# COMPUTER SIMULATION OF ANOMALOUS COMPOSITION OF Mg-Fe PLAGIOCLASE IN METEORITE

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***Abstract:*** The chemical anomalies of meteoritic plagioclase which appear also in lunar plagioclase, result in the difference between $An=100\cdot Ca/(K+Na+Ca)$ and $An(Al,Si)=(300\cdot(Al/Si)-100)/(1+Al/Si)$ caused by the various types of substitution which are dealt with computer simulation. Almost all average data are plotted close to the substitution vectors of Fe and Mg cations into T or M sites. Fe-Mg plagioclases are crystallized as Mg-rich plagioclases ($An_{67-91}$) in C3 or CV3 chondrites, whereas Fe-rich plagioclases ($An_{1-14}$) are predominantly crystallized in H6, L6 or LL6 chondrites. The maximum contents of Mg and Fe are 0.343 (per formula unit in O=8) in Allende (CV3) and 0.126 in Plainview (H5) chondrites, respectively, though maskelynite has much more Mg and Fe contents with excess total cations. Chemical heterogeneity of plagioclase in eight chondrites and Juvinas eucrite can be shown by the number of regions in An-content *vs.* Fe/(Fe+Mg) diagram; that is, three distinct regions of Willard (L6), ALH-769,75 (L6) and Plainview (H5); two regions of Holbrook (L6), Y-74640,81 (H6), Allende (CV3) and ALH-77307,85 (C3); and single region of Y-75258,97 (LL6). Wide variation of Fe/(Fe+Mg) in Juvinas with much more Fe- and Mg-substitutions indicates a mixture of various parent materials. The different values of Fe/(Fe+Mg) between chondrule and matrix with a nearly constant An-content in the Y-75135,93 (L5(67%)) chondrite suggest that chemical heterogeneity of plagioclase might have occurred in the formation of the chondrite.

## 1. Introduction

Among the constituent minerals of chondrites, the most structurally and chemically complicated mineral in both chondrule and matrix is plagioclase $MT_4O_8$ (M=K, Na, Ca, *etc.*; T=Si, Al, Mg, Ti, *etc.*) which exhibits various exsolution and ordering phenomena (VAN SCHMUS and RIBBE, 1968; MIÚRA, 1982a).

The term "stoichiometric" according to the definition used in chemistry describes a compound with rational coefficients in the structural formula. Therefore, as far as the site occupancies in the crystal structure are concerned, it does not apply to any solid solution. In fact, all plagioclases (except pure albite and anorthite) are non-stoichiometric, *i.e.* $Na_xCa_{(1-x)}Al_{(2-x)}Si_{(2+x)}O_8$ (WENK and WILDE, 1973). The terms "normal" and "anomalous (or defect)" are used in this study rather than "stoichiometric" and "non-stoichiometric", respectively, because the latter has been applied rather loosely so far. Chemical anomaly used in this study is related with the anomalous composition of plagioclase deviated further from the above-mentioned non-stoichiometry; *i.e.* $Na_{x-2\Delta}Ca_{(1-x+2\Delta)}Al_{(2-x-\Delta)}Si_{(2+x)}Z_\Delta O_8$ (where Z is cation ion and $\Delta$ is an amount of substitution by some divalent ion Z). Although plagioclase comprises such structurally different two M and T atoms that $TO_4$ tetrahedra link in an infinite three-dimensional array, and that charge-balancing M cations occupy large, irregular cavities in the tetrahedral framework, the compositions of both An- and An(Al, Si)-contents expressed by atomic ratios of the constituent M and T atoms, respectively, are almost the same in standard normal (without defect) terrestrial plagioclases (RIBEE and SMITH, 1966).

On the other hand, chemical anomalies of lunar plagioclase are described by substitutional vectors (WENK and WILDE, 1973). Nearly all deviations from normal Or-Ab-An chemistry which were observed in lunar plagioclases (*e.g.* LONGHI *et al.*, 1976) were explained by the additional components, Ca(Fe, Mg) $Si_3O_8$, (Fe, Mg) $Al_2Si_2O_8$ and $\square Si_4O_8$ where $\square$ signifies a Ca-site vacancy. In some chondritic plagioclases, MIÚRA (1982b) pointed out unusual compositional variations. The purpose of the present study is to elucidate chemical anomalies of meteoritic plagioclases, and then briefly to apply conclusions drawn from the result to consideration of the chemical heterogeneity and crystallization processes of meteorites, especially in the Y-75 chondritic meteorites for which a meteoritic shower was suggested by MIÚRA and MATSUMOTO (1981, 1982).

The samples used in this study include ALH-769,75 (L6), Holbrook (L6), Willard (L6), Plainview (H5), Y-74640,81 (H6), Y-75258,97 (LL6), ALH-77307,85 (C3) and Allende (CV3) chondrites and the Juvinas eucrite. The samples of ALH-769,75, Y-74640,81, Y-75258,97 and ALH-77307,85 chondrites were provided by the National Institute of Polar Research, and the rest samples were from the Yamaguchi University collections. Reported compositional data used in the calculation are the Y-75 Antarctic meteorites, namely Y-75102,74 (L4 (67%)), Y-75119,91 (L4 (67%)), Y-75124,91 (L5 (67%)), Y-75128,92 (L4 (83%)), Y-75133,93 (LL4 (67%)) and Y-75135,93 (L5 (67%)), classified by the statistical method of MIÚRA and MATSUMOTO (1982) (*cf.* MIÚRA and MATSUMOTO, 1981).

## 2. Experimental

### 2.1. EPMA analysis

The thin section labeled as Y-75135,93 (MIÚRA and MATSUMOTO, 1981) is $6\times9\times 0.01$ mm in size, and shows a large barred olivine chondrule of $3\times3$ mm in size with olivine rim (Fig. 1). The Y-75135,93 chondrite shows 73% matrix and 27% chondrules in volume percent; constituent minerals are 55% olivine, 23% plagioclase, 10% orthopyroxene, 2% clinopyroxene, 3%chromite, 3% phosphates, 2% troilite and 2% metal phases.

Plagioclases in ten meteorites (Y-75135,93, Y-75258,97, ALH-769,75, Y-74640,81, ALH-77307,85, Holbrook, Willard, Plainview and Allende chondrites, and Juvinas eucrite) were analyzed by using the JXA-50A electron probe microanalyzer (EPMA) at the Department of Mineralogical Sciences, Yamaguchi University. The instrument was operated at 15 kV accelerating voltage and $2.0\times10^{-8}$ A specimen current. To obtain constant peak-intensity of light elements, such as K and Na, a method of constantly moving the sample during analysis with a narrower beam diameter (*ca.* 2 $\mu$m) after checking the size of a plagioclase grain was used in this study.

