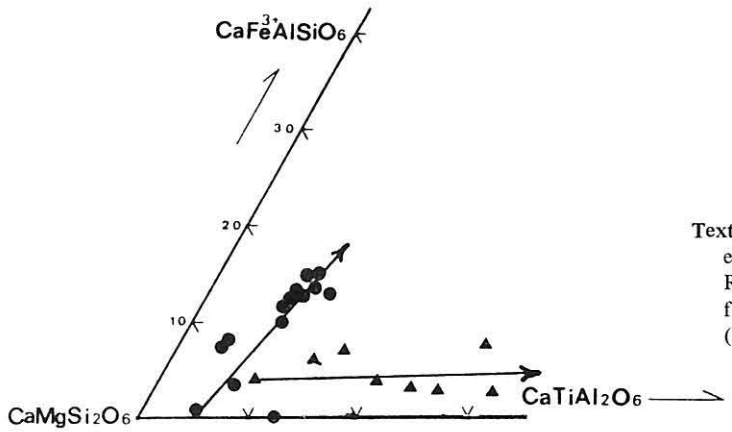
Text-fig 8 shows the plots of fassaitic pyroxenes from Hocheifel (Huckenholz et al.,



Text-fig. 8 Compositions of Ca-pyroxenes in alkalic rocks from (Huckenholz et al., 1965) and Westeifel (Becker, 1977) (Onuma et al., 1981)

1965 a, b, 1966) and Westeifel (Becker, 1977), West Germany in the Di-CaTs-FATs system. In general, the compositions of cores plot in the Di-richer portion, while those of rims in the Di-poorer potion, indicating that the pyroxenes gradually become rich in FATs as crystallization proceeds. The crystallization trends cross the stability limit of the pyroxene for fO_2. Since Fe^{2+} is calculated as $Ca(Mg, Fe^{2+})Si_2O_6$, an increase in FATs means a decrease in the hedenbergite component, in other wards, an increase in fO_2. For this reason, it is suggested that in the crystallization trends of these pyroxenes fO_2 increases as crystallization proceeds and temperature falls.

The plots of the clinopyroxene of Tahiti (Tracy and Robinson, 1977) and Hocheifel (Huckenholz, 1965) on the Di-FATs-Tp plane are shown in Text-fig 9, revealing two trends of clinopyroxene composition from core to rim; the trend of Tahiti pyroxene is approximately parallel to the Di-Tp join, indicating enrichment of Tp at constant FATs



Text-fig. 9 Plots of Tahiti pyroxenes (triangle) (Tracy and Robinson, 1977) and Hocheifel pyroxenes (circle) (Huckenholz et al., 1965)

(about 8 wt%), whereas in the Hocheifel pyroxene both Tp and FATs contents increase as crystallization proceeds, and FATs attains 18 wt%. Tracy and Robinson (1977) considered that low fO_2 is one cause of crystallization of pyroxenes extremely rich in Ti. The experimental results of the Di-FATs-Tp system in air however indicate that the pyroxene crystallizing in air can contain TiO_2 as much as 8 wt%, suggesting that when oxide minerals are absent low fO_2 is not a necessary condition to the entry of Ti into the pyroxene structure and the Ti-rich fassaitic pyroxenes are formed under equilibrium condition from the liquids rich in TiO_2 and poor in SiO_2. Based on the experimental results of the Di-FATs system at low fO_2, however, it can be said that a low FATs content in the Tahiti pyroxene implies the crystallization at low fO_2. Therefore, the difference in the pyroxene trend is probably due to the difference of fO_2 at which the pyroxenes crystallized from the liquid, and many intermediate trends of clinopyroxenes in undersaturated alkalic rocks between the extreme cases shown in Text-fig. 9 are postulated, depending on the bulk chemistry and fO_2 of the magma from which the pyroxene crystallized.

References

Akasaka, M., 1981. *Experimental study on the system $CaMgSi_2O_6$-$CaFeAlSiO_6$-$CaTiAl_2O_6$-$CaAl_2SiO_6$ at 1 atm and its bearing on the Tirich fassaitic pyroxenes.* D. Sc. dissertation to Hokkaido Univ. pp. 180.

Akasaka, M. & Onuma, K., 1980. The join $CaMgSi_2O_6$-$CaFeAlSiO_6$-$CaTiAl_2O_6$ and its bearing on the Ti-rich fassaitic pyroxenes. *Contrib. Mineral. Petrol.*, 71: 301-312.

Becker, H.J. 1977. Pyroxenites and hornblendites from the Maar-type volcanoes of the Westeifel, Federal Republic of Germany. *Contrib. Mineral. Petrol.*, 65: 45-52.

Bence, A.E. & Albee, A.L., 1968. Emperical correction factors for the electron microanalysis of silicates and oxides. *Jour. Geol.*, 76: 382-403.

