Experimental petrology of eucrite meteorites

by

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A thesis presented in partial fulfillment of the requirements for the degree of Master of Philosophy.

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DECLARATION

I hereby declare that the work presented in this thesis is my own, unless otherwise stated, and that the thesis has been composed by myself.

ABSTRACT

Low pressure melting experiments on eucrite meteorites demonstrate that the compositions of most eucrites can be generated by low pressure fractionation of pigeonite and plagioclase from liquids similar in composition to the Sioux County and Juvinas eucrites. It is unlikely that the liquids with compositions similar to Sioux County and Juvinas were themselves residual liquids produced by extensive fractionation of more magnesian parental liquids. The compositions of the Stannern and Ibitira eucrites cannot be produced by fractionation of liquids with compositions similar to other known eucrites. Liquids with compositions similar to the Stannern, Ibitira, and Sioux County sucrites could have been generated by increasing degrees of low pressure partial melting of source regions composed of olivine (~Fo65), pigeonite (~Wo5En65), plagioclase (~An94), Cr-rich spinel, and metal. These source assemblages may have been the primitive, undifferentiated material of the basaltic achondrite parent body and the eucrites may represent the melts produced in the early stages of melting and differentiation of this Further melting in the source regions of the eucrites after body. the exhaustion of plagioclase may have produced magnesian liquids capable of crystallizing the magnesian pyroxenes and olivines found in howardites, diogenites, and mesosiderites. Crystallization of these advanced partial melts in plutonic environments as closed systems can explain a number of the abundance patterns displayed by the basaltic achondrites. Most of the cumulate eucrites (e.g., Moama, Moore County, Serra de Magé) could not have crystallized from liquids similar in composition to known eucrites. These cumulates may have accumulated from liquids produced by extensive fractionation

of advanced partial melts of the source regions of eucritic liquids. A depletion in certain volatile alkalis in Ibitira is noted, but the cause is not certain.

I. INTRODUCTION

The mineralogical, textural, and compositional characteristics of eucrite meteorites suggest that they are closely related members of a suite of rocks whose evolution was dominated by igneous processes similar to those involved in the development of terrestrial and lunar basalts. The diogenites and the lithic fragments in howardites and in the silicate portions of mesosiderites appear to be related to the sucrites and to have formed by the same or similar igneous processes (MASON, 1962, 1967; DUKE and SILVER, 1967; POWELL, 1971). This paper reports the results of melting experiments on the 14 eucrite meteorites listed in Table 1. The results of these experiments help to establish which eucrite compositions represent quenched liquid compositions and which contain cumulus phases, the approximate values of P, T, and fO2 relevant to eucrite genesis, and the relative importance of partial melting and crystallization differentiation in the development of observed eucrite compositions. These experimental results can also place constraints on the mineralogical characteristics of the source regions from which eucritic magmas or the magmas parental to the eucrites were ultimately derived. A preliminary report of the results of experiments on the Juvinas eucrite has appeared elsewhere (STOLPER, 1975a).

The classification scheme of DUKE and SILVER (1967) is followed throughout this paper. Therefore, eucrites are achondritic meteorites which are <u>unbrecciated</u> or are <u>monomict</u> breccias and which consist principally of calcic plagioclase and low calcium pyroxene (primarily pigeonite or inverted pigeonite). Howardites are <u>polymict</u> achondritic breccias consisting principally of calcic plagioclase and

low calcium pyroxene. Although howardites usually contain significant amounts of primary orthopyroxene in addition to pigeonite, this is not used as a basis for classification. The value of this structural-compositional classification scheme in a discussion of igneous processes is that it clearly distinguishes the monomict breccias and unbrecciated meteorites, whose bulk compositions are the products of igneous processes alone and can thus provide constraints on the nature of these processes, from the polymict breccias, which are physical mixtures of diverse igneous rocks and whose bulk compositions are not the direct products of igneous processes. Table 1. Sample description.

Notes.

* Numbers in brackets are the identifying numbers of the museum specimens from which the samples used in this study were obtained.

Sample	Received as	Weight (grams)	Source*
Béréba	fragments	1.5	British Museum (BM1970,337)
Binda	fragments	2.0	Australian Museum
Cachari	chip	2.5	Harvard University (655)
Emmaville	fragments	0.5	Australian Museum
Haraiya	fragments	1.24	Arizona State University (637.1)
Ibitira	powder	0.23	H. Wänke
Jonzac	fragments	2.2	Vienna Museum (A419)
Juvinas	chip	2.5	Harvard University (87)
Lakangaon	fragments	0.55	British Museum (BM1915,142)
Millbillillie	powder	2.1	R.A. Binns
Noama	powder	0.22	J. Lovering
Pasamonte	chip	2.5	Harvard University (606)
Sioux County	fragments	3.0	British Museum (BM1959,1029)
Stannern	chip	2.0	Harvard University (55a)

Molting experiments were conducted at 1 atmosphere total pressure on rock powder starting materials held in molybdenum or iron capsules in vertical quenching furnaces with oxygen fugacities controlled by H_2 -CO₂ gas mixtures. Detailed descriptions of the apparatus and standard operating procedures were given by HUMPHRIES (1975). Temperatures were calibrated against the melting point of Au (1064.5°C), the liquidus of Li₂SiO₃ (1207.9°C), and the anorthite-wollastonite-gehlenite eutectic (1275.8°C). These temperatures were bracketed to within 2°C. Oxygen fugacities were calibrated against the Fe/FeO and Fe/FeTi₂O₅/FeTiO₃ buffers. These buffers were bracketed to within 0.1 log units of fO₂.

All samples were ground under acetone in an agate mortar to a maximum grain size of 30 microns. Three to 10 milligrams of rock powder were loaded into open molybdenum (Murex, >99.95%) or iron (Johnson-Matthey, >99.995%) foil capsules. Molybdenum was used as a container for experiments conducted within 0.1 log units of the oxygen fugacity of the Fe/FeO buffer and at 0.6 ± 0.1 log units below this buffer. Iron capsules were employed at lower oxygen fugacities.

Phase identifications were made by examining fragments of the quenched products in transmitted light under oils and in reflected light on polished surfaces prepared for microprobe analysis. Etching of these polished surfaces with dilute HCl aided phase identification and was found to be useful in distinguishing olivine from pyroxene. Thase compositions were determined with an electron microprobe. The correction procedures of SWEATMAN and LONG (1969) were employed.

Glasses from experiments conducted in molybdenum capsules within 0.1 log units of the oxygen fugacity of the Fe/FeO buffer contained

an average of 0.14 weight percent MoO2 (range: 0.07-0.21 weight percent). The MoO_2 contents of crystalline silicate phases from these experiments were below the detection limit (<0.05 weight percent). However, spinels with up to 5.8 weight percent MoO2 were produced in these experiments. Although spinels with negligible MoO_2 contents were also found, the concentration of molybdenum in some spinels suggests that the stability of this phase could be affected by the use of molybdenum containers near the Fe/FeO buffer. The extent of iron loss from the samples to the molybdenum capsules in experiments on the Juvinas and Sioux County eucrites has been calculated by a least squares mass balance between the bulk composition of the starting material (Table 3) and the compositions of the phases produced in each experiment. For experiments lasting 15-18 hours and conducted in molybdenum capsules within 0.1 log units of the fO₂ of the Fe/FeO buffer, an average loss of 3% of the iron in the starting material was calculated; the maximum calculated iron loss under these conditions was 7% of the iron in the starting material. For experiments lasting 15-18 hours and conducted in molybdenum capsules 0.6 log units of fO2 below the Fe/FeO buffer, an average loss of 7% of the iron in the starting material was calculated; the maximum calculated iron loss under these conditions was 14% of the iron in the starting material. Under these conditions, the MoO2 contents of glasses and all other silicate phases were below the detection limit. The low MoO2 contents of spinels (<0.6 weight percent) and silicates suggest that spinel stability is not significantly affected by the use of molybdenum capsules under these conditions.

The presence of iron metal in basaltic achondrites and the possibility that fractionation of metal played a role in the genesis

of eucrite compositions (DUKE, 1965) suggested the desirability of conducting experiments in iron capsules. Experiments were conducted on the Juvinas and Sioux County eucrites in open iron capsules with oxygen fugacities controlled by gas mixtures. This technique was employed by WALKER et al (1973) in an experimental study of lunar highland compositions. At a given temperature in such experiments, the FeO content of the sample matches the initial FeO content of the starting material only at a single fO_2 which is a function of the temperature and the composition of the starting material. At higher oxygen fugacities, the sample dissolves iron from the capsule; at lower oxygen fugacities, the sample loses FeO by precipitation of iron metal. For this reason, fO₂ must be carefully controlled in order to keep the sample on composition. The direction of iron exchange with the capsule was determined for each sample at each set of experimental conditions in order to bracket for each temperature the fO_2 at which the sample neither gains nor loses iron. At such a point, the bulk composition of the starting material is metal-saturated and its FeO content is maximized. The direction of iron exchange in a particular experiment was determined either by a least squares mass balance between the bulk composition of the starting material and the compositions of the phases present in the experiment or by examination of the probe mounts in reflected light, where the presence or absence of metal blebs in the silicates permitted location of the metal-saturation boundary to within 0.1 log units of fO_{2.}

III. RESULTS

The results and operating conditions of each experiment are recorded in Table 2. Diagrams based on these results are presented in Figures 1-3. Compositions of selected experimental liquids and the compositions of phases coexisting with these liquids are given in Table 3. The compositions of pyroxenes and olivines produced in experiments on Juvinas and Sioux County are shown in Figure 4 with compositions of natural pyroxenes and olivines from basaltic achondrites.

Average values of several crystal-liquid distribution coefficients in these experiments are given in Table 4. The Fe/Mg distribution coefficients for olivine-liquid and pigeonite-liquid are higher than corresponding distribution coefficients reported for lunar compositions under similar experimental conditions. This may reflect the low TiO₂ contents of eucrites relative to lunar basalts (LONGHI et al, 1975).

The value of the Cr distribution coefficient for olivine-liquid given in Table 4 shows no consistent variation with oxygen fugacity or temperature in the range studied and is similar to values reported by HUEENER and LIPIN (1976) and McKAY and WEILL (1976) at similar oxygen fugacities and temperatures. Although the distribution coefficient does not vary with fO_2 , the Cr contents of olivines decrease with increasing fO_2 due to the increased stability of spinel. The average Cr distribution coefficient for pigeonite-liquid increases with fO_2 . This may be due to increases in the Cr^{+3}/Cr^{+2} ratios of the samples with increasing fO_2 . A similar fO_2 dependence of the orthopyroxene-liquid distribution coefficient for Cr has been reported by McKAY and WEILL (1976). However, the magnitude of the

distribution coefficient which they report (5-9) is significantly greater than that given in Table 4. The values of the Cr distribution coefficient for pigeonite-liquid reported by HUEBNER and LIPIN (1976) are similar to those reported in Table 4.

Table 2. Experimental results.

Notes.

Oxygen fugacities calculated from the proportions of H_2 and CO_2 in the gas mixture by the method described in HUMPHRIES (1975).

(?) = Phase identification not positive; phase present in trace amounts, if at all.

* = Complete analysis of phase given in Table 3.

[phase] = Phase was positively identified, but was not used in constructing Figures 1-3, either because (i) the phase was never seen with other phases; (ii) the phase was only found at the capsule edge in iron-depleted or otherwise altered glass; or (iii) the phase was interpreted as a quench phase.

Abbreviations: gl=glass. cpx=clinopyroxene. plag=plagioclase. sp=spinel. ol=olivine.

Phase chemistry data: Fo(x) signifies an olivine with x = 100*Mg/(Mg+Fe) [molar]; $W_0(x)En(y)$ signifies a pyroxene with x = 100*Ca/(Ca+Mg+Fe+Mn) [molar] and y = 100*Mg/(Ca+Mg+Fe+Mn) [molar]; An(x) signifies a plagioclase with x = 100*Ca/(Ca+Na) [molar]; A, C, T, and M numbers are weight percent Al_2O_3 , Cr_2O_3 , TiO_2 , and MoO_2 , respectively. Phase compositions listed are averages when several phases in each experiment were analysed.

				Ĵ	uvinas experiments
Run#	т°с	%H ₂ (log[f0 ₂])	Hours	Capsule	Results
42	1200	75.0(-12.54)	15.3	Мо	gl + sp
40	1200	63.0(-11.94)	16,5	Mo	gl + sp
10	1194	86,6(-13,36)	15,3	Fø	g1
9	1194	85.4(-13.27)	15.0	Fe	gl
20	1193	84,9(-13,23)	15.3	Fo	gl
30	1189	75.0(-12.67)	15.6	Mo	gl + sp
12	1187	62,5(-12,08)	16.5	MO	
. 11	1180	85.0(-13.48)	10.3	FO	g1 + cpx(wo3,En68;A1.4,C.8,T.2) + plag(?)
13	1180	84.0(-13.41)	15.0	Ro	$g_1 + Foot(C, 3) + plag(7) + sp$
32	1178	63.0(-12.22)	15.3	Mo	$g_1 + r_{004}(0, 3) + sp$ $g_1 + r_{004}(0, 3) + sp$
33	1177	75.0(-12.83)	15.5	Mo	$p_1 + Fo_{1}(C, 3) + s_p(T3, 8, 412, 0, C48, 2, Mc, 1)$
16	1171	86.0(-13.59)	16.0	Fe	$g_1 + cpx(Wo6.En66:A1.1:C.7.T.1) + plag + sp$
14	1171	85.0(-13.51)	15.3	Fe	gl* + Fo66(C.3)* + cpx(Wo4.En65:A1.0.C.7.T.2)* + An94* + sp
18	1171	84,0(-13,44)	17.0	Fe	gl* + Fo63(C.3)* + cpx(Wo5,En63;A1.3,C.7,T.1)* + plag + sp
31	1168	75.0(-12.94)	16.7	Mo	gl + Fo67(C.2) + cpx(Wo6,En59;A1.1.C.7.T.1) + plag
30	1166	62.0(-12.32)	17.0	Мо	+ sp(T1.1,A20.6,C41.9,M.5) gl* + Fo66(C.1) + cpx(Wo5,En65;A1.1,C.5,T.1) + plag
					+ sp(T3.5,A11.3,C47.9,M<.1)
34	1165	86.0(-13.68)	15.5	Fe	gl + cpx(Wo6,En64;A1.1,C.7,T.3) + plag + sp
20	1165	85.0(-13.60)	16.7	Fe	g1 + o1 + cpx(Wo6,En62;A1.1,C.7,T.1) + plag + sp
22	1164	84.3(-13.56)	15,3	Fe	gl + Fo63(C.2) + cpx(Wo6,En62;A1.1,C.7,T.1) + plag
28	1156	63.0(-12.51)	16.5	Мо	+ sp(T1.5,A19.7,C42.1)* gl* + Fo62(C.2) + cpx(Wo5,En58;A1.1,C.4,T.1) + An94
00					+ sp(T4.1,A9.8,C41.7,M5.8)
29	1155	75.0(-13.10)	15.5	Mo	g1 + Fo63(C.2) + cpx(Wo6, En61; A1.0, C.5, T.1) + An94 + sp
38	1154	84.0(-13.67)	15.6	Fe	gl + cpx(Wo7, En 38; A1.2, C.8, T.2) + plag + sp
29	1154	83.0(-13.60)	16.5	Fe	g1 + cpx(Wo5, En56; A1, 1, C, 6, T, 1) + Fo57(C, 3) + plag
37	1153	85,1(-13,75)	16.5	Fe	+ sp(11.5,A18.8,C41.0) gl + cpx(Wo8,En59;A1.1,C.7,T.1) + plag + [ol]
27	1142	75.0(-13.27)	17.3	Мо	$ p_{1.4,3,114,0,047,27} = p_{1.4,3,114,0,047,27} = p_{1.4,3,114,0,047,12} + p_{1.4,3,114,0,047,12} = p_{1.4,3,114,0,047$
26	1140	61.0(-12.62)	16.5	Mo	r^{2} + cnx(Wo8 En55.41 0 C 5 T 1) + An92 + en
43	1139	83.9(-13.85)	18.6	Fe	$g_1 + c_{px} + c_{p$
44	1139	83.0(-13.79)	17.4	Fe	el + cox + plag + sp
41	1137	85.0(-13,96)	15.3	Fe	gl + cpx + plag + sp
25	1125	73.8(-13.44)	15.5	Mo	gl + cpx(Wo9, En50; A, 9, C, 5, T, 2) + plag + sp
24	1123	61,4(-12,88)	18.0	Mo	gl* + cpx(Wo8, En 46; A, 9, C, 4, T, 1) + An 91 + sp
17	1108	75.0(-13.73)	16.0	Mo	gl + cpx(Woll, En46; A1.0, C.5, T.3) + An91 + sp
15	1108	63.0(-13.16)	15.3	Mo	gl* + cpx(Wo7, En44; A.8, C.4, T.3) + An94 + sp
19	1093	61.0(-13.29)	17.0	Мо	gl + cpx + plag + sp
21	1076	60.0(-13.50)	18.5	Мо	gl + cpx + plag + silica + sp
	1060	59.0(-13.70)	17.0	Mo	gl(?) + cpx + plag + silica + sp
				Siou	x County experiments
97	1200	75.0(-12.54)	15.3	Мо	gl + sp
95 50	1200	63.0(-11.94)	16.5	Mo	gl + sp
50	1194	86,6(-13,36)	15.3	Fø	gl + cpx(Wo4,En65;A.7,C.6,T.1)
49	1194	85.4(-13.27)	15.0	Fe	g1 + cpx(Wo4, En68; A1.4, C.7, T.1)
48	1193	84.9(-13.23)	15.3	Fe	g1 + Fo67(C.3)
90	1189	75.0(-12.67)	15.6	Mo	gl + Fo69(C.3) + [cpx(Wo5,En66;A1,4,C.6,T.1)] + sp
50	1107	52.5(-12.08)	46.5	MO	gl = + Foo7(C, 2) + sp(X4, 2, A13, 6, C45, 3, M<.1)
51	1100	85.9(-13.48)	15.3	re Te	g1 + cpx(wob, Enb6; A1.0, C.6, T.1)
53	1180	83.0(-13.41) 84.0(-13.34)	16.0	re Re	$g_1 + Fob(C,3) + cpx(wob,Enb5;A1.0,C.7,T.1)$
87	1178	63.0(-12.22)	15.0	Mo	g1 + Fo64(C,3) + Ep(12,2,A14,9,C46,6) g1* + Fo66(C,2) + cpx(Wo5,En64;A,9,C,5,T,1)
88	1177	75.0(-12.83)	15,5	Мо	gl + Fo67(C,3) + cpx(Wo5,En64;A1.0,C.6,T.1) + SP(T1 & A17 3 (43.6 W 4)
56	1171	86.0(-13.59)	16.0	Fe	$g1 + cpx(W_{06}, En65: A1, 0, 0, 7, T, 1) \pm n100$
54	1171	85,0(-13,51)	15,3	Fe	$gl^* + Fo66(C, 3)^* + cpx(Wo5, En64; A1, 1, C, 7, T, 1)^* \perp nleg \perp en$
58	1171	84.0(-13.44)	17.0	Fe	gl* + Fo63(C,3)* + cpx(Wo5.En63:A1.2.C.7.T.1)* + plag + bp
73		75,0(-12,94)	16.7	Мо	+ sp(T2.7,A9.8,C50.3) gl + Fo66(C.2) + cpx(Wo6.En63;A1.1.C.6.T.1)
72	1166	62.0(-12.32)	17.0	Мо	+ sp(T5.1,A9.2,C47.3,M<.1) gl* + ol(?) + cpx(Wo5,En66;A1.4,C.6.T.1)
89	1165	86,0(-13,68)	15,5	Fe	+ sp(T5.2,A8.8,C48.1,M<.1) gl + cpx(Wo6,En61;A1.1,C.7,T.1) + plag
60	1165	85.0(-13.60)	16.7	Fe	+ $sp(T4.3,A16.6,C39.9)$ gl + $cpx(Wo7,En61;A1.0,C.7,T.2)$ + plag
62	1164	84.3(-13.56)	15,3	Fe	+ sp(T3.1,A13.2,C46.0) gl + cpx(Wo5,En62;A.9,C.5,T.1) + plag
68	1156	63.0(-12.51)	16.5	Mo	+ $sp(11.8,A17.9,C42.6)* + ol(?)$ gl* + cpx(Wo6,En60;A1.2,C.5,T,1) + An94 + $sp(T0, 1.6, 0, C42.0)* (1)$