The computer program of quantitative analysis by the Bence-Albee method (MIÚRA,

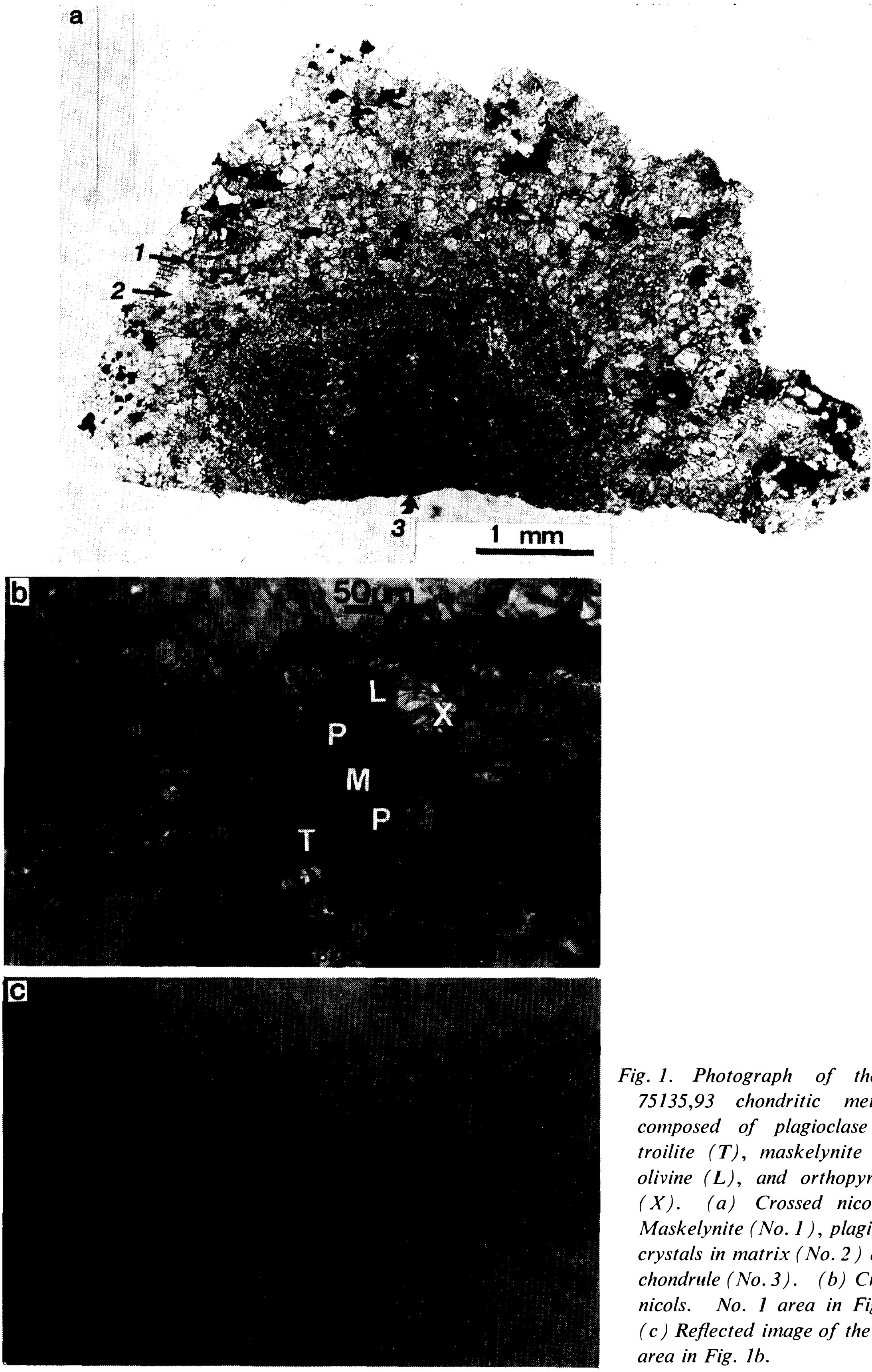


*Fig. 1. Photograph of the Y-75135,93 chondritic meteorite composed of plagioclase (P), troilite (T), maskelynite (M), olivine (L), and orthopyroxene (X). (a) Crossed nicols. Maskelynite (No. 1), plagioclase crystals in matrix (No. 2) and in chondrule (No. 3). (b) Crossed nicols. No. 1 area in Fig. 1a. (c) Reflected image of the same area in Fig. 1b.*

1978) was rewritten for this calculation with an NEC PC-9800 system computer.

Compositional data obtained in this study are used for the discussion with the total numbers of ions on the basis of 8(O) within the range between 4.95 to 5.05 (*i.e.* 1% deviation) and with the conditions of electrostatic neutrality fulfilled by making the subroutine of the computer program. The analytical data which do not satisfy the above both chemical conditions were discarded in this study, as shown in Table 1. The number of analyzed data used for discussion, therefore, is less than the original data (*i.e.* 61% of the total analyzed points).

*Table 1. Samples and number of analyzed points by EPMA of meteoritic plagioclase crystals in this study.*

| Meteorites | Sample No. | No. of analyzed points | No. of analyzed data used for discussion* |
|---|---|---|---|
| Chondrites | | | |
| L6 | ALH-769,75 | 14 | 7 |
| | Holbrook | 29 | 4 |
| | Willard | 25 | 12 |
| H5 | Plainview | 25 | 17 |
| H6 | Y-74640,81 | 12 | 12 |
| LL6 | Y-75258,97 | 10 | 10 |
| C3 | ALH-77307,85 | 5 | 2 |
| CV3 | Allende | 11 | 8 |
| Eucrites | Juvinas | 40 | 33 |
| | Total | 171 | 105 |

*Total number of cations in O=8 is from 4.95 to 5.05 (1% deviation), and charge valance is zero.

## 2.2. *Analytical error*

Because systematic differences, such as those introduced by using different analytical methods or even the same method but with different instruments, may affect the small variation in the amounts of any of major cations, only the data collected by the EPMA of Yamaguchi University have been used. Analyses for all elements were per-

*Table 2. Chemical uncertainties ($1\sigma$) for the analyzed data of meteoritic plagioclases in Y-75258,97.*

| Weight percents | | Cations for 8 oxygens | |
|---|---|---|---|
| $SiO_2$ | 68.9 (2) | Si | 2.959(12) |
| $Al_2O_3$ | 21.3 (1) | Al | 1.074( 5) |
| CaO | 2.05(5) | Ca | 0.094( 1) |
| $Na_2O$ | 7.55(5) | Na | 0.630( 5) |
| FeO | 0.32(1) | Fe | 0.020( 1) |
| MgO | 0.56(2) | Mg | 0.021( 1) |
| $K_2O$ | 0.30(1) | K | 0.022( 1) |
| An(mol %) | 12.6(2) | Al+Si | 4.026(2) |
| An(Al,Si) | 6.7(5) | Si–(Na+K) | 2.296(9) |
| An–An(Al,Si) | 5.7(5) | Fe/(Fe+Mg) | 0.49 (2) |

