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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LUNAR SAMPLE ANALYSIS PROGRAM

CATION DISTRIBUTION STUDIES IN CLINOPYROXENES, OLIVINES AND FELDSPARS
USING MÖSSBAUER SPECTROSCOPY OF ^{57}Fe.[1]

Final Technical Progress Report
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by

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ABSTRACT

Magnesium in clinopyroxenes with more than 20 percent wollastonite occurs almost exclusively at the M1 position. In calcium-poor pigeonites from rocks 12018, 12021, and 12053 Mg is significantly more disordered. An olivine from 12018 exhibits 20 percent ordering of iron in one of the M-positions. The Mg, Fe^{2+} distribution in clinopyroxenes and olivines is interpreted in terms of equilibrium distribution temperatures estimated from heating experiments and subsolidus cooling history. Fe^{2+} in feldspars occurs at calcium as well as aluminum positions. No Fe^{3+} has been detected in our mineral separates.

Contents

INTRODUCTION

The Mössbauer absorption spectra of ^{57}Fe in 15 clinopyroxenes, olivines, and feldspars separated from Apollo 11 and 12 rocks, and a pyroxene and a glass specimen from the Apollo 11 soil have been studied. The aim was to obtain information on the oxidation state of iron and the intracrystalline distribution of iron over the nonequivalent lattice sites. The distribution of Mg^{2+}, Fe^{2+} over the sites M1 and M2 in natural pyroxenes is known to be dependent on the cooling history of the rock. Similar relationships between Mg^{2+}, Fe^{2+}, M1, M2 and cooling history appear to exist in olivines. We have made a number of heating experiments with clinopyroxenes and olivines to determine the temperatures of equilibrium distribution in the natural crystals, and to investigate the ordering and disordering kinetics of the Mg^{2+}, Fe^{2+} exchange between the M1 and M2 sites.

EXPERIMENTAL AND RESULTS

X-ray emission microanalysis, Mössbauer spectroscopy and heating experiments were carried out as described previously[1]. The chemical compositions of the clinopyroxene separates from Apollo 11 and 12 are plotted on to the pyroxene quadrilateral En-Di-Hd-Fs in Figure 1. Plotted along the En-Fs join are the compositions of the olivines from 12053-79 and 12018,35. Site occupancy data for the Apollo 12 clino-pyroxenes are given in Table 1. Similar data on the Apollo 11 samples

were reported in reference 1, Table 6.

The Mössbauer spectra of ^{57}Fe in olivines were measured at absorber temperatures between 300 and 500°C since the quadrupole doublets at M1 and M2 are best resolved in that range[2]. Spectra of an iron-rich olivine (Rockport fayalite, Fa_{97}) and an iron-poor sample (rock 12018,35 Fa_{36}) are compared in Figure 2. The resolution of both the high and low velocity doublets shown in this figure is characteristic of the olivine solid solutions. We generally take the area ratio of the high velocity peaks as a measure for the distribution of Fe^{2+} over M1 and M2. Unfortunately the assignment of the doublets to the M-sites is not possible at this time[2]. The results which include distribution data of five terrestrial samples are shown in Table 2.

CONCLUSIONS

Oxidation state of iron

Ferric iron was not detected in any of the separates from the rocks or the soil. In clinopyroxenes the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio was 0+0.002; in the pyroxene and glass separates from soil 10084 this ratio was 0+0.01. Approximately 7 percent of the total iron in this soil was metallic[3]. The spectrum is indicative of the presence of some iron in a paramagnetic state (less than 3 percent).

Distribution of iron in feldspars

Iron in the plagioclase feldspars from 10044 and 12021 is in the ferrous state and occurs at two nonequivalent positions with different coordination. The nuclear quadrupole splittings, isomer shifts, linewidths and area ratios are shown in Table 3. Pattern 1 probably results

from Fe^{2+} at the tetrahedrally coordinated Al^{3+} positions whereas pattern 2 may be assigned to the Ca-sites.

