REVISION 1

The effects of contrasting Ti and Al activities on Mn/Fe systematics in pyroxene from lunar

mare basalts

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ABSTRACT

The usefulness of the Mn/Fe ratios of olivine and pyroxene to identify a sample's host parent body is well-established. Although there is an over-arching, defining slope for each planetary body, there is some scatter, or "dispersion" around the defining slope. This dispersion reveals important facts relating to the planetary body. The source regions of the three main types of lunar basalts (very high-Ti, low-Ti, and very low-Ti) have *f*O₂s near IW-1 or below, and all iron is either ferrous or metallic. The dispersion in the Mn/Fe ratios of pyroxene from the Moon is largely caused by differences in the Ti and Al concentrations in the mantle source regions and the resulting differences in Ti activity of the primary basaltic melts derived from those sources. Ti displaces ferrous iron in the pyroxene M1 site (in a coupled substitution with Al for Si in the tetrahedral site), and therefore, with increasing Ti activity the Mn/Fe ratio in pyroxene increases in all three suites studied. For lunar mare basalts, the effect of Ti activity on the occupancy of the pyroxene M1 site, and crystallization sequence differences among high-Ti, low-Ti, and VLT basalts account for almost all of the observed dispersion in the Mn/Fe ratios.

Keywords: pyroxene, basalt, manganese, iron, titanium, aluminum

INTRODUCTION

Papike et al. (2003) introduced a technique where the Mn/Fe ratios of olivine or pyroxene and the anorthite content of plagioclase provided a tool to identify the planetary parentage of newly discovered meteorites. A recent paper (Papike et al., 2017) refined this technique, focusing on the angrite meteorites, and a new, robust determinative curve was obtained. On a plot of Mn *vs*. Fe cations per formula unit for olivine from basalts, the slopes of the data trends decrease in the sequence Mars, Earth, angrite parent body (APB), and Moon. Vesta was not
included in the olivine discussion because basalts from Vesta (eucrites) have little or no olivine.
For pyroxene, the decreasing Mn *vs*. Fe slope sequence is Vesta, Mars, Earth, and Moon.
Analyses of angrite pyroxenes are not directly comparable to those from the other bodies because
in angrite pyroxenes the M2 sites are completely filled by Ca (e.g., Mittlefehldt et al., 1998;
Papike et al., 2016) and therefore have different substitution systematics.

17 Papike et al. (2017), however, did not discuss why we can compare relatively simple, 18 small bodies such as the Moon. Vesta and the angrite parent body, to much larger parental bodies 19 (for example Earth and Mars) that have undergone complex evolutionary histories including core 20 formation, magma ocean generation, and serial magmatism, yielding a range of basalt 21 compositions exposed to a large, dynamic range of oxygen fugacity, from three log units below 22 the iron-wüstite buffer to two log units above fayalite-magnetite-quartz (~IW-3 to FMQ+2). 23 Despite the fact that with enough high-quality electron microprobe data for olivine, pyroxene, 24 and plagioclase we find an over-arching fingerprint of planetary parentage, in any individual 25 suite there is significant scatter along the average trend line. The purpose of this paper is to 26 explore the dispersion of Mn/Fe ratios of pyroxene in lunar basalts and to illustrate the effect of 27 crystallization sequence upon this parameter.

Lunar mare basalts are divided into three main types: high-Ti (from Apollo 11 and 17 landing sites); low-Ti (mainly from the Apollo 12 and 15 landing sites); and very-low-Ti basalts (VLT; from the Soviet Luna 24 (L-24) mission and from the Apollo 17 (A-17) drill core). All of the Apollo samples were collected within or immediately adjacent to the Procellarum KREEP Terrane (PKT; Jolliff et al., 2000), whereas the L-24 basalts represent melts derived from outside this terrane. Most of the analysis of lunar samples indicates a fairly limited range of oxygen

fugacity, generally close to IW-1 (e.g., Wadhwa, 2008). Consistent with this estimate, direct measurements show that 60–100% of the Ti in lunar pyroxene is in the 4+ oxidation state, with up to 40% (but typically less) trivalent (Simon and Sutton, 2017; 2018). Rather than wide ranges in fO_2 or simply analytical error, the variability of Mn/Fe ratio in lunar basalt pyroxene is directly or indirectly dependent upon Ti concentrations in their mantle sources, as shown below.