*Table 3. Average values of chemical compositions and cations per 8 oxygens of the analyzed meteoritic plagioclases.*

| Samples<br>Oxides | Holbrook<br>[4]* | ALH-769,75<br>[7] | Willard<br>[12] | Plainview<br>[17] | Y-74640,81<br>[12] | Y-75258,97<br>[10] | ALH-77307,85<br>[2] | Allende<br>[8] | Juvinas<br>[33] |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 66.80(54)** | 66.79(55) | 65.31(81) | 65.63(66) | 66.09(66) | 66.34(71) | 56.96(51) | 49.76(114) | 47.02(165) |
| $Al_2O_3$ | 18.88(38) | 20.35(73) | 20.40(70) | 19.60(61) | 20.99(54) | 20.54(37) | 21.27(41) | 28.86(306) | 33.03(127) |
| $Cr_2O_3$ | 0.00 | 0.00 | 0.02 | 0.01( 1) | 0.01( 1) | 0.00 | 0.02( 1) | 0.04( 4) | 0.01( 1) |
| FeO*** | 0.86(53) | 0.15( 9) | 1.48(30) | 1.40(87) | 0.39(16) | 0.22( 9) | 1.20(70) | 0.37( 11) | 0.40( 39) |
| MnO | 0.05( 1) | 0.01( 1) | 0.01( 1) | 0.00 | 0.00 | 0.00 | 0.04( 1) | 0.04( 2) | 0.01( 1) |
| MgO | 0.09( 3) | 0.06( 4) | 0.49(27) | 0.52(58) | 0.01( 1) | 0.00 | 3.91(46) | 2.17(167) | 0.10( 16) |
| CaO | 2.29( 7) | 1.75(15) | 2.37(29) | 2.54(49) | 2.09(14) | 1.79( 9) | 13.17(28) | 16.73(170) | 17.27(115) |
| $Na_2O$ | 10.24(16) | 9.85(30) | 9.71(43) | 9.37(66) | 10.23(21) | 10.42(53) | 3.33(14) | 1.71( 59) | 1.37( 64) |
| $K_2O$ | 0.92(10) | 0.72(36) | 0.74(29) | 0.93(25) | 0.18(11) | 0.68(13) | 0.07( 1) | 0.00 | 0.09( 10) |
| Total | 100.13(61) | 99.68(31) | 100.53(61) | 100.00(121) | 99.99(29) | 99.99(30) | 99.97(18) | 99.68( 45) | 99.30(164) |
| An(mol %) | 10.5(2) | 8.6( 6) | 11.4(14) | 12.3(22) | 10.0( 6) | 8.4( 6) | 68.3(4) | 84.3( 51) | 87.1(62) |
| An(Al,Si) | 0.5(5) | 5.7(32) | 7.6(32) | 4.3(24) | 9.0(27) | 6.9(19) | 22.2(9) | 62.0(121) | 81.1(63) |
| Elements (in O=8) | | | | | | | | | |
| Si | 2.954(12)** | 2.941(24) | 2.885(26) | 2.913(29) | 2.907(25) | 2.922(19) | 2.592(10) | 2.292( 58) | 2.173(61) |
| Al | 0.984(13) | 1.056(36) | 1.062(36) | 1.025(31) | 1.088(29) | 1.066(20) | 1.141(16) | 1.565(158) | 1.799(68) |
| Cr | 0.000 | 0.000 | 0.001( 1) | 0.001( 1) | 0.000 | 0.000 | 0.000 | 0.001( 1) | 0.000 |
| Fe | 0.032(20) | 0.006( 4) | 0.055(11) | 0.052(32) | 0.014( 6) | 0.008( 4) | 0.046(27) | 0.014( 4) | 0.015(15) |
| Mn | 0.002( 0) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001( 1) | 0.002( 1) | 0.000 |
| Mg | 0.007( 2) | 0.004( 3) | 0.032(18) | 0.032(39) | 0.001( 1) | 0.001( 1) | 0.265(32) | 0.149(114) | 0.007(11) |
| Ca | 0.108( 3) | 0.083( 7) | 0.113(14) | 0.121(23) | 0.099( 7) | 0.084( 4) | 0.642(10) | 0.826( 92) | 0.856(59) |
| Na | 0.878(14) | 0.841(27) | 0.831(34) | 0.806(54) | 0.872(20) | 0.891(49) | 0.294(11) | 0.153( 52) | 0.122(57) |
| K | 0.052( 6) | 0.041(20) | 0.042(17) | 0.053(14) | 0.010( 6) | 0.038( 7) | 0.005( 1) | 0.000 | 0.005( 5) |
| Total | 5.017(17) | 4.972(17) | 5.021(25) | 5.003(30) | 4.991(18) | 5.010(33) | 4.986(14) | 5.002( 30) | 4.977(13) |
| Fe/(Fe+Mg) | 0.80(9) | 0.67(23) | 0.65(13) | 0.71(22) | 0.95(10) | 0.99(1) | 0.14(6) | 0.14(8) | 0.79(19) |

*Numbers of analyzed data used for discussion are shown in square brackets.

**Numbers in parentheses are standard deviation referring to the last decimal place of the analyzed data used in discussion.

***Total iron oxide as FeO.

formed consecutively on a single spot with JXA-50A interfaced to the PC-9800 (379K) computer for data-processing.

The calculated uncertainties ($1\sigma$, using Bernoulli counting statics) for the average amounts of any of major cations are $\pm 0.05\%$ for (Al+Si), $\pm 0.4\%$ for (Si-Na-K), $\pm 1.6\%$ for An-content and $\pm 7.5\%$ for An(Al, Si)-content, as shown in the example of a meteoritic plagioclase (*cf.* Table 2). The accuracy of the measurement listed in Table 2 is also similar to lunar plagioclases reported by BEATY and ALBEE (1980), and enough to discuss the chemical anomalies in the meteoritic plagioclases. Table 3 shows averages of chemical compositions of nine meteoritic plagioclases.

*2.3. Deviation from An and An (Al, Si) chemistry*

An ordinary An-content (mol%) is customarily shown as

$$An = 100 \times Ca/(Na + Ca + K). \quad (1)$$

However, as chemical anomalies have been reported in lunar plagioclases (WENK and WILDE, 1973), the expression of An-content in the overall plagioclases is not sufficient to discuss the real composition of plagioclase, except the information of the ratio among K, Na and Ca. Thus MIÚRA (1983) reported the other expression of An (Al, Si)-content. An An(Al, Si)-content (mol%) obtained by the Al/Si ratio can be expressed between albite $NaAlSi_3O_8$ and anorthite $CaAl_2Si_2O_8$ as follows:

$$Al/Si = (100 + An(Al, Si))/(300 - An(Al, Si)).$$

This An-content obtained by the Al/Si ratio, designated as An(Al, Si)-content, can be shown as the following non-linear equation:

$$An(Al, Si) = (300 \times (Al/Si) - 100)/(1 + Al/Si). \quad (2)$$

If the crystal has an ideal normal composition, the values of An- and An(Al, Si)-contents should be equal. Almost all analyzed and reported values of An-contents do not agree with the An(Al, Si)-contents. Moreover, the above (1) and (2) expressions are not enough to express the real compositions if there exist atomic substitutions of Fe, Mg and small amounts of vacancy to M or T site. The probable various types of substitution can be simulated by the computer.

