Pyroxene Chemistry in Polymict Eucrite Northwest Africa 6475: Contrasts with Juvinas, Stannern and Igdi, and Evaluation of Models for Eucrite Magmatic Evolution

Nicholas Castle[1], Olivier Bachmann[1], Anthony J. Irving[1], and Ryoji Tanaka[2]
[1]Dept. of Earth & Space Sciences, University of Washington, Seattle, WA 98195, USA (ncastle@uw.edu),
[2]Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan.

Précis

The eucrite meteorite suite is the mafic component of a silicate profile that formed from a magma ocean on a minor body, potentially the asteroid Vesta. There are four chemical divisions of eucrites: cumulate (CE), main group trend (MGT), Nuevo-Laredo trend (NLT), and Stannern trend (ST). This study examined pyroxenes in previously classified monomict eucrites Juvinas (MGT), Igdi (NLT), and Stannern (ST). The newly classified meteorite NWA 6475, a polymict eucrite with large igneous clasts, was also examined. All four meteorites are reequilibrated in major elements, so true liquid compositions cannot be calculated. Pyroxene major and minor element (Si, Ca, Fe, Mg, Cr, Ti, Al, Mn, Ni, Na) concentrations were determined by electron microprobe. Pyroxene trace element (Sc, V, Sr, Y, Zr, Nb, REE, Hf, Ta) concentrations were determined by laser-ablation sourced ICP-MS. MGT, NLT, and ST compositional trends are reproduced in pyroxene compositions. The modal NWA 6475 pyroxenes have major element chemistry similar to the MGT, but uncommon CE and NLT pyroxenes were observed. In trace element chemistry, NWA 6475 pyroxenes fall along the ST, but closer to Juvinas than Stannern. Oxygen isotopes in NWA 6475 are consistent with the main HED suite.

The presence of three major element groups in a single meteorite strongly suggests that all can originate on a single body. Contrasting this, the model relation between MGT and NLT magmas (pyroxene fractionation) is not consistent with observed pyroxene compositions in Juvinas and Igdi. NWA 6475 does not fall along a consistent silicate or oxide fractionation curve from Juvinas. CE pyroxenes remain an enigma and were observed not as individual clasts, but as inclusions in an MGT-dominated clast. Trace element mixing curves that connect MGT and ST magma compositions are not physically realistic. Assimilation and fractional crystallization curves fail to connect MGT and ST compositions. All of this suggests that while some may be, not all eucrites are cogenetic. Minor and trace element pyroxene compositions should be treated, along with oxygen isotopes, as a method for separating eucrites into cogenetic suites.

Introduction

The howardite, eucrite and diogenite (HED) meteorites are a related group of meteorites representing the profile of silicate mineralogy on a differentiated asteroid or asteroids, potentially associated with asteroid Vesta [*Larson and Fink*, 1975; *McCord et al.*, 1970]. HED meteorites date circa 4.5 Ga, among the oldest achondrites, so they provide a unique window into the first steps of planetary differentiation in the solar system [*Nyquist et al.*, 1997]. Eucrites are the mafic component of the eucrite parent body silicate profile [*Duke and Silver*, 1967], and it is believed that they formed the crustal lid above a magma ocean [*Righter and Drake*, 1997]. There are two primary divisions in eucrites [*Schnetzler and Philpotts*, 1969]: cumulate eucrites (CE) that have a coarse equant texture, lower Fe/Mg ratios, and lower incompatible element abundances; and non-cumulate eucrites (NCE) that vary in texture from granular to glassy, and always have a higher Fe/Mg ratio. The NCEs more directly represent the magmas they originate from, so they are more useful for close examination of magmatic process on the eucrite parent body [*Pun and Papike*, 1996]. Three chemical groupings of NCE have been observed [*Ahrens*, 1970]: the main group trend (MGT), comprising the majority of eucrites; the Nuevo-Laredo trend (NLT) with higher Fe content; and the Stannern trend (ST) with higher incompatible elements (eg: Ti, REE, etc) but similar bulk chemistry to MGT. Experimental petrology shows that the MGT eucrite composition is near the peritectic line between olivine and pyroxene, and saturation in plagioclase [*Stolper*, 1977]. Despite more than 40 years of research, there is still rigorous debate over the petrogenesis of eucrites, and the relation between eucrites and diogenites.

Existing models generally consider MGT eucrites to be the primitive eucrite magma composition. NLT eucrites have been related to MGT eucrites by crystal fractionation of pyroxenes [*Stolper*, 1977]. Originally, ST eucrites were related by differing degrees of partial melting of a eucritic source material [*Stolper*, 1977]. With the acceptance of a magma ocean on the parent [*Righter and Drake*, 1997], this hypothesis has lost favor and a number of alternatives proposed. One example is in-situ crystallization where a physical model describing crystal generation and fluid migration is used to modify the traditional picture of equilibrium crystallization [*Barrat et al.*, 2000; *Langmuir*, 1989]. Another is incorporation of partial melts of eucritic solids into primitive eucrite magmas during crystal fractionation [*Barrat et al.*, 2007; *DePaolo*, 1981].

This study begins by comparing the major, minor and trace element chemistry of pyroxenes in the monomict eucrites Juvinas (MGT), Igdi (NLT), and Stannern (ST). These results are compared to each other and to pyroxenes from compositionally diverse clasts in the polymict eucrite NWA 6475. The goals are to examine 1) the degree of chemical heterogeneity among the different trends of eucrites, and 2) the degree of chemical heterogeneity among different petrologies from a single meteorite. In light of our observations we discuss the viability of existing models relating the three trends and theories about the origin of and petrogenesis on the eucrite parent body.

A number of previous studies have examined eucrite mineral chemistries in an attempt to reconstruct the history of the eucrite parent body [*Hsu and Crozaz*, 1996; 1997a; b; *Mayne et al.*, 2009; *Pun and Papike*, 1995; 1996; *Pun et al.*, 1997]. It is important to consider mineral chemistry along with the bulk chemistry because it yields a

greater level of detail about the igneous process that formed the rock. For example, mineral compositions contrasted with the bulk rock composition can prove whether a rock represents the composition of the melt that the minerals formed from – an important consideration in the debate over the cumulate vs. non-cumulate nature of various eucrite meteorites, and determinations of the primitive magma composition. Mineral compositions are also especially important in examining clasts in a polymict breccia. Such clasts are generally too small to allow for representative bulk compositions of each clast to be obtained. However, it is important not to blindly calculate liquid compositions from mineral trace element compositions, since many eucrites (including all four in this study) have been metamorphically reequilibrated [*Treiman*, 1997; *Yamaguchi et al.*, 1996; 1997; *Yamaguchi et al.*, 2009]. This study focuses on pyroxene compositions to allow examination of clasts in NWA 6475, but will frequently reference bulk compositions obtained from the literature for comparison with calculated liquid compositions.

Samples and Methods

Four meteorite samples have been carefully described in this study (Tbl. 1). There is little evidence for terrestrial weathering on any of these samples. All of them have fresh fusion crusts, and lack metal hydrates or mineral concretions from desert weathering. NWA 6475 also contains unaltered CM chondrite clasts, which are especially susceptible to terrestrial weathering.

Table 1: Sample characteristics

Meteorite	Mass (sample)	Fall or find	Eucrite class	Eucrite chemistry
Juvinas	91 kg (3 g)	Fall	Monomict	Main Group Trend
Stannern	52 kg (2 g)	Fall	Monomict	Stannern Trend
Igdi	1470 g (3 g)	Find	Monomict	Nuevo Laredo Trend
NWA 6475	602 g (~200 g)	Find	Polymict	Unclassified

Polished slices were prepared from chips of the meteorites Juvinas, Stannern and Igdi. Four polished slices were prepared from the polymict eucrite NWA 6475. Polished slices of each meteorite were imaged by scanning electron microprobe (SEM). Backscatter electron (BSE) images of representative sections are included (Fig. 1). Pyroxene major and minor element concentrations were determined by electron microprobe analysis (EMPA) (University of Washington) using a JOEL 733 Superprobe. EMPA of pyroxenes was performed using wavelength dispersive spectrometers, analyzing for Si, Fe, Mg, Ca, Cr, Ti, Al, Ni, Mn, and Na. EMPA calibration was performed with well characterized mineral standards: Si and Ca on Cpx 69-27; Mg, and Al on Augite KH-1; Fe on Spinel 18; Ti on synthetic TiO2; Cr on synthetic magnesium chromite; Mn on Nuevo Garnet; Na on Tiburon. Calibration was verified using Alpine 7 (Opx) and Hess 31 (Cpx). Analyses were performed with 0.1 mm & 10 mm spot sizes to attempt to capture both original pigeonite and exsolution compositions.
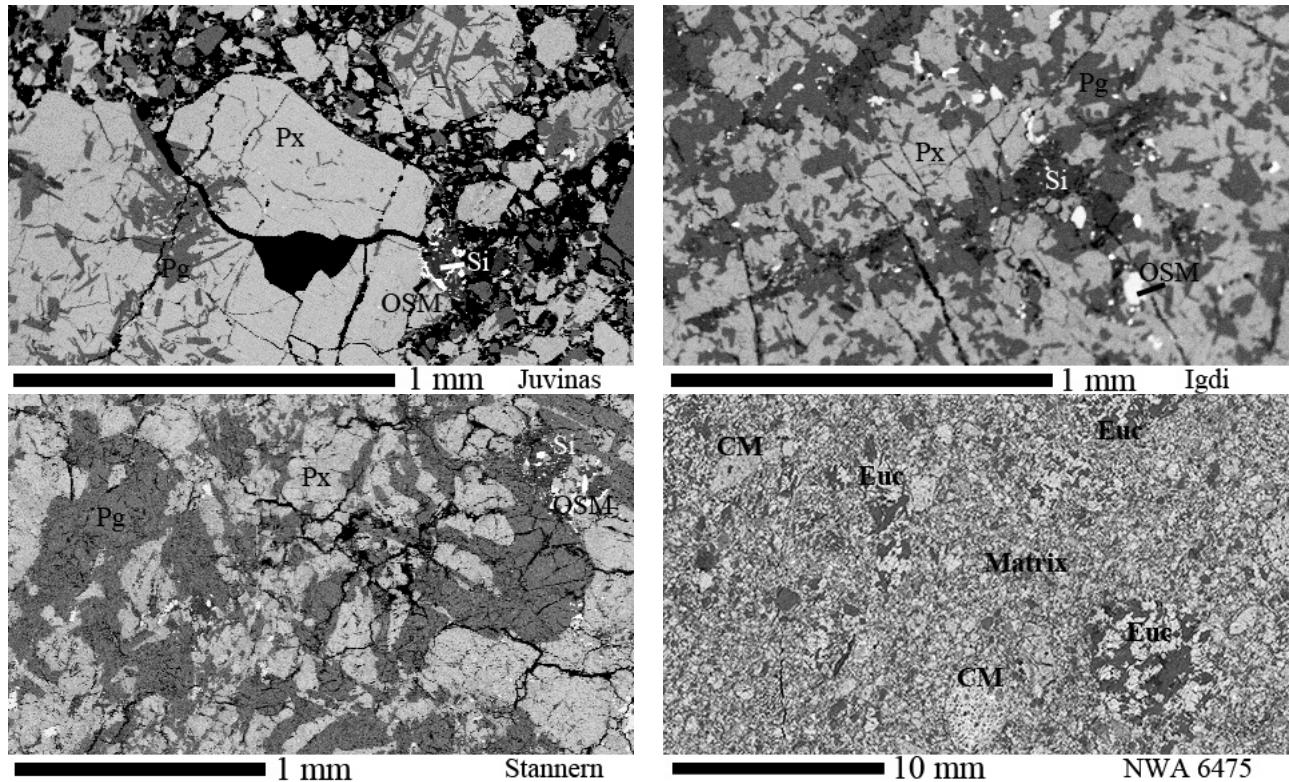
Figure 1: *BSE images with scales for representative sections of Juvinas (top left), Igdi (top right), Stannern (bottom left), and Northwest Africa 6475 (bottom right). NWA 6475 is a polymict sample, the rest are monomict, but Juvinas has been previously shown to contain regions of partial melt. Clasts in NWA 6475 range from ~1mm to ~1cm. Labels: pyroxene (Px), plagioclase (Pg), oxide/sulfide/metal (OSM), silica (Si), eucrite (Euc), CM chondrite (CM).*