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METHODS

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42 Data for pyroxene from high-Ti, low-Ti, and L-24 VLT basalts were taken from the 43 literature (Papike et al., 1976; 1998; Vaniman and Papike, 1977; Coish and Taylor, 1978) and are 44 tabulated in Tables A1-A3 of the supplemental material. The L-24 data were incorporated into this study to examine the potential variability in mantle Mn/Fe outside of the PKT. The A-17 45 46 VLT basalts considered here are those studied by Wentworth et al. (1979). New analyses of 47 pyroxene in these VLT samples (Tables 1 and A4) were obtained with a JEOL 8200 fully 48 automated electron microprobe at the University of New Mexico, operated at 15 kV. Counting 49 times on peaks ranged from 10 to 30 s; background count times equaled the peak counting 50 times for each analysis. Pure oxide, synthetic glass, and natural mineral standards were used. Average relative errors are ~6% for Ti and Mn, 2% for Al, and 0.5% for Fe. Fits to the 51 52 data, both linear and polynomial, were generated by curve-fitting algorithms built into the 53 KaleidaGraph v4.5 plotting software program. The polynomial fits are intended to be illustrative 54 rather than rigorous fits to the data.

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RESULTS

58 Crystal Chemistry of Lunar Pyroxenes

A review of pyroxene crystal chemistry is necessary for proper interpretation of the 59 60 results. Papike et al. (2005) summarized valence state partitioning of Cr. Fe, Ti, Al, and V among 61 crystallographic sites in olivine, pyroxene, and spinel from planetary basalts. That paper 62 illustrated the plethora of possible coupled substitution mechanisms in pyroxene using an 63 equation assuming stoichiometric formulae (where coefficients indicate the magnitude of the excess/deficiency, such that, for example, ^{VI}Al³⁺ is equivalent to a +1 charge excess, while 64 $2^{VI}Ti^{4+}$ indicates that for every Ti^{4+} substitution, there is a charge excess of +2). For lunar 65 pyroxene, the equation expressing this is: Excesses: $VIAl^{3+} + VICr^{3+} + VIV^{3+} + VITi^{3+} + 2^{VI}Ti^{4+} =$ 66 Deficiencies: ${}^{IV}A1^{3+} + {}^{M2}Na^{+}$. In lunar pyroxenes, no Fe³⁺ is detected in Mössbauer studies (e.g. 67 68 Hafner and Virgo, 1970). This is not surprising since metallic iron occurs in many samples. Coupled substitutions are required to incorporate trivalent cations and Ti⁴⁺ into the pvroxene 69 70 crystal structure because they replace divalent Mg and Fe in the M1 site (Papike et al., 2005). 71 thus creating an excess charge of +1 or +2, respectively. Crystal charge balance must be 72 maintained and can be accomplished by simultaneously substituting: 1) one Al cation into the 73 tetrahedral site for Si; or 2) one Na cation into the M2 site for Ca, per unit of excess charge. 74 Although pyroxenes from the three mare basalt groups exhibit a range of Mn/Fe ratios, the 75 positioning of an individual point on a plot of Mn vs. Fe cations does not follow a simple sweep 76 of Mn/Fe slope dependent only on Ti content. This is because, although $Ti^{4+}(M1) - 2AI$ (tet.) 77 exchange is very important, it is not the only coupled substitution in play. The second most 78 important is Al(M1) - Al(tet.). Therefore, the competing effects of variable Al vs. Ti content of 79 pyroxene can change the positioning of an individual point. Substitution of Ti into pyroxene 80 leads to increases in the Mn/Fe ratios; Ti⁴⁺ (and to a lesser extent Cr³⁺) preferentially replace Fe

relative to Mn because their ionic radii (0.605 and 0.615 Å, respectively) are closer to that of Fe