*2.4. Computer simulation of substitution*

It is found that all plagioclases including lunar and meteoritic plagioclases are chemically anomalous; in fact, value of An$-$An(Al, Si) does not become zero. It is important, therefore, to investigate the nature of this anomalous composition. In simulating a model for the anomalous chemical composition, the alumino-silicate framework remains intact. If there are site vacancies, they are more likely to involve the large-cation sites located in the interstices of the framework, because Na$-$O bond lengths are greater and the bond is weaker than those of T$-$O bonds. Normalization of the formula to 8 oxygens using only Si, Al, K, Na, Ca, Fe and Mg cations is applied in this simulation. It is found in meteoritic plagioclases that variation of Al+Si against Si$-$(Na+K) is the best combination, though WENK and WILDE (1973) reported the various combinations of plotting data in lunar plagioclases. Table 4 shows the bulk chemical composition of albite plagioclase from Monteagle Township (see RIBBE and

*Table 4. Chemical composition of the albite crystal used in computer simulation of chemical anomalies.*

| Samples | | Monteagle Township (RIBBE and SMITH, 1966; p. 220) | | |
|---|---|---|---|---|
| Weight percent oxides | | | | |
| $SiO_2$ | | 66.70 | | |
| $Al_2O_3$ | | 20.50 | | |
| FeO* | | 0.20 | | |
| MgO | | 0.00 | | |
| CaO | | 1.50 | | |
| $Na_2O$ | | 10.80 | | |
| $K_2O$ | | 0.20 | | |
| Total | | 99.90 | | |
| Cations per 8 oxygens | | | | |
| Si | | 2.932 | | |
| Al | | 1.062 | | |
| Fe | | 0.007 | | |
| Mg | | 0.000 | | |
| Ca | | 0.071 | | |
| Na | | 0.920 | | |
| K | | 0.011 | | |
| Total | | 5.003 | | |
| Or (mol %) | 1.1 | | Al+Si | 3.994 |
| An (mol %) | 7.1 | | Si−(Na+K) | 2.000 |
| Ab (mol %) | 91.8 | | Na+K+Ca | 1.002 |
| An(Al,Si) (mol %) | 6.4 | | Fe/(Fe+Mg) | 0.999 |

*Total iron oxide as FeO.

SMITH, 1966; p. 220) for computer simulation of probable substitutions. The following possible substitutions can be obtained (see Table 5):

(a) Added vacancy-producing substitution within large cation sites.
$\Delta Ca^{2+} + \Delta\square \rightarrow \Delta 2Na^{+}$ ($\Delta$: amount of substitution; $\square$ : vacancy).

(b) Alkali evaporation from large cation sites.
$\Delta\square \rightarrow \Delta Na$.

(c) Excess T cations into M large cation sites.
$\Delta T \rightarrow \Delta M$.

(d) Excess M cations into T tetrahedral sites.
$\Delta M \rightarrow \Delta T$.

(e) Fe and Mg cations into T tetrahedral sites.
$\Delta(Fe+Mg) \rightarrow \Delta T$.

(f) Fe and Mg cations into M large cation sites.
$\Delta(Fe+Mg) \rightarrow \Delta M$.

In the above substitutions, two types of substitution (e) and (f) are considered to have occurred drastically in meteoritic plagioclases, as shown in Fig. 2.

## 3. Results and Discussion

Table 5 and Fig. 2 show calculated results of computer simulation of possible types of substitutions, and plotting the average values of nine meteorites listed in Table 1.

*Table 5. Some calculated results of computer simulation in chemical anomalies of An-poor plagioclase from Monteagle Township (Table 4). Cations are normalized to 8 oxygens.*

| Substitution | | Al+Si | Si−(Na+K) | K+Na+Ca | Fe+Mg | An (mol %) | No. in Fig. 2 |
|---|---|---|---|---|---|---|---|
| 5% Ca excess+vacancy | →2% Na loss | | | | | | |
| | | 3.996 | 2.020 | 0.988 | 0.007 | 7.5 | (a) |
| 100% Ca excess+vacancy | →30% Na loss | | | | | | |
| | | 4.028 | 2.296 | 0.803 | 0.007 | 17.7 | |
| Vacancy | →2% Na loss | | | | | | |
| | | 3.998 | 2.021 | 0.985 | 0.007 | 7.2 | (b) |
| Vacancy | →30% Na loss | | | | | | |
| | | 4.064 | 2.316 | 0.739 | 0.007 | 9.7 | |
| 2% (Si+Al) excess | →10% (K+Na+Ca) loss | | | | | | |
| | | 4.025 | 2.127 | 0.891 | 0.007 | 7.1 | (c) |
| 5% (Si+Al) excess | →30% (K+Na+Ca) loss | | | | | | |
| | | 4.085 | 2.364 | 0.683 | 0.007 | 7.1 | |
| 10% (K+Na+Ca) excess | →2% (Si+Al+Fe) loss | | | | | | |
| | | 3.958 | 1.869 | 1.115 | 0.007 | 7.0 | (d) |
| 20% (K+Na+Ca) excess | →2% (Si+Al+Fe) loss | | | | | | |
| | | 3.931 | 1.763 | 1.208 | 0.007 | 7.0 | |
| 50% (Fe+Mg) excess | →2% (Si+Al) loss | | | | | | |
| | | 3.981 | 1.975 | 1.019 | 0.011 | 7.0 | (e) |
| 200% (Fe+Mg) excess | →2% (Si+Al) loss | | | | | | |
| | | 3.959 | 1.959 | 1.011 | 0.045 | 7.0 | |
| 50% (Mg+Fe) excess | →2% (K+Na+Ca) loss | | | | | | |
| | | 3.992 | 2.018 | 0.982 | 0.011 | 7.0 | (f) |
| 200% (Fe+Mg) excess | →10% (K+Na+Ca) loss | | | | | | |
| | | 3.982 | 2.088 | 0.899 | 0.045 | 7.0 | |

Table 6 shows the compositional data of the most Fe-rich and Mg-rich plagioclases in this study. Figures 3 and 4 show the variation of these data of the nine meteorites in the An-content *vs.* Fe/(Fe+Mg) diagram. Table 7 and Fig. 5 show Fe/(Fe+Mg) data in seven Y-75 chondrites. The term designated as "*plagioclase*" in this study indicates an intermediate (or metamict) state different from a perfect anisotropic crystal of plagioclase.

### *3.1. An- and An(Al, Si)-contents*

An ordinary An-content obtained by the atomic ratio of K, Na and Ca atoms given by eq. (1) shows only compositional information of M atoms, whereas the An(Al, Si)-content obtained by eq. (2) results in that of T atoms. These contents are surely inconsistent with each other in the anomalous plagioclase including much atomic substitution.

Table 3 shows that the average values of An- and An(Al, Si)-contents of nine meteorites. The larger values of An—An(Al, Si) are found in Holbrook (L6), Willard (L6) and Plainview (H5) chondrites including relatively higher Fe and Mg in Ab-rich plagioclases. The largest value is found in ALH-77307,85 (C3) chondrite; that is, An—An (Al, Si)=47.4 (see Table 3 and Fig. 6).

Although the most Mg-rich plagioclase is observed in the ALH-77307,85 (C3) chondrite, the most Fe-rich plagioclase in this study is found in the Plainview (H5)

*Table 6. Chemical compositions of Mg-rich and Fe-rich plagioclase crystals in the analyzed meteorites.*

| Samples | Allende-3 (CV3) | Plainview-3 (H5) |
|---|---|---|
| Weight percent oxides | | |
| $SiO_2$ | 49.31 | 65.26 |
| $Al_2O_3$ | 27.58 | 19.20 |
| FeO* | 0.25 | 3.39 |
| MnO | 0.04 | 0.00 |
| MgO | 5.01 | 0.88 |
| CaO | 16.96 | 2.77 |
| $Na_2O$ | 0.92 | 8.60 |
| $K_2O$ | 0.00 | 0.89 |
| Total | 100.07 | 100.99 |
| Cations per 8 oxygens | | |
| Si | 2.265 | 2.892 |
| Al | 1.493 | 1.003 |
| Fe | 0.010 | 0.126 |
| Mg | 0.343 | 0.058 |
| Mn | 0.002 | 0.000 |
| Ca | 0.835 | 0.132 |
| Na | 0.082 | 0.739 |
| K | 0.000 | 0.050 |
| Total | 5.030 | 5.000 |
| An(mol %) | 91.1 | 14.3 |
| An(Al,Si) (mol %) | 58.9 | 3.0 |
| Fe/(Fe+Mg) | 0.02 | 0.68 |

*Total iron oxide as FeO.