Pyroxene trace element concentrations were determined by LA-ICPMS (Washington State University) along 400 μm tracks with a 60 μm laser spot and an estimated trough depth of 12 μm. The carrier gas was He. Calibration was performed on NIST 610 & 612 glasses along with BCR2G basaltic glass, and was checked often to ensure instrument stability. Data was reduced on a spreadsheet developed by Charles Knaack and Scott Boroughs (Washington State University). Analysis was performed to measure: Ca, Sc, Ti, V, Cr, Mn, Sr, Y, Zr, Nb, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, and Ta. Si was used as an internal calibration since it has low variability in eucritic pyroxenes (absolute abundance was measured by electron microprobe). Ti, Cr, Sr and Mn were monitored to exclude analyses with significant mineral inclusions. Cr concentrations paralleled microprobe determinations but were systematically lower due to near saturation concentrations for the LA-ICPMS experimental setup.

Acid-washed subsamples of a eucrite clast in NWA 6475 were analyzed in replicate for oxygen isotopes by laser fluorination (Okayama University). More than 1000 microprobe and 80 LA-ICPMS analyses were performed (Fig. 3 & 4).

Data

Table 2: Average pyroxene compositions

Pyr. Meas.*		Juvinas		Igdi		Stannern		NWA 6475	
		30		24		16		102	
SiO$_2$	(wt%)	49.5	±0.1	49.02	±0.08	49.32	±0.09	50.42	±0.07
TiO$_2$	(wt%)	0.29	±0.02	0.37	±0.03	0.24	±0.02	0.37	±0.01
Al$_2$O$_3$	(wt%)	0.39	±0.02	0.31	±0.01	0.36	±0.02	0.48	±0.02
Cr$_2$O$_3$	(wt%)	0.52	±0.04	0.46	±0.03	0.43	±0.03	0.24	±0.01
FeO	(wt%)	32.3	±0.5	33.1	±0.5	29.9	±0.5	28.3	±0.3
MnO	(wt%)	1.00	±0.02	1.01	±0.02	1.04	±0.02	0.91	±0.01
MgO	(wt%)	12.0	±0.2	9.21	±0.03	11.01	±0.05	11.5	±0.2
NiO[††]	(wt%)	0.027	±0.001	0.040	±0.003	0.014	±0.002	0.029	±0.001
CaO[†]	(wt%)	4.2	±0.5	6.8	±0.5	7.2	±0.5	8.4	±0.3
Na$_2$O[††]	(wt%)	0.020	±0.003	0.020	±0.004	0.071	±0.002	0.034	±0.001
Total	(wt%)	100.2		100.3		99.6		100.4	
P/C Meas.**		**16**		**5**		**7**		**22°**	
Sc	(ppm)	52	±5	55	±3	45	±2	61	±3
V	(ppm)	126	±6	92	±3	84	±6	83	±6
Sr	(ppm)	1.0	±0.3	27	±2	5.8	±0.9	6	±1
Y	(ppm)	12	±2	19	±2	11	±1	20	±2
Zr	(ppm)	12	±1	17	±3	5.7	±0.5	25	±4
Nb[††]	(ppm)	0.17	±0.02	1.1	±0.2	0.5	±0.1	0.12	±0.02
La	(ppm)	0.11	±0.03	1.6	±0.4	0.9	±0.3	0.37	±0.06
Ce	(ppm)	0.5	±0.2	3.3	±0.6	2.4	±1.0	1.7	±0.4
Pr	(ppm)	0.11	±0.03	0.6	±0.1	0.4	±0.1	0.37	±0.08
Nd	(ppm)	0.8	±0.2	3.1	±0.7	2.1	±0.8	2.2	±0.5
Sm	(ppm)	0.5	±0.1	1.1	±0.2	0.8	±0.2	1.1	±0.2
Eu	(ppm)	0.014[††]	±0.004	0.12	±0.02	0.059	±0.008	0.021	±0.003
Gd	(ppm)	1.1	±0.2	1.7	±0.23	1.1	±0.2	2.1	±0.3
Tb	(ppm)	0.23	±0.04	0.37	±0.04	0.25	±0.05	0.40	±0.06
Dy	(ppm)	2.0	±0.3	2.9	±0.3	2.0	±0.4	3.0	±0.4
Ho	(ppm)	0.50	±0.08	0.69	±0.06	0.50	±0.07	0.70	±0.08
Er	(ppm)	1.7	±0.2	2.3	±0.2	1.7	±0.2	2.3	±0.2
Tm	(ppm)	0.28	±0.04	0.36	±0.02	0.30	±0.02	0.37	±0.03
Yb	(ppm)	2.0	±0.3	2.7	±0.1	2.4	±0.1	2.6	±0.1
Lu	(ppm)	0.36	±0.05	0.45	±0.02	0.43	±0.02	0.45	±0.03
Hf[††]	(ppm)	0.33	±0.03	0.9	±0.1	0.35	±0.07	1.1	±0.2
Ta[††]	(ppm)	0.012	±0.001	0.061	±0.009	0.026	±0.006	0.012	±0.001

* Pyroxenes (or, in the case of NWA 6475, pyroxenes averaged by clast) measured by EMPA. A subset of these was then measured by LA-ICPMS (UW).

** Pyroxenes or clasts measured by LA-ICPMS (WSU).

[†] Although an effort was made to not preferentially sample CPX vs OPX exsolution lamellae, this number should be considered questionable.

[††] These elemental abundances are near method detection limit and are therefore questionable.

° CE and NLT type clasts were excluded from the trace element calculated average. 3 Additional clasts were measured, 2 from NLT and 1 from CE.

Meteorite pyroxene compositions were computed by averaging all analyses of a single pyroxene grain (or all pyroxene grains within a single igneous clast for NWA 6475 values), and then averaging the pyroxene compositions (Tbl. 2). This approximates primitive pigeonite compositions, although it may artificially favor the augite exsolution to a minor degree. Variations reported are distribution statistics calculated as 1σ standard errors from population variance and the number of pyroxenes. This approach uses replicate analyses to characterize single pyroxenes and minimize the effect of instrumental error. Population deviations were reported instead of instrumental errors as, in most cases, the population variation greatly exceeded the instrumental error (exceptions are noted, see comment ††). Oxide abundances are unnormalized.

Results

Table 3: Major meteorite chemical features

Meteorite	FeO/MgO*	La (ppm)**	Ce (ppm)**	La/Sm**	Cr (wt%)
Juvinas	2.69	0.36	0.6	0.1_5	0.52
Igdi	3.59	5.1	4.0	0.90	0.46
Stannern	2.71	2.8	3.0	0.73	0.43
NWA 6475	2.46	1.2	2.0	0.21	0.24

* FeO/MgO is based on the weight percent ratios. This can be a biased statistic, since the Fe/Mg depends on the Ca content of the pyroxene. See figure 7 for a comparison attempting to remove the Ca-bias of this number.
** REE values and ratios in this table are average chondrite normalized (R. Korotev, private communication).

There are a number of ways to divide these four meteorites into groups (Tbl. 3). The MGT/NLT distinction is reproduced in major element compositions. Juvinas and Igdi are clearly separated by FeO/MgO, while Stannern and NWA 6475 both overlap with Juvinas (Fig. 3). Of the three with low FeO/MgO, NWA 6475 is the lowest. The MGT/ST distinction is reproduced in trace element concentrations. La and Ce concentrations readily separate Juvinas and Stannern, as does LREE slope. NWA 6475 is intermediate between them (Fig. 4). Igdi pyroxenes have the highest concentration of both La and Ce, contrary to expectations from the bulk compositions. Further, although La/Sm shows a reasonable progression from Juvinas to Stannern (and on to Igdi), the shape of the REE curve in NWA 6475 is nearly identical to Juvinas despite its much higher La. Cr readily separates Juvinas and Igdi from the majority of NWA 6475. Stannern shows a range of Cr consistent with a fractionation process, but without as strong of a clustering around a given concentration as the other three meteorites.