Run#	т°с	%H2(log[f02])	Hours	Capsule	Results
69	1155	75.0(-13.10)	15.5	Мо	gl + cpx(Wo6,En60;A1.3,C.6,T.2) + plag
94	1154	83.0(-13.60)	16.5	Fe	f = p(11, 1, A10, 7, C43, 5, m, 6) gl + cpx(W_{06} , En58; A1, 1, C, 6, T, 2) + plag + ol(?) + sp
93	1154	84.0(-13.67)	15,6	Fe	gl + cpx(Wo7,En58:A1.0,C.6,T.1) + plag
92	1153	85 1/-13 75)	18 5	Po	+ sp(T1.7, A15.6, C44.4)
02	1100	83.1(-13.137	10.5	re	$g_1 + cpx(mo_1, Eno_1; A1, 0, C, 7, T, 2) + plag + sp(T2, 8, A9, 3, C50, 8)$
20	1142	87.7(-14.12)	17.0	Fe	gl + cpx + plag + sp
67 66	1142	75.0(-13.27)	17.3	Mo Mo	g1 + cpx(Wo7, En55; A.9, C.6, T.2) + An94 + sp
21	1140	89.1(-14.26)	16.6	Pe	$gi^{*} + cpx(*00, m04; A, 9, C, 4, T, 2) + An93 + sp$ $gi^{*} + cpx + plag + silica + sp$
15	1140	88.0(-14.16)	1.0	Fø	gl + cpx + plag + sp + silica(?)
98	1139	83.9(-13.85)	18.6	Fe	gl + cpx + plag + sp
99 96	1139	83.0(-13.79) 85.0(-13.96)	17.4	Fe	gl + cpx + plag + sp
65	1125	73.8(-13.44)	15.5	Mo	g1 + cpx + p1ag + sp g1 + cpx(Wo8, En48; A, 8, C, 4, T, 2) + An93
					+ sp(T2.9,A14.0,C44.5,M<.1)
64 57	1123	61.4(-12.88)	18.0	Mo	gl* + cpx(Wo9,En50;A.9,C.5,T.2) + An93 + sp
57	1108	75.0(-13.73) 63.0(-13.16)	16.0	Mo	g1 + cpx(Wo10, En46; A.9, C.6, T.3) + An93 + sp g1* + cpx(Wo10, En46; A.9, C.6, T.3) + An93 + sp
2.					+ sp(T4,2,A9,3,C47.0.M<.1)
59	1093	61.0(-13.29)	17.0	Мо	gl + cpx + plag + sp
61 63	1076	60.0(-13.50) 59.0(-13.70)	18.5	Mo	gl + cpx + plag + silica + sp gl(2) + cpx + plag + cilica + sp
					gi(// + cpx + piag + silica + sp
				1	Bereba experiments
35	1187	62.5(-12.08)	15.5	Мо	gl + sp
32	1178	63.0(-12.22)	15.3	Мо	g1 + sp + o1(?)
30	1166	62.0(-12.32)	17.0	Mo	gl + sp + cpx + plag
26	1130	61.0(-12.62)	16.5	Mo	gI + cpx + plag + sp + [ol]
24	1123	61,4(-12,88)	18.0	Mo	gl + cpx + plag + sp
15	1108	63.0(-13.16)	15.3	Mo	gl + cpx + plag + sp
19 21	1093	61.0(-13.29) 60.0(-13.50)	17.0	Mo Mo	gl + cpx + plag + silica + sp
23	1060	59.0(-13.70)	17.0	Mo	gl(?) + cpx + plag + silica + sp
				I	Binda experiments
3	1277	88.6(-12.57)	16.0	Fe	gl + px(\overlap{wo2.En77:A.7.C1.3.T<.1}
2	1277	87.7(-12.49)	16.6	Fe	gl* + Fo76(C.5) + px(Wo3, En72; A.7, C.9, T.3)
1 5	1277	86.2(-12.36)	16.5	Fe /	g1 + px(Wo2, En73; A.6, C1.0, T<.1) + o1
4	1276	80.6(-11.97)	3.2	No	$g_1 + f_0/2(C,7) + p_x(m_02,En/3;A,5,C1,0,T<.1)$ $g_1 + f_0 + p_x(m_03,En/5;A,8,C,9,T<.1) + g_n(2)$
2 ₀	1200	63.0(-11.94)	16.5	Mo	gl + px + ol + sp
18	1187	62.5(-12.08)	16.5	Mo	gl + px + ol + sp
16 14	1178	63.0(-12.22) 62.0(-12.32)	15.3	Mo No	gl + px + ol + sp gl + px + ol(2) + on
12	1156	63.0(-12.51)	16.5	Mo	$g_1 + px + plag + ol + soc$
10	1140	61.0(-12.62)	16.5	Мо	gl(?) + px + plag + sp
8	1123	61.4(-12.88)	18.0	Mo	subsolidus, silica(?)
	1100			m0	BUDSOILGUB
·				Ca	achari experiments
35	1187	62.5(-12.08)	16.5	Мо	gl + sp
32 30	1178	63.0(-12.22)	15.3	Mo	gI + sp
28	1156	63.0(-12.52)	16.5	Mo	$g_1 + p_{12}g_2 + cp_x(\gamma) + sp_z$ $g_1 + cp_x + p_{12}g_2 + g_2$
26	1140	61.0(-12.62)	16.5	Mo	gl + opx + plag + sp
24	1123	61.4(-12.88)	18.0	Мо	gl + cpx + plag + sp(?)
10 19	1093	03.0(-13.16) 61.0(-13.20)	15.3 17 0	Mo	$g_{\perp} + c_{px} + plag + sp$
21	1076	60.0(-13.50)	18.5	Мо	gl + cpx + plag + silica + sp gl + cpx + plag + silica + sp
23	1060	59.0(-13,70)	17.0	Мо	gl + cpx + plag + silica + sp
				Emp	naville experiments
35	1187	62.5(-12.08)	16.5	Мо	gl + sp
		63 0(-12 22)	15.3	Mo	gl + sp
32	1178	62 0(-10 20)	177 ~		
32 30 28	1178 1166 1156	62.0(-12.32) 63.0(-12.51)	17.0 16.5	Mo Mo	gl + sp gl + cpx + plag + sp

Run#	т°с	% ^H 2(log[f0 ₂])	Hours	Capsule	Results		
.——-							<u></u>
24	1123	61.4(-12.88)	18.0	Mo	gl + cpx + plag + sp		
15	1108	63.0(-13.16)	15.3	Mo	gl + cpx + plag + sp		
19	1093	61.0(-13.29)	17.0	Mo	gl + cpx + plag + sp		
21	1076	60.0(-13.50)	18.5	Мо	gl + cpx + plag + silica + sp		
23	1060	59.0(-13.70)	17.0	Мо	gl(?) + cpx + plag + silica + sp		
				He	araiya experiments	•	
35	1187	62 5(-12 08)	16 5		/////////////////////////////////////		
32	1178	63 0(-12.08)	15.3	Mo	$g_1 + c_0 \pi(2) + g_0$		
30	1166	62 0(-12 32)	17 0	Mo	$g_1 + c_{DX} + n_{eg}(2) + g_{D} + [o]]$		
28	1156	63.0(-12.51)	16.5	Mo	$p_1 + c_{DX} + p_{10} = p_{10} + c_{DY} + p_{10} = p_{10}$		•
26	1140	61.0(-12.62)	16.5	Мо	gl + cpx + plag + sp		
24	1123	61.4(-12.88)	18.0	Мо	gl + cpx + plag + sp		
15	1108	63.0(-13.16)	15.3	Мо	gl + cpx + plag + sp		- ·
19	1093	61.0(-13.29)	17.0	Mo	gl + cpx + plag + silica + sp		
21	1076	60.0(-13.50)	18.5	Mo	g1 + cpx + plag + silica + sp		
23	1060	59.0(-13.70)	17.0	Мо	subsolidus (?)		• •
				. 11	bitira experiments		
39	1200	63.0(-11.94)	16.5	Mo	$g_{L} + s_{P}$		
34	1187	62,5(-12,08)	16.5	Mo	$g_{\perp} + c_{px}(7) + s_{p}$	• .	
31	1178	63.0(-12.22)	15.3	MO	$g_1 + o_1 + c_px + plag(?) + s_p$		
29	1166	62.0(-12.32)	17.0	Mo	gl + ol + cpx + plag + sp		
27	1136	63.0(-12.51)	16.5	MO	gi + cpx + plag + sp		
20	1140	61.0(-12.62)	10.0	MO	$g_1 + c_{px} + p_{1ag} + s_{p}$		
14	1123	61,4(-12,00)	15.2	MO	$g_1 + c_p x + p_{1ag} + s_p$		
19	1003	63,0(-13,16)	17.0	No	$g_1 + c_p x + p_{1ag} + s_p$	1	
20	1035	60.0(-13.29)	18 5	Mo	$g_1 + c_{px} + p_{1ag} + silica + sp$		
22	1060	59.0(-13.70)	17.0	Мо	gl(?) + cpx + plag + silica + sp gl(?) + cpx + plag + silica + sp		
				3	Jonzac experiments		
<u> </u>							
28	1187	62.5(-12.08)	16.5	Mo	gl + sp		
25	1178	63.0(-12.22)	15.3	Mo	gl + ol + sp		
23	1166	62.0(-12.32)	17.0	Mo	gl + ol + cpx + sp		
21	1156	63.0(-12.51)	16.5	MO	gl + cpx + plag + sp		
19	1140	61.0(-12.62)	10.0	MO	$g_1 + c_p x + p_{1ag} + s_p$		
311	1109	63.0(-13.16)	15.0	MO . No	$g_1 + c_{px} + p_{1ag} + s_{p}$		•
12	1003	61.0(-13.16)	17.0	No	$g_1 + c_p x + p_{1ag} + sp$		
14	1035	61.0(-13.29) 60.0(-13.50)	18 5	MO Mo	$g_1 + c_p x + p_{12} g_1 + g_{11} c_2 + g_p$		
16	1060	59.0(-13.70)	17.0	Mo	gl(?) + cpx + plag + silica + sp gl(?) + cpx + plag + silica + sp		
							· · · · · · · · · · · · · · · · · · ·
<u> </u>					angaon experiments		
10	1162	69.3(-12.72)	16.0	Мо	gl + sp		
11	1151	69.4(-12.86)	16.0	· Mo	$g_{1} + s_{p} + o_{1}(7)$		
13	1145	09.3(-12.95)	18.1	MO	$g_1 + o_1 + c_{px} + s_p$		
10	1144	00.7(=12.06) 70.0(=12.04)	10.1	MO	$a_1 + cbx + c_1 + a_2 + a_2 + c_2$		
22	1130	10.0(-13.04) 60 7(-19 79)	16 0	Mo	al + ony + blog + ap		
5	1122	60 7(-12 PC)	-0.0	жо Мо	oj t cux t bjeg t se Pr , chy i bigg t sh		
4	1112	59 6(-12 05)	16 5	Mo	ol T CUX T DJ8G T 60		<i>?</i>
3	1102	59.8(-13 11)	15 5	Mo	of t cox t plag t of t an		
2	1087	59.8(-13.32)	15.5	Mo	gl + cpx + plag + sp		
1	1079	59.8(-13.45)	17.1	Mo	gl + cpx + plag + sp + silica		
				Millt	billillie experiments	· · · · · · · · · · · · · · · · · · ·	
	1107	£9 5/_10 09)	16 E	Ne			
30 37	1170	04.0(-12.08) 63.0(-10.00)	15.3	100 140	$a_1 + a_2 + [o_1] + a_1 - (o_1)$ RT + ab		
31	1166	62 0(-12,22)	17 0	Mo	er + eh + forl + bres(1)		
20	1156	63.0(-12.51)	16 5	Mo	o] + CDX + Dlag ⊥ SN P= I of I frag		
27	1140	61.0(-12.62)	16.5	Mo	$p_{1} + c_{2} + p_{3} + p_{4} + s_{5}$		•
25	1123	61.4(-12.88)	18.0	Mo	g_{-} + c_{px} + p_{ag} + s_{p}		
16	1108	63.0(-13.16)	15.3	Mo	gl + cpx + plag + sp + [ol]		
20	1093	61,0(-13,29)	17.0	Мо	gl + cpx + plag + sp		
22	1076	60,0(-13,50)	18.5	Мо	gl + cpx + plag + silica + sp		
24	1060	59.0(-13.70)	17.0	Мо	gl(?) + cpx + plag + silica + sp		-

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Run#	т°с	%H ₂ (log[f0 ₂])	Hours	Capsule	Results
	<u>.</u>	······································]	Moama experiments
1	1282	70.8(-11.36)	18.2	Mo	gl + Fo ⁸² (C.4) + sp
23	1200	63.0(-11.94)	16.5	Мо	gl + ol + px + plag + sp
21	1187	62.5(-12.08)	16.5	Mo	gl + px + plag + ol + sp
19	1178	63.0(-12.22)	15.3	Mo	gl + px + ol + plag + sp
17	1166	62.0(-12.32)	17.0	Mo	gl + px + plag + ol + sp
15	1156	63.0(-12.51)	16.5	Mo	gl + px + plag + ol + sp
13	1140	61.0(-12.62)	16.5	Mo	gl + px + plag + ol + sp
11	1123	61.4(-12.88)	18.0	Mo	subsolidus
9	1108	63.0(-13.16)	15.3	Мо	subsolidus
				Pa	samonte experiments
35	1187	62.5(-12.08)	16.5	Mo	Pl + 8D
32	1178	63.0(-12.22)	15.3	Mo	$s \rightarrow sp$
30	1166	62.0(-12.32)	17.0	Mo	$r_{\rm s} = 1 + r_{\rm s}$
28	1156	63.0(-12.51)	16,5	Mo	r = r + r = r + r = r = r = r = r = r =
26	1140	61.0(-12.62)	16.5	Mo	$g_1 + c_{px} + p_{lag} + s_{p} + ol(2)$
24	1123	61.4(-12.88)	18.0	Mo	gl + cpx + plag sp
15	1108	63.0(-13.16)	15.3	Mo	gl + cpx + plag + sp
19	1093	61.0(-13.29)	17.0	Mo	gl + cpx + plag + sp
21	1076	60,0(-13,50)	18.5	Mo	gl + cpx + plag + silica + sp
23	1060	59.0(-13.70)	17.0	Mo	gl(?) + cpx + plag + silica + sp
	<u> </u>	· · · · · · · · · · · · · · · · · · ·		S	tannern experiments
	1197	£2 5(-12 09)	16 5		
-30	1179	63 0(-12 22)	10.0	Mo	ST T DY
30	1166	62 0(-12 32)	17 0	Mo	$a_1 + a_2 + n \log(2)$
28	1156	63 0(-12 51)	16 5	Mo	0] + 017 + 1]90 + 85 5- 1 00 7 F-05/1/
26	1140	61 0(-12.01)	16 5	Mo	al t und t blog t ab
24	1123	61 4(-12 88)	18 0	Mo	aj tour tujea teu Et tohu thraf teh
15	1108	63.0(-13.16)	15.3	Mo	r = r r r r r r r r r r r r r r r r r r
19	1093	61 0(-13 29)	17 0	Mo	$a_1 + a_2 + b_3 + a_5 + a_5$
21	1076	60.0(-13.50)	18 5	Mo	ol + one + nlog + silice + sn
23	1060	59 0(-13 70)	17 0	Mo	gi t opa t plag t ciling t cp
20	2000		±1.0		BUILL AND I ATTAC I ATTAC I AN

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Table 3. Microprobe analyses (weight percent) of experimentally

produced phases.*

Notes.

- Conditions of the experiments and the phases identified in the experimental products are listed in Table 2. Jv14=Juvinas, run 14. SC58=Sioux County, run 58. Bi2=Binda, run 2. ol=olivine. cpx=clinopyroxene. plag=plagioclase. sp=spinel.
- ** Bulk compositions based on average composition of glasses produced in experiments conducted above the liquidus. Because of iron loss from experiments conducted in molybdenum capsules, the FeO contents of the bulk compositions listed were arbitrarily adjusted to give Fe/(Fe+Mg) ratios matching those given in the literature for Juvinas (DUKE and SILVER, 1967; McCARTHY et al, 1973), Sioux County (DUKE and SILVER, 1967; McCARTHY et al, 1973) and Emmaville (MASON, 1974). The Fe/(Fe+Mg) [molar] ratio of Jonzac was arbitrarily adjusted to 0.60.

- = Not analysed.

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		Jv 14	Jv14	Jv14	Jv14	Jv 18	Jv 18	Jv18	Jv22	Jv32	Jv30	Jv28	Jv26
		glass	ol	срх	plag	glass	01	срж	вр	glass	glass	glass	glass
	SiO ₂ TiO ₂	49.39	36.72	53.33 .21	45,36	49.08	36.75	52.70 .15	1.30	49,53	49.24	49,26	49.20
	A1203	13.07	.09	.99	33.86	12.78	.10	1.30	19.71	12.85	13.03	12.51	11.74
	FeO	17.35	30,06	.65 18,52	.01	19.03	31.68	.72 19.42	42.08 26.69	.14 17.44	.14 17.54	.13 18.77	.16 20.06
	м _л о Моо	.57 6.41	.74 31.84	.68 23.18	.05 .17	.58 6.50	.72 30,23	.72 22,13	.62 6.53	.52 7 12	.56	.60	.66 5.26
	CaO	10.47	.40	2.18	18,54	10.28	.39	2.45	.42	10.20	10.29	10.36	10.41
	Na 20	. 53	.01	.03	.70	. 51	.03	.00	.01	.66	.51	.62	.59
	Total	98.82	100.13	99.77	99.69	99.75	100.21	99.59	98.81	99.02	98.71	99.08	98,95
		J _v 24	J v 15	SC 54	\$C54	SC54	SC58	SC58	SC58	SC62	SC90	SC87	SC72
		glass	glass	glass	0 1	срх	glass	ol	срх	вр	glass	glass	glass
	siO ₂	49.00	49.75	49.38	36.89	53.45	48.90	36.92	53.47	.82	49.45	49.90	49.05
	TiO ₂	1,18	1.28	.70 12.85	.05	.11	.67 12 48	.02	.11	1.77	.64	.62	.67
	Cr ₂ O ₃	.15	.12	.31	.31	.66	.32	.30	.73	42.61	.23	.22	.16
	FeO MnO	21.86 .65	21.46 .66	17.88	30.04 .76	18.87 .71	19.13	32.21	19,40	28.06	18.70	17.92	18.27
	MgO	4.44	3.64	6.44	31,86	23.03	6.40	30.51	22.55	6.06	7.36	7.16	6.64
	Na ₂ O	.64	.76	.44	.01	2.40 .00	.47	.01	2.53 .03	.44	9.84 .59	10.29 .66	10.20 .50
	Total	99.46	98.44	98,96	100.46	100.29	99.15	101.13	100.70	98.28	99.58	99.69	98,73
	_ _,	5069	5066	5054					.	• 61			
		glass	glass	glass	glass	glass	glass	glass	JUVINAS+	County	Jonzac		/1110**
	SiO ₂	49.12 73	49.05	49.42	50,16	53,93	50.63	50,43	48.5	48.8	49.1	48,	,8
	A1203	12.36	12.20	10,95	10.63	11.78	8,99	8,25	12.7	12.2	12.4	12.	.3
	Cr ₂ 0 ₃ FeO	.15 19.18	.12 19.99	.13 21.10	.13 21.32	14.31	.66 18,63	.80 19.17	.26 18.6	.31 18.7	.27 18.4	7 . 19.	,26 .4
·	MnO Mar	.64	.60	.62	.58	.78	.64	.64	.54	.63	. 50)	54
• .	Ca O	10.31	4.93	4.32	3.54 10.37	4.59	8,27	8.48	7.18	7.22 9.8	6.87 10.2	6. 10	.39 .2
	Na ₂ O	. 52	. 59	.62	.71	. 53	.32	. 36	.49	.47	. 58	3.	, 53
	Total	99.08	98.83	98,55	98.69	97.87	98.89	99.14	98,98	98.75	99.04	99.	19
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Table 4. Average solid-liquid distribution coefficients determined

in experiments on the Juvinas and Sioux County eucrites.

Notes.

K_D(Fe/Mg)=[Fe/Mg(crystal)]/[Fe/Mg(liquid)]. Molar ratios. Averages
for all experiments.

K_D(Fe/Mn)=[Fe/Mn(crystal)]/[Fe/Mn(liquid)]. Molar ratios. Averages
for all experiments.

D(Cr)=[Cr(crystal)]/[Cr(liquid)]. Weight ratios. Averages for

experiments conducted at the indicated values of fO2.

n=number of crystal-liquid pairs used to obtain average.

s=standard deviation.

IW=experiments conducted with oxygen fugacity near the iron-wustite buffer.

IW-0.6=experiments conducted with oxygen fugacity approximately 0.6 log units below the iron wustite buffer.

IW-1.25=experiments conducted with oxygen fugacity approximately 1.25 log units below the iron-wustite buffer (experiments in equilibrium with metallic iron).