Clark, S.P., Schairer, J.F. & de Neufville, J., 1962. Phase relations in the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-SiO_2 at low and high pressure. *Carnegie Inst. Wash. Yearb.*, 61: 59-68.

Deer, W.A., Howie, R.A. & Zussman, J., 1978. *Rock-forming minerals,* 2nd ed. vol. 2A, Longman Group Ltd. London.

Hays, J.F., 1966. Stability and properties of the synthetic pyroxene $CaAl_2SiO_6$. *Am Mineral.*, 51: 1524-1529.

Hijikata, K., 1968. Unit-cell dimensions of the clinopyroxenes along the join $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$. *Jour Fac. Sci., Hokkaido Univ.*, Ser. IV, 14: 149-159.

Hijikata, K., 1973. Phase relations in the system $CaMgSi_2O_6$-$CaAl_2SiO_6$ at high pressures and temperatures *Jour. Fac. Sci., Hokkido Univ.*, Ser. IV, 16: 167-177.

Hijikata, K. & Yagi, K., 1967. Phase relation of Ca-Tschermak's molecule at high pressures and temperatures. *Jour. Fac. Sci., Hokkaido Univ.* Ser. IV, 13: 407-417.

Hijikata, K. & Onuma, K., 1969. Phase equilibria of the system $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ in air. *Jour. Japan Assoc. Min. Pet. Econ. Geol.*, 62: 209-217.

Huckenholz, H.G., 1965a. Der petrogenetische Werdegang der Klinopyroxene in den tertiaren Vulkaniten der Hocheifel. I. *Beitr. Min. Petrogr.* 11: 138-195.

Huckenholz, H.G., 1965b. Die petrogenetische Werdegang der Klinopyroxene in den tertiaren Vulkaniten der Hocheifel. II. *Beitr. Min. Petrogr.* 11: 415-448.

Huckenholz, H.G., 1966. Die petrogenetische Werdegang der Klinopyroxene in den tertiaren Vulkaniten der Hocheifel. III. *Beitr. Min. Petrogr.* 12: 73-95.

Huckenholz, H.G., Lindhuber, W., & Springer, J., 1974. The Join $CaSiO_3$-Al_2O_3-Fe_2O_3 of the CaO-Al_2O_3-Fe_2O_3-SiO_2 quaternary system and its bearing on the formation of grandic garnets and fassaitic pyroxene. *Neu. Jb. Min. Abh.*, 121: 160-207.

Oba, T. & Onuma, K., 1978. Preliminary report of the join $CaMgSi_2O_6$-$CaFe^{3+}AlSiO_6$ at low oxygen fugacity. *Jour. Fac. Sci., Hokkaido Univ.*, Ser. IV, 18: 433-444.

Ohashi, H. & Hariya, Y., 1975a. Phase relation of $CaFeAlSiO_6$ pyroxene at high pressures and temperatures. *Jour. Japan. Assoc. Min. Pet. Econ. Geol.*, 70: 93-95.

Ohashi, H. & Hariya, Y., 1975b. Decomposition of $CaFe^{3+}AlSiO_6$ pyroxene at high pressure and low oxygen partial pressure. *Jour. Japan. Assoc. Min. Pet. Econ. Geol.*, 70: 347-351.

Onuma, K. & Akasaka, M., 1980. Clinopyroxene with $Si < Al_{IV}$ in the join $CaFeAlSiO_6$-$CaTiAl_2O_6$. *Mineral. Mag.*, 43: 851-6.

Onuma, K., Akasaka, M. & Yagi, K., 1981. The bearing of the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFeAlSO_6$ on fassaitic pyroxene. *Lithos*, 14: 173-182.

Onuma, K. & Yagi, K., 1971. The join $CaMgSi_2O_6$-$Ca_2MgSi_2O_7$-$CaTiAl_2O_6$ in the system CaO-MgO-Al_2O_3-TiO_2-SiO_2 and its bearing on the titanpyroxenes. *Mineral. Mag.*, 38: 471-480.

Onuma, K. & Yagi, K., 1975. The join $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaFe^{3+}AlSiO_6$ in air and its bearing on fassaitic pyroxene. *Jour. Fac. Sci.*, Ser. IV, 16: 343-356.

Schairer, J.F. & Yoder, H.S., Jr., 1970. Critical planes and flow sheet for portion of the system CaO-MgO-Al_2O_3-SiO_2 having petrological applications. *Carnegie Inst. Wash. Yearb.*, 68: 202-214.

Tracy, R.J. & Robinson, P., 1977. Zoned titanian augite in alkali olivine basalt from Tahiti and the nature of titanium substitutions in augite. *Am. Mineral.*, 62: 634-645.

Yang, H.Y., 1975. Al- and Ti-rich clinopyroxene in the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaTiAl_2O_6$. *Proc. Geol. Soc. China*, 18: 48-58.

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