Despite the wide textural variation among the approximately 100 analyzed NWA 6475 eucritic clasts, the majority of pyroxenes have a narrow compositional range. Within the main clustering of pyroxenes FeO/MgO varies between 1.9 and 3.2, averaging 2.5. A few pyroxenes were analyzed with resulting compositions significantly lower than the MGT, consistent with CE pyroxenes [*Hsu and Crozaz*, 1997a]. A few clasts are separable from the main cluster at high FeO/MgO, more consistent with NLT eucrites.
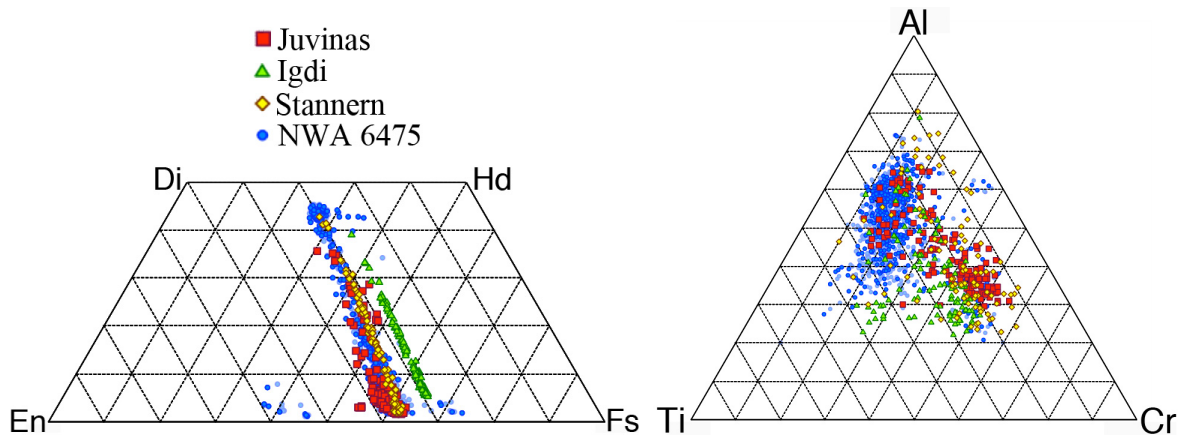
Figure 3: *Pyroxene major and minor element compositions for four eucrites: Juvinas (red squares), Stannern (yellow diamonds), Igdi (green triangles) and NWA 6475 (blue circles).*
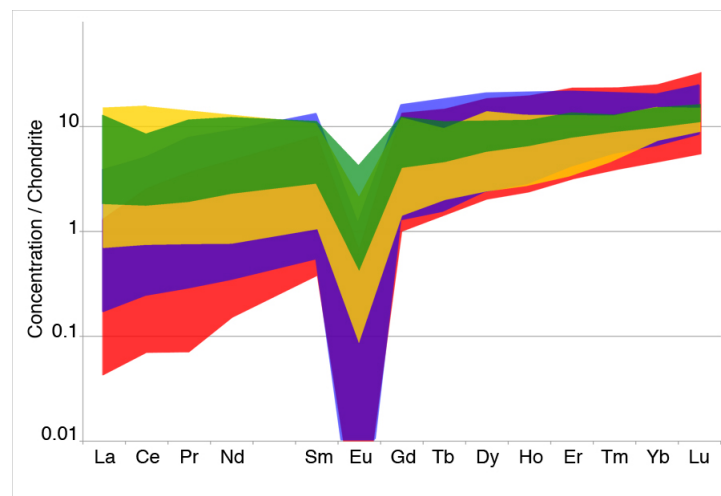

Figure 4: *Pyroxene REE ranges for four eucrites. Both LREE (eg: La or Ce) and LREE slope distinguish the three monomict eucrites. NWA 6475 has an average La abundance closest to Stannern, and a LREE slope closest to Juvinas.*

NWA 6475 oxygen isotope replicate analyses yielded (in per mil):

$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$
3.557, 3.550	1.630, 1.639	-0.242, -0.230

Since these results plot in the field for typical eucrites [*Greenwood et al.*, 2005; *Wiechert et al.*, 2004], they are inconclusive in establishing whether NWA 6475 was derived from a separate parent body than most eucrites (including Juvinas and Stannern). They do exclude any genetic relationship with otherwise similar eucrites such as Ibitira, NWA 2824 and Bunburra Rockhole [*Bland et al.*, 2009; *Bunch et al.*, 2009] that have less negative $\Delta^{17}O$ value (Fig. 5).
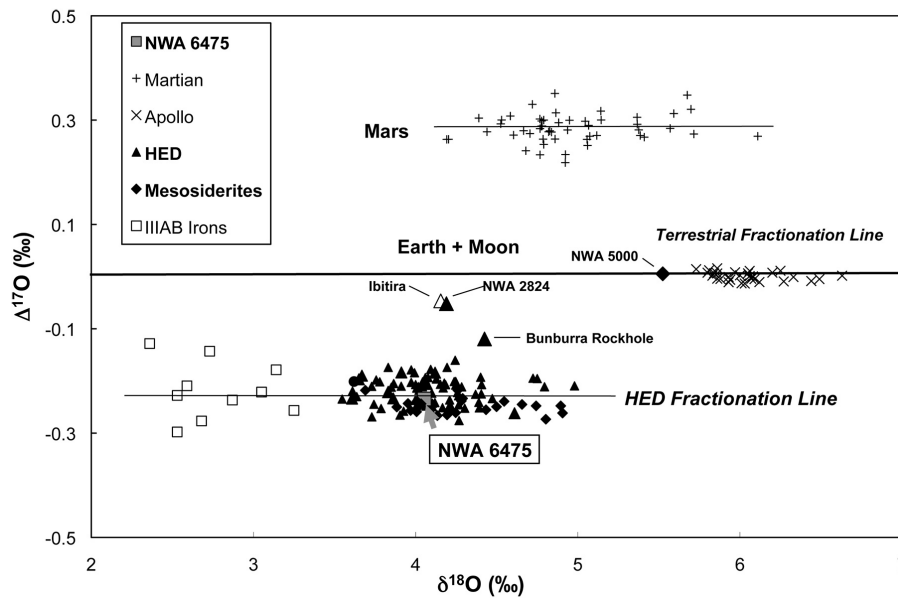
Figure 5: *Oxygen isotope values for NWA 6475 plotted along with the main HED trend, anomalous eucrites, the terrestrial fractionation line, and angrites. Note that NWA 6475 is indistinguishable from other eucrites in oxygen isotopes.*

Discussion

There are a number of inconsistencies between our current theories for eucrite formation and the observed pyroxenes. To illuminate these difficulties, two geochemical models have been examined. The first model examines the theoretical evolution of a MGT magma during crystallization. This approach directly examines the difference between the MGT and NLT eucrites. The second model examines the evolution of a MGT magma by assimilating or mixing material during fractional crystallization. This is one of the present models for relating the MGT and ST eucrites [*Barrat et al.*, 2007]. After discussing these models we will examine them in the context of the polymict eucrite NWA 6475. Before discussing these models it is important to examine what information may be gleaned from first order observations of and comparisons between the four samples included in this study.

Chemical Variability in Eucrites

The first area for consideration is the range of compositions observed in the polymict breccia NWA 6475. Although their presence within a single breccia does not prove that none of the associated clasts are xenoliths, the simplest conclusion is that similar materials within the breccia coorginate. Obvious examples of xenolith impactor materials are the CM chondrite clasts commonly observed in eucrites, including NWA 6475. Metal fragments may also be achondrite xenoliths, but this is more difficult to

determine since some eucrites contain native metals in igneous or metamorphic textures (Fig. 6).

The easiest compositional heterogeneity to observe is the major element difference between the MGT and the NLT (eg: FeO/MgO ratio). Unfortunately, this is somewhat obscured in pyroxene analysis because Fe/Mg in pyroxene exsolution varies with Ca content. Since the exsolution process is thermodynamically controlled, the FeO/MgO at an arbitrary CaO concentration can be calculated. The populations of the estimated FeO/MgO of the Ca-free equivalent compositions are reported (Fig. 7). In preference to the full thermodynamic calculation, this data was regressed by treating the slope of the FeO/CaO dependence to depend solely on the CaO + FeO sum, a roughly constant value in each MGT & NLT pyroxene analyzed.

The result of this analysis is to show that although clasts within the polymict breccia contain principally MGT pyroxenes, minor amounts of non-MGT pyroxenes are observed. This includes both NLT pyroxenes (a total of three clasts could be distinguished from the MGT mode), and pyroxenes broadly consistent with CE compositions. Although no cumulate eucrites were included in this study for comparison, pyroxene compositions from existing work are consistent with the observed low Fe/Mg pyroxene compositions in NWA 6475 [*Hsu and Crozaz*, 1997a; *Pun and Papike*, 1995]. These pyroxene populations will be considered separately from the meteorite to meteorite comparisons in the major and minor element models of the next two sections.

It is interesting to note that although there is a significant textural difference between many of pyroxene clasts in NWA 6475 (Fig. 8), there is very little chemical variation in the overwhelming majority of clasts. Of the three clasts that are more ferric than average, two have an unusual texture (Fig. 9). These two clasts are dominated by large pyroxene crystals rather than the usual mixture of plagioclase and pyroxene (±silica, oxides, etc). Equally unusual, both of these grains are made of orthopyroxene lamellae in a clinopyroxene host; more commonly the reverse is observed. The third clast is texturally indistinguishable from several other, more magnesian, clasts.
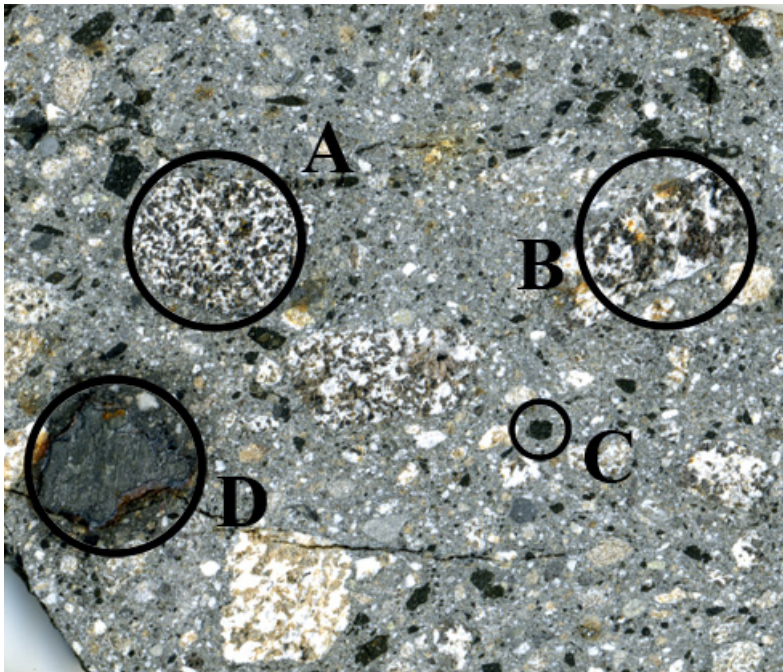