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•		K _D (Fe/Mg)	K _D (Fe/Mn)	D(Cr) fO ₂ =IW	D(Cr) fO ₂ =IW-0.6	D(Cr) fO ₂ =IW-1.25					
	olivine	0.35 (n=24,s=0.01)	1.24 (n=24,s=0.11)	1.0 (n=5,s=0.2)	1.1 (n=8,s=0.1)	1.0 (n=11,s=0.1)					
	pigeonite	0.30 (n=48,s=0.01)	0.88 (n=48,s=0.06)	3.2 (n=11,s=0.5)	2.7 (n=12,s=0.5)	2.2 (n=23,s=0.4)					
	spinel	1.60 (n=33.s=0.22)	1.33 (n=33.s=0.15)	-	-	-					

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Figure 1. Summary of results of 1 atmosphere quenching experiments on eucrite meteorites. In samples other than Binda and Moama, spinel begins crystallizing at approximately the same temperature as the silicate phases under metal-saturated conditions. At higher oxygen fugacities, spinel is the sole liquidus phase.



Figure 2. Summary of results of 1 atmosphere quenching experiments on the Juvinas and Sioux County eucrites. Solid squares show the conditions of each experiment. Liquid is present in all fields. Solid boundaries separate regions in which a given phase was present in experimental products from those in which it was absent. Dashed lines are inferred extensions of the solid boundaries. Dotted lines are the locations of oxygen buffers determined in this study. Abbreviations: ol=olivine, pig=pigeonite, plag=plagioclase, sp=spinel, Fe=iron metal, wu=wustite, il=ilmenite, fb=ferropseudobrookite.



pig in

plag in ol out

Figure 3. Summary diagram showing the proportions of phases present in the products of experiments on the Juvinas and Sioux County eucrites as a function of temperature. Proportions of phases in each experiment were determined by least squares solution of a set of mass balance equations for the following oxides: SiO_2 , TiO_2 , Al_2O_3 , Cr_2O_3 , FeO, MnO, MgO, CaO, and Na₂O. Each mass balance equation was of the form:

 $\sum_{i} X(i) * W(i,j) = W(initial,j)$

where X(i) is the mass fraction of phase i in the experimental product, W(i,j) is the weight percent of oxide j in phase i, and W(initial,j) is the weight percent of oxide j in the starting material. Starting material compositions are given in Table 3. The compositions of the phases in each experiment were determined by electron microprobe. Filled circles are calculated percentages of liquid in experiments. Open circles are calculated percentages of olivine. Open triangles are calculated percentages. Open squares are calculated plagioclase percentages. Calculated percentages of spinel were less than 1% in all experiments.



Figure 4. Compositions of natural and experimentally produced pyroxenes and olivines. Filled circles are pyroxenes from experiments on Sioux County. Open circles are pyroxenes from experiments on Juvinas. Open triangles are pyroxenes in basaltic achondrites: Bi=Binda pigeonite (ISHII et al, 1976). Jv=Juvinas pigeonite (DWKE and SILVER, 1967). Ka=most magnesian pyroxene in the Kapoeta howardite (FREDRIKSSON and KEIL, 1963). MC=pigeonite in Moore County (DUKE and SILVER, 1967). Me=orthopyroxene host in inverted pigeonite in Medanitos (SYMES and HUTCHISON, 1970). Mo=pigeonite in Moama (LOVERING, 1975). NL=pigeonites in Nuevo Laredo (DUKE and SILVER, 1967). SDM=pyroxene in Serra de Magé (DUKE and SILVER, 1967). Dotted region in pyroxene quadrilateral labelled Di is the range of diogenite pyroxene compositions (DYMEK et al, 1976). Range of compositions of Kapoeta olivines from FREDRIKKSON and KEIL (1963).



IV. LIQUID COMPOSITIONS AND P-FO2-T DURING EUCRITE GENESIS

In each of the eucrite compositions shown in Figure 1, excluding Binda and Moama, pigeonite, ±olivine, and plagioclase crystallize within 25°C of each other at low pressure and low oxygen fugacity. Figure 2 shows that although the temperatures of olivine, pigeonite, and plagioclase crystallization are not greatly altered by changes in fO_2 between the Fe/FeO buffer and the fO_2 levels at which Juvinas and Sioux County are metal-saturated (the Fe in boundaries in Figure 2), the temperature of spinel crystallization is strongly dependent on fO_2 . At metal-saturation, the liquidi of these compositions are approximately saturated with olivine, pigeonite, plagioclase, and spinel. The temperature of spinel appearance rises sharply with increases in fO2 and spinel becomes the sole liquidus phase. It is probable that this is primarily due to increases in the Cr^{+3}/Cr^{+2} ratios of the melts with increasing fO₂. The possibility that stabilization of spinel by molybdenum contributes to the positive slope of the spinel liquidi in Figure 2 cannot be ruled out entirely. However, this is considered unlikely because of the low MoO2 contents (<0.05 weight percent) of most of the analysed spinels. At values of fO2 below metal-saturation, the FeO contents of the experimental charges drop rapidly as iron metal is precipitated; the temperatures of pyroxene and plagioclase appearance rise while the temperatures of spinel and olivine appearance fall. It is probable that increased pressure would remove both olivine and pyroxene from the metal-saturated liquidi of these compositions (O'HARA, 1968; MERRILL and WILLIAMS, 1975).

The slight departures from truly cotectic behavior of some of the samples shown in Figure 1 may reflect the difficulty in obtaining

representative samples of heterogeneous and coarse-grained rocks when only small samples are available for study. The sample showing the greatest departure from multiple saturation at its liquidus, Sioux County, is also one of the coarsest eucrites (DUKE and SILVER, 1967) and it is likely that poor sampling is responsible for its departure from a cotectic condition. One measure of the degree to which a given sample approaches a cotectic or multiply saturated condition is the degree of crystallinity of the sample when it becomes multiply saturated. This has been estimated by a mass balance calculation involving the compositions of the phases present in each charge and the initial composition of the sample for Juvinas and Sioux County experiments. The amounts of liquid and other phases in each experiment are shown as functions of temperature in Figure 3. Even Sioux County is less than 5 percent crystalline when it becomes saturated with olivine, pyroxene, and plagioclase.

Therefore, at pressures close to one atmosphere and oxygen fugacities near $10^{-13.3\pm0.2}$ atmospheres, the liquidi of the eucrites shown in Figure 1 (excluding Binda and Moama) are approximately saturated with four or five phases - pigeonite, ±olivine, plagioclase, spinel, and metal. In general, if conditions of pressure and oxygen fugacity can be found at which a given rock composition has more than three phases at its liquidus, it is probable that this rock was produced by quenching of a liquid and that the generation of this liquid involved equilibria between the liquid and the liquidus phases at the conditions at which the liquid indicates that these meteorites are probably quenched liquids whose compositions were controlled by equilibria with pigeonite, ±olivine, plagioclase, spinel, and metal at low pressures,

at temperatures between 1150° C and 1190° C, and at oxygen fugacities near $10^{-13.3}$ atmospheres.

The multiple saturation of the liquidi of these eucrite compositions was anticipated by MASON (1962) and by DUKE and SILVER (1967) who predicted that pigeonite, plagioclase, and perhaps olivine would crystallize simultaneously from these compositions. DUKE and SILVER (1967) also noted that if, as they predicted, the liquidi of eucrite compositions were cotectic, this would support their texturally-based conclusion that the eucrites were produced by the quenching of non-porphyritic magmas near the surface of some body. The conclusion of DUKE (1965) that these eucritic magmas were approximately metal-saturated at their liquidi is corroborated by the experimental data presented above.

The low pressure multiple saturation of eucrite compositions suggests that these compositions were controlled by low pressure igneous processes. This is consistent with the absence of mineralogical evidence of high pressure igneous processes in basaltic achondrites (DJKE and SILVER, 1967).

The level of fO_2 during eucrite genesis inferred from the oxygen fugacities at which the eucrite liquidi are approximately saturated with five phases is virtually coincident with the iron-ilmenite-ferropseudobrookite buffer at liquidus temperatures. Lunar basalts appear to have evolved at similar fO_2 levels (SATO et al, 1973; SATO, 1976). In contrast, comparisons of the Eu^{+3}/Eu^{+2} ratios of eucrites and of lunar rocks suggest that eucrites evolved at fO_2 levels several orders of magnitude below those experienced by lunar magmas (PHILPOTTS, 1970; DRAKE, 1975). Neither the data presented above nor the Eu^{+3}/Eu^{+2} ratios of eucrites are consistent with the suggestion of KIMURA et al (1974) that eucrites may have

evolved at fO_2 levels as high as those experienced by terrestrial basalts. The low Fe_2O_3 contents of eucrites and the presence of metal in some eucrites as a magmatic phase (DuKE and SILVER, 1967) are also inconsistent with the high fO_2 levels suggested by KIMURA et al (1974).

A. Graphical representations.

It is in general helpful to be able to make graphical representations of the results of experiments on natural rocks involving coexisting crystals and liquid. One way to display the changes in composition of coexisting crystals and liquid is through the use of variation-type diagrams where mineral compositions are used as coordinates instead of oxides. Such diagrams may closely resemble the liquidus diagrams of simple systems. Such a pseudo-liquidus diagram can, with a judicious choice of coordinates, be a useful tool for understanding crystallization sequences and the relationships between members of a given suite of rocks. Figures 5 and 6 illustrate diagrams of this type. The locations of the field boundaries in these diagrams are based on microprobe analyses of multiply saturated liquids produced in experiments on the Juvinas and Sioux County eucrites (Table 3). The field boundaries in Figures 5 and 6 can be used as in ternary liquidus diagrams to predict crystallization sequences and liquid lines of descent of liquids similar in composition to the experimentally produced liquids on which they are based. However, they will in general be of limited value in elucidating the behavior of liquids even broadly similar in composition to these experimentally produced liquids.

The behavior of olivine in the sucrite experiments demonstrates that olivine is in reaction relation with liquids on the olivine + pigeonite boundary curve in Figure 5 and on the olivine + pigeonite + plagioclase curve in Figure 6. The peritectic natures of the olivine + pyroxene boundary in Figure 5 and the olivine + pyroxene +

Figures 5 and 6. Pseudo-liquidus diagrams for eucrite compositions. Molar units are used throughout. Compositions may be projected into these diagrams by recalculating SiO_2 , Al_2O_3 , FeO, MnO, MgO, CaO, Na₂O, and K₂O into the coordinates SiO_2

 $(SiO_2-0.5*[FeO+MgO+MnO]-5*[Na_2O+K_2O]-Al_2O_3-CaO); CaAl_2Si_2O_8$ $(Al_2O_3-Na_2O-K_2O); Fe_2SiO_4$ (0.5*FeO); Mn_2SiO_4 (0.5*MnO); Mg_2SiO_4 (0.5*MgO); CaSiO_3 (CaO+K_2O+Na_2O-Al_2O_3); NaAlSi_3O_8 (2*Na_2O); and KAlSi_3O_8 (2*K_2O) and then recalculating the SiO_2, CaAl_2Si_2O_8, and (Fe,Mn,Mg)_2SiO_4 components to 100% (Figure 5) or the SiO_2, (Fe,Mn)_2SiO_4, and Mg_2SiO_4 components to 100% (Figure 6).

Residual liquids produced by equilibrium crystallization of pigeonite and plagioclase from liquids at A follow the path AB. At B, these residual liquids become saturated with a silica polymorph. The Fe/Fe+Mg ratios of liquids increase from <u>A</u> to <u>B</u>. This path is based on the compositions of multiply saturated liquids produced in experiments on the Sioux County and Juvinas eucrites (Table 3). Residual liquids produced by fractional crystallization of liquids at <u>A</u> would follow the schematic path <u>AB</u>. At <u>B</u>, these residual liquids would become saturated with a silica polymorph. The remaining field boundaries in Figure 5 delineate the olivine, pyroxene, and plagioclase liquidus fields for liquids with Fe/(Fe+Mg)[molar]=0.60-0.65. B" is the point at which such liquids are saturated with pyroxene, plagioclase, and a silica polymorph. The field boundaries in Figure 6 delineate the plagioclase-saturated liquidus fields of olivine, pyroxene, and silica for liquids similar in composition to sucrites and their derivatives. Compositions of eucrite meteorites have been projected into these diagrams. Solid circles are "non-cumulate" eucrites: Be=Béréba. Ca=Cachari. Em=Emmaville. Ha=Haraiya. Ib=Ibitira. Jo=Jonzac. Jv=Juvinas.
Lk=Lakangaon. Mi=Millbillillie. NL=Nuevo Laredo. Pa=Pasamonte. SC=Sioux County. St=Stannern. Open circles are cumulate eucrites: Bi=Binda. Br=Brient. Me=Medanitos. Mo=Moama. MC=Moore County. Po=Pomozdino. SDM=Serra de Magé. <u>Rho</u>=fragment from Kapoeta. Analyses from: Table 3, DYAKONOVA and KHARITONOVA (1961), DUKE and SILVER (1967), VON MICHAELIS et al (1969), SYMES and HUTCHISON (1970), WANKE et al (1972, 1974), KVASHA and DYAKONOVA (1972), ALLEN and MASON (1973), McCARTHY et al (1973,1974), LOVERING (1975), DYMEK et al (1976), R. HUTCHISON (pers. comm.), and R.A. BINNS (pers. comm.). Multiple analyses of a single meteorite were averaged before projecting into these diagrams. Multiple analyses from a single author were averaged before averaging with analyses from other authors.





plagioclase boundary in Figure 6 (and <u>A</u>, the piercing point of this peritectic in the diagram in Figure 5) indicate that olivine will not crystallize from liquids with compositions on these boundaries even though such liquids are saturated with olivine at their liquidi.

The compositions of those eucrites for which modern analyses are available have been projected into the pseudo-liquidus diagrams in Figures 5 and 6. The clustering of eucrite compositions (excluding those which on textural grounds and for other reasons to be discussed below are believed to contain significant cumulus material) about the olivine + pigeonite + plagioclase peritectic (A) in both of these diagrams confirms the conclusion reached earlier that these eucrite compositions are approximately saturated with these three phases near their low pressure liquidi. The detailed variations in crystallization sequences of the eucrites studied (Figure 1) do not all match those expected on the basis of the locations of their compositions in Figures 5 and 6. Since most of the analyses projected into these diagrams are from the literature, these differences could reflect slight differences between the compositions of different subsamples of a single meteorite. Also, since the location of a composition in either of these diagrams is extremely sensitive to its silica concentration, some of the scatter of eucrite compositions around A may be due to uncertainties in the published analyses.

The petrographically determined crystallization sequence of silicates in eucrite meteorites is pigeonite, closely followed by plagioclase (DUKE and SILVER, 1967). Silica and ferroaugite were relatively late crystallizing phases. The idealized crystallization sequence of silicates from a eucritic liquid at <u>A</u> is simultaneous crystallization of pigeonite and plagioclase. The composition of the

residual liquid changes on a path between <u>AB</u> and <u>AB</u> and silica begins to crystallize along with pigeonite and plagioclase when the residual liquid reaches a composition between <u>B</u> and <u>B</u>. The absence of olivine in the actual crystallization sequences of eucrites and the rarity of olivine in basaltic achondrites as a whole are consistent with the crystallization sequences of liquids at <u>A</u>. The appearance of olivine on some of the experimentally determined liquidi probably reflects small sampling biases; actual eucritic liquids were probably at <u>A</u> or slightly more silica-oversaturated. Variations in conditions of pressure or oxygen fugacity could have moved liquids at <u>A</u> into the olivine field, resulting in crystallization of the rare olivines in basaltic achondrites.

Controlled cooling rate experiments on lunar basaltic compositions have demonstrated that rapid cooling can depress the temperatures at which pyroxene and plagioclase begin to crystallize from a liquid but that the temperature of plagioclase appearance is depressed significantly more than that of pyroxene (WALKER et al, 1976b). The observation of DUKE and SILVER (1967) that pyroxene appears to have slightly preceded plagioclase in eucrite crystallization sequences could reflect such undercooling, but the magnitude of the effect, if present, was smaller than that which has been observed in many lunar basalts.

B. Eucrite cumulates.

In large flows or magma chambers, slower cooling rates could have resulted in accumulation of the phases crystallizing from eucritic liquids. Three meteorites have been suggested as such cumulates on the basis of textural evidence: Moama (LOVERING, 1975), Moore County (HESS and HENDERSON, 1949), and Serra de Magé (DUKE and

SILVER, 1967). Four other eucrites, Binda, Brient, Medanitos, and Pomozdino, have compositions which are significantly displaced from those of the eucrites at <u>A</u> and which could be interpreted as cumulates of pyroxene and plagioclase.

The compositions of the pyroxenes in these meteorites have been plotted in Figure 4 along with the compositions of pyroxenes produced in experiments on the Juvinas and Sioux County eucrites. The trend of experimental pyroxene compositions is similar to that found in the cumulates. Assuming a pyroxene-liquid distribution coefficient (Fe/Mg) of 0.30 (Table 4), the Fe/(Fe+Mg) ratios of the liquids with which the cumulates could have equilibrated can be calculated from the compositions of the pyroxenes in the cumulates. This calculation assumes that the composition of the pyroxene as now observed is the same as it was when it separated from the liquid. Subsolidus homogenization of original zoning or extensive reaction of the pyroxene with an intercumulus liquid would invalidate this assumption. The results of this calculation are shown in Table 5. The pyroxenes in Binda could have precipitated from a liquid with an Fe/(Fe+Mg) ratio similar to Juvinas and Sioux County. However, the pyroxenes in Medanitos, Moama, Moore County, and Serra de Magé could only have equilibrated with liquids significantly more iron-rich than any known sucrites. Liquids as iron-rich as these hypothetical liquids are found in experiments on the Sioux County eucrite at temperatures of less than 1140°C when the sample is 45-65 percent crystalline (Figure 9).

If these calculations are meaningful, they cast doubt on: (i) the suggestions of SCHNETZLER and PHILPOTTS (1969) and McCARTHY et al (1973) that the compositions of Moore County and Serra de Magé approximate the bulk composition of the phases crystallizing from

Table 5. Fe(/Fe+Mg) [molar] ratios of liquids with which cumulate eucrites could have equilibrated, calculated from the Fe/(Fe+Mg) ratios of the pyroxenes in the cumulates (references in parentheses) and a pigeonite-liquid distribution coefficient of 0.30 (Table 4). For comparison, the Fe/(Fe+Mg) ratios of Juvinas, Pasamonte, Nuevo Laredo, and Lakangaon are 0.60, 0.62, 0.67, and 0.69, respectively (DUKE and SILVER, 1967; McCARTHY et al, 1973, 1974).

References: (1) DUKE and SILVER (1967); (2) MASON (1974); (3) SYMES and HUTCHISON (1970); (4) LOVERING (1975); (6) McCARTHY et al (1974).

	Fe/(Fe+Mg) (pyroxene)	Fe/(Fe+Mg) (liquid, calculated)
Binda	0.32-0.36 (1,2)	0.61-0.65
Medanitos	0.42 (3)	0.71
Moama	0.42 (4)	0.71
Moore County	0.50 (1)	0.77
Serra de Magé	0.44 (1)	0.72

liquids similar in composition to Sioux County and Juvinas; (ii) the suggestion of LOVERING (1975) that Moama might be a good approximation to the bulk composition of this extract; and (iii) the suggestion of BUNCH (1976) that the eucrites similar in composition to Juvinas and Sioux County are quenched residual liquids produced by the fractionation of the phases in these cumulates from more primitive parental liquids.

A rough experimental test of these calculations may be based on the fact that the temperature at which olivine first appears in the equilibrium melting sequence of an unzoned pyroxene plus plagioclase cumulate must be an upper limit to the temperature at which the cumulate crystallized. Therefore, the experimental data on Moama (Figure 1) support the suggestion that the phases in Moama did not equilibrate with liquids similar in composition to Juvinas since the temperature at which olivine appears in the Moama melting sequence, ~1140°C, is significantly lower than the liquidus temperature of Juvinas.

