

1 **Magma chamber dynamics recorded by oscillatory zoning in pyroxene and**
2 **olivine phenocrysts in basaltic lunar meteorite Northwest Africa 032**

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11 **ABSTRACT**

12 Oscillatory zoning in silicate minerals, especially plagioclase, is a common feature found
13 in volcanic rocks from various terrestrial tectonic settings, but is nearly absent in the lunar
14 environment. Here we report backscattered electron images, quantitative wavelength dispersive
15 spectrometry (WDS) analyses, and qualitative WDS elemental X-ray maps that reveal oscillatory
16 zoning of Mg, Ca, Fe, Ti, Al, Cr, and Mn in euhedral pyroxene phenocrysts, and faint oscillatory
17 zoning of P in olivine phenocrysts in basaltic lunar meteorite Northwest Africa (NWA) 032. This
18 is only the third known occurrence of oscillatory zoning in lunar silicate minerals. Zoning bands
19 in pyroxene range from ~3-5 μm up to ~60 μm in width, but are typically ~10-20 μm in width.
20 Oscillatory bands are variable in width over short distances, often within a single grain. Most
21 oscillatory bands preserve a euhedral form and have sharp edges; however some bands have
22 jagged or uneven edges indicative of resorption surfaces. The short-scale oscillatory nature of the
23 zoning in pyroxene is overprinted on longer-scale core to rim normal magmatic zoning from
24 pigeonite to augite compositions. Oscillatory zoning of P in olivine is faint and only resolvable
25 with high beam current (400 nA) mapping. Bands of higher P are typically only a few microns in
26 width, and although they preserve a euhedral form, they are not traceable around the full
27 circumference of a grain and have variable spacing.

28 Resorption surfaces, longer-scale normal magmatic zoning, and relatively thick
29 oscillatory bands are indicative of the formation of these chemical oscillations as a result of
30 variable magma composition. Pyroxenes likely experienced variable liquid compositions as a
31 result of convection in a differentially cooling, chemically stratified magma chamber. Periodic
32 replenishments of progressively decreasing volumes of primitive parental magma are also
33 permissible and may have enabled convection. In a convection model, Mg-rich bands reflect
34 growth in the lower, warmer, more crystal-poor regions of the chamber whereas Ca-Al-Ti-Cr-
35 rich bands reflect growth in the upper, cooler, more crystal-rich regions of the chamber. The
36 limited duration of crystallization in the magma chamber and the slow diffusion rates of multiple
37 elements amongst multiple crystallographic sites in clinopyroxene, combined with fast cooling
38 upon eruption, act to preserve the oscillatory zoning. Oscillatory zoning of P in olivine is a
39 product of solute trapping resulting from the slow diffusion of P in silicate melts and minerals,
40 and relatively fast magma cooling rates that may be related to magma chamber convection.
41 Differential cooling of the chamber and the fast cooling rates within the chamber are likely a
42 product of the thermal state of the lunar crust at 2.93 Ga when NWA 032, which is currently the
43 youngest dated lunar igneous rock, erupted onto the surface of the Moon.

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46 Keywords: Oscillatory zoning, magma chamber, convection, Moon, basalt, lunar meteorite,
47 zoning, NWA 032, pyroxene.