Distribution of iron in clinopyroxenes

The exchange energy of the reaction

$$Fe(M2) + Mg(1) \rightleftharpoons Mg(M2) + Fe(M1) \tag{1}$$
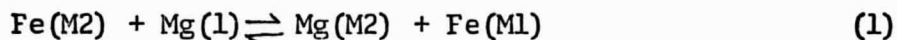
in pyroxenes within the enstatite-diopside-hedenbergite-ferrosilite quadrilateral is primarily determined by the amount of calcium present at the M2 sites, i.e. the amount of wollastonite component in the solid solution. Space group symmetry and the presence of small amounts of foreign cations at the M-sites appear to be of minor importance. Our limited data suggest a simple, linear relationship between the standard Gibbs-free energy difference, ΔG_E^o and the wollastonite concentration; but more data will be needed to establish this precisely. Based on this assumption, plots of temperature versus the equilibrium distribution constant k can be drawn where k is equal to the ratio $(Fe/Mg)_{M1}/(Fe/Mg)_{M2}$. The equilibrium temperature which corresponds to the observed Mg,Fe site occupancy (Table 1) can thus be determined from this plot. This principle is shown in Figure 3.

ΔG_E^o in clinopyroxenes with $\underline{Wo}_{25-36}$ is approximately 8-10 kcal per formula unit $M_2Si_2O_6$. Therefore, only very small changes in the equilibrium site occupancy of Mg and Fe at M1 and M2 are expected in the temperature range from 0 to $1000^{\circ}C$. This has been confirmed by experiments (Table 1). Precise occupancy determinations are hampered

by the large chemical zoning and the pigeonite exsolution, character-
istic of these crystals. Our data indicate, however, complete ordering,
at least within the experimental error, with Mg exclusively at the M1
sites (cf. also ref. 1). We do not believe that there is any indication
of Ca disordering. The apparent excess of cations Ca and Fe at M2 in
some samples of Table 1 can be largely accounted for by corrections
which result from the elements Ti, Mn, Cr, Al.

ΔG_E^O in apparently homogeneous pigeonites with compositions Wo_{5-10}
is approximately 4-5 kcal per formula unit. Disordering as well as
ordering experiments of the yellow-green colored pigeonite, 12021,150
suggest a close similarity to that of the orthopyroxene system[4]. Some
data for ortho- and clinopyroxenes with compositions within the pyroxene
quadrilateral are plotted in Figure 3. The natural Mg,Fe distribution
observed in the yellow-green pigeonite 12021,150-Pl corresponds to an
equilibrium temperature of 570°C. This temperature is substantially
lower than the quench-in temperature for the short range ordering
(rate constant K_{12}', cf. ref. 1) which was determined from an ordering
experiment (Table 1) to be 810°C. The natural Mg,Fe distributions in
orthopyroxenes from Hawaiian lavas[1] correspond to equilibrium tempera-
tures generally higher than the quench-in temperature for orthopyroxenes.
The Mg,Fe distribution observed in the pigeonite 12053,79-Pl (Table 1)
represents an equilibrium temperature of 710°C. Ordering experiments
have not been carried out but the equilibrium temperature does suggest
a more rapid cooling of rock 12053 through the critical range of 600-500°C,
compared with rock 12021.

In <u>clinopyroxenes</u> with compositions Wo_{10-20} the observed degree of Mg,Fe disorder over M1 and M2 is high. It seems likely that the ordering processes in these chemically inhomogeneous pyroxenes are hindered by the complexity of the augite-pigeonite exsolution.

Distribution of iron in olivines

The natural Mg,Fe distribution in an olivine separate (Fa_{36}) from rock 12018 exhibits approximately 20 percent more iron in one of the two nonequivalent M-positions (Table 2). After heat treatment at 1155°C for 7 days the distribution was found to be almost completely disordered. A somewhat ordered terrestrial olivine (B1) did not show disorder after heating at 915°C for 1 day or 1050°C for 5 days. It appears that the Mg,Fe exchange in olivines is quenched-in at much higher temperatures than in pyroxenes. But more experiments will be needed on olivines to establish the nature of this exchange reaction between the M-sites and its relationship to the cooling history of the mineral.

Publications

H. Fernandez-Moran, S.S. Hafner, M. Ohtsuki and D. Virgo: Mössbauer
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H. Fernandez-Moran, M. Ohtsuki, S.S. Hafner and D. Virgo: High voltage
    electron microscopy and electron diffraction of lunar pyroxenes.
    Proc. Apollo 11 Lunar Sci. Conf. Vol. 1, 409-417 (1970).

S.S. Hafner and D. Virgo: Temperature-dependent cation distributions
    in lunar and terrestrial pyroxenes. Proc. Apollo 11 Lunar Sci.
    Conf. Vol. 3, 2183-2198.