In addition to these difficulties, other data suggest that the view that the cumulate eucrites crystallized from liquids similar in composition to known eucrites may need revision: (i) Although the major element chemistries of the pyroxenes in the cumulate eucrites are similar to those of experimentally produced pyroxenes, the minor element chemistries are significantly different. In particular, the Al_2O_3 content (0.47 weight percent) and Cr_2O_3 content (0.27 weight percent) of the primary pigeonite in Moama (LOVERING, 1975) are significantly lower than those found in any experimentally produced pyroxenes (Table 2). (ii) Abundances of Sr, Ba, Rb, and certain rare earth elements in a plagioclase separate from the Moore County eucrite were given by SCHNETZLER and PHILPOTTS (1969) and PHILPOTTS

and SCHNETZLER (1970a). Using the experimentally determined distribution coefficients of DRAKE and WEILL (1975) for Sr, Ba, and the rare earths and the phenocryst-matrix distribution coefficient for Rb of PHILPOTTS and SCHNETZLER (1970b), the concentrations of these elements in the liquid from which the Moore County plagioclase crystallized can be calculated. This calculation assumes that the plagioclase is homogeneous and that its composition is the same as it was when it separated from the liquid. The results of such a calculation are shown in Figure 7. These demonstrate that the composition of the liquid with which the Moore County plagioclase could have equilibrated is different from that of any known eucrite. In addition, the data of McCARTHY et al (1973) suggest that fractionation of eucritic magmas produced Sr enriched liquids. It would therefore be difficult to produce the liquid with which the Moore County plagioclase could have equilibrated, which would have had an Sr concentration lower than any known eucrite, by fractionation of liquids similar in composition to known eucrites. (iii) At 1175°C, the densities of liquids similar in composition to Juvinas would be approximately 2.8-2.9 g/cc based on the data of BOTTINGA and WEILL (1970). Plagioclase would be expected to float rather than sink in such liquids. Therefore, if these calculations are valid, they suggest that it might be difficult to produce pyroxene plus plagioclase cumulates from eucritic liquids since pyroxene would sink and plagioclase would float in these liquids.

Figure 7. The shaded region shows the range of chondrite normalized REE, Sr, Ea, and Rb abundances (weight percent) in eucrites with compositions near peritectic <u>A</u> in Figures 5 and 6 (SCHNETZLER and PHILPOTTS, 1969; PHILPOTTS and SCHNETZLER, 1970a; GAST and HUBBARD, 1970). Dots show the chondrite-normalized concentrations of these elements in the hypothetical liquid with which the plagioclase in the Moore County eucrite could have equilibrated. This was calculated from: an analysis of a plagioclase separate from Moore County (SCHNETZLER and PHILPOTTS, 1969; PHILPOTTS and SCHNETZLER, 1970a); experimentally determined plagioclase-liquid distribution coefficients for 1150° C given by DRAKE and WEILL (1975) for REE, Sr, and ^Ba; and a plagioclase-liquid distribution coefficient for ^Rb of 0.07 (PHILPOTTS and SCHNETZLER, 1970b).



C. Augite crystallization.

Most petrographic and crystallographic studies of the pyroxenes in oucrites have suggested that early-formed pyroxenes crystallized as pigeonite and reacted to varying extents into augite and orthopyroxene or clinohypersthene (DUKE and SILVER, 1967: TAKEDA et al, 1976). However, DYMEK et al (1976) have interpreted some of the augite which they observe in lithic clasts in the Kapoeta howardite as primary. Their interpretation of augite as a primary phase crystallizing along with pigeonite and plagioclase early in the crystallization sequences of eucrites and related magmas is difficult to reconcile with the results of the melting experiments. Although ferroaugite coexists with pigeonite and liquid late in the crystallization sequences of some eucrites (DUKE and SILVER, 1967), no augite was detected in any of the experiments listed in Table 2. The discussion presented below on the variation of Ca/Al ratios in eucrites and in experimental liquids, in which it is shown that the Ca/Al ratios of residual liquids increase continuously with increasing degrees of fractionation (Figure 12), is consistent with the interpretation that pigeonite was the only pyroxene present in the experiments and involved in the fractionation of actual eucrite compositions. Otherwise, a discontinuity in the Ca/Al ratio versus Ti concentration trends of experimental and natural compositions (Figure 12) would be expected if augite began to crystallize after pigeonite and plagioclase. Either the petrographic observations of DYMEK et al (1976) are invalid, or there existed a variety of liquid which had a composition unlike any eucrite which has yet been sampled and which was capable of crystallizing augite near its liquidus.

D. Spinel crystallization.

Chromian spinel is a minor but ubiquitous phase in basaltic achondrite meteorites. If the eucrites crystallized at oxygen fugacities substantially above metal-saturation; spinel would have been the sole liquidus phase. Therefore, eucritic magmas probably crystallized at oxygen fugacities near metal-saturation since: (i) spinel-rich cumulates are unknown among basaltic achondrites; and (ii) the iron-rich eucrites such as Nuevo Laredo and Lakangaon, which appear to have evolved as residual liquids produced by differentiation of more Mg-rich eucrites (see below), are not significantly depleted in Cr relative to the more primitive eucrites such as Juvinas and Sioux County. This supports the earlier conclusion that eucritic magmas evolved at fO2 levels near metal-saturation and close to lunar basalt fO₂ levels. Spinel appears virtually simultaneously with the crystalline silicate phases in the experimental crystallization sequences of eucrites at these fO_2 levels. No petrographic determination of the role of spinel in the crystallization of eucrites is yet available. However, if Binda is regarded as a cumulate from eucritic liquids, the presence of some relatively large, euhedral spinels in this meteorite is consistent with the suggestion that spinel may have been an early, though minor, phase in the crystallization of eucritic magmas.

The spinel compositions listed in Table 3 are typical of the experimentally produced spinels. Natural spinels in basaltic achondrites are generally richer in Fe and Cr and poorer in Al and Mg than these experimentally produced phases (BUNCH and KEIL, 1971). The departures of natural spinel compositions from the compositions of the experimentally produced spinels are smallest in diogenites and

mesosiderites (BUNCH and KEIL, 1971).

The differences between the natural and experimental spinel compositions may result from re-equilibration of basaltic achondrite phase assemblages during cooling. The tendency of spinels to re-equilibrate during subsolidus cooling of igneous rocks is well documented in lunar rocks (HAGGERTY, 1972). STEELE and SMITH (1976) describe features in the oxides of the Ibitira eucrite which appear to result from subsolidus re-equilibration. The rarity of zoning in eucrite pyroxenes despite textures which in lunar rocks are often accompanied by strong zoning, the prolonged thermal metamorphism and subsequent shock metamorphism inferred by STEELE and SMITH (1976) to account for some of the features of the Ibitira eucrite, and the petrographic data presented by DUKE and SILVER (1967) are consistent with a complex thermal history for these meteorites which could have resulted in extensive re-equilibration between spinels and other

E. Metal crystallization.

Although the multiple saturation arguments, the minor role of spinel in eucrite crystallization sequences, and the low levels of siderophiles in eucrites (DUKE, 1965; LAUL et al, 1972) suggest that eucritic magmas were approximately metal-saturated at near liquidus temperatures, metal does not appear to have played a major role in the crystallization sequences of the eucrites. This is suggested by the following observations: (i) petrographic observations indicate that the small amount of magmatic metal which occurs in some eucrites did not crystallize until late in the crystallization sequences of these meteorites (DUKE, 1965); (ii) the evolved eucrites such as Nuevo Laredo and Lakangaon do not appear to be significantly depleted

in siderophile elements relative to the more primitive eucrites such as Juvinas and Sioux County; (iii) Lakangaon and Nuevo Laredo have higher Fe/Mn ratios than most other eucrites (Figure 11), as opposed to the lower Fe/Mn ratios which might be expected if crystallization of metal had played a major role in their development from more primitive eucritic liquids; and (iv) although there is some question concerning the relation between those eucrites which appear to represent quenched liquids and the cumulate eucrites, the rarity of cumulus metal in the cumulate eucrites is consistent with a minor role of metal in the crystallization sequences of the liquids from which the cumulates crystallized.

BOWEN and SCHAIRER (1935) demonstrated that liquids in equilibrium with metal and olivine or pyroxene in simple synthetic systems contain some Fe^{+3} and that metal is in reaction relation with such liquids. Therefore, under conditions of constant bulk composition, metal will not crystallize from such metal-saturated liquids on cooling. The crystallization of natural liquids is complicated by the presence of cations such as Ti and Cr which can exist in several oxidation states. Also, it is unlikely that crystallization ever takes place at constant bulk composition: loss of volatiles during eruption and cooling would change the bulk composition of the magma and result in either its oxidation or reduction. Nevertheless, the probable existence of a metal-silicate reaction relation near the liquidi of the relatively Cr- and Ti-poor oucrites provides, in principle, a means of accounting for the rarity of metal crystallization from approximately metal-saturated eucritic magmas.

Equilibria involving $Ti^{+3}-Ti^{+4}$ and $Cr^{+2}-Cr^{+3}$ may have been responsible for the crystallization of metal late in eucrite

crystallization sequences (BRETT et al, 1971). Alternatively, the reducing effects of progressive loss of volatiles such as sulfur (GIBSON and MOORE, 1974; BRETT, 1976) or oxygen (O'HARA et al, 1970) during crystallization could have resulted in late-stage metal precipitation.

F. Fragment Rho

DYMEK et al (1976) concluded on the basis of textural evidence that "fragment <u>Rho</u>", an unusual lithic fragment from the Kapoeta howardite, represents a quenched liquid. If this conclusion is valid, the composition of <u>Rho</u> could place important constraints on basalt genesis on the Kapoeta parent body since it is significantly more magnesian and chromian than any of the known eucrites which are believed to represent quenched liquids. However, several aspects of the composition and mineralogy of this fragment suggest that it does not represent a quenched liquid.

If pyroxene were on the liquidus of <u>Rho</u>, as DYMEK et al contend (although the location of <u>Rho</u> in Figure 5 suggests that olivine would be the first silicate to crystallize from a liquid with the composition of <u>Rho</u>), the first pyroxene to crystallize would have a molar Fe/(Fe+Mg) ratio of ~0.24 based on an Fe/Mg distribution coefficient of 0.30 (Table 4). Yet the most magnesian pyroxene reported from <u>Rho</u> has an Fe/(Fe+Mg) ratio of ~0.4. Rapid cooling rates, resulting in delayed pyroxene nucleation, can produce porphyritic rocks in which the most magnesian pyroxenes are more iron-rich than those produced in equilibrium experiments (LOFGREN et al, 1974). LOFGREN et al (1974) studied the crystallization of an average Apollo 15 quartz normative basalt composition at a variety of cooling rates. The composition which they studied was similar to Rho

in its major element chemistry. These experiments demonstrate that there are no conditions at which a liquid of the composition of <u>Rho</u> will crystallize core pigeonites as iron-rich as those found in <u>Rho</u>. Hence, it is difficult to reconcile the phase chemistry of <u>Rho</u> with that of a quenched liquid as suggested by DYMEK et al (1976).

The discrepancy between the composition of the most magnesian core pigeonite in <u>Rho</u> and the composition of the pigeonite expected near the liquidus of <u>Rho</u> suggests that fragment <u>Rho</u> may contain some cumulus pyroxene (GREEN et al, 1971). The textural evidence on which DYMEK et al (1976) base their conclusion that <u>Rho</u> is a quenched liquid is ambiguous. The specimen is porphyritic and the distinction between a quenched liquid and a sample containing up to 20-30 percent cumulus phenocrysts is subjective.

This line of reasoning does not imply that the bulk composition of Rho resulted from a concentration of pyroxene produced by differential movement of crystals and liquid in a gravitational field. More properly, this argument implies that there is an excess of pyroxene in the small thin section (15 square millimeters) on which the bulk composition of Rho is based, over the composition of the liquid from which the pyroxenes in Rho crystallized. This excess could be due to accumulation of pyroxenes or poor sampling due to heterogeneities in the proportions of phases in different regions of the flow from which Rho originated. The heterogeneities in lunar rock 70215 reported by WALKER et al (1976a) show that even large samples of a quenched liquid may, due to heterogeneous distribution of phases or complex diffusion processes, be unrepresentative of the liquid composition itself. Alternatively, there may be problems with the technique used by DYMEK et al (1976) to estimate the composition of Rho.

An alternative interpretation of fragment Rho is suggested by the observation that its most magnesian core pigeonites are similar in composition to the pyroxenes expected near the liquidus of an Feand Ti-rich eucrite such as Nuevo Laredo. Rapid cooling of a liquid similar in composition to Nuevo Laredo would produce a rock with a texture and core pigeonite compositions similar to those found in Rho. The delayed nucleation of plagioclase in Rho inferred by DYMEK et al (1976) could have been due to the rapid cooling rate (WALKER et al, 1976b). Either slight settling of pyroxene and spinel phenocrysts or a heterogeneous distribution of these phases in the quenched liquid could then have produced small Mg- and Cr-rich regions such as Rho containing an excess of pyroxene and chromite over the bulk composition of the Nuevo Laredo-like liquid. According to this interpretation, instead of providing information concerning the compositions of liquids more magnesian and hence more primitive than the common eucrites as suggested by DYMEK et al (1976), the phases in Rho would have crystallized from a liquid similar in composition to Nuevo Laredo which was more iron-rich than most eucrites.

VI. PRIMARY AND DERIVATIVE MAGMAS

"Primary" magmas are magmas whose compositions have not been modified since separation from the source regions in which they were produced by melting. These magmas are of special interest in igneous petrology since they provide direct evidence relating to the mineralogies and compositions of the source regions of magmas and the nature of igneous processes in these source regions. Hence, one of the most fundamental problems facing the igneous petrologist is the discrimination of primary magmas from magmas whose compositions have been modified since separation from their source regions. No generally applicable criteria have yet been developed for recognizing primary magmas, and for this reason, identification of primary magmas has long been one of the most difficult and controversial problems in igneous petrology.

One feature of the mineralogy of basaltic achondrites has dominated considerations of the petrogenesis of these meteorites and the identification of primary and differentiated liquid compositions among these meteorites: The pyroxenes in diogenites and the most magnesian pyroxenes in the polymict howardite and mesosiderite breecias are significantly more magnesian than the pyroxenes which crystallize near the liquidi of the eucrites with compositions near peritectic <u>A</u> (Figures 5 and 6). This is demonstrated in Figure 4 where the compositions of diogenite and howardite pyroxenes are plotted with the compositions of pyroxenes produced in melting experiments on the Juvinas and Sioux County eucrites. If one accepts, as nearly all researchers have done, that all of these meteorites developed in a single igneous "province" on a single body or on a group of closely related bodies, then the existence of phases

more magnesian than those which could have crystallized from eucritic liquids suggests that liquids more magnesian than eucrites but closely related to the eucrites must have existed.

The requirement that liquids more magnesian than the Juvinas and Sioux County eucrites must have existed has led to a remarkable uniformity of opinion on the general features of the petrogenesis of igneous rocks on the basaltic achondrite parent body: Highly magnesian liquids were produced by either partial or total melting in some source regions. Phases at least as magnesian as the most magnesian pyroxenes and olivines found in basaltic achondrites crystallized from these liquids. Crystallization of pyroxene and perhaps minor olivine, metal, and spinel from these liquids resulted in pyroxene-rich cumulates and fractionated liquids with a variety of Fe/(Fe+Mg) ratios. The magnesian phases found in mesosiderites, howardites, and diogenites are the phases crystallized from these primary liquids and their derivatives. Liquids similar in composition to the Sicux County and Juvinas eucrites were late-stage; highly fractionated residual liquids produced by the differentiation of these phases from the primary liquids. According to this model, the compositions of all known eucrites are far removed from primary liquid compositions and provide little information on the nature of the primary liquids or their source regions. Models along these lines have been developed by a number of authors (MASON, 1962, 1967; MOORE, 1962; DUKE and SILVER, 1967; SCHNETZLER and PHILPOTTS, 1969; McCARTHY et al, 1973; REID, 1974; SHIMIZU and ALLEGRE, 1975; BUNCH, 1975, 1976; DYMEK et al, 1976).

The existence of liquids more magnesian than the Sioux County and Juvinas eucrites does not, however, require that these and the other eucrites with compositions near peritectic <u>A</u> (Figures 5 and 6)

are the fractionated derivatives of the more magnesian liquids. Nor does it imply that eucritic liquids cannot be primary. If eucritic liquids were produced by partial melting of some source region, increasing degrees of partial melting of this same source region would lead to melts with lower Fe/(Fe+Mg) ratios. Hence, intermittent or continuous tapping of melts from a single source region could produce a range of primary magma compositions varying from the relatively iron-rich eucritic compositions to compositions magnesian enough to crystallize the most magnesian phases in howardites and mesosiderites. Crystallization and accumulation of phases from these magmas could lead to a sequence of cumulates with variable Fe/(Fe+Mg) ratios similar to the phases in howardites and mesosiderites. Only GAST and HUBBARD (1970) and RINGWOOD (1970) seem to have seriously considered the possibility that eucritic liquids were not highly differentiated residual liquids. Although these authors clearly recognized the possibility that eucritic liquids may have been primary, their main concorn was the genesis of lunar basalts and the eucrites were only briefly mentioned with no attempt being made to present detailed models.

In the remainder of this paper, a number of aspects of the phase equilibria and major and minor element chemistry of eucrites with compositions near peritectic \underline{A} (Figures 5 and 6) are examined in an attempt to establish the importance of partial melting and crystallization differentiation processes in the evolutions of these meteorites. A general pattern emerges from these considerations: both partial melting and crystallization differentiation probably played important roles in the genesis of these eucrites and the other basaltic achondrites. However, most of these eucrites appear to have been produced by the quenching of nearly primary liquids and models

which produce eucritic compositions by extensive fractionation of magnesian liquids are unsatisfactory. A model is presented to explain the phase equilibria of eucrites and the detailed chemical and mineralogical relationships between the individual eucrites and between the other basaltic achondrites. This model involves variable amounts of differentiation of a range of primary magmas produced by variable degrees of partial melting of a single type of source region. It could be argued that it is pointless to explain the detailed chemical differences between eucrites with such a model when there are so few eucrites and when there is no concrete evidence that they are even distantly related, let alone that they come from a single parent body. Clearly, alternative models which attribute chemical differences between eucrites to variable source region chemistry or to derivation from different planets are possible. Nevertheless, the model presented, which relates all of the eucrites and the other basaltic achondrites to melts derived from a single type of source region, does make specific predictions, and can thus be tested. Only when models such as this can no longer be developed should models invoking unverifiable factors such as source region variability be seriously considered.

VII. PHASE EQUILIBRIA

The multiply saturated condition of the liquidi of the eucrites which plot near peritectic <u>A</u> in Figures 5 and 6 is consistent with an origin of these eucrites as liquids produced either by low pressure fractionation of olivine, pyroxene, plagioclase, spinel, and metal from some parental liquid or by low pressure partial melting of an assemblage consisting of these five phases. However, since olivine is in reaction relation with such liquids under these conditions, there are restrictions on the ways in which the eucrites can have developed into this multiply saturated condition. These restrictions are most easily understood with the aid of the pseudo-liquidus diagram shown in Figure 8.

A. Crystallization differentiation.

The model of eucrite genesis originally proposed by MASON (1962) in which the eucrites are interpreted as residual liquids resulting from extensive fractional crystallization of magnesian parental liquids is illustrated in Figure 8 by the liquid path <u>P-Q-R-B</u>. A parental magma such as <u>P</u> begins differentiation by crystallizing olivine. Accumulation of this olivine may have produced the pallasites. The residual liquid becomes pyroxene-saturated at <u>Q</u> when it reaches the olivine + pyroxene boundary curve. Because olivine is in reaction relation with the liquid on this boundary, olivine is removed from the crystallization sequence at <u>Q</u>. During further fractional crystallization, the liquid crystallizes only pyroxene and changes along the path <u>Q-R</u>. At <u>R</u>, the residual liquid begins to crystallize plagioclase. Further fractional crystallization of the residual liquids at <u>R</u> results in liquids between R and <u>B</u>.

Figure 8. Schematic pseudo-liquidus diagram for basaltic achondrite compositions. Projection as in Figure 5. The liquid path AB, taken from Figure 5, is the path followed by residual liquids produced by equilibrium crystallization of pyroxene and plagioclase from liquids at <u>A</u>, with $F_{\Theta}/(F_{\Theta}+M_g)[molar]=0.60$. The $F_{\Theta}/(F_{\Theta}+M_g)$ ratios of these residual liquids increase continuously from <u>A</u> to <u>B</u>. These liquids become saturated with a silica polymorph at <u>B</u>. The shaded region around peritectic A shows the projected locations of "non-cumulate" eucrites. The path CA is the path along which undersaturated liquids such as \underline{P} could produce residual liquids similar in composition to the eucrites at \underline{A} by equilibrium crystallization of pyroxene and resorption of olivine. The $F_{e/(Fe+Mg)}$ ratios of liquids on CA increase continuously from C to A. This path is based on the compositions of multiply saturated liquids produced in experiments on the Binda eucrite (Table 3). The path Q A is the path along which liquids such as P and P' can produce residual liquids similar in composition to the eucrites at A by fractional crystallization of olivine and plagioclase. The Fe/(Fe+Mg) ratios of liquids on $\underline{Q'A}$ increase continuously from $\underline{Q'}$ to \underline{A} .