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INTRODUCTION

52 Many early studies of mare basalts returned by the Apollo and Luna missions
53 demonstrated the effects of cooling rate on mineral chemistry and the usefulness of crystal
54 zoning, particularly in pyroxene, as a means of unraveling the cooling history of a mare basalt
55 (e.g. Boyd and Smith, 1971; Bence and Papike, 1972; Donaldson et al., 1975; Lofgren, 1975;
56 Papike et al., 1976; Grove, 1978). Mineral chemical constraints, such as the changes of Ti/Al in
57 pyroxenes as a response to plagioclase and ilmenite saturation during crystallization of a non-
58 tholeiitic basalt (Bence and Papike, 1972), can be powerful recorders of changes in the
59 composition and/or conditions of a liquid crystallizing in a magma chamber or surface flow.
60 Oscillatory zoning, or nanometer- to micron-scale cyclic and concentric compositional crystal
61 zoning, is a phenomenon that has been observed in various magmatic minerals (e.g. plagioclase,
62 pyroxene, olivine, zircon) from multiple terrestrial tectonic settings, and has received much
63 attention due to its potential as a recorder of the physiochemical conditions of magma
64 crystallization and potentially complex conditions of formation (e.g. Vance, 1962; Downes,
65 1974; Sibley et al., 1976; Allegre et al., 1981; Anderson, 1984; Clark et al., 1986; Ortoleva,
66 1990; Pearce and Kolisnik, 1990; Shimizu, 1990; Halden and Hawthorne, 1993; Pearce, 1994;
67 L'Heureux and Fowler, 1996; Shore and Fowler, 1996; Ginibre et al., 2002a; Milman-Barris et
68 al., 2008; Shearer et al., 2013).

69 In the lunar literature, reports of oscillatory zoning in minerals are scarce. The apparent
70 rarity of oscillatory zoning in lunar minerals may be due, at least in part, to the lower viscosities
71 of lunar basalts compared to terrestrial counterparts (e.g. Murase and McBirney, 1970; Weill et
72 al., 1971; Wilson and Head, 1981; Head and Wilson, 1992). The lower viscosities of mare
73 basalts may act to increase cation diffusion rates in the melt and suppress the efficacy of solute

74 diffusion rate-based mechanisms for the development of oscillatory zoning. However, Boyd and
75 Smith (1971) and Weill et al. (1971) reported oscillatory zoning of pyroxenes in low-Ti lunar
76 basalt 12021, and Crawford (1973) reported oscillatory zoning of plagioclase in the same
77 sample. Gotze et al. (1999) reported oscillatory zoning revealed by cathodoluminescence in
78 plagioclase grains from the lunar regolith. Burger et al. (2009) first reported oscillatory zoning in
79 both olivine and pyroxene in lunar meteorite Northwest Africa (NWA) 032, which is the focus of
80 this study. The mare basaltic meteorite NWA 032 (and its pairing NWA 479) is particularly
81 interesting, as it is currently the youngest dated lunar igneous rock (2.93 Ga; Borg et al., 2009). It
82 is one of five mare basaltic meteorites (NWA 773, LaPaz Icefield 02205, Northeast Africa 003A,
83 NWA 4734) with ages younger than the basaltic units sampled during the Apollo and Luna
84 missions (Borg et al., 2004; Rankenburg et al., 2007; Borg et al., 2009; Haloda et al., 2009;
85 Elardo et al., In Review). Previous workers have shown that NWA 032 sampled a low-Ti (1-6
86 wt. % TiO₂; Neal and Taylor, 1992) basaltic flow that is also compositionally and geochemically
87 distinct from the Apollo 12 and 15 low-Ti basalt suites (Fagan et al., 2002; Barrat et al., 2005;
88 Zeigler et al., 2005; Elardo et al., In Review). Its bulk composition and age are nearly identical to
89 LaPaz Icefield (LAP) 02205 and NWA 4734, which has led to the suggestion that the three are
90 source crater paired (Zeigler et al., 2005; Day et al., 2006; Joy et al., 2006; Day and Taylor,
91 2007; Elardo et al., In Review), despite their differing Nd isotopic compositions (Borg et al.,
92 2009). Its young age indicates that NWA 032 samples a basaltic flow erupted at the end of the
93 main pulse of mare magmatism on the Moon (Nyquist and Shih, 1992; Hiesinger et al., 2000;
94 Shearer et al., 2006). Not only do its bulk composition and isotopic compositions preserve a
95 record of source regions and magmatic processes involved in young mare magmatism (see
96 Elardo et al., In Review), but the zoning patterns in its phenocrysts record the cooling history of