S.S. Hafner, B. Janik and D. Virgo: State and location of iron in
    Apollo 11 samples. Mössbauer Effect Methodology Vol. 6
    (E. Gruverman ed.), 193-207 (1971).

Submitted, being submitted: Three additional papers on Apollo 11 and
                             12 samples.

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1. S.S. Hafner and D. Virgo: Temperature dependent cation distributions in lunar and terrestrial pyroxenes. Proc. Apollo 11 Lunar Sci. Conf. Vol. 3, 2183-2198 (1970), and references therein.

2. W.R. Bush, S.S. Hafner, and D. Virgo: Some ordering of iron and magnesium at the octahedrally coordinated sites in a magnesium-rich olivine. Nature 227, 1339-1341 (1970).

3. S.S. Hafner, B. Janik, and D. Virgo: State and location of iron in Apollo 11 samples. Mössbauer Effect Methodology Vol. 6, 193-207(1971).

4. D. Virgo and S.S. Hafner: Fe^{2+},Mg order-disorder in heated ortho-pyroxenes. Mineral. Soc. Amer. Spec. Pap. 2, 67-81 (1969), and references therein.

Figure captions

Fig. 1. Average compositions (molecular percents) of clinopyroxene separates from rocks 12018 (▢), 12021 (X) and 12053 (△). The compositions of two olivine separates from 12018 (▨) and 12053 (▲) are plotted on the En-Fs join. Also plotted are the previously published data from Apollo 11 rocks[1].

Fig. 2. ^{57}Fe resonant absorption spectra of an olivine separate from rock 12018 Fa_{36}(top), and a fayalite Fa_{97}(bottom).

Fig. 3. Plot of temperature against the equilibrium distribution constant k $(Fe/Mg)_{M1}/(Fe/Mg)_{M2}$ for orthopyroxenes($(Mg,Fe)SiO_3$); pigeonite 12021,150-P1 ($(Mg,Fe)_{0.93}Ca_{0.07}SiO_3$); pigeonite 12053,79-P1 ($(Mg,Fe)_{0.90}Ca_{0.10}SiO_3$), and augite 10044,26-P2 ($(Mg,Fe)_{0.64}Ca_{0.36}SiO_3$). The slopes of the lines are constructed assuming a constant standard Gibbs free energy, ΔG_E^o, determined from a linear plot of ΔG_E^o and molecular percent

Fig. 3.
(cont'd.) wollastonite in the sample (numbers in kcal per mole). The crosses (X) correspond to the respective measured k values for the unheated samples. For the orthopyroxene line, the crosses correspond to volcanic samples from Hawaii[1]. The circles (O) correspond to the final distributions in ordering runs of initially disordered samples. For the $(Mg,Fe)_{0.93}Ca_{0.07}SiO_3$ and $(Mg,Fe)SiO_3$ samples, these were respectively $600^{\circ}C$ for 7 days and $550^{\circ}C$ for 7 days.

Table 1   Estimated Mg, Fe, Ca site occupancies in clinopyroxenes from Apollo 12.

Clinopyroxene	En	Fs	Wo	$\frac{A(M1)}{A(tot)}$	$\frac{I(M1)}{I(tot)}$	Estimated site occupancy					
						M1			M2		
						Mg	Fe	Ca	Mg	Fe	Ca
12018,35-P1	50	35	14	0.250	0.263	0.814	0.186	-	0.192	0.520	0.288
12018,35-P2	46	41	13	0.332	0.351	0.715	0.285	-	0.212	0.527	0.261
12021,150-P1 natural	61	33	6	0.176	0.189	0.873	0.127	-	0.343	0.543	0.114
12021,150-P1 555°C	61	33	6	0.172	0.186	0.875	0.125	-	0.341	0.545	0.114
12021,150-P1 800°C	61	33	6	0.248	0.258	0.827	0.173	-	0.389	0.497	0.114
12021,150-P1 1000°C	61	33	6	0.273	0.290	0.806	0.194	-	0.410	0.476	0.114
12021,150-P1 1000°C,600°C	61	33	6	0.234	0.253	0.831	0.169	-	0.386	0.500	0.114
12021,150-P2	31	42	27	0.401	0.403	0.618	0.342	-	-	(0.506)	(0.533)
12021,150-F2 800°C	31	42	27	0.418	0.430	0.618	0.365	-	-	(0.483)	(0.533)
12021,150-P2 1000°C	31	42	27	0.414	0.448	0.618	0.380	-	-	(0.468)	(0.533)
12021,150-P3	17	56	27	0.506	0.516	0.335	0.581	-	-	(0.545)	(0.539)
12053,79-P1	59	31	10	0.183	0.220	0.861	0.139	-	0.314	0.492	0.194

Table 2. Nuclear hyperfine doublets of ^{57}Fe in olivines: line widths and area ratios.