- 82 (0.77 Å) than Mn (0.82 Å) (Shannon and Prewitt, 1969).
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Pyroxenes as recorders of lunar basalt petrogenesis

84 Bence and Papike (1972) demonstrated how zoning in mare basalt pyroxene recorded the 85 chemical evolution of the residual melt. They noted two dominant atomic Ti/Al ratios in pyroxene: a "low" value, ~¹/₄, reflecting crystallization before plagioclase, and a "high" value 86 87 $\sim \frac{1}{2}$, reflecting crystallization after plagioclase. This is very important for the present subject: the 88 variation of the Mn/Fe ratio with melt crystallization is a function of the competing activities of 89 Ti and Al and crystallization sequence. Crystallization sequences for many of the crystalline 90 mare basalts are summarized by Papike et al. (1976). The influence of crystallization history on 91 pyroxene chemistry is summarized by Bence and Papike (1972). Many of these magmas 92 represent only a part of the crystallization history of the primary mare basalts. For all primary 93 basalt compositions that have been examined, olivine is the first phase to crystallize (Longhi, 94 1987)

95 The data for the high-Ti basalts are given in Table A1 (high-Ti basalts) and are illustrated 96 in Fig. 1. A plot of Mn cations per formula unit as a function of Fe# (Fe/(Fe + Mg) cations per 97 formula unit) shows, with increasing Fe#, a somewhat sinusoidal trend with a positive trajectory 98 (Fig. 1a). The linear fit has a slope of 0.022 ± 0.005 and is shown for comparison, illustrating the 99 better fit of the sinusoidal curve, except, in both cases, for the steep increase in Mn content at 100 low Fe#. This near-vertical trend is a result of rapid, early incorporation of Ti into the pyroxene 101 M1 site and a consequent displacement of Fe, leading to increasing Mn/Fe ratios. For Apollo 17 102 and Apollo 11 basalts, early liquidus phases include olivine, ilmenite (Fe²⁺,Mg)TiO₃ and 103 armalcolite (Fe²⁺,Mg)Ti₂O₅ (Papike et al., 1976; Taylor et al., 1991). These phases sequester Fe

104 effectively and early, competing with pyroxene while increasing the alumina activity, which 105 facilitates Ti substitution into pyroxene. This near-vertical trajectory continues until the Ti-106 oxides stop crystallizing. Next is a segment (Fe# from ~ 0.5 -0.9) with a shallower slope. This is 107 after plagioclase crystallizes, so the Ti/Al ratio is relatively high, $\sim \frac{1}{2}$ (Bence and Papike, 1972). The inflection before (i.e., at lower Fe#) the flattened part of the trajectory occurs when 108 109 plagioclase comes onto the liquidus and competes with pyroxene for Al, causing sharp drops in 110 both Ti and Al contents in pyroxene (Fig. 1b). The last upturn, at Fe# $>\sim 0.9$, involves a second 111 increase of Ti activity in the residual melt due to plagioclase crystallization. The Ti enters the 112 late-stage pyroxene and again displaces Fe, causing an increased Mn/Fe ratio and resulting in the 113 crystallization of late-stage ilmenite and Ti-rich spinel.

The enrichment of early pyroxene in Ti and Al is illustrated in Fig. 1b. Abundances of both of these cations in pyroxene decrease as Fe# increases. Despite the early crystallization of Fe-Ti oxides, early pyroxene has higher Ti contents than late pyroxene, due to the availability of Al for coupled substitution prior to plagioclase crystallization, after which both decrease. The strong correlation (R^2 = .973) of Ti and Al cation contents in high-Ti mare basalt pyroxene can be seen in Fig. 1c. The slope is very close to ½, reflecting the dominance of the Ti⁴⁺ + 2Al³⁺ for M²⁺ + 2Si⁴⁺ coupled substitution.