*Table 7. An-contents and Fe/(Fe+Mg) ratios of plagioclase-like compositions in several Y-75 Antarctic meteorites.*

| Sample No. | Type and group | | An-content (mol %) | Fe/(Fe+Mg) ratio |
|---|---|---|---|---|
| Y-75128,92 | L4(83%) | | 29.1 | 0.70 |
| | | | 15.8 | 0.50 |
| Y-75119,91 | L4(67%) | | 11.0 | 0.64 |
| Y-75102,74 | L4(67%) | | 14.2 | 0.76 |
| | | | 12.1 | 0.76 |
| Y-75133,93 | LL4(67%) | | 10.1 | 0.81 |
| Y-75124,91 | L5(67%) | | 10.1 | 0.84 |
| Y-75135,93 | L5(67%) [4]* | (maskelynite in matrix) | 10.9(28)** | 0.89(8)** |
| | | (crystal in matrix) | 10.4 | 0.83 |
| | | (crystal in chondrule) | 10.4 | 0.69 |
| Y-75258,97 | LL6 [10]* | | 8.4(6)** | 0.99(1)** |

*Numbers of analyzed data used in discussion are shown in square brackets.

**Numbers in parentheses are standard deviation referring to the last decimal place of the analyzed data used in discussion.

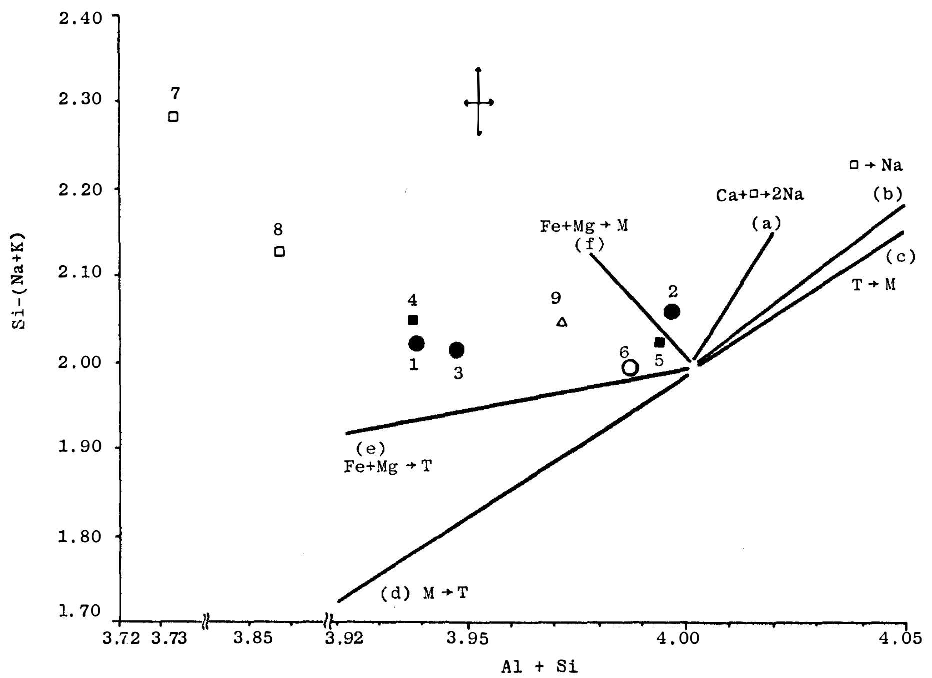


*Fig. 2. Variation of Si-(Na+K) and Al+Si in nine meteoritic plagioclases. Microprobe analyses of Si, Al, Ca, Na, K, Fe and Mg are normalized to 8(O). 1. Holbrook(L6), 2. ALH-769,75(L6), 3. Willard(L6), 4. Plainview(H5), 5. Y-74640,81(H6), 6. Y-75258,97(LL6), 7. ALH-77307,85 (C3), 8. Allende(CV3), 9. Juvinas eucrite. The error bar is the calculated absolute uncertainty, as shown in Table 2.*

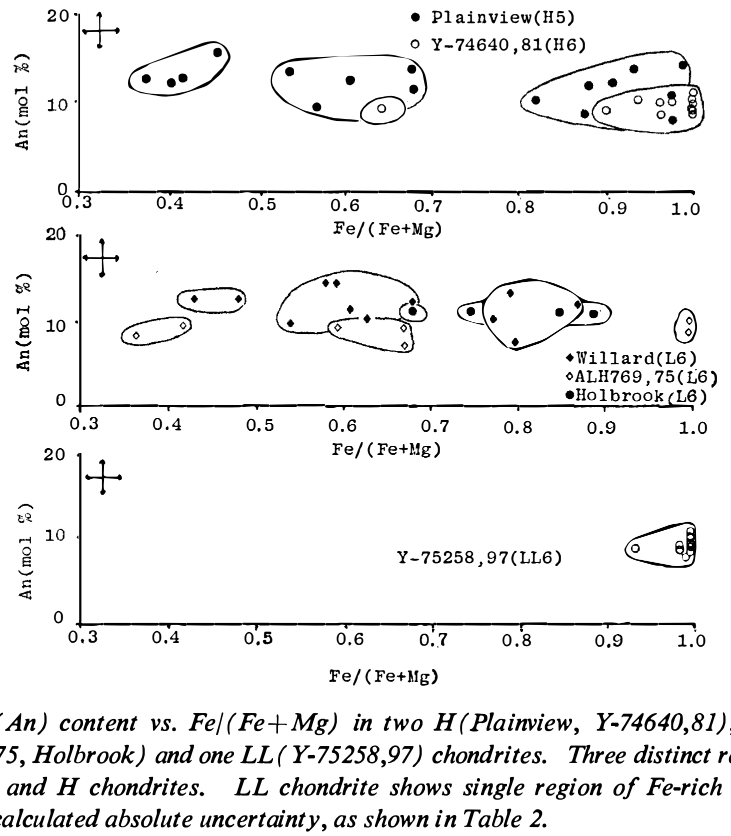


*Fig. 3. Anorthite (An) content vs. Fe/(Fe+Mg) in two H(Plainview, Y-74640,81), three L(Willard, ALH-769,75, Holbrook) and one LL(Y-75258,97) chondrites. Three distinct regions are observed in some L and H chondrites. LL chondrite shows single region of Fe-rich albite. The error bar is the calculated absolute uncertainty, as shown in Table 2.*