One difficulty of this model as it is stated is that after the liquid becomes pyroxene-saturated at \underline{Q} , the path of residual liquids moves away from olivine-saturation, making it difficult to produce late-stage liquids similar in composition to the eucrites near peritectic A. The only ways in which liquids at A could be produced by fractional crystallization at low pressure is from liquids such as <u>P</u> along a path such as $\underline{P}'-\underline{Q}'-\underline{A}$ or from liquids such as \underline{P}'' along a path such as $\underline{P}' \underline{Q}' - \underline{A}$. Generation of eucritic liquids along these paths would not be consistent with: (i) the rarity of olivine in basaltic achondrites; (ii) the rarity of cumulates containing plagioclase without pyroxene among basaltic achondrites; (iii) the flat rare earth patterns of some of the eucrites with compositions near A (SCHNETZLER and PHILPOTTS, 1969) which suggest that they could not have evolved by significant fractionation of plagioclase from parental liquids; and (iv) the existence of howardite, diogenite, and mesosiderite pyroxenes more magnesian than those crystallizing near the liquidi of eucrites near peritectic A.

Polybaric fractionation of olivine and pyroxene from a liquid such as <u>P</u> could produce liquids at <u>A</u> (O[°]HARA, 1963). However, such processes were probably unimportant in the genesis of eucritic compositions in view of: (i) the small size usually inferred for the eucrite parent body; (ii) the rarity of olivine in the basaltic achondrites; and (iii) the absence of any indications of high pressure crystallization in the magnesian pyroxenes in howardites, diogenites, and mesosiderites.

The compositions of residual liquids produced by fractionation of <u>P</u> change continuously during fractional crystallization, never pausing at any one composition. Hence it would be difficult for a differentiation process such as that proposed by MASON (1962,1967) to

produce a cluster of liquid compositions as tight as the eucrites unless some tectonic control existed which caused eruption or cessation of fractionation after exactly the same degree of fractionation in the derivation of all eucritic liquids.

During equilibrium crystallization of a liquid at P, the residual liquid follows the path P-Q-A. Along this path, the composition of the residual liquid pauses at peritectic \underline{A} while the liquid reacts away completely. Therefore, in contrast to the fractional crystallization process outlined above, equilibrium crystallization of <u>P</u> could produce residual liquids at <u>A</u>. However, it is unlikely that the delicate chemical and mechanical balance required by equilibrium crystallization could ever be achieved in nature. Indeed, the existence of diogenites, the pyroxenes in howardites and mesosiderites, and the cumulate eucrites clearly demonstrate that phases were quite free to separate from their parental liquids during cooling. Liquids at A could also be produced by imperfect fractional crystallization of a liquid at P if olivine were prevented from separating from the fractionating liquid. However, it is unlikely that olivines were somehow prevented from settling out of liquids along $\underline{P-Q-A}$ while pyroxenes were free to do 80.

BUNCH (1976) proposed a model similar to that of MASON (1962,1967) only he further suggested that eucritic liquids were residual liquids produced by fractionation of the pyroxenes and plagioclases in cumulates such as Moama, Moore County, and Serra de Magé from more primitive magnesian liquids. This model is particularly difficult to reconcile with the observed features of eucrites since substantial fractionation of pyroxene and plagioclase from liquids at <u>R</u> (Figure 8) would result in liquids even more

silica-oversaturated and further removed from olivine-saturation than the liquids at <u>R</u>. Also, it is difficult to reconcile the flat rare earth pattern of the Juvinas eucrite with its generation as a residual liquid produced by extensive fractionation of pyroxene and plagioclase from more primitive liquids unless these primitive liquids had positive europium anomalies. As mentioned above, the pyroxenes in Moama, Moore County, and Serra de Magé appear to have crystallized from liquids more iron-rich than known eucrites. Therefore, it is unlikely that liquids similar in composition to the eucrites near peritectic <u>A</u> evolved by fractionation of the phases in these cumulate eucrites from other liquids.

B. Partial melting.

In contrast to the difficulties encountered by these crystallization differentiation models of eucrite genesis, models in which the eucrites with compositions near peritectic \underline{A} are viewed as quenched primary magmas or liquids developed by only minor fractionation of primary magmas have little difficulty in accounting for the main features of the phase chemistry and compositions of basaltic achondrites. Consider the low pressure melting of an olivine + pyroxene + plagioclase + spinel + metal assemblage. The compositions of liquids produced by this melting would be at peritectic A in Figure 8 and would remain at peritectic A with the continuous addition of heat to the source region until either pyroxene or plagioclase were exhausted from the residue. Therefore, partial melting provides a means of producing liquids similar in composition to the eucrites whose compositions are tightly clustered at A.

Under conditions of fractional fusion, where liquid is

continuously separated from the source as it is generated by melting (PRESNALL, 1969), the generation of liquid by further addition of heat to the source region would be nearly halted after pyroxene or plagioclase were exhausted from the residue. Under conditions of equilibrium fusion or imperfect fractional fusion, if plagioclase were the first phase exhausted from the source assemblage during melting, further addition of heat to the source region would result in melts moving from A to C on the olivine + pyroxene boundary curve (Figure 8), continuously decreasing in Fe/(Fe+Mg) ratio. When pyroxene becomes exhausted from the source assemblage, say at Q, the composition of the melt would leave the curve AC and move back towards the olivine corner. Each of the melts from A to Q would be olivine-saturated, but as pointed out in the discussion of eucrite crystallization sequences, pyroxene would be the only ferromagnesian silicate to crystallize from these liquids because of the olivine-liquid reaction relation. Hence, this partial melting model provides, in principle, a means of producing liquids which could crystallize the range of pyroxene compositions found in howardites, mesosiderites, diogenites, and eucrites by variable degrees of partial melting of a single type of source region. This model also accounts for the rarity of olivine in these meteorites. The occasional olivine in basaltic achondrites could be due to a slight drop in pressure between the source regions and environments of crystallization of this range of primary magmas or from crystallization of the liquids produced by further melting after the exhaustion of pyroxene from the source regions.

Therefore, from the point of view of phase equilibria, the fractionation model of eucrite genesis first proposed by MASON (1962) and subsequently restated by many authors is difficult to reconcile

with the clustering of eucrite compositions at any point, least of all at peritectic <u>A</u>, without the introduction of restrictions which do not appear to be consistent with the mineralogy of the basaltic achondrites. On the other hand, the partial melting model outlined above is consistent with the clustering of eucrite compositions at peritectic <u>A</u> and the dominance of pyroxene in the crystallization of liquids more magnesian than the eucrites at <u>A</u>.

A. Incompatible elements.

When considered with major element chemistry, minor element abundance patterns can be sensitive indicators of the degree and mechanism of differentiation of a suite of igneous rocks. SCHNETZLER and PHILPOTTS (1969) and McCARTHY et al (1973) suggested on the basis of incompatible element distributions in eucrites that crystallization and separation of pyroxene and plagioclase from liquids similar in composition to Haraiya and Juvinas produced a sequence of differentiated liquids with variable enrichments of incompatible elements. The composition of Stannern, the eucrite with the highest concentrations of nearly all incompatible elements and a negative europium anomaly in its rare earth pattern, was regarded as an example of the composition of a highly differentiated liquid. Based on similar minor element data, GAST and HUBBARD (1970) and RINGWOOD (1970) suggested that the Stannern - Nuevo Laredo -Pasamonte - Juvinas sequence was produced by increasing degrees of partial melting of a single source. Consideration of both major and minor element chemistry reveals that neither of the above models are entirely valid and that both partial melting and crystal fractionation processes probably played important roles in the development of these meteoritic basalts.

(i) Crystallization differentiation.

The Ti concentrations of the eucrites with compositions near peritectic <u>A</u> are plotted against their Fe/(Fe+Mg) ratios in Figure 9. The Ti concentrations and Fe/(Fe+Mg) ratios of liquids produced in melting experiments on the Juvinas and Sioux County eucrites are also

Figure 9. Relationship between Ti concentration and Fe/(Fe+Mg) ratio in eucrites with compositions near peritectic <u>A</u> in Figures 5 and 6 (shown as asterisks, sources of data and abbreviations as in Figures 5 and 6) and in liquids produced in melting experiments on the Sioux County eucrite (filled circles) and on the Juvinas eucrite (open circles). The number adjacent to each experimental liquid data point is the calculated percentage crystallinity of the experiment (calculated as in Figure 3). The trend of experimentally produced liquids defines the trend of Ti concentrations and Fe/(Fe+Mg) ratios expected in liquids produced by crystallization differentiation of liquids similar in composition to Sioux County and Juvinas.



Fe/(Fe+Mg) molar

plotted in Figure 9. The trend of experimental liquids in Figure 9 indicates that incompatible element enrichments in residual liquids produced by crystallization of pyroxene and plagioclase from liquids similar in composition to Sioux County and Juvinas are accompanied by increases in the Fe/(Fe+Mg) ratios of the liquids. Neglecting Stannern and Ibitira, there is a positive correlation between the Fe/(Fe+Mg) ratios and Ti concentrations of natural eucrites which is similar to the experimental liquid line of descent of the Juvinas and Sioux County compositions. This suggests that these sucrites were produced by quenching of a series of liquids produced by low pressure crystallization differentiation of liquids with compositions similar to Sioux County. These eucrites can be placed in a sequence of increasing degree of fractionation: Sioux County, Juvinas + Cachari, Pasamonte + Béréba + Millbillillie, Nuevo Laredo + Lakangaon. Although complete data are not available for some of these eucrites, the increases in Ti concentration and Fe/(Fe+Mg) ratio observed in this sequence are paralleled by increases in other incompatible elements; for example, the rare earths (SCHNETZLER and PHILPOTTS, 1969; GAST and HUBBARD, 1970), K, Na, Rb, Cs, Ba, Sr, and Zr (TERA et al, 1970; LAUL et al, 1972; McCARTHY et al, 1973).

If zirconium is assumed to be a perfectly incompatible element, zirconium concentrations in eucrites (SCHMITT et al, 1964; McCARTHY et al, 1973) can be used to estimate the percentages of crystallization of liquids similar in composition to Sioux County which could have produced residual liquids similar in composition to other eucrites. Independent estimates of these percentages can be based on the crystallinities of the products of melting experiments on the Sioux County eucrite in which the Fe/(Fe+Mg) ratios and Ti concentrations of the experimental liquids are similar to those of

other eucrites (Figure 9). On these bases, it can be estimated that: (i) approximately 30-40% crystallization of liquids similar in composition to Sioux County could have produced residual liquids similar in composition to Nuevo Laredo and Lakangaon; (ii) less than 10-20% crystallization differentiation of a liquid similar in composition to Sioux County could have produced a liquid similar in composition to Sioux County could have produced a liquid similar in composition to the Pasamonte eucrite; (iii) less than 5-10% crystallization of a liquid similar in composition to Sioux County could have produced the Cachari and Juvinas compositions. If this model is correct, the gap between Millbillillie and Nuevo Laredo and Lakangaon in Figure 9 reflects the poor sampling of eucrites available to us rather than a real gap in permissible compositions of eucritic liquids.

In addition to an increase in Fe/(Fe+Mg) ratio, other variations in major element chemistry would be expected from Sioux County to Nuevo Laredo if this is a low pressure differentiation sequence. The variation in Ca/Al ratio is discussed below. Figure 8 illustrates that during crystallization of pyroxene and plagioclase from a liquid at peritectic <u>A</u>, the liquid composition moves on the pyroxene + plagioclase cotectic towards the eutectic-like point <u>B</u>. Figures 5 and 6 show that, as expected, Nuevo Laredo and Lakangaon project at higher silica levels than other known eucrites. The effects of the smaller amounts of fractionation involved in generating the Pasamonte, Bereba, and Millbillillie eucrites cannot be distinguished in the projections of the compositions of these eucrites into these diagrams.

The liquidus temperatures determined in this study tend to decrease with increasing level of fractionation from Sioux County to Lakangaon (Figure 10). This is expected in a series of liquids
Figure 10. Relationship between liquidus temperature and Ti concentration in eucrites with compositions near peritectic A (Figures 5 and 6) and in experimentally produced liquids. Asterisks give the liquidus temperatures of eucrites determined in this study (sources of Ti data and abbreviations as in Figures 5 and 6). The lines extending down from the asterisks extend from the liquidus temperature to the temperature at which the composition studied is saturated with plagioclase, pigeonite, ±olivine. The circles show the Ti concentrations of liquids produced in melting experiments on the Sioux County (filled circles) and Juvinas (open circles) eucrites and the temperatures of the experiments. These experimental liquid points define the relationship between Ti concentration and liquidus temperature expected in liquids produced by crystallization differentiation of liquids similar in composition to Sioux County and Juvinas. Note that of the compositions studied, only Stannern, Ibitira, and perhaps Jonzac are displaced from the experimentally defined trend and that the liquidus temperature of Lakangaon is similar to that expected in a differentiated liquid.



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related by crystal fractionation.

The Fe Mn distribution coefficient between pigeonite and liquid of 0.88 determined in this study suggests that the Fe/Mn ratios of . residual liquids produced by fractionation of pigeonite and plagioclase should increase slightly with increasing fractionation. The Fe/Mg ratios of eucrites are plotted against their Fe/Mn ratios in Figure 11. There may be a positive correlation between the Fe/Mg and Fe/Mn ratios. This is consistent with the conclusion that the Nuevo Laredo and Lakangaon compositions were produced by fractionation of pyroxene and plagioclase from liquids similar in composition to Sioux County. It is of interest to note from Figure 11 that the constancy of Fe/Mn ratio observed in lunar rocks (SCHMITT and LAUL, 1973) is not observed in the basaltic achondrites. This suggests that assumptions of constancy of the Fe/Mn ratio during igneous processes employed in calculations of the bulk compositions of planets (GANAPATHY and ANDERS, 1974; WANKE et al, 1974) should be viewed with caution.

(ii) Stannern and Ibitira.

The Ibitira and Stannern eucrites do not plot near the fractionation trend followed by the other eucrites on the Ti concentration versus Fe/(Fe+Mg) ratio diagram (Figure 9). Neither Stannern, with the highest concentrations of nearly all incompatible elements, nor Ibitira, with incompatible element enrichments intermediate between Stannern and Sioux County, has the increased Fe/(Fe+Mg) ratio expected if these enrichments resulted from fractionation of pyroxene and plagioclase from liquids similar in composition to Sioux County and Juvinas. Stannern and Ibitira plot with the unfractionated eucrites in Figures 5 and 6 and do not show

Figure 11. Relationship between Fe/Mg and Fe/Mn ratios in monomict basaltic achondrites. Filled circles are eucrites with compositions near peritectic <u>A</u> (Figures 5 and 6). Open circles are cumulate eucrites. Filled squares are diogenites. Sources of eucrite data and abbreviations as in Figures 5 and 6. Diogenite abbreviations are: El=Ellemeet, Jn=Johnstown, Ma=Manegaon, Sh=Shalka, and Ta=Tatahouine. Dicgenite data from McCARTHY et al (1972,1974) and MASON and JAROSEWICH (1971).



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the silica enrichment found in Nuevo Laredo and Lakangaon and expected in fractionated liquid compositions. In contrast to Nuevo Laredo and Lakangaon, which have higher Fe/Mn ratios than Sioux County and Juvinas, Stannern has an Fe/Mn ratio similar to the unfractionated eucrites (Figure 11). The Fe/Mn ratio of Ibitira is, however, slightly higher than that of Nuevo Laredo. The liquidus temperature of Stannern, though lower than those of Sioux County and Juvinas, is not as low as expected in an extensively fractionated eucrite such as Lakangaon (Figure 10). These factors all suggest that models such as those of McCARTHY et al (1973) and SCHNETZLER and PHILPOTTS (1969) in which the enrichments of incompatible elements and the negative europium anomaly of Stannern are produced by substantial amounts of low pressure fractionation of pyroxene and plagioclase from a liquid similar in composition to Juvinas or Sioux County are incorrect and that alternative explanations of the compositions of the Ibitira and Stannern eucrites are necessary.

McCARTHY et al (1973) noted that extraction of pyroxene and plagioclase from a liquid similar in composition to Juvinas in quantities sufficient to produce the incompatible element enrichments observed in Stannern would result in an extremely iron-rich liquid. They suggested that cumulates more iron-rich than Moore County and Serra de Magé may have separated from primitive liquids, producing residual liquids enriched in incompatible elements but not in Fe/(Fe+Mg) ratio. Such cumulates would need Fe/(Fe+Mg) ratios similar to the liquids from which they crystallized in order to produce residual liquids similar in composition to Stannern and Ibitira with Fe/(Fe+Mg) ratios as low as the primitive liquids. If a phase with an Fe/(Fe+Mg) ratio greater than the liquid fractionated along with pyroxene and plagioclase, this could have produced

incompatible element enrichments in the residual liquids without increasing their Fe/(Fe+Mg) ratios. Only phases near the liquidi of the Ibitira and Stannern compositions could have been involved in this fractionation. Spinel and metal both have higher Fe/Mg ratios than the liquids from which they crystallize and substantial crystallization of these phases could, in principle, have kept the Fe/(Fe+Mg) ratios of fractionated liquids from increasing along with incompatible element concentrations. Significant spinel fractionation can be ruled out because the Cr concentrations of Stannern and Ibitira are not depleted relative to Lakangaon and Nuevo Laredo (data in DUKE and SILVER, 1967; McCARTHY et al, 1973,1974; WANKE et al, 1974). Metal fractionation can also be ruled out because siderophile elements (especially Au, which does not appear to fractionate between crystalline silicates and silicate melts) are not depleted in Stannern and Ibitira relative to the other eucrites (data in LAUL et al, 1972; SCHMITT et al, 1972; McCARTHY et al, 1973; WANKE et al, 1974; HIGUCHI and MORGAN, 1975; CHOU et al, 1976). Also, since Mn is lithophile at the fO2 levels relevant to eucrite crystallization, extensive fractionation of metal might lower the Fe/Mn ratios of residual liquids. Figure 10 shows that the Fe/Mn ratios of Stannern and Ibitira are not lower than those of the unfractionated eucrites.

Although the compositional differences between the Stannern, Ibitira, and Sioux County eucrites cannot be easily explained by crystallization differentiation processes, they are similar to the compositional variations expected in a sequence of liquids produced by increasing, but small, degrees of partial melting of a single source (RINGWOOD, 1970). If liquid <u>M</u> is produced by X% melting of some source and liquid <u>N</u> is produced by 2X% melting of the same

source, the concentrations of perfectly incompatible elements in M are twice the concentrations in N. If X is small and the mineralogy of the source is unchanged between X and 2X percent melting and can buffer the major element chemistry of the melt, the decreasing concentrations of incompatible elements from M to N are accompanied by negligible changes in the major element chemistry of the melt (including the Fe/(Fe+Mg) ratio). Such variability in trace element chemistry coupled with relative constancy of major element chemistry, especially Fe/(Fe+Mg) ratio, is precisely what is found in the Stannern - Ibitira - Sioux County sequence. GAST and HUBBARD (1970) and RINGWOOD (1970) suggested this type of model to explain the decrease in incompatible elements in the sequence Stannern - Nuevo Laredo - Pasamonte - Juvinas. However, as discussed earlier, the composition of Nuevo Laredo was probably considerably modified by low pressure differentiation. The same may be true, though to a lesser extent, of Pasamonte. If zirconium and uranium are assumed to be perfectly incompatible elements, their concentrations in Stannern and Sioux County (McCARTHY et al, 1973; MORGAN and LOVERING, 1973) can be used to estimate that if a liquid similar in composition to Stannern was produced by X% melting, a Sioux County-like melt could have been produced by 2.0-2.5X% melting of the same source. The position of Haraiya in Figure 9 could indicate that its composition represents that of a liquid produced by small amounts of fractionation of a liquid generated by a greater degree of melting than that which produced the Sioux County composition.

One restriction on this type of partial melting model is that the degree of partial melting involved in the generation of the Stannern and Sioux County compositions must have been small. Just what is meant by "small" degrees of partial melting? Intuitively,

there might be some difficulty in separating melt from a source region at the 1% melting level. Five or 10 percent melting is probably the lower limit on the degree of melting at which liquid could be separated from the solid residue. However, although simplifying the problem of separating the melt from the residue, larger degrees of partial melting increase the variation in the Fe/(Fe+Mg) ratios of melts produced between X and 2.5X percent melting. In order to establish the absolute degrees of partial melting needed to produce the trace element characteristics of the different eucritic compositions, it is necessary to assume a bulk composition and mineralogy of the source and solid-liquid distribution coefficients for the elements being modelled. On the basis of an assumed source of olivine + clinopyroxene + orthopyroxene + plagioclase with a chondritic rare earth pattern, GAST and HUBBARD (1970) showed that liquids with rare earth element concentrations similar to Stannern could have been produced by approximately 6% melting of such a source; liquids with rare earth element concentrations similar to Juvinas could have been produced by about 14% melting. Compositions similar to Sioux County could presumably have been generated by slightly greater degrees of melting since the incompatible element concentrations of Sioux County are lower than those of Juvinas. The proportion of plagioclase in the hypothetical source would have to be smaller than the value chosen by GAST and HUBBARD (1970) (25%) in order to account for the absence of a europium anomaly in Juvinas. However, this calculation demonstrates that the degrees of partial melting needed to produce liquids with trace element characteristics similar to Sioux County and Stannern from a reasonable source are not unrealistically large or small. However, even at these levels of partial melting a slight, but

noticeable, decrease in the Fe/(Fe+Mg) ratios of the melts might be expected with increasing degrees of melting. A slight increase in Fe/(Fe+Mg) ratio is indeed observed from Sioux County to Stannern (Figure 9).