Olivine	Composition mol.percent Fa	Absorber temperature °C	Line widths (FWHH) (mm/sec)				Area ratios[a]	
			A_1[a]	A_2[a]	B_2	B_1	$\dfrac{B_1 + B_2}{\text{total area}}$	$\dfrac{B_1}{B_1+B_2} = \dfrac{Fe_1^{2+}}{Fe_1^{2+}+Fe_2^{2+}}$
Apollo 12								
12018,35-01 (natural)	36	273	0.300		0.312	0.241	0.507	0.422
"	36	315	0.305		0.297	0.222	0.497	0.416
"	36	350	0.306		0.285	0.207	0.491	0.394
12018,35-01 (1155°C, 7 days)	36	303	0.326		0.299	0.265	0.492	0.464
"	36	316	0.304		0.273	0.229	0.490	0.448
"	36	353	0.306		0.263	0.239	0.488	0.467
"	36	402	0.331		0.275	0.278	0.488	0.506
Terrestrial								
Rockport fayalite	97	269	0.222	0.257	0.231	0.221	0.493	0.500
"	97	336	0.227	0.241	0.228	0.224	0.495	0.506
"	97	368	0.227	0.243	0.228	0.219	0.494	0.508
"	97	420	0.224	0.243	0.235	0.219	0.494	0.500
Ho-A	74	315	0.364		0.297	0.286	0.485	0.489
"	74	571	0.361		0.291	0.302	0.485	0.485
B-16	23	273	0.330		0.361	0.275	0.509	0.381
"	23	334	0.333		0.323	0.288	0.502	0.454
"	23	372	0.340		0.335	0.281	0.501	0.429
Modoc	22	353	0.335		0.307	0.298	0.497	0.501
"	22	431	0.330		0.302	0.286	0.496	0.497

Table 2. (continued)

Olivine	Composition mol.percent Fa	Absorber temperature °C	Line widths (FWHH) (mm/sec)				Area ratios [a]		
			A_1 [a]	A_2 [a]	B_2	B_1	$\dfrac{B_1 + B_2}{\text{total area}}$	$\dfrac{B_1}{B_1+B_2} = \dfrac{Fe_1^{2+}}{Fe_1^{2+}+Fe_2^{2+}}$	
B1 (natural)	18	301	0.280		0.274	0.227	0.494	0.451	
"	18	337	0.284		0.274	0.232	0.495	0.452	
B1 (915°C 1 day)	18	360	0.326		0.309	0.282	0.498	0.445	
"	18	390	0.322		0.298	0.273	0.492	0.456	
"	18	510	0.332		0.311	0.294	0.494	0.470	
B1 (1055°C, 5 days)	18	341	0.297		0.282	0.245	0.498	0.450	
"	18	376	0.302		0.287	0.252	0.498	0.449	
"	18	412	0.301		0.282	0.250	0.497	0.452	
S14	8	416	0.315		0.297	0.286	0.495	0.486	
"	8	460	0.314		0.305	0.287	0.497	0.486	

[a] Determined from four-line fits (13 variables) in the case of fayalite and from three-line fits (10 variables) for the remaining samples; A and B refer to the low and high velocity peaks of the doublets, respectively (cf. Fig. 2).

Table 3. Hyperfine interaction of ^{57}Fe in lunar feldspars at 298°K.