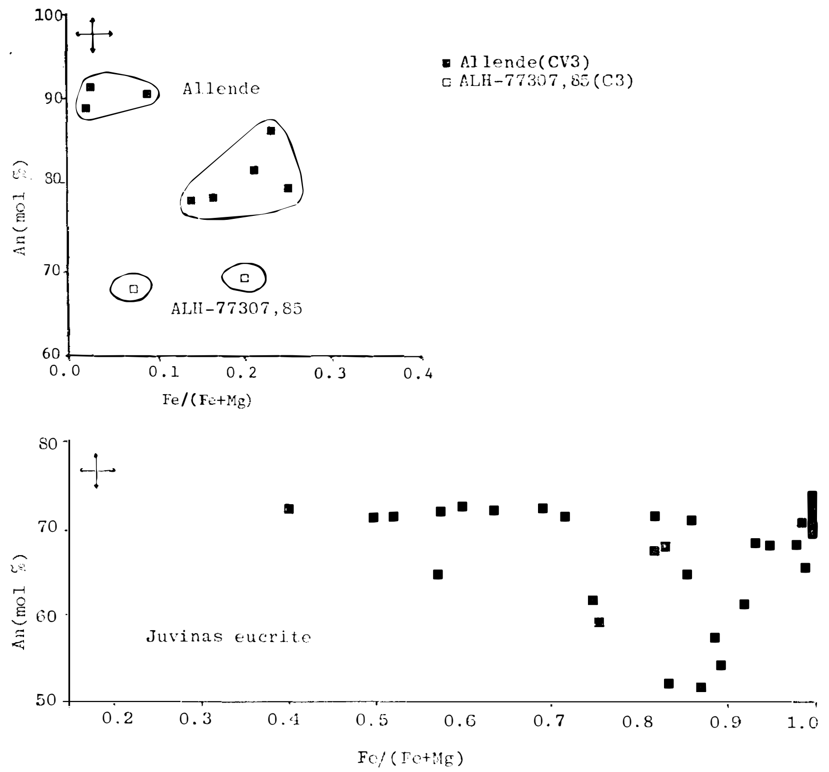


*Fig. 4. An-content vs. Fe/(Fe+Mg) in Allende(CV3) and ALH-77307,85(C3) chondrites. Two regions are observed in two chondrites. This shows, as well as Fig. 3, that much more Mg- and Fe-substitutions are observed in An-rich (C3 or CV3) and An-poor(L6, H6 or LL6) plagioclases. The Juvinas eucrite shows random distribution of value of Fe/(Fe+Mg), resulted from chemical heterogeneity of the parent materials. There is no preferential substitution of Fe and Mg to An-rich plagioclases. The error bar is the calculated absolute uncertainty, as shown in Table 2.*

chondrite (*cf.* Table 6). This indicates that much more Fe and Mg substitution in plagioclase results in larger difference between An- and An (Al, Si)-contents. As the difference between An- and An (Al, Si)-contents is, therefore, caused by atomic substitution with electrostatic neutrality, the An—An (Al, Si) value is simply regarded as a useful indicator of chemical anomalies of plagioclase deviated from the ideal composition.

### *3.2. Substitution obtained by computer simulation*

Figure 2 shows variation of Al+Si and Si—(Na+K) in the meteorites listed in Table 1, and the substitution vectors labeled in Table 5. Probable substitution in each sample can be obtained simply by the nearest substitution vector in Fig. 2. Almost all average data are plotted between type (e) and (f) substitutions. The amount of substitution is simply determined by the distance from the center of Al+Si=4.00 and Si—(Na+K)=2.00. The maximum amount of substitution is found in the ALH-77307,85 (C3) chondrite, as shown in Fig. 2. Although there exists a trace amount of substitution in type (a), (b) or (d) substitution (but no example of type (c) substitution), almost all cases are that Fe and/or Mg cations substitute T and/or M site.

Five types of substitution, (a), (b), (d), (e) and (f) in meteoritic plagioclases are probably caused by the atomic proportions of cations in the silicate melt from which

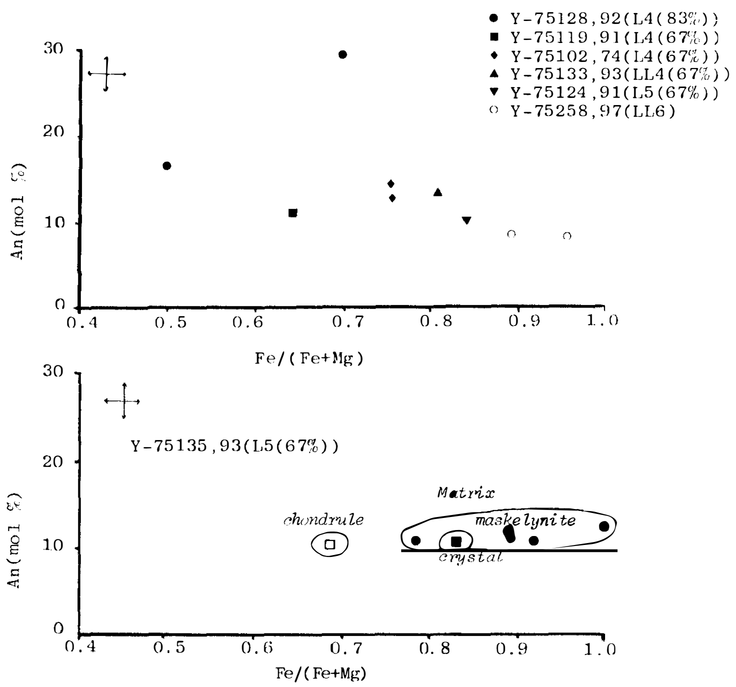


*Fig. 5. An-content vs. Fe/(Fe+Mg) in six Y-75 chondrites and Y-75135,93 chondrite (cf. Fig. 1). Petrologic type increases toward type 6 (Fe/(Fe+Mg)=1.00 and An=8 mol %). The values of matrix and chondrule of the Y-75135,93 chondrite are completely different. The error bar is the calculated absolute uncertainty, as shown in Table 2.*