B. Ca/Al ratios.

According to AHRENS(1970), the Ca/Al ratios in chondrites, howardites, and eucrites are nearly constant at 1.08. The constant ratio of these two elements in chondrites reflects their geochemical similarities in the processes which produced these meteorites. However, in view of the ease with which Ca and Al can be fractionated from each other during igneous processes, such coherence of Ca and Al would be remarkable in a suite of igneous rocks such as the basaltic achondrites and would provide rigid constraints on petrogenetic models if it occurred. Examination of modern analyses of the eucrites demonstrates that, although small, the variations in Ca/Al ratio between eucrites are not negligible and do not simply reflect uncertainties in the analytical data. The patterns of Ca/Al ratio variations in these meteorites provide important data on their origins and inter-relationships.

The Ca/Al ratios of eucrites with compositions near peritectic <u>A</u> (Figures 5 and 6) are plotted against their Ti concentrations in Figure 12. There is a positive correlation between Ti concentration and Ca/Al ratio in these eucrites. Figure 12 also shows that the relationship between Ti concentration and Ca/Al ratio in the liquids produced in melting experiments on the Juvinas and Sioux County eucrites is similar to that observed in actual eucrites. The correspondence between the Ti concentrations and Ca/Al ratios of Nuevo Laredo and Lakangaon and evolved experimental liquids supports

Figure 12. Relationship between Ti concentration and Ca/Al ratio in eucrites with compositions near peritectic <u>A</u> in Figures 5 and 6 (shown as asterisks, sources of data and abbreviations as in Figures 5 and 6) and in liquids produced in experiments on the Sioux County (filled circles) and Juvinas (open circles) eucrites. The experimentally produced liquids define the relationship between Ti concentration and Ca/Al ratio expected in liquids produced by orystallization differentiation of liquids similar in composition to Sioux County and Juvinas.



the earlier suggestion that these two eucrites represent quenched liquids whose compositions were produced by low pressure fractionation of pigeonite and plagioclase from liquids similar in composition to Juvinas and Sioux County. The continuous increase in Ca/Al ratio with fractionation in natural and experimental liquids suggests, as mentioned above, that augite was not involved in the early portions of eucrite crystallization sequences.

Although the high levels of incompatible elements, the Ca/Al ratios, and the Fe/(Fe+Mg) ratios in Nuevo Laredo and Lakangaon can be produced by differentiation, it was argued previously that the increases in incompatible elements from Sioux County to Stannern are inconsistent with such a differentiation sequence because they are not accompanied by a significant increase in the Fe/(Fe+Mg) ratio. Can the high Ca/Al ratios in Stannern and Ibitira (Figure 12) be explained by the partial melting processes which can explain the incompatible element enrichments of these meteorites? The 1 atmosphere liquidus diagram for olivine-saturated equilibria in the system CaO-MgO-FeO-Al₂O₃-SiO₂ at Fe/(Fe+Mg) [molar] = 0.60 and at oxygen fugacities near the iron-wustite buffer (HUMPHRIES, 1975) demonstrates that the Ca/Al ratios of liquids generated by melting of an olivine + pigeonite + plagioclase assemblage will decrease with increasing degrees of partial melting until either pyroxene or plagioclase is exhausted from the source. Therefore, the decrease in Ca/Al ratio observed from Stannern to Sioux County is consistent with a partial melting sequence since in the early stages of partial molting, before pyroxene or plagioclase has been exhausted from a source region, the Ca/Al ratios of the melts will decrease along with the concentrations of incompatible elements with increasing degrees of partial melting.

C. Siderophile elements.

The low levels of siderophile elements and of Ni in particular in eucrites and eucrite metal led DUKE (1965) to suggest that eucritic magmas or the magmas from which they differentiated had equilibrated with a metal phase. LAUL et al (1972) and KIMURA et al (1974) pointed out that although siderophile element concentrations in eucrites are indeed low, Ni is depleted in these meteorites relative to Au (relative to their cosmic abundances). It is unlikely that this Ni-Au fractionation is due to metal fractionation since the metal-silicate distribution coefficient for Au is significantly higher than that for Ni. Both the generally low levels of siderophile elements and the Ni-Au fractionation in eucrites can be qualitatively explained by a partial melting model if both olivine and metal were present in the source regions of eucritic liquids, since olivine concentrates Ni but not Au over the liquid phase (LEEMAN, 1973; KIMURA et al, 1974). Low calcium pyroxenes in the source regions would also concentrate Ni over the melt (D. LINDSTROM, cited by DRAKE, 1976), contributing to the depletion of Ni in the The presence of Cr-rich spinel and olivine in these source melt. regions could account for the depletion of Ir relative to Au observed in eucrites (GREENLAND, 1971; KIMURA et al, 1974). These features could also be produced, at least qualitatively, by fractional crystallization of metal, olivine or pyroxene, and spinel from some parental liquid.

D. Alkali depletion in Ibitira.

Many aspects of the chemistry of the Ibitira eucrite can be explained if its composition is interpreted as that of a liquid produced by an intermediate degree of partial melting of the same type of source region which generated the Stannern and Sioux County compositions. However, the data presented in Table 6 demonstrate that relative to the other eucrites with compositions near peritectic \underline{A} (Figures 5 and 6), Ibitira is significantly depleted in several alkalis - Na, K, and Hb. Ibitira does not appear to be depleted in Cs relative to the other eucrites.

There are several possible interpretations of the low alkali concentrations in Ibitira: (i) Ibitira could have been derived from a source region depleted in alkalis relative to the source regions of the other eucrites. Although this is possible, it is difficult to devise a test of this hypothesis. However, if the proposed variability of alkali levels in these source regions were produced by nebular fractionations, it would be difficult to explain why Cs was not depleted in the source region of Ibitira along with the other volatile alkalis. (ii) STEELE and SMITH (1976) suggested that Ibitira had a complex thermal history including a prolonged thermal metamorphism followed by shock metamorphism. It is possible that loss of alkalis from Ibitira could have been produced during thermal or shock metamorphism. The experiments of GIBSON and HUBBARD (1972) demonstrated that alkalis can be lost from lunar basalt compositions in subsolidus thermal metamorphism and the experiments of JEANLOZ and AHRENS (1976) suggest that under appropriate conditions, shock metamorphism could also result in loss of alkalis. However, since most of the other eucrites appear to have experienced thermal and

Table 6. Alkali concentrations in eucrites with compositions near peritectic <u>A</u> (Figures 5 and 6). Values listed are averages of analyses from the literature. Multiple analyses from a single source were averaged separately before averaging with analyses from other sources.

'-' = no data.

References: (1) McCARTHY et al (1973); (2) DUKE and SILVER (1967); (3) SCHMITT et al (1972); (4) TERA et al (1970); (5) WÄNKE et al (1972); (6) ALLEN and MASON (1973); (7) R.A. BINNS (pers.comm.); (8) HIGUCHI and MORGAN (1975); (9) WÄNKE et al (1974); (10) ALLEGRE et al (1975); (11) PHILPOTTS and SCHNETZLER (1970a); (12) McCARTHY et al (1974); (13) LAUL et al (1972); (14) PAPAMASTASSIOU and WASSERBURG (1969); (15) VON MICHAELIS et al (1969).

• - · · ·	Na (wgt%)	K (ppm)	Rb (ppm)	Cs (ppb)	References
Béréba	0.321	277	0.178	6.9	1.3.4.13
Cachari	0.394	410	-	-	1,3
Haraiya	0.313	230	-	-	1,3,6
Ibitira	0.141	119	0.125	8.3	8,9
Juvinas	0.311	286	0.203	7.0	1-5,10,11,13,14
Lakangaon	0.375	640	-	-	3,12
Millbillillie	0.341	-	-	-	7
Nuevo Laredo	0.388	414	0.352	13.8	2-4,14
Pasamonte	0.337	331	0.236	9.5	1-4,14,15
Sioux County	0.314	300 [`]	0.218	8.5	1-4,13-15
Stannern	0.429	631	0.784	15.2	1-4,11,13,14

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shock histories at least as complex as Ibitira, it would be difficult to understand why Ibitira is the only alkali-depleted eucrite if either of these processes were responsible for its alkali-depletion. (iii) Alkali loss could have occurred during eruption of the Ibitira eucrite. Alkali volatilization has been observed in experiments conducted on lunar and terrestrial basalts (GIBSON and HUBBARD, 1972; STOREY, 1973). Since the rate at which a volatile element is lost from a magma is dependent on its activity in the melt (STOREY, 1973), the low initial concentration of Cs in eucritic compositions might explain why in spite of its volatility, Cs is not depleted in Ibitira. The presence of vesicles in Ibitira (WILKENING and ANDERS, 1975) would be consistent with degassing of the Ibitira magma on eruption, but it does not demand it. Juvinas is reported to be vesicular (LACROIX, 1926) and it is not depleted in alkalis and none of the vesicular lunar rocks have been found to be alkali-depleted relative to non-vesicular rocks. Any petrographic evidence of alkali loss on eruption would probably have been obscured during subsequent thermal metamorphism.

Even if the low levels of alkalis in Ibitira resulted from loss of alkalis on eruption, this process was probably not important in the evolution of the other eucrites. Otherwise, it would be difficult to account for the positive correlations of volatile alkalis such as potassium and rubidium with involatile trace elements which are observed in eucrites other than Ibitira (McCARTHY et al, 1973).

If loss of alkalis on eruption was responsible for the alkali-depletion of Ibitira, the rarity of alkali depletion among known eucrites could be due to rapid chilling of the exposed surfaces of lava flows preventing loss of volatiles from the interiors of

flows, or to emplacement of most eucrites below the surface of their parent body. Volatile-depleted rock might therefore have been limited to vesicular flowtops which constituted only a small proportion of the rocks in a given flow. The calculations of WILKENING and ANDERS (1975) suggest that Ibitira was derived from a depth of 2.5 meters from the flowtop, and if valid, would indicate that the unique alkali-depletion of Ibitira could not be due to its derivation from the vesicular top of a eucrite flow. However, the calculations of WILKENING and ANDERS (1975) only indicate that if the assumptions which they made are valid, Ibitira resided at least 2,5 meters from the surface of its parent body over much of its residence time on this body. STEELE and SMITH (1976) concluded from their petrological study of Ibitira that it experienced a period of prolonged thermal metamorphism after eruption. From this they inferred that after eruption, the Ibitira flow was buried either under an ejecta blanket or by further basalt flows. The Rb-Sr internal isochron age of Ibitira (4.53 b.y., BIRCK et al, 1975) presumably dates this thermal metamorphism or the shock metamorphism which followed it. Therefore, the Ibitira flow must have been buried soon after its eruption. Hence, the 2.5 meter lower limit on depth calculated by WILKENING and ANDERS (1975) gives an estimate of the lower limit of the depth of burial of the Ibitira flow, rather than any constraints on the distance of Ibitira from the flowtop.

These considerations of the phase equilibria and the major and minor element chemistry of eucrites suggest the following model of eucrite genesis: A sequence of melts was generated by increasing degrees of low pressure partial melting of a single type of source region composed of olivine (~Fo65), pyroxene (~Wo5En65), plagioclase (-An94), Cr-rich spinel, and metal. Increasing degrees of partial melting resulted in: (i) minor decreases in the Fe/(Fe+Mg) ratios of the melts; (ii) decreases in the Ca/Al ratios and incompatible element concentrations of the melts; (iii) diminishing negative europium anomalies in the melts as the amount of plagioclase in the residue decreased; and (iv) increases in the liquidus temperatures of the melts. The composition of Stannern may represent that of a liquid produced by 5-10% melting while the Sioux County composition may have been produced by 15-20% melting of such a source. The composition of Haraiya may have developed by minor fractionation of a liquid produced by a greater degree of partial melting of the same type of source. The compositions of most of the other eucrites could have been produced by minor (<20%) low pressure fractionation of plagioclase and pigeonite from primary liquids with compositions similar to Sioux County. Liquids with compositions similar to Nuevo Laredo and Lakangaon could have evolved by more significant amounts (~40 percent) of fractionation of these phases from primary liquids similar in composition to Sioux County. Fractionation of pigeonite and plagioclase from primary eucritic liquids resulted in: (i) increases in the Fe/(Fe+Mg), Ca/Al, and Fe/Mn ratios of the residual liquids; (ii) increases in the levels of silica-oversaturation of the residual liquids; (iii) increases in the concentrations of

incompatible elements in the residual liquids; (iv) the development of negative europium anomalies in the residual liquids; and (v) decreases in the liquidus temperatures of the residual liquids.

A. Limits on permissible source regions.

The compositions of the silicates and spinel in the source regions can be estimated from the compositions of the phases near the liquidi of the primary eucrites (Table 3). Since the metal-saturated experiments were conducted in high purity iron containers, the composition of the metal phase with which eucritic liquids could coexist must be estimated in a less direct manner. The composition of metal found in the eucrites may have no relation to the composition of the metal with which the eucrites could coexist at their liquidi, because the metal in the sucrites crystallized well below their liquidi. One way of estimating the composition of the metal which could coexist with sucritic liquids is to use available metal-silicate distribution coefficients. Metal-liquid distribution coefficients of 6000-8000 for Ni and about 1000 for Co were estimated by HEWINS and COLDSTEIN (1974) for Apollo 12 basalts. KIMURA et al (1974) determined a lower limit to the metal-liquid distribution coefficient for Au of 20000 for a high titanium lunar basalt composition at 1500°C. CHOU et al (1973) suggested that 1100 is a lower limit to the distribution coefficient of Ge between metal and silicates in H-group chondrites. Although the temperature dependence of this distribution coefficient is unknown, the data of WASSON and BAEDECKER (1970) and BAEDECKER et al (1971) demonstrate that fractionation of Ge between crystalline and liquid silicates is negligible in basaltic compositions and suggest that 1100 may also be a lower limit to the metal-liquid distribution coefficient for Ge in

basaltic compositions. CHOU et al (1976) have estimated average concentrations of 13 ppm Ni, 0.4 ppb Au, and 25 ppb Ge for eucrites. An average Co concentration in eucrites of about 5 ppm can be estimated from the data of SCHMITT et al (1972) and LAUL et al (1972). Applying the distribution coefficients discussed above, this suggests that eucritic liquids could have equilibrated with metal containing approximately of 6-8 percent Ni, 0.5 percent Co, 8 ppm Au, and >28 ppm Ge. Despite the approximate nature of this result, it suggests that eucritic liquids could have equilibrated with metal similar in composition to the metal in mesosiderites (WASSON et al, 1974) or pallasites (SCOTT and WASSON, 1975). This is consistent with an indigenous origin of the metal in mesosiderites and it may suggest that this metal played an important role in the genesis of magmas on the basaltic achondrite parent body. This result might also support the relationship between pallasites and basaltic achondrites suggested by oxygen isotope data (CLAYTON et al, 1976).

The multiple saturation of the eucrite liquidi can help determine the nature of the phases present in the source regions of eucritic melts but not their relative proportions. Any mixture of the five phases near the eucrite liquidi would produce eucrite-like liquids at peritectic <u>A</u> on melting (Figure 8). However, petrological and geochemical arguments can set rough limits on the mineralogy of permissible source regions.

Since the Juvinas eucrite has a flat rare earth pattern (SCHNETZLER and PHILPOTTS, 1969), plagioclase must have been approximately exhausted from the source regions when melts similar in composition to Juvinas and Sioux County were generated. If Sioux County was produced by 15-20% melting of the source, the normative mineralogy of Sioux County (37 weight percent plagioclase) can be

used to estimate that plagioclase constituted 5-8% of the initial silicate portion of the source.

In the Kapoeta howardite, plagioclase first appears intergrown with pyroxenes when the pyroxenes are similar in Fe/(Fe+Mg) ratio to the pyroxenes near the liquidi of the Juvinas and Sicux County eucrites and are never found intergrown with more magnesian pyroxenes (DYMEK et al, 1976). This observation is consistent with the conclusion that plagioclase was exhausted from source regions at approximately the degree of partial melting which produced melts similar in composition to Sioux County. However, WEIGAND (1975) concluded that plagioclase coprecipitated with pyroxenes more magnesian than the pyroxenes near the Sioux County liquidus in the igneous rocks sampled by the mixing processes which produced the Patwar mesosiderite. If valid, this conclusion would indicate that at least in the source regions of the liquids which produced the phases in the Patwar mesosiderite, plagioclase could not have been exhausted from the source regions until the pyroxenes in these source regions were at least as magnesian as Fe/(Fe+Mg) [molar] = 0.24. However, WEIGAND's conclusion, based on the observation that the Al₂O₃ contents of pyroxenes in Patwar decrease slightly as the Fe/(Fe+Mg) ratios of these pyroxenes increase from 0.24 to 0.35, is unjustified since, as demonstrated by CAMPBELL and BORLEY (1974), decreases in the Al₂O₃ contents of pyroxenes with increasing Fe/(Fe+Mg) ratios can be produced when pyroxene is the only crystallizing phase.

Limits on the initial proportions of olivine and pyroxene in permissible source regions can be estimated if it is assumed that the bulk Ca/Al ratios of these source regions were 1.08 (AHRENS, 1970) and that these source regions initially contained 5% plagioclase.

Assuming pyroxene, plagioclase, and olivine compositions from Table 3, such sources would contain approximately 5% plagioclase, 30% pyroxene, and 65% olivine. Because of the aluminous nature of spinels which can coexist with eucritic liquids (Table 3), this calculation is only valid if the initial amounts of spinel in these source regions were negligible. If there were negligible amounts of olivine in the initial sources, assemblages with 90% pyroxene, 5% plagioclase, and 5% spinel would be required by the Ca/Al ratio constraint. If olivine and pyroxene were initially present in equal proportions, spinel would have constituted less than 2% of these source regions.

In an earlier attempt to set limits on the relative proportions of pyroxene and olivine in the source regions of eucritic liquids (STOLPER, 1975b), the restriction was imposed that pyroxene could not have been exhausted from these sources before the residual pyroxenes in these source regions were at least as magnesian as the most magnesian pyroxenes found in howardites (~En85, FREDRIKSSON and KEIL, 1963). Otherwise, liquids produced by melting of these sources would have been unable to crystallize pyroxenes as magnesian as these howarditic phases. Although this restriction is valid in principle, the result obtained is dependent on whether it is assumed that melting took place under conditions of equilibrium or fractional fusion. In equilibrium fusion, at least 75% of the initial silicate fractions of these sources would have to be pyroxene. However, the results of PRESNALL (1969) demonstrate that under conditions approaching fractional fusion, sources containing smaller initial proportions of pyroxene could satisfy this constraint. Therefore, contrary to my earlier conclusion (STOLPER, 1975b), pyroxene need not have dominated over olivine in the source regions.

No attempt has been made to estimate the initial proportion of metal in permissible source regions. In principle, this could be done by assuming that the source had a cosmic Ni/Au or Co/Au ratio and carrying out an exercise similar to that used above to estimate the relative proportions of phases of known composition for an assumed bulk Ca/Al ratio. However, the detailed distributions of Ni, Co, and Au among the silicates, spinel, metal, and perhaps sulfide in the sources are not well enough known to make such a calculation meaningful. If it were assumed that the metal in mesosiderites was indigenous to the basaltic achondrite parent body, the existence of these metal-rich meteorites could suggest that some source regions were metal-rich. However, the concentration of metal in these meteorites could be secondary, perhaps due to sinking or coalescence of initially less concentrated metal.