Figure 6: *Reflected light image of a slice of NWA 6475. Highlighted regions include: a,b) common eucrite igneous textures; c) CM chondrite inclusions; d) metal fragments.*
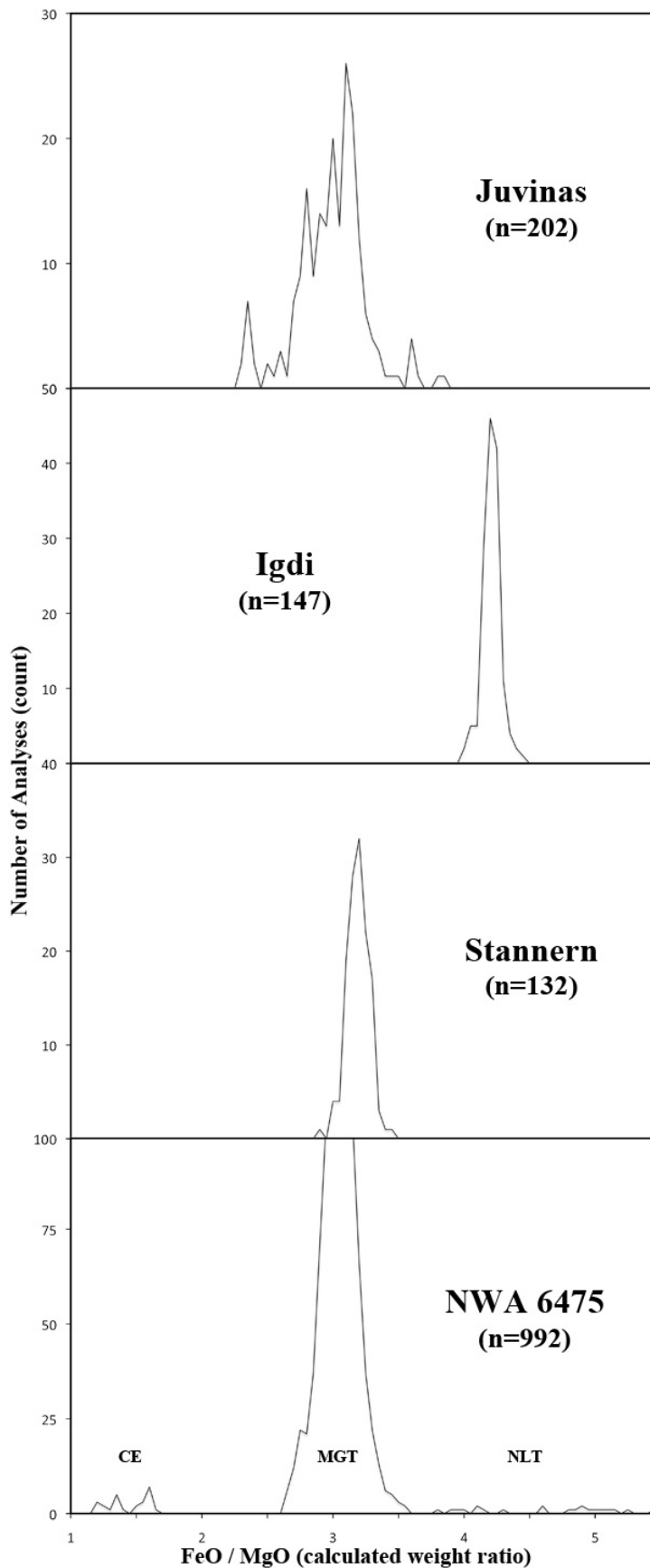
Figure 7: *Calculated Ca-free pyroxene compositions binned in increments of 0.05. Juvinas has a wider distribution of compositions than the modal group of pyroxenes in the other three meteorites. Also note that NWA 6475 has both MGT and NLT pyroxenes, as well as some magnesian pyroxenes consistent with CE pyroxenes. This is strong evidence that all three major element compositions of eucrites are present on a single body. This plot does not differentiate the ST from the MGT, so the two are treated as the same in major elements.*
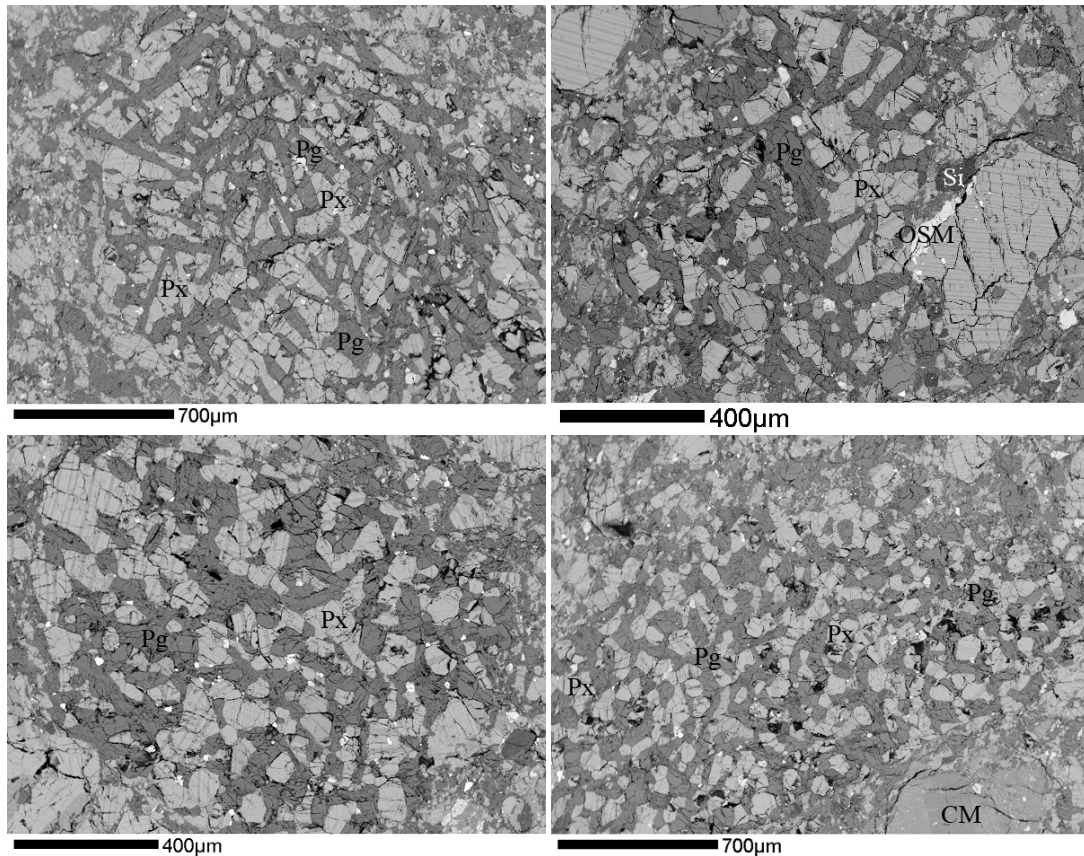
Figure 8: *BSE images of MGT clasts in NWA 6475. Despite the textural variation, these clasts have a very narrow range of compositions and comprise the majority of clasts on NWA 6475, much as the MGT comprises the majority of eucrites.*

A startling observation is that all CE pyroxenes measured were in clasts dominated by MGT pyroxenes (Fig. 10). This suggests several possibilities. If the CE grains are inherited from a source rock or earlier differentiation process, then MGT magmas do not represent the primitive eucrite magma composition. The assumption that MGT magmas are the primitive magma composition is based on their dominant abundance, and that they are neither obviously cumulates or the result of a large degree of fractionation. This possibility will be revisited in light of major element modeling. CE grains could also be remnants of magma mixing. If a partially crystalline CE mush were recharged by a larger MGT magma body near its liquidus, then the CE grains might be mobilized and incorporated into the crystallizing MGT magma. This possibility does not seem likely from the observed petrography. If the mixed magma crystallized slowly, then the CE grains should have equilibrated with the magma composition and only one population should be observed. If the magma crystallized rapidly, then the CE grains should have formed nucleation centers for overgrowths of MGT pyroxenes. This is not observed. A final possibility is that the two populations of pyroxenes represent different formation mechanisms in an inhomogeneous system. No such mechanism has been identified. The presence of CE pyroxenes in MGT-dominated clasts raises questions about the primitive nature of MGT magmas, and may provide insight into their relation on the eucrite parent body.
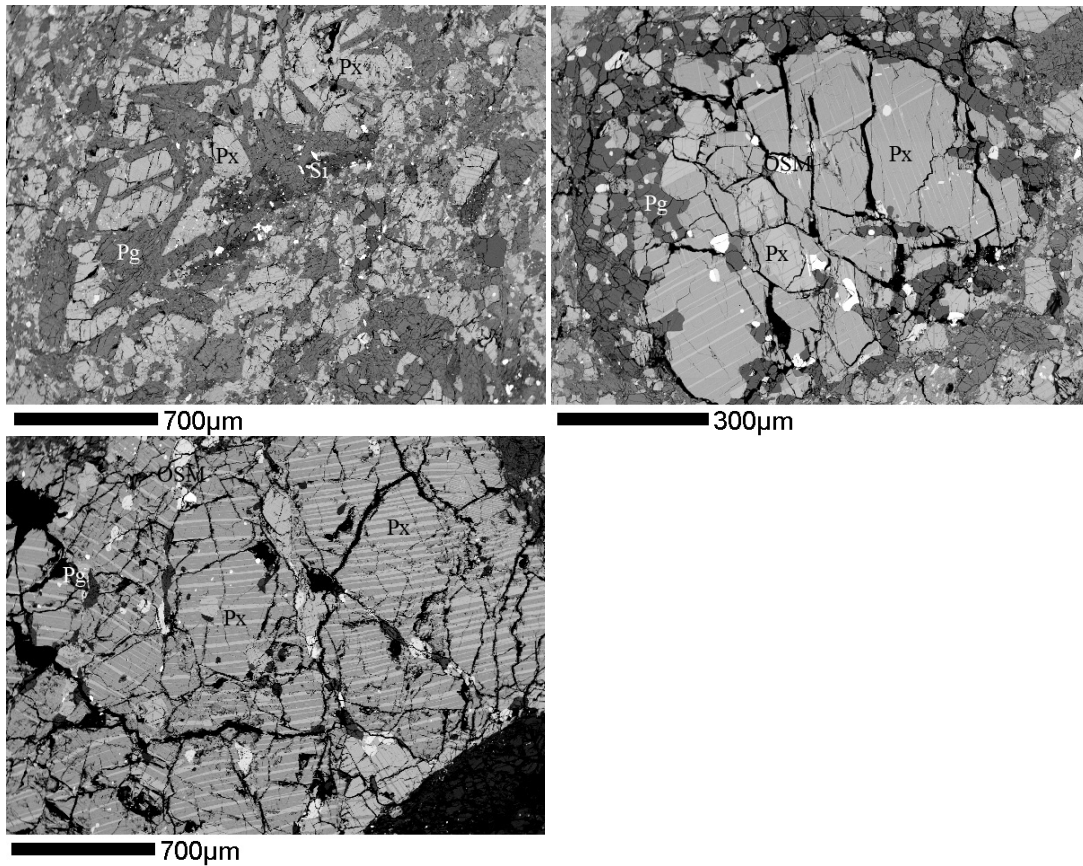
Figure 9: *BSE images of ferroan clasts in NWA 6475. Note that two of the clasts have an unusual texture while the third has a common igneous texture indistinguishable from the main group of clasts.*
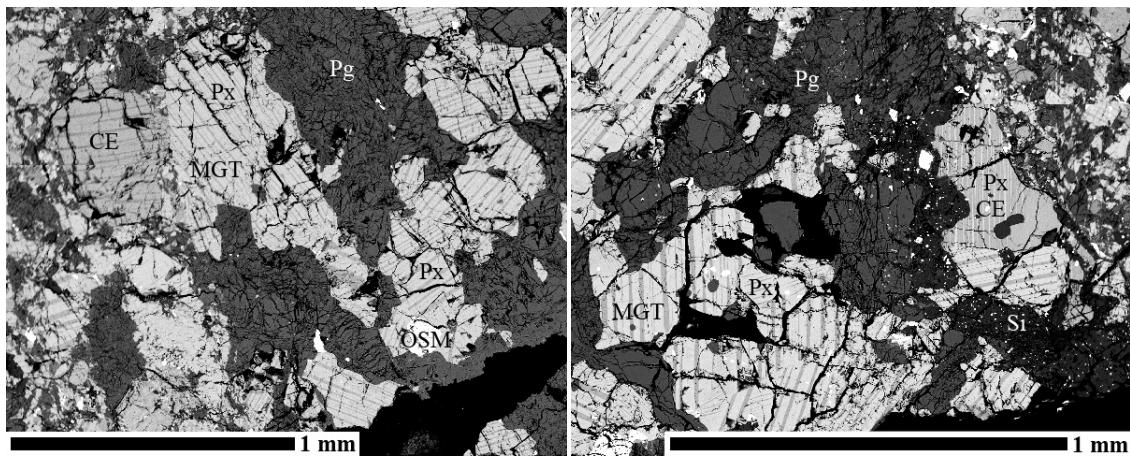