97 a basalt that passed through the lunar crust at a time when the elastic lithosphere had thickened
98 significantly, to perhaps as much as 150 km, and mid-crustal temperatures had decreased to less
99 than 400 °C (Solomon and Head, 1980; Parmentier and Hess, 1998; Hess, 2000; Wieczorek and
100 Phillips, 2000; Hess and Parmentier, 2001; Spohn et al., 2001). In this study, we present major,
101 minor, and trace element analyses of both olivine and pyroxene phenocrysts in NWA 032
102 combined with textural analysis from backscattered electron (BSE) images and WDS elemental
103 X-ray maps. We discuss the possible roles of crystallization kinetics, specifically solute trapping,
104 as well as magma recharge events and magma chamber convection to constrain the origin of
105 oscillatory zoning in olivine and pyroxene, and the thermal history of a young lunar basalt. We
106 also investigate whether these data can be used to constrain the relationship between NWA 032,
107 NWA 4734, and LAP 02205.

108 **SAMPLE DESCRIPTION AND ANALYTICAL METHODS**

109 **Northwest Africa (NWA) 032**

110 NWA 032 and NWA 479 are paired samples of an unbrecciated mare basaltic lunar
111 meteorite found in the Saharan desert that have a combined weight of ~456 g. With a Sm-Nd age
112 of 2931 ± 92 Ma, it is currently the youngest dated igneous rock from the Moon (Borg et al.,
113 2009). The basalt consists of 11.3% olivine phenocrysts, 4.8% pyroxene phenocrysts, and 0.3%
114 chromite phenocrysts set in a fine-grained groundmass of pyroxene, feldspar, ilmenite, troilite,
115 and Fe-Ni metal (Fagan et al., 2002; Barrat et al., 2005; Zeigler et al., 2005; Day and Taylor,
116 2007; Elardo et al., In Review). BSE images showing representative textures in NWA 032 are
117 shown in Fig. 1. Shock melt veins make up 3.2% of the sample. The sample has experienced
118 terrestrial contamination from desert weathering that is apparent in the Rb-Sr and Sm-Nd
119 isotopic systematics (Borg et al., 2009). NWA 032 is classified as a low-Ti, low-Al, low-K mare

120 basalt based on the scheme developed by Neal and Taylor (1992). The bulk rock composition
121 reported by Fagan et al. (2002) and Zeigler et al. (2005) show it to be a relatively evolved, Fe-
122 rich mare basalt with an Mg* (molar $[Mg/Mg+Fe]*100$) of 39. It is also enriched in incompatible
123 trace elements (i.e. Th, Zr, LREEs) relative to mare basalt of similar TiO₂ content (Papike et al.,
124 1998) and has a deep, negative Eu anomaly ($Eu/Eu^* = 0.46$). It has been determined that NWA
125 032 is close to a magmatic liquid composition. Zeigler et al. (2005) recalculated the bulk
126 composition to remove 4.8% accumulated olivine, 2.7% accumulated pigeonite, and 0.2%
127 accumulated chromite to reconstruct the liquid composition. The compositions of phenocryst
128 phases in NWA 032 span a narrow range (Fagan et al., 2002; Zeigler et al., 2005; Elardo et al., In
129 Review). Olivine phenocrysts are normally zoned in Mg-Fe and vary in composition from Fo₆₅
130 in the most primitive cores to ~Fo₅₀ at the rim. They contain abundant poly-phase melt
131 inclusions, as well as inclusions of primary chromite. Chromite compositions span a narrow
132 range and sometimes have *ülvospinel* rims (Fagan et al., 2002). Pyroxenes span a narrow range
133 from pigeonite to augite. The details of pyroxene compositions will be discussed in more detail
134 below.