B. Differentiation of the basaltic achondrite parent body.

No known meteorites satisfy the requirements of the proposed source regions of eucritic liquids. However, the normative mineralogy of the non-metallic portion of the bulk composition of the eucrite parent body estimated by WANKE and PALME (1974) is 17% plagioclase (An92), 49% pyroxene (Wo6,En72), 34% olivine (Fo76), and <1% spinel. The normative mineralogy of an independent estimate of the bulk composition of the eucrite parent body (VIZGIRDA and ANDERS, 1976; E. ANDERS, pers.comm.) is 6% plagioclase (An90), 48% pyroxene (Wo2,En80), 46% olivine (Fo81), and <1% spinel. The mineralogies of these estimates of the bulk composition of the eucrite parent body are similar to the mineral assemblages of permissible eucrite source regions as estimated above. Although these bulk planet compositions are too magnesian to produce eucritic melts, the Fe/(Fe+Mg) ratios of

these compositions are poorly constrained (GANAPATHY and ANDERS, 1974). The mineralogical similarities between the inferred eucrite source regions and these estimates of the bulk composition of the eucrite parent body suggest that the eucrites may have been produced by partial melting of the primitive material of the eucrite planet. With the age of the eucrites, 4.5 to 4.6 AE (ALLÈGRE et al, 1975; BIRCK et al, 1975), this possibility further suggests that the eucrites may have been produced during the early stages of the differentiation of the eucrite parent body.

The first stage in the differentiation of a homogeneous planet would have been the generation of melts produced by small degrees of melting of the bulk composition of the planet. On large bodies such as the earth or moon, these early melts would have been consumed in the more extensive planetary melting which occurred in the later stages of differentiation. On the smaller eucrite parent body, where the mechanism of differentiation might have been different or on which differentiation may not have proceeded to complete planetary melting or even beyond the initial stages of melting, it is possible that these early products of partial melting might have been preserved and perhaps would have formed the crust of such a planet.

Peritectic <u>A</u> (Figure 8) moves towards silica-undersaturated compositions with increasing pressure and becomes silica-undersaturated at some pressure less than 5 kilobars (O'HARA, 1968). Therefore, the melting which produced the oversaturated eucrite compositions must have occurred at pressures considerably less than 5 kilobars. Since pressures at the centers of the asteroidal bodies which may have been parental to the eucrites are probably less than this, eucrite genesis could have occurred at any depth in these bodies.

C. The relationship of the eucrites to stony-irons and other

basaltic achondrites.

Further melting of the source regions of eucritic melts after the exhaustion of plagioclase from the residues would produce melts which could crystallize the magnesian pyroxenes found in the howardites, diogenites, and mesosiderites. The residue left after the separation of such melts from their source regions would be an olivine + low calcium pyroxene + spinel + metal assemblage. If the source region were metal-poor, the olivine-bearing diogenites could represent such residua. However, since such an origin is not possible for the diogenites which contain no olivine, a cumulate origin is preferred for all of the diogenites. Although the major constituents of the Lodran meteorite are similar to those expected in such a residue, the presence of Cr-diopside and a K-rich phase in Lodran (BILD and WASSON, 1976) suggest that this meteorite is not such a residue.

Further melting would eventually exhaust pyroxene from the source regions, producing melts which could crystallize the magnesian olivines found in howardites and mesosiderites. Separation of these advanced partial melts from their source regions would leave pallasite-like residues of olivine + spinel + metal.

If the basaltic achondrites are ejecta from the near-surface regions of undisrupted planets, residual and unmodified source materials would remain unsampled in the planetary interiors, perhaps accounting for the rarity of such material among known meteorites. This would be consistent with derivation of the eucrites and other basaltic achondrites from the surface of the Vesta asteroid (McCORD et al, 1970) or from the differentiated stony surface regions which

may have been stripped from those asteroids which appear to have stony-iron surfaces (GAFFEY and McCORD, 1976).

D. Abundance patterns.

Although the model of eucrite petrogenesis outlined above can account for the compositions, mineralogies, and relationships between the eucrite meteorites and at least in principle for the existence and crystallization histories of melts more magnesian than known eucrites, there are some rather curious patterns in our sampling of the basaltic achondrites which suggest that refinement of this model is possible. The most conspicuous of these apparent sampling biases is that although melts more magnesian than the eucrites with compositions near peritectic A (Figures 5 and 6) must have existed, no quenched examples of these magnesian liquids have yet been identified either as whole unbrecciated or monomict meteorites or as lithic fragments in polymic: breccias. Fragment Rho in Kapoeta (DYMEK et al, 1976) is the only possible example of such a quenched liquid and, as pointed out earlier, such an interpretation of this fragment appears unjustified. Although the model developed above would predict a bias towards the products of smaller degrees of partial melting under conditions of fractional and imperfect fractional fusion, it cannot in its present form account for the complete absence of examples of quenched liquids whose compositions were produced by larger degrees of melting than the eucrites with compositions near peritectic A.

The coarse-grained pyroxcne fragments in diogenites, howardites, and mesosiderites provide abundant evidence that liquids more magnesian than the eucrites fractionated quite efficiently by crystallization of pyroxene in plutonic environments. If the

eucrites are not the residual liquids produced by this fractionation, why are there no known meteorites with compositions similar to these residual liquids?

Figure 9 shows that of known eucrites, only two, Lakangaon and Nuevo Laredo, have compositions which were produced by significant fractionation of primary eucritic liquids. All of the others suffered only minor (<20%) fractionation. In contrast, the elusive magnesian liquids seem to have fractionated quite efficiently as demonstrated by the abundance of phases which appear to have crystallized from them. It is even more curious that although fractionated eucrites such as Nuevo Laredo and Lakangaon are rare, most of the cumulate eucrites (e.g., Moama, Moore County, Serra de Magé) appear to have crystallized from liquids even more fractionated and iron-ricn than these two late-stage liquids.

It is tempting to disregard these anomalies and to attribute them to the incomplete and statistically insignificant nature of our sample of rocks from basaltic achondrite parent bodies. Meteoriticists rarely place much emphasis on abundance patterns and, in view of our lack of understanding of the factors which affect our sample of fragments from a given body, this is in general a wise policy. Nevertheless, it is desirable to be aware of abundance patterns and although they can always be attributed to sampling biases, it would obviously be more desirable to have a model which is consistent with observed abundance patterns than one which is not.

One possible interpretation of these abundance patterns is that eucritic melts generally crystallized in near-surface environments while the more advanced partial melts of the same sources developed as lower level plutonic rocks. Thus, if the eucritic liquids suffered only minor fractionation en route from their source regions

to their near-surface environments of crystallization, quenching of these liquids in these environments could have produced rocks similar in composition to these primary liquids. If later partial melts of the same sources were limited to plutonic environments, perhaps by the presence of a relatively thick and rigid crust composed of earlier sucritic flows, this could explain the rarity of meteorites produced by the quenching of magmas more magnesian than Sioux County. Crystallization and differentiation of these magnesian plutons might first have led to the formation of minor olivine cumulates, overlain by pyroxene cumulates. Plagioclase would have started to accumulate when the composition of the crystallizing pyroxene was at least as iron-rich as Wo 5En65. Continued accumulation of pyroxene and plagioclase would have produced a series of pyroxene-plagioclase cumulates with increasing Fe/(Fe+Mg) ratios. Moama, Moore County, Serra de Mage, and the other known cumulate eucrites may have crystallized in such plutons from residual liquids produced by the fractionation of liquids more magnesian than known eucrites, rather than from liquids similar in composition to known sucrites or their derivatives. This could explain why most of the known pyroxene + plagioclase cumulates appear to have crystallized from liquids more iron-rich and with different trace element characteristics than known eucrites. The iron-rich residual liquids in these plutons (e.g., liquids between R and B in Figure 8) would have been richer in silica than liquids similar in composition to known sucrites (liquids near A in Figure 8); if cumulates such as Moama crystallized from such late-stage liquids, this silica enrichment might explain why the pyroxenes in these cumulates are lower in Al and Cr than the pyroxenes produced in experiments on known eucrites (CAMPBELL and BORLEY, 1974).

As in late-stage terrestrial plutonic rocks, ferrohedenbergite and silica would have eventually crystallized from the residual plutonic liquids. This could account for some of the ferrohedenbergite in howardites (REID, 1974; DYMEK et al, 1976). The crystallization of these plutons as closed systems could explain the low abundance of known meteorites or fragments which could represent quenched examples of the extremely iron- and silica-rich residual liquids produced by fractionation in these plutons.

Figure 9 shows that although eucrites such as Stannern and Ibitira which could have been produced by the quenching of liquids produced by small (~5-10 percent) degrees of partial melting of the proposed source regions are known, nearly all of the known eucrites developed from liquids similar in composition to Sioux County which were generated by approximately the same degree of partial melting (~15-20 percent). The bias towards liquids produced by about 20% partial melting suggests that there may have been a critical degree of partial melting at which separation of the melt from residual crystals became probable. It may be significant that the degree of melting at which nearly all eucritic liquids separated from their source regions appears to have coincided with the exhaustion of plagioclase from these source regions. Perhaps the presence in the residues of a phase such as plagioclase, with a density close to that of the melt, inhibited the separation of melts from source regions. If it is valid, this concept of a critical degree of melting suggests that eucrite compositions were in general produced by nearly perfect equilibrium fusion, rather than fractional fusion (PRESNALL, 1969); since melts were rarely removed from their source regions before this critical degree of melting was attained.

The importance of a critical degree of melting in controlling

when a melt separated from its source region can also explain, at least qualitatively, why melts produced by greater degrees of partial melting than Sioux County may have been limited to plutonic environments. When a melt separated from its source region, some liquid would usually have been left behind interstitial to the residual crystals. Thus, even though plagioclase had been exhausted when most of the eucritic melts separated from their source regions, melting would have continued with further addition of heat to these source regions after the removal of the eucritic melts. However, the amount of liquid remaining in the source regions would probably have been considerably less than the minimum percentage of liquid which could have been easily removed. In addition, due to a steepening of the solidus path of the source regions after plagioclase exhaustion (WYLLIE, 1963), a considerable further increase in temperature would probably have been required before significant amounts of melt would again have been present in the source regions. Hence, one might expect a considerable gap in temperature, melt composition, and perhaps time between the separation of melts similar in composition to Sioux County from source regions and the point at which there was a sufficient quantity of more advanced partial melt in the source regions so that it could be easily separated from the residual crystals. This suggests that there might have been at least two discrete stages in the differentiation of a basaltic achondrite parent body: In the early stages of melting, while plagioclase remained in the residues, melts did not often separate from their source regions, although liquids similar in composition to Stannern and Ibitira did occasionally erupt. When plagioclase was exhausted from the residues, separation of melts from the source regions almost invariably occurred. Eruption of these liquids built up a crust of

eucrite flows. After the exhaustion of plagioclase and the eruption of eucritic liquids, melting in the source regions continued, but initially the advanced melts were unable to separate from their source regions. When the percentage of melt in the source regions again reached a level at which melt-residue separation became likely, the melts were considerably hotter and more magnesian than were the Sioux County-like melts when they separated from these source regions. A crust of earlier eucrite flows may have acted as an impermeable cap, preventing these magnesian liquids from erupting and limiting them to crystallization and differentiation in plutonic environments. Though admittedly speculative, this type of model of the early differentiation of basaltic achondrite planets is consistent with both the petrologic constraints discussed earlier and the suggestions of the abundance patterns of these meteorites.

X. CONCLUSIONS

1. Low pressure fractionation of pigeonite and plagioclase from liquids similar in composition to the Sioux County and Juvinas eucrites can explain the compositional variations of most eucrite meteorites. However, the compositions of the Stannern and Ibitira eucrites cannot be produced by low pressure fractionation of liquids similar in composition to Sioux County, Juvinas, or any other known eucrites.

2. With the possible exception of Binda, it is unlikely that the cumulate eucrites (e.g., Moama, Moore County, Serra de Magé) crystallized from liquids similar in composition to any known eucrites.

3. It is unlikely that liquids similar in composition to the Stannern, Ibitira, and Sioux County eucrites were residual liquids produced by extensive low pressure fractionation of more magnesian liquids.

4. Melts similar in composition to the Stannern, Ibitira, and Sioux County eucrites could have been produced by increasing degrees of low pressure partial melting of an olivine (~Fo65), pigeonite (~Wo5En65), plagioclase (~An94), Cr-rich spinel, and metal (~6-8% Ni, 0.5% Co) assemblage. The composition of Stannern may have been produced by 5-10% melting of such a source region; plagioclase would still have been present in the residue at this degree of melting. The composition of Sioux County may have been produced by 15-20% melting of such a source region; plagioclase would have been just exhausted from the source region at this degree of melting. The rarity of eucrites with compositions similar to Ibitira and Stannern among known eucrites may not be fortuitous and may reflect the

difficulty in extracting melts from source regions at small degrees of melting and when a low density phase such as plagioclase remains in the residue.

5. The proposed mineralogy of the source regions of the eucritic melts resembles the mineralogy of estimates of the bulk composition of the eucrite parent body. This suggests that the eucritic melts may have been the first melts produced in the early melting and differentiation of the basaltic achondrite parent body.

6. Ibitira is depleted in several volatile alkalis relative to other eucrites. This could be due to alkali depletions in its source region, alkali loss during thermal or shock metamorphism, or loss of alkalis on eruption.

7. Further melting of the source regions of eucrite melts after the exhaustion of plagioclase from the residues could have produced melts capable of crystallizing the magnesian pyroxenes and rare olivines in howardites, diogenites, and mesosiderites. These magnesian liquids may have been restricted to crystallization in plutonic environments by a crust of earlier eucrite flows. This could explain the rarity of meteorites with compositions produced by quenching of these magnesian liquids. It is proposed that most of the cumulate eucrites (e.g., Moama, Moore County, Serra de Mage) crystallized in such plutons from liquids produced by advanced fractionation of these magnesian melts rather than from liquids similar in composition to known sucrites or their derivatives. Closed system crystallization of these magnesian plutons could explain the rarity of meteorites with compositions resulting from the quenching of liquids produced by advanced fractionation of these magnesian melts.

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Petrogenesis of eucrite, howardite and diogenite meteorites

THE mineralogical, textural and compositional characteristics of the eucrite meteorites suggest that they are the products of igneous processes. Howardites are polymict breccias containing a variety of fragments, the bulk of which are thought to have crystallised from eucrite and eucrite-related melts¹. Diogenites are orthopyroxene-rich stones which may represent cumulates from eucrite-related melts². I relate here experimentally determined phase equilibria to the igneous processes which produced the eucrites and their associates.

I conducted melting experiments on a sample of the Juvinas eucrite (Harvard 87) at 1 atm total pressure and various oxygen fugacities. Samples were held in iron or molybdenum foil capsules in quenching furnaces with oxygen fugacity controlled by H_2 -CO₂ gas mixtures³. Phase compositions were determined with an electron microprobe. At $f_{O_2} = 10^{-13.4}$ atmospheres and less than 10 °C below the metal-saturated olivine liquidus (FO₆₇; 1,183 °C), the sample is saturated with olivine (FO₆₅), pigeonite (WO₅En₆₅), plagioclase (An₉₄), chrome-rich spinel and iron metal. On cooling, olivine reacts out by 1,150 °C and a silica polymorph crystallises from 1,085 °C.

Figure 1 is a projection of a low pressure liquidus diagram relevant to eucrite crystallisation. Olivine is in reaction relation with liquids at peritectic A (Fig. 1), and on the olivine +pyroxene boundary curve. Eucrite compositions have been projected onto this diagram. The clustering of non-cumulate eucrite compositions about the olivine + low calcium pyroxene + plagioclase + chrome spinel + metal peritectic (A, Fig. 1) indicates that like Juvinas, these other eucrites are probably multiply saturated near their liquidi. This emphasises the role of low pressure crystal-liquid equilibria in the genesis of the eucrites: all known eucrites can be designated as either multiply saturated liquids at A (Fig. 1) or cumulates or partial cumulates of the pyroxene and plagioclase near the liquidi of such liquids. Any model of the igneous processes which produced the eucrites must account for this preferential generation of liquids at peritectic A (Fig. 1).

The compositions of pyroxenes produced in the Juvinas experiments are similar to the compositions of pyroxenes in cumulate and non-cumulate textured eucrites and to those of many pyroxenes in howardites, but are more Fe-rich than the pyroxenes and olivines in diogenites and the most magnesian pyroxenes and olivines in howardites. These natural Mg-rich phases would have equilibrated with liquids more magnesian than the eucrite magmas at A (Fig. 1), and any model of eucrite petrogenesis should account for the existence of such liquids.

Reduction of eucrite magma resulting in crystallisation of iron metal and a decrease in the Fe/Mg and Fe/Mn of the magma could produce magmas which would crystallise magnesian diogenitic and howarditic pyroxenes. The pyroxenes crystallised from such liquids would have a higher Mn/Fe than those crystallised from unreduced eucrite magmas. Such an origin for diogenitic and the most magnesian howarditic pyroxenes is, however, unlikely since the Mn/Fe ratios of these phases are nearly identical to those of pyroxenes in cumulate and non-cumulate eucrites and of the more iron-rich howarditic pyroxenes^{2,4}.

Models which produce eucrite liquids by the differentiation of magnesian parental magmas and which invoke the fractional crystallisation of eucrite magmas to explain the bulk of the chemical variation observed in eucrites² encounter several difficulties. First, as pointed out in connection with Fra Mauro rocks and soils, which display a similar clustering about an olivine + plagioclase + low calcium pyroxene peritectic, it is



Fig. 1 Projection of low pressure liquidus diagram valid for molar Fe/Fe+Mg ≈ 0.60 . Field boundaries were located by microprobe analyses of multiply saturated liquids from experiments on the Juvinas eucrite. Iron metal and chrome-rich spinel are present in all fields. \blacktriangle , Projected analyses of cumulate eucrites: Moore County (2 analyses), Serra de Magé (2 analyses), Moama, Medanitos; \textcircledlimits , Projected analyses of other eucrites. Pre-1960 analyses are plotted only when a more recent analysis of the same stone is not available. Analyses are plotted on this diagram by recalculating SiO₂, Al₂O₃, FeO, MgO, CaO, Na₂O and K₂O in terms of molar SiO₂, CaAl₂Si₂O₈, Fe₂SiO₄, Mg₂SiO₄, CaSiO₃, NaAlSi₃O₈ and KAlSi₃O₈ and then projecting on to the olivine–anorthite–silica plane. Analyses which plot below the pyroxene–plagioclase join do so because of the effects of modal iron metal, troilite, chromite, ilmenite and calcite on the projection. A and the shaded region, are explained in the text.

difficult to preferentially generate liquids at peritectic A (Fig. 1) by low pressure differentiation of other magmas through the action of crystallisation processes⁵. Second, if the proposed parental magmas ever passed through a stage in their evolution in which pyroxene was the only crystallising phase (required by such models to produce the diogenites and magnesian pyroxenes in howardites), the liquid lines of descent of such magmas would never encounter the peritectic at A (Fig. 1). Third, low pressure fractional crystallisation paths which can produce liquids at A (Fig. 1) involve the crystallisation of plagioclase and olivine, but not of pyroxene. At low oxygen fugacities, the fractionation of plagioclase would rapidly differentiate europium from the other rare earth elements. Models which attempt to derive magmas at peritectic A (Fig. 1) by the low pressure fractional crystallisation of more magnesian magmas are, therefore, not easily reconciled with the primitive rare earth distributions of some eucrites⁶, the existence of diogenitic and howarditic pyroxenes more magnesian than the pyroxenes at the liquidi of magmas at A (Fig. 1), or the rarity of olivine in diogenites, howardites and eucrites. Fourth, these models cannot easily reconcile the constancy of the major element chemistry (particularly the Fe/Fe + Mg ratios) of eucrites which cluster at A (Fig. 1) with their variations in rare earth and incompatible element concentrations⁶. Though the variations in the concentrations of rare earths and incompatible elements in the eucrites at A (Fig. 1) apparently suggest that these eucrites could be related to each other through the fractional crystallisation of up to 60% of a liquid of the composition of Haraiya² (another eucrite which projects at A (Fig. 1)), that suggestion is incompatible with the fact that all of these eucrites have nearly identical major element chemistries. A liquid which has reached A (Fig. 1) will not remain there during fractional crystallisation; as it loses heat it will change composition along the pyroxene + plagioclase cotectic and trend toward iron enrichment. Fifth, if these models are valid, the total volume of the magnesian parental magma must have greatly exceeded the volume of eucrite magma. Examples of magmas more primitive than the eucrites should predominate among falls and the distribution of fragments in howardites should be strongly skewed toward the products of magmas more magnesian than the eucrites at peritectic A (Fig. 1). These relationships are not observed.

I propose the following model to account for the observed features of the eucrites and their associates. The eucrite magmas at the peritectic A (Fig. 1) are interpreted as the products of small degrees of low pressure partial melting of an olivine + low calcium pyroxene + plagioclase + chrome spinel + iron metal source which projects in the shaded region of Fig. 1. Compositional variation of the eucrites is the result of variable degrees of partial melting and subsequent fractional crystallisation and crystal accumulation. Diogenites are regarded as cumulates of phases separated from more advanced partial melts of the same source. Howardites are polymict breccias containing fragments sampling the spectrum of differentiated liquids and cumulates developed from the range of primary magmas produced by variable degrees of partial melting of this source.