Figure 10: *BSE images of clasts containing anomalously magnesian pyroxenes. Note that these pyroxenes exist as a second pyroxene population within a MGT-dominated clast. The anomalous CE pyroxenes appear darker than the prevalent MGT pyroxenes in these contrast-exaggerated BSE images. Labels: cumulate eucrite (CE); main group trend (MGT), pyroxene (Px), plagioclase (Pg), silica polymorph (Si), oxide/sulfide/metal (OSM).*

MGT → NLT Modeling

Ferroan eucrites are probably the product of crystal fractionation from other eucritic magmas, as has been demonstrated in the past [*Stolper*, 1977]. The question raised here is whether or not all eucrites originate from the same magma body. In order to be considered cogenetic, a mechanism must be identified that connects the observed compositions. Most commonly this is some combination of crystal fractionation, magma mixing, or assimilation. The existing mechanism relies fractionation of pyroxene to generate the FeO/MgO difference between the trends.

When relying on meteorite bulk compositions, the pure fractionation relation between the NLT and MGT eucrite compositions is demonstrably false. Cr is one of the most abundant minor elements in eucrites, and it is compatible in pyroxenes. A simple major element fractionation model was calculated for both pure pyroxene and a typical eucrite (52% pyroxene, 48% plagioclase [*Mayne et al.*, 2009]) fractionation from the Juvinas bulk composition (fig. 11). This is compared to the bulk compositions of Nuevo-Laredo and Igdi. (Unfortunately the Cr-content of Igdi is not reported in the literature due to experimental considerations [*Barrat et al.*, 2003], so the Cr-content of Igdi was estimated from Nuevo-Laredo, a very similar eucrite) The resulting fractionation trend does not connect Juvinas with either bulk composition.
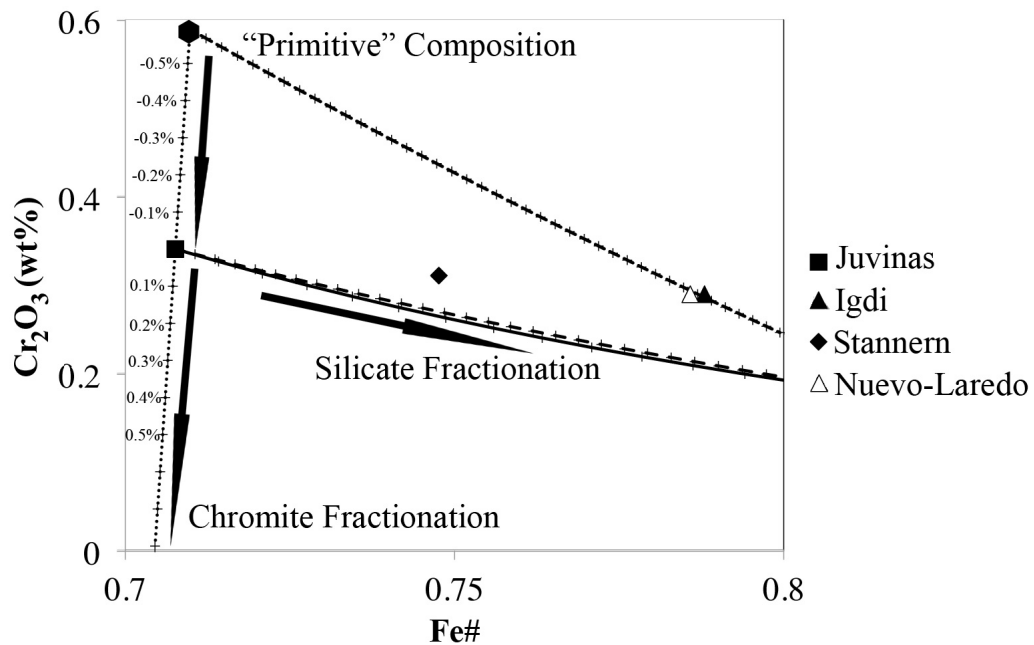

Figure 11: *In the Cr-Fe-Mg system, pure pyroxene fractionation (solid line) and fractionation of an average eucrite (52% pyroxene, 48% plagioclase; dashed lines) follow nearly identical paths. Small amounts of chromite precipitating (39% FeO, 42% Cr_2O_3; dotted line) can have a profound effect on the system. Direct fractionation from the Juvinas bulk composition does not generate Igdi, but addition of 0.6% chromite to form a 'primitive' composition can fractionate to form Igdi. Stannern was also included for reference. Bulk compositions are from the literature [Barrat et al., 2007; Barrat et al., 2003].*

Minor minerals crystallizing early in the crystallization sequence may offer a solution to this conundrum. Theoretical models for eucrite crystallization show four minerals forming for reasonable ranges of oxygen fugacity: chromite, pyroxene, plagioclase, and olivine (in order of decreasing liquidus temperature, calculated in MELTS) [*Asimow and Ghiorso*, 1998; *Ghiorso and Sack*, 1995]. The experimental crystallization sequence varies on the order, but agrees on the phases present [*Stolper*, 1977]. Literature values for average eucrite chromite show that it is properly ferrichromite with ~40% FeO and ~40% Cr_2O_3 [*Mayne et al.*, 2009]. Experimentally formed chromites are less ferroan, with ~27% FeO and ~42% Cr_2O_3 [*Stolper*, 1977]. With either composition, small amounts of chromite crystallizing would strongly affect the Cr-content of the magma (and, incidentally, have a modest effect on the Fe/Mg of the magma). If Juvinas pyroxenes formed from a primitive magma that had formed chromite before pyroxene fractionation, then an initial magma composition can be found that ties Juvinas and Igdi pyroxenes.
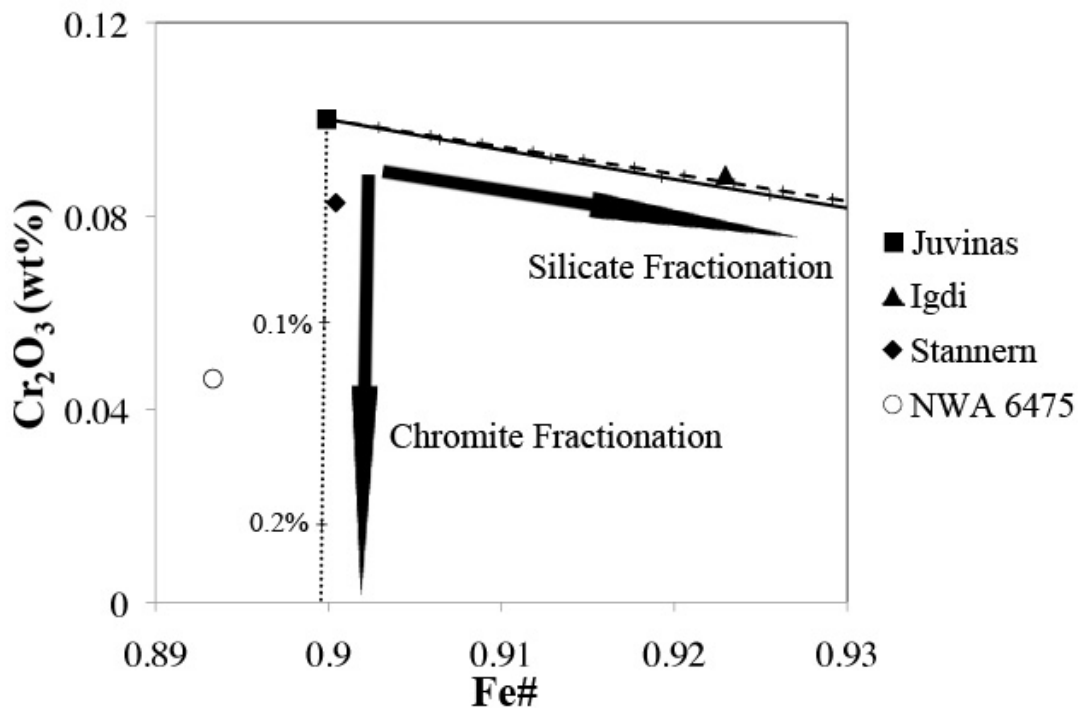

Figure 12: *As in figure 11, three fractionation models have been calculated for eucrite evolution: pure pyroxene fractionation (solid line), average eucrite fractionation (52% pyroxene, 48% plagioclase; dashed line), and ferri-chromite removal (dotted line). This time the model is started from the liquid composition calculated from Juvinas pyroxenes, and compared to calculated liquids from the other three examined eucrites. Note that Igdi now lies along the silicate fractionation curves without a modification to the original Juvinas liquid. NWA 6475 calculated liquid is too magnesian to be accounted for in this simple model, but variation within the pyroxene compositions of both meteorites will show some overlap with model results, suggesting that chromite fractionation played a role in generating NWA 6475 from the primitive liquid. Stannern has again been included for reference.*

Calculated liquid compositions may resolve the conflict with the expected model results. The bulk composition of Juvinas is significantly less ferroan than the equilibrium liquid composition calculated from the average pyroxene compositions. This suggests that the Juvinas meteorite does not represent a direct sample of the magma it crystallized from, so use of the bulk composition is inappropriate. Substituting the calculated liquid compositions, either pyroxene or average eucrite fractionation from Juvinas generates a liquid consistent with Igdi (Fig. 12).