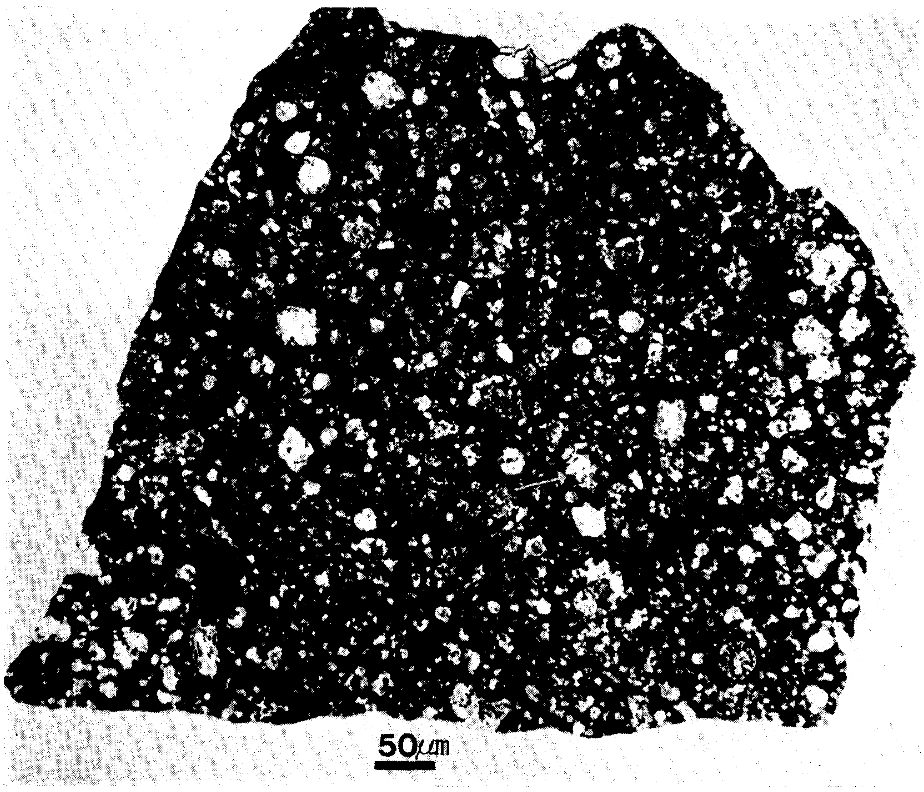


*Fig. 6. Photograph of the ALH-77307,85(C3) chondrite. Analyzed point listed in Table 3 is shown by white arrow.*

the plagioclase feldspar is crystallized. The various types of substitution by which plagioclase departs from ideality could probably give valuable information about the chemical and thermal history of the parent bodies of meteorites. The detailed discussion will be given in another paper.

### 3.3. *Mg-Fe substitution and value of Fe/(Fe+Mg)*

It is found in Tables 3 and 7 that An-rich chondrites have much more Mg-substitution mainly to Al-site, and that An-poor chondrites have much more Fe-substitution. If crystallization index of Fe/(Fe+Mg) reported by LONGHI *et al.* (1976) is applied to the detailed mechanism of Fe and Mg substitution in plagioclase, it is found that Fe-Mg plagioclases are crystallized predominantly as Mg-plagioclase ($An_{67}$ to $An_{91}$) in C3 or CV3 chondrite, and as Fe-plagioclase ($An_1$ to $An_{14}$) in H6, L6 or LL6 chondrite. In this study, the deficiency in Al+Si (up to 0.29 per formula unit in O=8) is compensated by Fe, Mg and small amounts of excess Na or Ca, whereas the (K+Na+Ca) site is also substituted by Fe, Mg and small amounts of vacancy (up to 0.08 per formula unit in O=8). The maximum contents of Mg and Fe are 0.343 (MgO=5.01 wt %) and 0.126 (FeO=3.39 wt %) per formula unit in O=8, respectively, in crystalline plagioclases.

Maskelynite (glassy plagioclase) has larger total cations and higher contents of Mg and Fe; that is, FeO=18.70 wt % and total cations=5.078 (in O=8) in the Adams County (H5) chondrite (FODOR *et al.*, 1980), and MgO=12.20 wt % and total cations=5.132 (in O=8) in the Allende (CV3) chondrite ($An_{89.7}$). These maskelynites are easily found out by the chemical restriction in this study (*i.e.* within 1% deviation of total cations and electrostatic neutrality). Although the sharp boundary between crystal plagioclase and maskelynite is difficult to define, a plot of the An-content *vs.* Fe/(Fe+Mg) diagram is useful, especially in expression of an intermediate (or transition) state between maskelynite and plagioclase crystal. Chemical compositions of plagioclase from the Plainview (H5) chondrite are divided into three different regions; that is, Fe/(Fe+Mg)=0.38 to 0.46; 0.54 to 0.68 and 0.83 to 0.99, as shown in Fig. 3. As the maskelynite has Fe/(Fe+Mg)<0.38 in composition of Plainview, the value of Fe/(Fe+Mg)=0.68 listed in Table 6 is considered to suggest an intermediate (or metamict) state of maskelynite (Fe/(Fe+Mg)<0.38) and plagioclase crystal (Fe/(Fe+Mg)=0.99) (*cf.* Fig. 3). Figure 4 shows that the data of the ALH-77307,85 (C3) chondrite with Fe/(Fe+Mg)=0.20 are also assumed to indicate an intermediate (or metamict) state between maskelynite and plagioclase crystal, which is designated as "*plagioclase*" in this study. Although X-ray and electron microscopic data on larger grain may be informative to confirm the relationship between the compositional ratio of Fe/(Fe+Mg) and the structural state, the structural state of high, intermediate or low temperature type is difficult to determine in smaller grains of the above chondrites.

The Plainview (H5), ALH-769,75 (L6) and Willard (L6) chondrites show three different regions of Fe/(Fe+Mg); *i.e.* 0.36–0.48, 0.54–0.68 and 0.83–0.99. The Y-74640,81 (H6) and Holbrook (L6) chondrites have two different regions; Fe/(Fe+Mg) =0.64–0.68 and 0.75–0.99. The Y-75258,97 (LL6) chondrite shows only one region of Fe/(Fe+Mg)=0.94–0.99. If the number of isolated region of Fe/(Fe+Mg) indicates the chemical heterogeneity of parent bodies of meteorite, the existence of different regions in the An-content *vs.* Fe/(Fe+Mg) diagram has information of the formation process of meteorite (*e.g.* mixing up of fragments, *etc.*) which is not necessarily consistent with petrologic type, as follows:

Willard (L6)[3]<ALH-769,75 (L6) [3]<Plainview (H5) [3]<Holbrook (L6) [2]
<Y-74640,81 (H6) [2]<Y-75258,97 (LL6) [1],

where the number of different regions is shown in square bracket [ ], and the average value of Fe/(Fe+Mg) increases from Willard to Y-75258,97. It is interesting to note in Fig. 3 that the values of Fe/(Fe+Mg)=0.49–0.54, and 0.69–0.75 are the regions without plotted data and are considered to be boundaries of these Fe-Mg substitution in H, L and LL chondrite.

On the other hand, the Allende (CV3) chondrite has two different regions in the An-content *vs.* Fe/(Fe+Mg) diagram; that is, 0.02–0.09 in $An_{90}$, and 0.14–0.25 in $An_{80}$. This result indicates that An-poor plagioclase in the Allende chondrite has much more Fe-substitution. But although only two data of the ALH-77307,85 (C3) chondrite give no further information of Fe-preferential substitution (that is, 0.08 and 0.20 in $An_{67.9}$ and $An_{68.7}$, respectively), the similar Fe-preferential substitution in the Allende chondrite may hold if the two discarded analyzed data (*cf.* Table 1) of maskelynite of Fe/(Fe+Mg)=0.01–0.02 and $An_{78.0-87.7}$ (total cations=4.861–4.917 in O=8) are plotted in the diagram of Fig. 4.

The Juvinas eucrite with compositions of $An_{71-90}$ (*i.e.*, An(Al, Si)=66 to 88) shows no regular variation of the values of Fe/(Fe+Mg) and An-content; that is, Fe/(Fe+Mg)=0.40 ($An_{92}$, An(Al, Si)=88) to 0.99($An_{94}$, An(Al, Si)=85). The interesting result in Fig. 4 is that much more Fe-substitution, together with Mg-substitution, in plagioclase $An_{70\pm}$, is the unique type of substitution which could not be observed in chondritic meteorites. This indicates that the Juvinas eucrite consists of chemically different various sources of the parent bodies (*cf.* Fig. 4).