Data for low-Ti basalts are given in Table A2 and illustrated in Figure 2. The linear fit has a slope of 0.013±0.003. As observed for the high-Ti pyroxene, a sinusoidal pattern with three main segments is observed for low-Ti basalt pyroxene on a plot of Mn cations against Fe# (Fig. 2a). The first segment reflects co-crystallization of olivine and pyroxene, with pyroxene incorporating Ti and Al in a ratio of ~¹⁄₄ and Mn increasing sharply over a narrow range of Fe#. The second is a flattening when plagioclase comes onto the liquidus. This sharply increases the

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127 Ti/Al ratio of the pyroxene to $\frac{1}{2}$, but also causes the Ti content of the pyroxene to drop, but not 128 as sharply as that of Al (Fig. 2b). This sequence of changes in the Ti/Al ratios of the pyroxene is 129 indicated with arrows showing the trend with crystallization progress in Fig. 2c. The contents of 130 Al and Ti cations are not as strongly correlated in the low-Ti basalts as they are in the high-Ti 131 basalts (Fig. 1c) because, with the lower initial Ti/Al in the parental melts of the former, two 132 substitutional couples are involved. The first is, as above, Ti⁴⁺(M1)- 2Al³⁺(Tet site, tetrahedral). 133 The second is Al³⁺(M1)- Al³⁺(Tet-site). Once plagioclase comes onto the liquidus, it sequesters 134 Al and the slope rises from $\frac{1}{4}$ to $\frac{1}{2}$. Thus, pyroxene in low-Ti mare basalts, unlike that in high-Ti 135 basalts, does not have a constant Ti/Al ratio of ¹/₂ (Fig. 2c,d). 136 Sinusoidal crystallization trajectories are also observed on a plot of Mn cations vs. Fe# 137 for both A-17 VLT and Luna 24 VLT pyroxenes (Fig. 3a). The linear fits have the same slope as 138 each other and the low-Ti basalt data. Representative electron probe analyses of A-17 VLTs are 139 given in Table 1. A rise in the activity of Ti in late-stage liquids due to fractional crystallization 140 of plagioclase and Ti-poor pyroxene causes the upswing of all trajectories and leads to the 141 crystallization of Ti-rich spinel and ilmenite, which preferentially take up Fe relative to Mn. The 142 abundances of Ti and Al cations per formula unit for A-17 VLT basalt pyroxenes are plotted 143 against Fe# in Fig. 3b. Some early pyroxene is Al-rich, but overall, Al contents are relatively 144 constant with crystallization progress. Early pyroxene is Ti-poor, and Ti contents increased 145 significantly as crystallization proceeded. Fewer analyses of L-24 pyroxene are available but 146 similar trends can be seen (Fig. 3c): some relatively Al-rich early pyroxene occurs but otherwise 147 there is no strong trend, and Ti contents increase with Fe# as in A-17 VLTs.

148 The Mn-Fe trends for all suites considered here are compared in Fig. 4. All of the data 149 are shown in Fig. 4a. The associated sinusoidal trends are shown in Fig. 4b; the high-Ti and Luna

150 24 trends are the most strongly sinusoidal, with the other suites having flatter trends. The linear 151 fits are illustrated in Fig. 4c. The high-Ti (HT) basalts have a relatively steep slope 152 (0.022 ± 0.005) and the other suites have slopes of ~0.013, typical of lunar pyroxene (Papike et 153 al., 2003).

154 These data imply that differences in the activity of Ti in the basalts, their crystallization 155 sequences, and the nature of the M1 site in pyroxene result in minor variations in lunar pyroxene, 156 vet they do not radically reduce the usefulness of Mn/Fe in pyroxene as an indicator of planetary 157 heritage. Increasing Ti activity should increase the polymerization of melt, and as Ti⁴⁺ abundances in the silicate melt increase, ^[IV]Ti⁴⁺ and ^[IV]Fe²⁺ tend to change to ^[VI]Ti⁴⁺ and ^[VI]Fe²⁺ 158 159 in the melt structure (Vander Kaaden et al., 2015). The role of melt structure due to changes in the Ti content of the melt does not, however, appear to be significant. The limited data available 160 161 for Mn partitioning in silicates over this range (e.g., Longhi et al., 1978) show no correlation 162 with melt structure.