A trace element model shows that the major element model for eucrite fractionation is flawed. It is important in any geochemical model to consider more than just a single chemical system before accepting it. The trace element system of La and Sc has been identified as a potent tool for examining eucrite chemistry (Fig. 13) [*Mittlefehldt and Lindstrom*, 1993]. In this system Sc acts as a proxy for magmatic evolution, much as Fe# does for major elements. La is a sensitive indicator of low degrees of partial melting, so for high partial melt systems, like this fractional crystallization model, it should remain relatively constant. Since Sc is vaguely compatible in pyroxene, and very incompatible in plagioclase, it can also act as a sensitive tool to determine the composition of a fractionating solid from a eucritic magma. It should also be noted that this system is insensitive to chromite fractionation. For bulk compositions, Nuevo-Laredo is consistent with the fractional crystallization model, but Igdi is near the limit of fractional crystallization of a pyroxene-enriched eucritic fractionate. In calculated liquid compositions, it is impossible to achieve the Igdi composition from Juvinas. It is also apparent that although the Cr content of NWA 6475 can be accounted for by small amounts of chromite formation, in the La-Sc system NWA 6475 liquids would require significant eucritic crystal fractionation to achieve from the Juvinas liquid, in sharp contradiction with the major element system model. It is therefore apparent that fractionation within the pyroxene-plagioclase-chromite system cannot relate all MGT and NLT magmas.

MGT → ST Modeling

It is difficult to relate the MGT and ST as cogenetic sequences. The initial model was to relate the two as a partial melting sequence: ST eucrites represented a lower degree of partial melting than MGT eucrites [*Stolper*, 1977]. A more recent attempt functions in the magma ocean paradigm [*Righter and Drake*, 1997], and involves mixing of primitive MGT magmas with partial melts of existing eucrites [*Barrat et al.*, 2007]. This model will be examined and demonstrated to be false by the systematics of observed pyroxene compositions. Since this debate centers on trace element compositions in homogenized pyroxenes, it is important to consider the effect of metamorphic overprinting [*Treiman*, 1996].

Any fractionation model used to relate the various eucrite trends must be tied to reasonable chemical, thermal, and physical constraints. A first order observation of eucrite compositions shows that any melt formed from a eucrite, whether at high or low degrees of melting, will be more ferroan than the solid it is in equilibrium with. To this end, it is difficult to rationalize any material formed from a primitive MGT composition
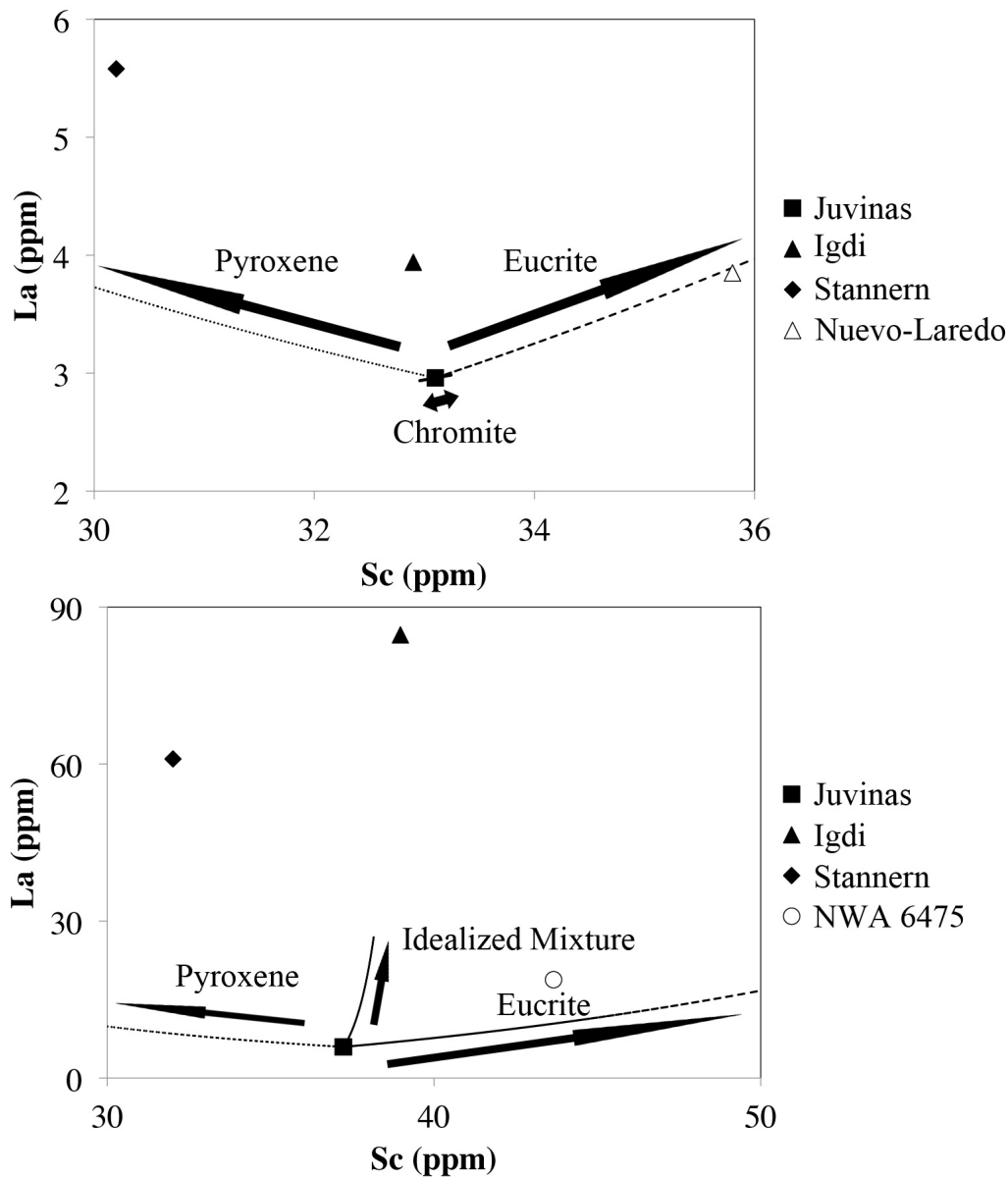
Figure 13: *As in figures 11 & 12, comparison of three fractionation models for eucrite evolution: pure pyroxene fractionation (dotted line), average eucrite fractionation (52% pyroxene, 48% plagioclase; dashed line), and ferri-chromite removal (solid line). Models are calculated based on meteorite bulk compositions (above) and liquids calculated from pyroxene compositions (below). This time a trace element system is considered. In this system Sc is generally considered a proxy for magmatic evolution, much as Fe# was previously [Mittlefehldt and Lindstrom, 1993]. Pure pyroxene fractionation and the average eucrite fractionation follow nearly opposite vectors, so an arbitrary vector between them can be calculated. The 'idealized mixture' (70% pyroxene, 30% plagioclase) vector points at Igdi, but does not enrich La sufficiently for even exaggerated ranges of crystallization. (the 'ideal curve' here is for 0.2<f<1. In reality the system runs out of pyroxene close to f≈0.3)*

that has higher incompatible element concentrations and lower FeO/MgO. Juvinas and Stannern are within reasonable error of an identical FeO/MgO, but as we will discuss later, the average NWA 6475 pyroxene has higher REE and lower FeO/MgO than Juvinas. This is problematic, as it doesn't follow the expected chemical trend.

The effect of differential metamorphic overprinting is likely to be minimal in these eucrites. Although the major elements have been equilibrated across the pyroxenes, pyroxene is still the major reservoir for both Mg and Fe in these eucrites. To alter the average pyroxene Fe and Mg content would require the formation of additional minor phases, such as troilite and ferri-chromite. Metamorphic troilite is unlikely as there is no excess sulfur in the system. Metamorphic chromite is possible, but its effect on the FeO/MgO of the pyroxene is limited by the low concentration of Cr in eucrites. Further, all of these eucrites have been subjected to similar metamorphic events, as evidenced by similar separations between the high- and low-Ca pyroxene compositions in exsolution and similar lamellae widths. Although this overprinting may exclude the calculation of a robust magma composition, it still allows a comparison between similarly metamorphosed materials.

A pure fractional crystallization model has not yet been identified to relate the ST eucrites to MGT magmas. Experimental results show that olivine, pyroxene and plagioclase are the main silicate phases stable at low degrees of crystallization from Juvinas bulk composition [*Stolper*, 1977]. None of these minerals fractionate the magma along a vector that ties Juvinas pyroxenes to Stannern pyroxenes. Theoretical modeling results do not suggest another phase to consider. All of these models fail because they do not sufficiently enrich the fractionated magma in La compared to Sc (or FeO/MgO). This leads us to consider alternate geochemical models.