Eucrite magmas produced by the partial melting of such a source would plot at the peritectic A (Fig. 1) until plagioclase was exhausted from the source region; this explains the observed clustering of eucrite compositions. If the eucrites represent small degrees of partial melting, variations in the degrees of partial melting which produced different eucrite liquids could have produced the significant variations in the concentrations of incompatible elements which are observed between eucrites of indistinguishable major element chemistry and Fe/Fe+Mg ratios⁶. If plagioclase becomes exhausted from the source region at small degrees of partial melting, this model can also explain the variations in rare earth distributions and the magnitudes of europium anomalies which are observed between eucrites of nearly identical major element chemistry⁶.

The subsequent crystallisation and separation of pyroxene and plagioclase from the primary magmas at A (Fig. 1) would be expected to produce cumulates and silica and incompatible element enriched liquids of higher Fe/Fe+Mg ratios projecting near the pyroxene + plagioclase cotectic emanating from A(Fig. 1). Moore County and Serra de Magé are examples of these cumulates¹. The bulk chemistry and mineralogy of Binda, considered by some to represent a magma parental to the eucrites² are compatible with such a cumulate origin. Nuevo Laredo and Lakangaon may represent liquid differentiates from the crystallisation of magmas at A (Fig. 1). Both are enriched in incompatible elements and display the iron enrichment expected in differentiated liquids. It is unlikely that they represent smaller degrees of partial melting of the same source that produced the eucrites which are not iron enriched, for at least in the case of Nuevo Laredo, rare earth distributions are not compatible with this interpretation⁶. Other eucrites may have been affected to a lesser extent by fractional crystallisation.

Though olivine would be present in the source rock and the residue left after melting, it would not be present at the liquidi of the partial melts at A (Fig. 1), (provided there was little fall in pressure accompanying eruption) because it is in reaction relation with these liquids. This is consistent with the absence of olivine in eucrites and its rarity in howardites.

If the reaction relationship between iron metal and silicate liquids observed in synthetic systems⁷ extends to this natural system, metal would remain in the source region until all crystalline silicate phases were removed by melting. The probable reaction relation between chrome-rich spinel, low calcium pyroxene and liquid⁸ suggests that chrome spinel would remain in the source region until all the pyroxene had been removed by melting.

In conditions of fractional fusion⁹, the production of magma

by further melting would be nearly halted after the exhaustion of plagioclase from a source projecting in the shaded region of Fig. 1. If equilibrium fusion or imperfect fractional fusion took place, the melts produced after the exhaustion of plagioclase from the source would move up the olivine + pyroxene curve (Fig. 1), continuously decreasing the Fe/Fe+Mg ratio, until pyroxene was exhausted from the source. The diogenites and magnesian pyroxenes in howardites can be interpreted as cumulates of the pyroxene crystallising near the liquidi of these more advanced partial melts. The rarity of olivine in these meteorites is predicted since these liquids would not ordinarily crystallise olivine. The occasional presence of olivine in these meteorites (and Chassigny) could result from variations in source composition, variations in conditions of melting or crystallisation (for example, a small drop in pressure between the source region and the environment of crystallisation), or xenocrysts from the imperfect separation of the magma from the source. The absence of cumulate plagioclase in the diogenites or in intergrowths with the most magnesian howarditic pyroxenes⁴ can be expected since plagioclase would not be present at the liquidi of these magmas.

The residue left in the source region after the exhaustion of plagioclase by partial melting would be olivine + low calcium pyroxene + chrome spinel + metal. If metal were a major constituent of the source, this residue would approximate the Lodran meteorite¹⁰. If the source were low in metal, the olivine-bearing diogenites could represent such residues. Since such an origin is not possible for the olivine-free diogenites, a cumulate origin is preferred for the entire diogenite group.

Further equilibrium fusion or imperfect fractional fusion of this same source after the exhaustion of pyroxene from the source region would produce liquids moving away from the olivine + pyroxene reaction curve (Fig. 1) towards the olivine composition, leaving a pallasite-like residue of olivine + chrome spinel + metal. The olivines crystallised near the liquidi of such melts may account for some howarditic and diogenitic olivines.

The abundance patterns of fragments in howardites⁴ and the lack of known meteorites with compositions which could represent partial melts more advanced than the eucrites at A (Fig. 1) are consistent with the bias toward the products of smaller degrees of partial melting which is expected in conditions of imperfect fractional fusion.

Though eucrite liquids would have equilibrated with the metal of the residue left in the source region after partial melting, metal would not be at the low pressure liquidi of these melts because of the probable reaction relation between metal and silicate liquid (provided no change in oxidation state of the magmas occurred between the source region and the environment of crystallisation). This is compatible with both the observed low Ni contents of the eucrites, which suggest they have equilibrated with metal, and the petrographic observations that metal is never found as a cumulate phase in diogenites and cumulate eucrites, is rarely enclosed in pyroxenes, and is usually a late, interstitial phase when it occurs¹¹. The late stage crystallisation processes similar to those which have been proposed to account for metal in lunar mare basalts¹².

A partial melting model requires a suitable low pressure source assemblage in the eucrite parent body. A primitive type of mesosiderite (perhaps a condensate¹³ or the product of early differentiation and brecciation on the eucrite planet or on some other body which was subsequently incorporated into the eucrite planet) could be suitable source material. The low pressure mineralogy (< 8 kbar) of the bulk composition of the eucrite parent body calculated by Wänke and Palme¹⁴ is similar to the source assemblage required by this model. This similarity raises the possibility that the eucrites may have formed by partial melting of the primitive material of the eucrite parent body at 4.6×10^9 yr BP.

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ORIGIN OF THE BASALTIC ACHONDRITES. E. Stolper, Grant Institute of Geology, University of Edinburgh, Scotland.

Melting experiments on Juvinas and other eucrite meteorites have shown that near their liquidi, most of these compositions are saturated with iron metal, olivine(Fo65), pigeonite(Wo5En65), plagioclase(An94), and Cr-rich spinel (TAC=.04, Fe/Fe+Mg=.65) at 1 atm pressure, $fO_2=10^{-13}\cdot^4$ atm, and T=1175°C¹. Liquidus diagrams based on probe analyses of glasses from these experiments are shown in fig 1 and 2, along with projections of known eucrite analyses. The clustering of projected eucrite compositions about the olivine, pyroxene, plagioclase, Cr-spinel, metal peritectic (<u>A</u>) restates the results of the melting experiments and emphasizes the role of the low pressure crystal-liquid equilibria in the genesis of the eucrites: all known eucrite compositions can be designated as liquids on this peritectic or cumulates of the pyroxene and plagioclase present at the low pressure liquidi of these liquids. Any model of the igneous processes which produced the eucrites must account for the preferential generation of liquids at peritectic <u>A</u>.

At low pressure, liquids at peritectic <u>A</u> simultaneously crystallize pigeonite and plagioclase. The residual liquids move from <u>A</u> to <u>B</u> (fig 1). A silica polymorph begins crystallizing at <u>B</u>. This crystallization sequence reproduces the sequence petrographically deduced for eucrites². Spinel is present at all stages of predicted and observed crystallization sequences. Though olivine and metal are stable in equilibrium with a liquid at <u>A</u>, they are in odd reaction relation with the liquid and will not crystallize from it. This is consistent with the absence of olivine in eucrites and the observation that metal was not an early crystallizing phase in the eucrite crystallization sequence¹.

The failure of models which produce eucrite liquids by differentiation of more magnesian magmas and of models which explain the bulk of chemical differences between the eucrites by differentiation of eucrite magmas during fractional crystallization³⁻⁵ has been discussed elsewhere¹. Briefly, these models encounter the following difficulties:(a) preferential generation of liquids at a peritectic as the products of differentiation by fractional crystallization is unlikely⁶; (b) if parental liquids ever passed through a stage in their evolution in which pyroxene was the only crystallizing phase (required by such models to account for the diogenites), the liquid line of descent would never encounter the peritectic at A;(c) liquid lines of descent resulting from fractional crystallization which reach peritectic A undergo only olivine and/or plagioclase fractionation in reaching the peritectic; such paths are inconsistent with the existence of diogenites and the abundance of magnesian pyroxenes in howardites, the absence of olivine in eucrites and its rarity in diogenites and howardites, the rarity of plagioclase cumulates which contain no cumulate pyroxene, and the primitive REE distributions of some eucrites⁷, indicating that these liquids did not develop from parental magmas by fractionation of plagioclase; (d) these models cannot reconcile the constancy of major element chemistry (particularly Fe/Fe+Mg) of the eucrites which cluster around \underline{A} with their wide variations in the concentrations of REE and incompatible elements⁴.

The observed features of the eucrites can be explained if these meteorites are interpreted as the brecciated products of low pressure melting of an olivine+low-Ca pyroxene+plagioclase+Cr-spinel+metal source which projects in the shaded region of fig 1, with compositional variation the result of variable

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degrees of partial melting and subsequent fractional crystallization and crystal accumulation. Diogenites are regarded as brecciated cumulates separated from more advanced partial melts of the same source. Howardites and mesosiderites are polymict breccias which contain lithic and mineral fragments sampling the spectrum of differentiated liquids and cumulates developed from the range of primary magmas produced by variable degrees of partial melting of this source. Magmas produced by partial melting would plot at peritectic A until plagioclase was exhausted from the source region; this explains the observed clustering of eucrite compositions. If the eucrites represent small degrees of partial melting, small variations in the degrees of partial melting which produced different eucrites could have produced the significant variations in the concentrations of incompatible elements which are observed between eucrites of indistinguishable major element chemistry and Fe/Fe+Mg⁸. If plagioclase were completely exhausted from the source at small degrees of partial melting, this model can explain the variations in REE distributions and the magnitudes of Eu anomalies which are observed between eucrites of nearly identical major element chemistry^{7,8}. This model predicts the absence of olivine in the eucrites. Differentiation of eucrite liquids at \underline{A} by crystallization and separation of pyroxene and plagioclase would be expected to produce the eucrite cumulates (e.g. Moore County, Serra de Magé, Binda) and silica and trace element enriched liquids of higher Fe/Fe+Mg (e.g. Nuevo Laredo, Lakangaon). Under conditions of fractional fusion, the production of magma by further melting after the exhaustion of plagioclase in the source would be nearly halted. If imperfect fractional fusion took place, the more advanced partial melts would move up the olivine+pyroxene curve in fig 1, continuously decreasing Fe/Fe+Mg until pyroxene were exhausted from the scurce. The diogenites and magnesian pyroxenes in howardites can be interpreted as cumulates of the low-Ca pyroxenes crystallizing near the liquidi of these more advanced partial melts. The rarity of olivine in these meteorites is predicted since these liquids would not ordinarily crystallize olivine. The occasional olivine in these meteorites (and Chassigny) could be due to variations in source composition, small variations in conditions of melting or crystallization (e.g. a small drop in pressure between the source region and the environment of crystallization), or xenocrysts from imperfect separation of the magma from the source. Further melting after the exhaustion of pyroxene in the source would produce liquids which move away from the olivine+pyroxene curve in fig 1 toward the olivine corner. The olivines crystallized near the liquidi of these magmas could account for some of the diogenitic and howarditic olivines. The observed abundance patterns of rockand mineral fragments in howardites⁹ and the lack of known meteorites with compositions which could represent partial melts more advanced than the plagioclasesaturated eucrites are consistent with the bias toward the products of smaller degrees of partial melting which is expected under conditions of imperfect fractional fusion. Models which require fractional crystallization of magnesian parental magmas to produce the eucrites should produce the opposite of observed trends; i.e. examples of magmas more primitive than the eucrites should predominate and the abundance of mineral and rock fragments in the howardites should be strongly biased towards more magnesian compositions.

The equilibria shown in fig 1 and 2 are relatively insensitive to pressure and are probably broadly valid for pressures up to 5 kb. The melting which

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produced the eucrite magmas could therefore have occurred at depths greater than 100 km if the parent planet was smaller than the moon.

If a partial melting model is accepted, constraints can be set on the mineralogy and nature of the source region. The low pressure phase equilibria only dictate the phases present in the source region, not their proportions. The proposed model requires that plagioclase be exhausted from the source at small degrees of partial melting, so the source would project near the olivine-pyroxene join in the shaded region of fig 1. The bulk Fe/Fe+Mg of the silicates would be .30-.35. Mesosiderites show that concentrations of metal were present in the eucrite planet and probably near its surface. This suggests that metal may have been a major phase in the source region.

The residue of partial melting after the exhaustion of plagioclase in the source would be olivine+pyroxene+Cr-spinel+metal. If the source were metal-poor, the olivine-bearing diogenites could represent such residua. Since such an origin is not possible for the olivine-free diogenites, a cumulate mode of origin is preferred for the entire diogenite group. If metal were a major constituent of the source, as suggested above, the residue would approximate the Lodran meteorite¹⁰. Further melting of such a metal-rich source would leave a pallasite-like residue after the exhaustion of pyroxene from the source.

If Lodran is assumed to be such a residue, its modal mineralogy 10,11 and the form of phase relations in the system SiO₂-CaAl₂Si₂O₈-Fe₂SiO₄-Mg₂SiO₄¹² can be used to estimate the proportions (by weight) of phases in the source: metal/ metal+silicate=.08; olivine/olivine+pyroxene=.14; minor calcic plagioclase, Cr-spinel, and sulfide. The same phase relations can be used to make an independent estimate of the initial source assemblage by assuming that the most magnesian howarditic pyroxenes(~ En85)⁹ crystallized from partial melts produced just as pyroxene was exhausted from the source region: olivine/olivine+ pyroxene=.21; the metal content cannot be estimated in this case. These estimates demonstrate that pyroxene must dominate over olivine in permissable source assemblages.

No known meteorites satisfy the requirements of this source region. A primitive and as yet unsampled type of mesosiderite, formed either as condensates¹³ or as the crust of the eucrite body (or some other planet which was subsequently incorporated into the eucrite planet) produced by large scale melting and planetary differentiation similar to that inferred for the moon could offer a satisfactory source assemblage.

Wanke and $Palme^{14}$ have estimated the bulk composition of the eucrite parent body. The low pressure (<8kb) mineralogy of such a composition is nearly an exact match for the source region required to produce the eucrites and related partial melts; the only difference is that the source of the eucrite melts would have to be slightly more iron-rich. Though the eucrite source would have to be more iron-rich, the bulk composition and low pressure mineralogy of the primitive moon inferred by Ringwood⁸,¹⁵ are also an excellent match to the requirements of the eucrite source region. These similarities raise the possibility that the eucrite melts may have formed by partial melting of the primitive material of the eucrite planet.

Though the gravitational field of the eucrite planet was sufficient to separate crystals from eucrite melts and to produce crystal alignment in cumulates, Page 2 - Fourth Annual Lunar Science Conference

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the planet is inferred to be smaller than the moon and possibly of asteroidal dimensions¹⁶. The rarity of olivine in basaltic achondrites, the absence of fragments similar to high- or low-Ti mare basalts, and the rarity of plagioclase-rich fragments in basaltic achondrites are other differences between these meteorites and lunar rocks⁹. These differences may simply reflect the smaller size of the eucrite planet, as illustrated in the following possible scenarios of its evolution:(1) Energy from homogeneous accretion of the outer portions of the eucrite planet of material corresponding to the source of the eucrite melts (possibly similar to the material from which the moon accreted) resulted in melting in the outer portions of the eucrite planet. Unlike on the moon, where larger size resulted in accretional energy sufficient to completely melt its outer portions, the degrees of melting were restricted on the eucrite planet, though melting probably occurred over much of the planet. The widespread partial melting, controlled by the low pressure equilibria shown in fig 1, resulted in eruption of eucritic and more advanced partial melts and perhaps in the formation of large lava lakes. Differentiation of these melts and accumulation of crystallizing phases produced the variety of rock types represented in lithic and mineral clasts in basaltic achondrites. Continued bombardment of the planet resulted in brecciation and mixing of these igneous products. Impact melting of the basaltic achondrites occurred. Due to the small size of the planet, heating from interior radioactive sources was never sufficient to produce a later period of melting from the interior. The young ages of some clasts in howardites¹⁷ must represent impact melts or ages reset by impact. (2) Early evolution of the planet is similar to (1), but in this case radioactive heat sources in the interior produce melting between 3-4 AE. The small size of the planet restricts pressures even deep in its interior to K5 kb so that magma genesis is controlled by the low pressure equilibria in fig 1. Since the source is identical to that involved in the earlier episode of melting, the character of these eucrite magmas and the associated cumulates differentiates, etc. will be nearly identical to those formed at 4.6 AE by accretional, near surface melting. The pressure drop accompanying eruption would result in small amounts of olivine crystallization due to the expansion of the olivine field with decreasing pressure.

The incomplete melting of the planet's outer regions envisaged in these scenarios and the lowered effectiveness of crystal fractionation due to the smaller gravitational field of the eucrite planet relative to the moon suggest that neither the mafic cumulates which could represent sources for low-Ti mare basalts, nor the high-Ti cumulates or residua which could produce high-Ti mare basalts, nor a plagioclase-rich crustal accumulate would be present on this eucrite planet. In addition, the high pressure control of phase equilibria needed to produce mare-like basalts would have been unavailable in this eucrite planet. Thus the smaller size of the eucrite planet could account for the differences between basaltic achondrites and lunar rocks even if the bulk compositions of the planets are similar.

If the basaltic achondrites are indeed the products of magmas formed by small amounts of partial melting, they must be less abundant than the residua left by this melting. This relationship is not observed among recorded falls. If, however, the eucrite body were never completely disrupted and sampling of material from this planet were restricted to ejecta from near surface regions,

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the observed abundance pattern would be expected. The brecciated character of nearly all basaltic achondrites and mesosiderites indicate that sampling of this planet has indeed been biased toward rocks from its regolith and near surface regions. Estimates of the surface compositions of asteroids indicate that Vesta (which was never disrupted) has a basaltic achondrite surface¹⁸. Perhaps the basaltic achondrites were ejected from the surface of Vesta. It should be noted that if Vesta or a body of similar dimensions (radius~200 km) is indeed the source of the basaltic achondrites, an alternative to accretional energy as the heat source for the low pressure melting which produced the eucrites at 4.6 AE may be necessary, since the temperature increase from gravitational energy would be negligible on a body this small.

I thank the Marshall Aid Commemoration Commission for financial support. <u>References</u>. (1) Stolper E.(1975)<u>Met.Soc.38th Ann.Mtg</u>.,31;(1975)Nature(in press). (2)Duke M.B. and Silver L.T.(1967)<u>G.C.A.</u> 31,1637-1665.(3)Mason B.(1962)<u>Meteorites</u>(Wiley,N.Y.).(4)McCarthy T.S. et al(1973)<u>E.P.S.L.</u> 18,433-442(5) Shimizu N. and Allegre C.J.(1975)<u>Met.Soc.38th Ann.Mtg</u>.,32. (6)Walker D. et al(1972) <u>Proc</u>. <u>3rd Lunar Sci.Conf</u>.,797-817.(7)Gast P.W. and Hubbard N.J.(1970)<u>E.P.S.L.10</u>,94-101.(8)Ringwood A.E.(1970)<u>J.G.R.</u> 75,6453-6479.(9)Dymek R. et al(1975)<u>Lunar Sci</u>. <u>VI</u>,227-229.(10)Bild R.W. and Wasson J.T.(1974)<u>Meteoritics</u> 9,315-316.(11) Tschermak G.(1870)<u>Sitz.Math.-Natur.Classe</u>, <u>Akad.Wiss.Wien</u> 61,465-475.(12) Roeder P.L. and Osborn E.F.(1966)<u>Am.J.Sci</u>. 264,428-480.(13)Ganapathy R. and Anders E.(1974)<u>Proc.5thLunar Sci.Conf</u>.,1181-1206.(14)Wanke H. and Palme H. (1974)<u>Meteoritics</u> 9,414-415.(15)Ringwood A.E.(1975)<u>Lunar Sci</u>. VI,674-676.(16) Brownlee D. and Rajan R.(1973)<u>Science</u> 182,1341-1344.(17)Papanastassiou D.A. et al(1974)<u>Lunar Sci.-V</u>,583-585.(18)Chapman C.R.(1974)<u>Meteoritics</u> 9,322-324.



Analyses recast to molar $SiO_2-CaAl_2Si_2O_8-Fe_2SiO_4-Mg_2SiO_4-CaSiO_3-NaAlSi_3O_8-KAl-Si_3O_8$. Field boundaries located by probe analyses of experimental glasses. Cr-spinel and iron metal present in all fields. Triangles are projected analyses of cumulate-textured eucrites. Dots are other eucrites. (1)Projection onto ol-ivine-anorthite-silica plane. Valid for molar Fe/Fe+Mg~.60. (2)Plagioclase-saturated equilibria projected onto silica-forsterite-fayalite plane.