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IMPLICATIONS

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165 Basalts are considered by many petrologists as windows into the nature of planetary 166 mantles. Not all basalts are equal in this regard, however. Primary basalts (derived from a 167 planetary mantle without gain or loss of material) are the most valuable "recorders". In terms of 168 using Mn/Fe ratios for determining planetary parentage and the reasons for dispersion in this 169 trend for each body, variation in oxygen fugacity appears to be the most important factor for 170 martian basalts (Papike et al., 2017). For lunar mare basalts, high Ti activity in the melting zone 171 and the melts, and crystallization sequence differences among high-Ti, low-Ti, and VLT basalts 172 account for almost all of the observed dispersion in the Mn/Fe ratios.

173 The Mn and Fe contents of pyroxene from four Solar System bodies are compared in Fig. 174 5. From highest Mn/Fe ratio to lowest, the sequence is Vesta, Mars, Earth, and Moon. The 175 dispersion in 4 Vesta pyroxene can be attributed mostly to analytical error. For Mars, the 176 dispersion results from a combination of analytical error plus variation in oxygen fugacity 177 (Papike et al., 2018). For Earth, the dispersion can be entirely explained by the range in oxygen 178 fugacity over which the terrestrial basalts crystallized. The low Mn/Fe ratios of lunar pyroxenes 179 compared to those from other parent bodies could be due to volatilization and loss of Mn relative 180 to Fe in the Moon-forming event, and distinct conditions (e.g., lower fO_2 and P compared to 181 Mars and Earth) of core formation and core composition.

Similarities in Mn/Fe between pyroxenes from mare basalts within and outside the PKT indicate a limited range of Mn/Fe on the planetary mantle scale. This limited range is further substantiated by the Mn/Fe of lunar pyroxenes from basaltic meteorites of different ages that were randomly sampled from the lunar surface (Elardo et al., 2014). The mantle sources for all of these magmas must have had nearly identical Mn/Fe, suggesting that the Moon-wide primordial melting and differentiation event had little effect on this ratio in silicates.

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269 270	FIGURE CAPTIONS
271	Figure 1. a) Mn vs. Fe# for high-Ti basalt pyroxene with a linear and a sinusoidal curve fitted to
272	the data. The polynomial curve fit (4^{th} order) was calculated with KaleidaGraph v 4.5
273	software. b) Abundances of Al and Ti cations per formula units plotted against Fe#. Both
274	Al and Ti decrease with increasing Fe#. c) Ti vs. Al cations per formula unit showing a
275	strong positive correlation and a slope of $\sim 1/2$. This is because the dominant charge
276	balance mechanism for incorporation of Ti into the pyroxene M1 site is $\mathrm{Ti}^{4+}(\mathrm{M1})$ -
277	2Al ³⁺ (T-site, tetrahedral). The Ti-Al substitution displaces ferrous iron, causing increases
278	in the Mn/Fe ratio. Data from Papike et al. (1976, 1998).
279	
280	Figure 2. Analyses of pyroxene in low-Ti basalts. a) Plot of Mn cations per formula unit vs. Fe#,
281	with both a linear and a sinusoidal curve fitted to the data. The polynomial curve fit (4 th
282	order) was calculated with KaleidaGraph v 4.5 software. b) Ti (apfu) and Al (apfu) vs.
283	Fe#. Note contrast with data for high-Ti basalts (Fig. 1b). c) Plot of Ti (apfu) vs. Al
284	(apfu), showing different Ti/Al slopes for pyroxene crystallized before $(\frac{1}{4})$ and after $(\frac{1}{2})$
285	plagioclase crystallization. Arrows indicate trends with continued crystallization. d) Plot
286	of atomic Ti/Al vs. Fe#. Pyroxenes in low-Ti mare basalts do not have a constant slope of
287	$\frac{1}{2}$, because with the higher initial Al/Ti in the melt, two substitutional couples are
288	involved: Ti ⁴⁺ (M1)-2Al ³⁺ (T-site, or tetrahedral); and Al ³⁺ (M1)-Al ³⁺ (T-site). Once
289	plagioclase comes on the liquidus, it sequesters Al and the slope rises from $\frac{1}{4}$ to $\frac{1}{2}$. Data
290	from Papike et al. (1976, 1998).