It is possible that assimilation may play an important role in the evolution of eucritic magmas, but present models are not able to clearly reconcile the ST and MGT within reasonable thermal and physical scenarios. Barrat et al. generated a geochemical model based on magma mixing of a 10% eucritic melt that approximately relates ST and MGT magmas [*Barrat et al.*, 2007]. Fractional crystallization was considered along with assimilation, so the equations for AFC magmatic evolution were used [*DePaolo*, 1981]. An important variable in this model is "r", which represents the ratio of the rates of material being assimilated ($\dot{M}_a$) to material being crystallized ($\dot{M}_c$). In the scenario where two existing magmas are mixing while cooling, this ratio describes the net rate of change in the size of the original magma chamber. The Barrat model requires values above r=5 (Fig. 14), meaning that the magma chamber is growing rapidly. This model could only operate where the partial melt is essentially recharging the primitive magma chamber. Physically, this requires a significant input from a large, and pre-existing magma chamber, not small amounts of assimilation along the primitive magma chamber walls. In the scenario where significant amounts of the chamber walls are being assimilated into the magma chamber, the bulk rock is added as the assimilant, not a partial melt of it. The AFC model for eucritic assimilation is shown below (Fig. 15). It is worth noting that high degrees of assimilation buffer the magma near to the primitive eucrite composition, so there is little change for even large amounts of assimilation (the r=5 arrow points to the composition from assimilating a mass equal to the original magma). Further, in the example of eucrites melting eucrites, the thermodynamic upper bound is r=1, as the latent heat of both the assimilant and the crystallizing fraction are the

same. This model also fails to show a robust connection between the MGT and ST compositions.
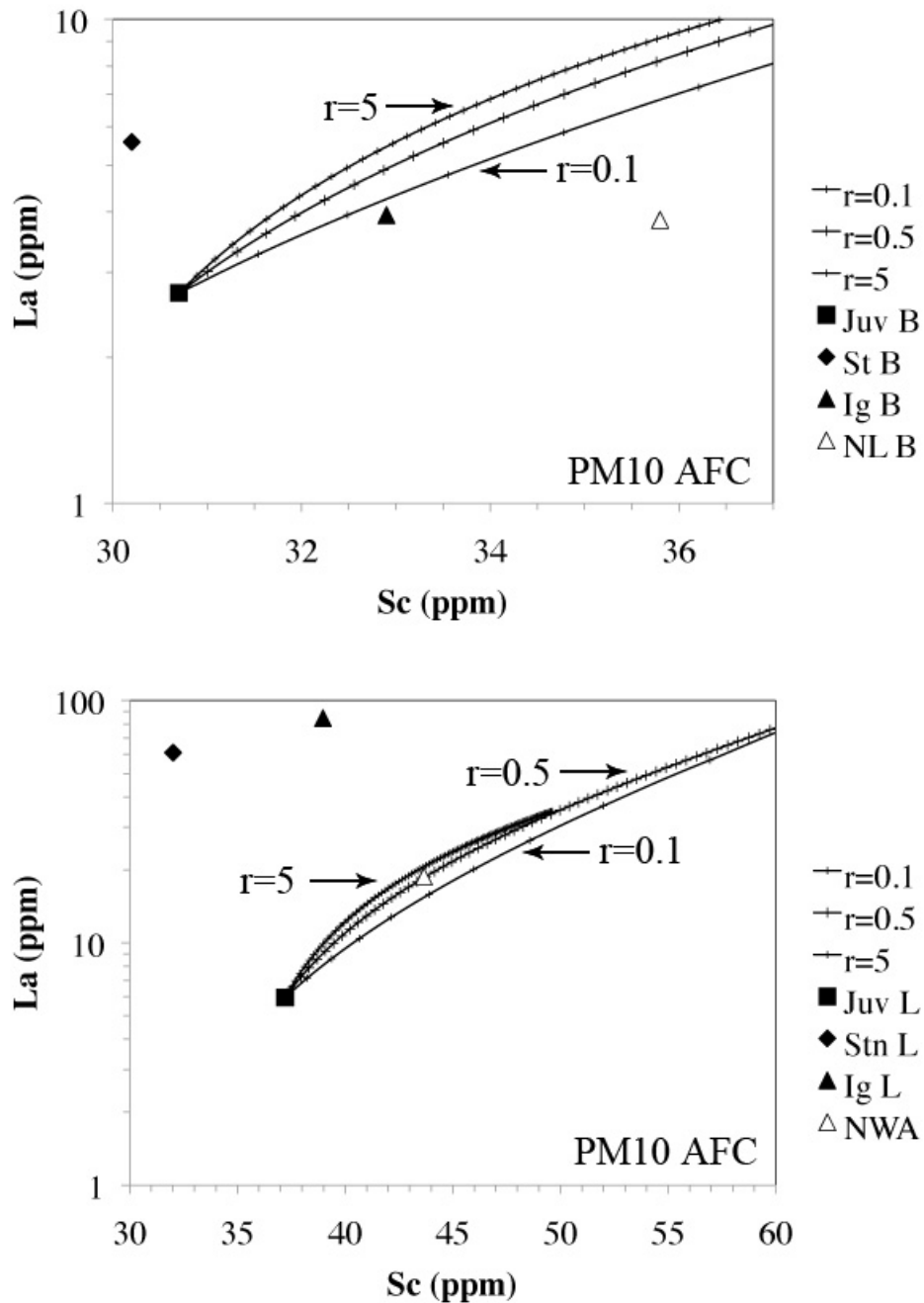

Figure 14: *AFC magma compositions for mixing of a 10% partial melt starting from the Juvinas bulk composition (above), and starting from the calculated liquid compositions (below). Each point along the curves represents a 1% mass addition to the original magma. Diagrams are after Barrat et al., 2007, and bulk compositions are from literature [Barrat et al., 2007; Barrat et al., 2003]. In terms of modal composition ties, this model fails to correlate the two trends.*
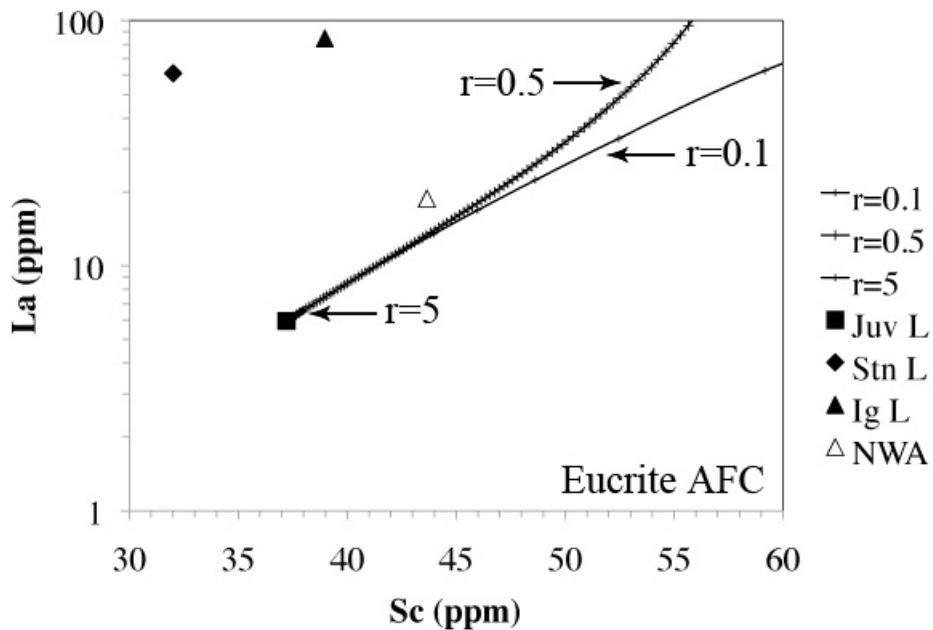
Figure 15: *AFC magma compositions for simple AFC of a MGT eucrite magma intruding into a MGT eucritic host rock. As a physical model this is the simpler, and more plausible, model for eucritic magma interaction with existing rock, but fails to evolve a MGT magma to the ST composition.*

NWA 6475 Modeling Results

NWA 6475 is more complicated to relate to a primitive, Juvinas-like magma than the others. It has a major element composition that is centered on the MGT, but with NLT clasts and cumulate eucrite grains in some MGT-dominated clasts. It also has a REE content that is intermediate between the MGT and the ST.

In terms of major elements, NWA 6475 clasts are primarily within the main group, and so provide a reasonable estimate of the primitive, or at least the modal, magma composition. Relative to Juvinas, these clasts are low in Cr and slightly more magnesian. To a first order, this is consistent with a higher degree of chromite fractionation before pyroxene saturation (See Fig. 12).

In terms of trace elements, NWA 6475 is almost entirely homogeneous. The exception to this is the CE pyroxenes. It is interesting to note that the CE pyroxenes in NWA 6475 are in clasts dominated by MGT pyroxenes, not in separate clasts. LA-ICPMS analysis of two pyroxenes in one such mixed clast shows different REE contents in the two groups. Unfortunately, the REE abundance of the CE pyroxene was near the method detection limit, so the absolute concentration is not reliable for modeling.

The presence of all three major-element groups (CE, MGT, NLT) within a single breccia confirms that these trends can form on a single parent body. Each chemical trend also displays a systematic decrease in Cr with increase in Fe/Mg (Fig. 16), as expected for a crystallization relationship, suggesting that within NWA 6475 the three trends are cogenetic. A search of literature values shows that this is not always the case. Of the 29

eucrite meteorites examined by Mayne et al., very few show a coherent variation of Cr content with Fe/Mg [*Mayne et al.*, 2009].
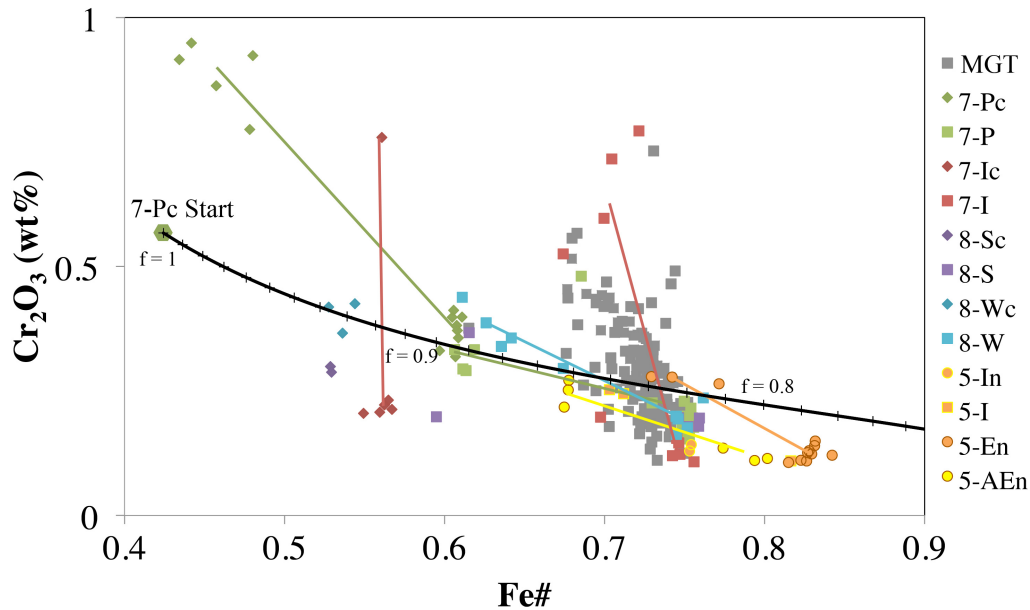

Figure 16: *Cr-content as a function of Fe# for representative pyroxenes in NWA 6475. Pyroxenes from the same clast have the same color. Pyroxene symbols vary by grouping: MGT (square), CE (diamond), NLT (circle). Vertical spread within a grain is due primarily to the Cr dependence on Ca content – tie lines are provided between groups of exsolved pyroxene compositions. Note the inverse dependence between Cr and Fe.*

Other Implications for Discussion

Through geochemical modeling of major elements it has become clear that even 'primitive' eucrites, like Juvinas, show signs of cumulate process. If an igneous sample represents a closed system affected only by crystal accumulation, then the mineral compositions must be in equilibrium with the bulk composition. This would be most apparent if the system crystallized in total equilibrium, so that the calculated liquid composition matches the bulk composition. For a fractional crystallization process, the mineral compositions need only match the liquid at some stage in its evolution. In Juvinas, there is a significant offset between the calculated liquid composition from pyroxene averages and the bulk composition as reported in the literature. The calculated Juvinas liquid is significantly more ferroan than the bulk composition, suggesting that an evolved liquid escaped incorporation into the bulk rock. This is consistent with a mixture of average eucrite silicates and minor amounts of oxides fractionating from the primitive composition through the liquid composition, and extracting a residual liquid to achieve the bulk composition. This should be confirmed in trace elements to constrain exactly what crystallized, and what composition of magma escaped.