### 3.4. *Value of Fe/(Fe+Mg) in Y-75 chondrites*

If the compositional restriction is applied to the Y-75 chondrites (L4–5), almost all data of "*plagioclase*" in the Y-75 chondrites show the total numbers of cations in O=8 exceeded 1% deviation; that is, from 4.733 in Y-75102,74 to 5.094 in Y-75128,92. Although "*plagioclases*" of the Y-75 chondrites listed in Table 7 are almost maskelynite (or partly metamict or microcrystalline phase), interesting relationships are found among petrologic type, An-content and value of Fe/(Fe+Mg). As the petrologic type increases from 4 to 6 in the Y-75 chondrites, the Fe/(Fe+Mg) ratio of "*plagioclase*" remarkably increases, as follows:

Y-75128,92 (L4 (83%))<Y-75119,91 (L4 (67%))<Y-75102,74 (L4 (67%))
Y-75133,93 (LL4 (67%))<Y-75124,91 (L5 (67%))<Y-75135,93 (L5 (67%))
Y-75258,97 (LL6).

The increased petrologic type, together with both increased Fe substitution and decreased An-content in the Y-75 chondrites (L4–5), indicates an increase in degree of crystallinity from petrologic type 4 to 6. Although the relatively uniform inverse relationship between Fe substitution and An-content may be informative to progressive crystallization from maskelynite to plagioclase crystal probably within the same meteoritic bodies of the Y-75 chondrites, further examples will be required to support the results of the probable meteorite shower.

*3.5. Value of Fe/(Fe+Mg) in chondrule and matrix*

The value of Fe/(Fe+Mg) is assumed to be a crystallinity index, because maskelynite, either crystalline or intermediate in state, can be distinguished in the An-content *vs.* Fe/(Fe+Mg) diagram. Thus, the crystallinity index of Fe/(Fe+Mg) is also informative of plagioclase state in three different regions of the Y-75135,93 chondrite (L5 (67%)) (*cf.* Fig. 5). Table 7 and Fig. 5 show that plagioclase crystal in the chondrule has lower value of Fe/(Fe+Mg) (0.69), and that crystal (0.83) and maskelynite (0.89) in the matrix are relatively higher in value, though the values in the maskelynite are variable (0.77–0.99). As the values of Fe/(Fe+Mg) of crystal and masklynite in the matrix are plotted almost in the same region (but average values are slightly different from each other), the plagioclase crystal of the matrix may have been crystallized from the maskelynite. Anyhow, the experimental result that the values of Fe/(Fe+Mg) in the crystals both of chondrule and matrix are completely different indicates the chemical heterogeneity in the Y-75135,93 chondrite. Thus, since no remarkable change of the An-content, together with the above different values of Fe/(Fe+Mg), is observed in the Y-75135,93 chondrite, then the different chemical sources between the chondrule and the matrix are probably mixed up in the formation of the chondrite.

## 4. Conclusions

The following results are summaried in this study:

1) The difference between An- and An(Al, Si)-contents expressed by eqs. (1) and (2), respectively, is caused by the various types of substitution which were obtained by computer simulation, and is regarded as a useful indicator of chemical anomalies in meteoritic plagioclase.

2) Substitution vectors plotted in the Al+Si *vs.* Si−(Na+K) diagram are simulated from the Monteagle Township albite for the original data, resulted in much more Fe and Mg substitution for T or M site.

3) An-rich chondrite has much more Mg-substitution mainly for Al-site, whereas An-poor chondrite has much more Fe-substitution mainly for Al-site. Fe-Mg plagioclases are crystallized as Mg-plagioclase ($An_{67}$ to $An_{91}$) in studied C3 or CV3 chondrites, and as Fe-plagioclase ($An_1$ to $An_{14}$) in studied H5, H6, L6 or LL6 chondrites. The maximum contents of Mg and Fe are 0.343 and 0.126 per formula unit (in O=8), respectively, in crystalline plagioclases. Maskelynites have higher Mg and Fe contents of 0.838 and 0.778 (in O=8), respectively. The maskelynite can be easily distinguished by the chemical restriction; that is, total cations within 1% deviation and electrostatic neutrality.

4) The Willard (L6), ALH-769,75 (L6) and Plainview (H5) chondrites show clearly three different values of Fe/(Fe+Mg), whereas Holbrook (L6) and Y-74640,81 (H6) show two regions and Y-75258,97 (LL6) has only one region. The Allende (CV3) and ALH-77307,85 (C3) chondrites two different regions in the An-content *vs.* Fe/(Fe+Mg) diagram. The Juvinas eucrite with much more Fe-substitution of plagioclase shows chemical complex heterogeneity, which can be explained chiefly as a mixture of various parent materials. The number of constituent regions in the An-content *vs.* Fe/(Fe+Mg)

diagram is consistent rather with the chemical heterogeneity from parent bodies of meteorite, than with the petrologic type.

5) The petrologic types increased from 4 to 6 as the value of Fe/(Fe+Mg) remarkably increased in seven Y-75 chondrites from Y-75128,92 (L4 (83%)), Y-75119,91 (L4 (67%)), Y-75102,74 (L4 (67%)), Y-75133,93 (LL4 (67%)), Y-75124,91 (L5 (67%)), Y-75135,93 (L5 (67%)) to Y-75258,97 (LL6), though all the L4-5 chondrites show almost composition of maskelynite. The decreased An-content, together with both the increased value of Fe/(Fe+Mg) and the increased petrologic type (4 to 6), indicates progressive crystallization from maskelynite to plagioclase crystal within the parent bodies of the Y-75 chondrites.

6) The different values of Fe/(Fe+Mg) with nearly constant An-content of the Y-75135,93 (L5 (67%)) chondrite suggest that the chemical heterogeneity between chondrule and matrix might have occurred in the formation of the chondrite.

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## Appendix

The calculation procedure of the computer simulated values on Table 5 obtained from the original value in Table 4 is summarized as follows:

1) Various amounts and types of substitution are changed in each oxide to obtain the appropriate value of substitution.

2) The computer simulated data satisfying the charge balance are selected in each M (Na, K, Ca etc.) and/or T(Al, Si, etc.) atomic site.

3) The most suitable amounts and type of substitution are determined, as shown in Table 5. For example, (a) type of substitution $x\Delta Ca^{2+}\Delta\square \rightarrow y\Delta 2Na^{+}$ shows the most suitable combination in lower value is x=5% and y=2%. Compositional data of (x, y)=(5, 2) in (a) type of substitution is shown as follows:

| Weight percents | | Cations for 8 oxygens | |
|---|---|---|---|
| $SiO_2$ | 66.70 | Si | 2.934 |
| $Al_2O_3$ | 20.50 | Al | 1.063 |
| CaO | 1.575 | Ca | 0.074 |
| $Na_2O$ | 10.584 | Na | 0.903 |
| $K_2O$ | 0.20 | K | 0.011 |
| FeO | 0.20 | Fe | 0.007 |
| MgO | 0.00 | Mg | 0.000 |
| An(mol %) | 7.5 | Al+Si | 3.996 |
| Fe+Mg | 0.007 | Si−(Na+K) | 2.020 |
| K+Na+Ca | 0.988 | Fe/(Fe+Mg) | 1.0 |