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292 Figure 3. a) Plot of Mn cations per formula unit vs. Fe#, showing different sinusoidal and linear

293	trajectories for pyroxenes from A-17 and Luna 24 VLT basalts. b) Ti and Al abundances
294	per formula unit vs. Fe# for A-17 VLT basalt pyroxene. Aluminum contents are relatively
295	constant with crystallization but Ti contents increase significantly because, unlike the
296	high-Ti and low-Ti basalts, in the VLTs there are negligible proportions of Ti-oxides
297	competing with pyroxene for Ti. c) Ti and Al abundances per formula unit vs. Fe# for
298	Luna 24 VLT basalt pyroxene. The trends are similar to those observed for A-17 VLT
299	pyroxene.

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Fig. 4. a) Summary diagram showing the crystallization trajectories of the four suites for Mn
cations per formula unit vs. Fe#. Note the generally sinusoidal distribution. b) Polynomial
(4th order) fits to the Mn vs. Fe# data shown in (a). The high-Ti basalts have the steepest
trend and the L24 VLTs the most sharply curved, but only seven analyses with Mn cation
abundances reported are available for the latter suite, so its curves may not be very
representative. c) Linear fits to the data shown in (a). The VLT and low-Ti suites have

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Figure 5. Plot of Mn vs. Fe cations per formula unit for pyroxene from Vesta, Mars, Earth and
Moon; Mn/Fe ratios decrease in that order. Slopes of the linear fits to the data have a
range of a factor of 2. Mars and Earth have similar slopes. After Papike et al. (2009).

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	1.	2.	3.	4.	5.	6.	7.	8.	9.			
MgO	22.34	16.38	14.00	9.82	23.80	20.72	13.07	4.76	0.61			
Al_2O_3	1.64	1.78	1.20	1.09	1.25	1.94	1.98	1.03	0.82			
SiO ₂	53.40	51.73	51.14	49.32	53.56	52.71	51.02	47.30	45.75			
CaO	4.35	9.12	7.97	8.98	3.14	5.66	15.78	8.46	8.54			
TiO ₂	0.18	0.31	0.52	0.97	0.09	0.18	0.43	1.01	0.91			
Cr_2O_3	0.86	0.75	0.46	0.18	0.79	1.06	0.82	0.17	0.03			
MnO	0.34	0.39	0.39	0.43	0.36	0.37	0.30	0.45	0.57			
FeO	16.40	19.16	23.52	28.27	16.07	17.65	16.71	36.38	42.64			
Total	99.72	99.85	99.39	99.22	99.08	100.31	100.15	99.58	99.89			
Total 99.72 99.85 99.39 99.22 99.08 100.31 100.15 99.58 99.89 Mg 1.225 0.923 0.806 0.583 1.306 1.141 0.740 0.293 0.039 A1 0.071 0.079 0.054 0.054 0.084 0.089 0.050 0.041												
Mg	1.225	0.923	0.806	0.583	1.306	1.141	0.740	0.293	0.039			
Al	0.071	0.079	0.054	0.051	0.054	0.084	0.089	0.050	0.041			
Si	1.964	1.955	1.976	1.964	1.971	1.947	1.940	1.956	1.953			
Ca	0.171	0.369	0.330	0.383	0.124	0.224	0.643	0.375	0.391			
Ti	0.005	0.009	0.015	0.029	0.003	0.005	0.012	0.031	0.029			
Cr	0.025	0.022	0.014	0.006	0.023	0.031	0.025	0.006	0.001			
Mn	0.011	0.012	0.013	0.014	0.011	0.012	0.010	0.016	0.021			
Fe	0.504	0.606	0.760	0.941	0.495	0.545	0.531	1.258	1.522			
Total	3.991	3.993	3.982	3.984	3.988	3.991	3.992	3.986	3.998			
En	64.45	48.62	42.54	30.57	67.86	59.73	38.67	15.22	1.99			
Wo	9.01	19.46	17.40	20.08	6.44	11.74	33.58	19.45	20.02			
Fs	26.53	31.92	40.07	49.35	25.70	28.54	27.75	65.32	77.99			
Mn/Fe	0.021	0.021	0.017	0.015	0.023	0.021	0.018	0.013	0.014			
Fe#	29.16	39.63	48.51	61.75	27.47	32.33	41.78	81.10	97.52			
	1 1 -							>				