Conclusions

New observations confirm some of our understanding of eucrite petrogenesis, but also show a number of inconsistencies with our present models and interpretations. These observations are based on detailed chemical descriptions of pyroxene populations in monomict eucrites of known bulk classification and pyroxene populations in igneous clasts in a polymict eucrite. These observations have been incorporated into contemporary models of assimilation and fractional crystallization within the suite.

Chemical diversity in the pyroxene population of polymict eucrite NWA 6475 strongly suggests that cumulate eucrites, main group eucrites and Nuevo-Laredo trend eucrites can all originate on a single parent body. Contrasting this, chemical homogeneity in the face of petrologic diversity suggests a ubiquitous process that is insensitive to cooling rate or emplacement mechanism forms the main group eucrites. This means that major element changes to eucritic magma are comparatively rare, so the mechanism(s) that relates each of the eucrite groups to the MGT is the exception on the eucrite parent body.

Pyroxene crystal fractionation is not ubiquitously supported as a mechanism to relate primitive (MGT) eucrites to evolved (NLT) eucrites by meteorite mineral compositions in the observed eucrites. Solutions can be found to relate both Nuevo-Laredo and Igdi to Juvinas by crystal fractionation in the Fe-Mg-Cr system from bulk compositions and calculated liquids from pyroxenes. The Nuevo-Laredo bulk composition falls along a crystal fractionation curve from Juvinas in the La-Sc system, but the Igdi bulk composition does not. Igdi pyroxene compositions also fall outside of the possible crystal fractionation curves.

The proposal to form ST eucrites by assimilation of or mixing with low percentage melts of existing eucritic material into MGT magma is thermodynamically and physically unreasonable. With reasonable constraints from thermodynamics, the AFC equations do not connect the trends by assimilation during fractional crystallization. Although magma mixing with low partial melts of eucritic material comes close to reconciling the chemistry of the trends, the existence of such a melt in sufficiently large quantities is physically unlikely.

Pyroxene clast compositions within NWA 6475 broadly support pyroxene crystal fractionation as a mechanism to generate CE, MGT and NLT eucrites from MGT magmas. This shows that crystal fractionation did differentiate magmas on the eucrite parent body, but that not all eucrites are cogenetic. Pyroxene mineral compositions and simple models for eucrite fractionation should be considered as another tool for separating various genetic sequences of eucrites.

Use of bulk compositions when modeling eucrite fractionation relations is inappropriate. MGT eucrites do not represent unaltered primitive liquids. CE pyroxene grains in a MGT clast represent a non-equilibrium mineral assemblage. This can be explained one of three ways: 1) MGT magmas inheriting CE pyroxenes from a source magma or rock, 2) magma mixing between partially crystallized CE magma and entirely molten MGT magma, 3) two different formation mechanisms for pyroxenes operating without complete equilibrium. Further, calculated major element liquid compositions do not agree with bulk compositions, showing that the meteorites do not represent closed systems.

References

Ahrens, L. H. (1970), The composition of stony meteorites (VII) the special significance of eucrites Stannern and Nuevo Laredo in lunar-meteorite comparative studies, *Earth and Planetary Science Letters*, *9*(4), 341-344.

Asimow, P. D., and M. S. Ghiorso (1998), Algorithmic modifications extending MELTS to calculate subsolidus phase relations, *American Mineralogist*, *83*(9-10), 1127-1132.

Barrat, J. A., J. Blichert-Toft, P. Gillet, and F. Keller (2000), The differentiation of eucrites: The role of in situ crystallization, *Meteoritics & Planetary Science*, *35*(5), 1087-1100.

Barrat, J. A., A. Yamaguchi, R. C. Greenwood, M. Bohn, J. Cotten, M. Benoit, and I. A. Franchi (2007), The Stannern trend eucrites: Contamination of main group eucrite magmas by crustal partial melts, *Geochimica et Cosmochimica Acta*, *71*, 4108-4124.

Barrat, J. A., A. Jambon, M. Bohn, J. Blichert-Toft, V. Sautter, C. G√∂pel, P. Gillet, O. Boudouma, and F. Keller (2003), Petrology and geochemistry of the unbrecciated achondrite Northwest Africa 1240 (NWA 1240): an HED parent body impact melt, *Geochimica et Cosmochimica Acta*, *67*(20), 3959-3970.

Bland, P. A., et al. (2009), An Anomalous Basaltic Meteorite from the Innermost Main Belt, *Science*, *325*(5947), 1525-1527.

Bunch, T. E., A. J. Irving, D. Rumble, R. L. Korotev, J. H. Wittke, and P. P. Sipiera (2009), Northwest Africa 2824: Another Eucrite-like Sample from the Ibitira Parent Body?, *Meteoritics and Planetary Science Supplement*, *72*, 5367.

DePaolo, D. J. (1981), Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization, *Earth and Planetary Science Letters*, *53*(2), 189-202.

Duke, M. B., and L. T. Silver (1967), Petrology of eucrites, howardites and mesosiderites, *Geochimica et Cosmochimica Acta*, *31*(10), 1637-1665.

Ghiorso, M. S., and R. O. Sack (1995), Chemical mass transfer in magmatic processes IV. A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures, *Contributions to Mineralogy and Petrology*, *119*(2), 197-212.

Greenwood, R. C., I. A. Franchi, A. Jambon, and P. C. Buchanan (2005), Widespread magma oceans on asteroidal bodies in the early Solar System, *Nature*, *435*(7044), 916-918.

Hsu, W., and G. Crozaz (1996), Mineral chemistry and the petrogenesis of eucrites: I. Noncumulate eucrites, *Geochimica et Cosmochimica Acta*, *60*(22), 4571-4591.

Hsu, W., and G. Crozaz (1997a), Mineral chemistry and the petrogenesis of eucrites: II. Cumulate eucrites, *Geochimica et Cosmochimica Acta*, *61*(6), 1293-1302.

Hsu, W., and G. Crozaz (1997b), Ion microprobe study of the Pomozdino and Peramiho eucrites, *Meteoritics & Planetary Science*, *32*(2), 271-280.

Langmuir, C. H. (1989), Geochemical consequences of in situ crystallization, *Nature*, *340*(6230), 199-205.

Larson, H. P., and U. Fink (1975), Infrared spectral observations of asteroid 4 Vesta, *Icarus*, *26*(4), 420-427.

Mayne, G. R., H. Y. McSween Jr., T. J. McCoy, and A. Gale (2009), Petrology of the unbrecciated eucrites, *Geochimica et Cosmochimica Acta*, *73*, 794-819.

McCord, T. B., J. B. Adams, and T. V. Johnson (1970), Asteroid Vesta: Spectral Reflectivity and Compositional Implications, *Science*, *168*(3938), 1445-1447.

Mittlefehldt, D. W., and M. M. Lindstrom (1993), Geochemistry and petrology of a suite of ten Yamato HED meteorites, *Procedings of the NIPR Symposium on Antarctic Meteorites*, *6*, 268-292.

Nyquist, L., D. Bogard, H. Takeda, B. Bansal, H. Wiesmann, and C. Y. Shih (1997), Crystallization, recrystallization, and impact-metamorphic ages of eucrites Y792510 and Y791186, *Geochimica et Cosmochimica Acta*, *61*(10), 2119-2138.

Pun, A., and J. J. Papike (1995), Ion microprobe investigation of exsolved pyroxenes in cumulate encrites: Determination of selected trace-element partition coefficients, *Geochimica et Cosmochimica Acta*, *59*(11), 2279-2289.

Pun, A., and J. J. Papike (1996), Unequilibrated eucrites and the equilibrated Juvinas eucrite; pyroxene REE systematics and major, minor, and trace element zoning, *American Mineralogist*, *81*(11-12), 1438-1451.

Pun, A., J. J. Papike, and G. D. Layne (1997), Subsolidus REE partitioning between pyroxene and plagioclase in cumulate eucrites: An ion microprobe investigation, *Geochimica et Cosmochimica Acta*, *61*(23), 5089-5097.

Righter, K., and M. J. Drake (1997), A magma ocean on Vesta: Core formation and petrogenesis of eucrites and diogenites, *Meteoritics & Planetary Science*, *32*(6), 929-944.

Schnetzler, C. C., and J. A. Philpotts (1969), Genesis of the calcium-rich achondrites in light of rare-earth and barium concentrations, edited, pp. 206-216, International Atomic Energy Agency : Vienna, International D. Reidel Publishing Co., International.

Stolper, E. (1977), Experimental petrology of eucritic meteorites, *Geochimica et Cosmochimica Acta*, *41*(5), 587-611.

Treiman, A. H. (1996), The perils of partition: Difficulties in retrieving magma compositions from chemically equilibrated basaltic meteorites, *Geochimica et Cosmochimica Acta*, *60*(1), 147-155.

Treiman, A. H. (1997), The parent magmas of the cumulate eucrites: A mass balance approach, *Meteoritics & Planetary Science*, *32*(2), 217-230.

Wiechert, U. H., A. N. Halliday, H. Palme, and D. Rumble (2004), Oxygen isotope evidence for rapid mixing of the HED meteorite parent body, *Earth and Planetary Science Letters*, *221*(1-4), 373-382.

Yamaguchi, A., G. J. Taylor, and K. Keil (1996), Global Crustal Metamorphism of the Eucrite Parent Body, *Icarus*, *124*(1), 97-112.

Yamaguchi, A., G. J. Taylor, and K. Keil (1997), Metamorphic history of the eucritic crust of 4 Vesta, *J. Geophys. Res.*, *102*(E6), 13381-13386.

Yamaguchi, A., J. A. Barrat, R. C. Greenwood, N. Shirai, C. Okamoto, T. Setoyanagi, M. Ebihara, I. A. Franchi, and M. Bohn (2009), Crustal partial melting on Vesta: Evidence from highly metamorphosed eucrites, *Geochimica et Cosmochimica Acta*, *73*(23), 7162-7182.