Specimen	Wt. percent natural iron	Quadrupole splitting		Isomer shift[b]	
		1 mm/sec	2 mm/sec	1 mm/sec	2 mm/sec
10044,26	0.4[a]	1.54	2.01	0.90	·1.13
12021,150	?	1.49	2.03	0.87	1.13

Specimen	Peak widths			Area ratio (2)/(1+2)
	A mm/sec	B mm/sec	C mm/sec	
1044,26	0.52	0.35	0.65	0.65
12021,150	0.51	0.36	0.65	0.88

[a]from J. V. Smith et al., Proc. Apollo 11 Lunar Sci. Conf. Vol. 1, 897-925 (1970)

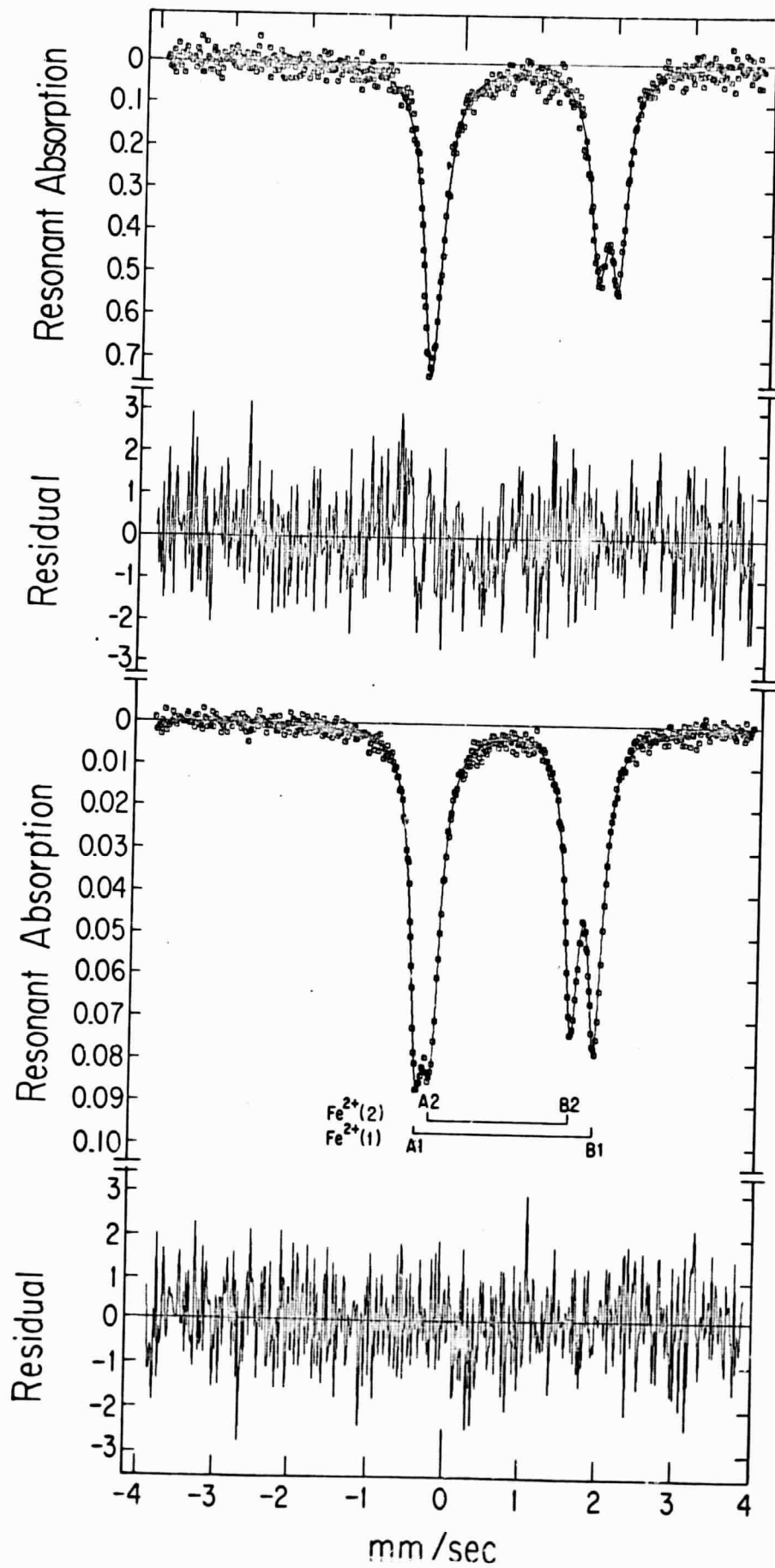[b]referred to a metallic iron absorber

Fig. 1

Fig. 2

Fij. 3

°C

$(Mg , Fe)_{.64} Ca_{.36} SiO_3$ 8

$(Mg , Fe)_{.90} Ca_{.10} SiO_3$ 4.5

$(Mg , Fe)_{.93} Ca_{.07} SiO_3$ 4

$(Mg , Fe) SiO_3$ 3.6

k