316 Table 1. Representative electron probe analyses of pyroxene in A-17 VLT basalts.

317 Analyses 1.-4.: 70007,289; 5.-9.: 70007,296. Fe# = 100 x atomic Fe/(Fe+Mg).

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)	•		1	2	17			
	10.	11.	12.	13.	14.	15.	16.	17.	18.
MgO	23.97	19.57	7.30	2.58	23.97	18.28	16.10	6.13	3.01
Al ₂ O ₃	1.44	1.74	0.78	1.25	1.54	0.87	1.20	1.54	0.73
SiO ₂	53.93	52.63	48.48	46.92	53.99	52.58	51.32	47.95	46.93
CaO	3.71	6.07	5.82	10.97	3.69	4.98	5.64	11.71	9.09
TiO ₂	0.12	0.19	0.52	1.18	0.14	0.13	0.25	0.91	0.83
Cr_2O_3	0.83	0.79	0.27	0.04	0.85	0.48	0.55	0.51	0.06
MnO	0.32	0.37	0.53	0.54	0.32	0.37	0.43	0.42	0.52
FeO	15.59	18.48	36.01	36.20	15.82	22.38	23.84	30.48	38.21
Total	99.91	99.83	99.72	99.69	100.34	100.08	99.35	99.67	99.37
			C	Cations per	r 6 oxyger	ı			
Mg	1.303	1.087	0.444	0.160	1.299	1.028	0.922	0.370	0.188
AĨ	0.062	0.077	0.038	0.061	0.066	0.039	0.054	0.074	0.036
Si	1.966	1.961	1.977	1.952	1.962	1.983	1.972	1.942	1.968
Ca	0.145	0.242	0.254	0.489	0.144	0.201	0.232	0.508	0.408
Гі	0.003	0.005	0.016	0.037	0.004	0.004	0.007	0.028	0.026
Cr	0.024	0.023	0.009	0.001	0.024	0.014	0.017	0.016	0.002
Mn	0.010	0.012	0.018	0.019	0.010	0.012	0.014	0.014	0.018
Fe	0.475	0.576	1.228	1.260	0.481	0.706	0.766	1.032	1.340
Total	3.988	3.983	3.984	3.980	3.990	3.987	3.986	3.986	3.987
En	67.74	57.05	23.04	8.37	67.53	53.12	48.02	19.38	9.72
Wo	7.54	12.72	13.20	25.62	7.47	10.40	12.09	26.59	21.08
Fs	24.72	30.23	63.76	66.01	25.00	36.48	39.89	54.03	69.19
Mn/Fe	0.021	0.020	0.015	0.015	0.021	0.017	0.018	0.014	0.014
	26 74	31 63	73 15	88 75	27.02	40 71	45 37	73 61	87.68

Table 1 (cont). Representative electron probe analyses of pyroxene in A-17 VLT basalts.





Al cations per 6 Ox

aton Ti/





Figure 4