135 **Analytical Methods**

136 We examined two sections on NWA 032 that are part of the meteorite collection at the
137 Institute of Meteoritics, University of New Mexico (UNM). The samples were documented via
138 backscattered electron (BSE) imaging to understand textural relationships before analyses.
139 Quantitative wavelength dispersive spectrometry (WDS) analyses were conducted on the
140 pyroxene phenocrysts using the JEOL JXA 8200 electron microprobe (EMP) operated by the
141 Institute of Meteoritics, UNM. Analyses of olivine were collected during a companion study and
142 are available in the supplementary material of Elardo et al. (In Review). Quantitative WDS

143 analyses were conducted using an accelerating voltage of 15 kV, a beam current of 30 nA, a spot
144 size of 1 μm . Standards were a mix of both natural and synthetic minerals and oxides, and the
145 quality of analyses were assessed based on stoichiometric constraints. Multiple core to rim and
146 multi-grain traverses were made to assess compositional profiles across grains.

147 Qualitative K_{α} X-ray mapping was conducted using the same instrument. Maps of an area
148 of interest were made in a single accumulation by utilizing five WDS spectrometers
149 simultaneously. K_{α} X-ray maps of Mg, Ti, Al, Ca, Fe, and Cr in pyroxene grains were made at an
150 accelerating voltage of 15 kV and a beam current of 100 nA. Dwell times were 60-180 ms and
151 pixel sizes were 1-2 μm depending on the size of the mapped area. K_{α} X-ray maps of Mg, Al, Ti,
152 Cr, and P in olivine were made at an accelerating voltage of 15 kV and a beam current of 400
153 nA, after the methods of Milman-Barris et al. (2008) and Shearer et al. (2013). Dwell times were
154 800-850 ms and nominal pixel size was 2 μm , although the high beam current likely resulted in a
155 larger effective pixel size. Resultant maps of both olivine and pyroxene were interpolated and the
156 color contrast was adjusted to best show the details of the zoning patterns of the element of
157 interest in a particular grain. Therefore, similar color levels in the maps presented here are not
158 necessarily correlated to similar concentrations in maps of the same element in different grains.

159 RESULTS

160 Olivine Phenocrysts

161 Olivine is the most abundant phenocryst in NWA 032. It ranges in size from 10's to
162 100's of μm in length and sometimes form glomerocrysts with other olivine grains or, less
163 frequently, pyroxene phenocrysts. We have observed no evidence for a reaction relationship
164 existing between olivine and liquid. Olivine grains are typically euhedral and often contain
165 euhedral chromite grains as inclusions in addition to polyphase melt inclusions (Fig. 1). Olivine

166 in NWA 032 in normally zoned in all elements measured in this study with the exception of faint
167 oscillatory zoning of P. Their compositions are continuously zoned and range from $\sim\text{Fo}_{65}$ in the
168 cores to 1-3 μm Fe-rich rims of $\sim\text{Fo}_{42}$ (Figs. 1, 2), the latter likely having formed during rapid
169 cooling upon eruption (Fagan et al., 2002). All olivine analyses presented in Fig. 2 can be found
170 in the supplementary data tables of a companion study by Elardo et al. (In Review).

171 Olivine phenocrysts contain faint oscillatory zoning in P that is only resolvable during
172 high beam current (i.e. 400 nA) WDS mapping. Examples of this zoning are shown in Figs. 3
173 and 4. Oscillatory bands are thin, typically a few microns in width and, at least at the analytical
174 conditions used here, are not traceable around the full circumference of a crystal. The bands are
175 parallel to crystallographic planes, indicating constant euhedral crystal growth throughout the
176 crystallization history of the basalt. Spacing between P-rich oscillatory bands is not constant and
177 can vary from microns to many 10's of microns. Some crystals have broad euhedral cores that
178 have relatively higher P contents than the mantles of the crystal where thin high-P oscillatory
179 bands occur (Figs. 3, 4). However, P content does not correlate with detectable variations of any
180 other element investigated here. Concentrations of P in olivine are very low, typically less than
181 250 ppm, and usually below the detection limit of the EMP. In the grains mapped in this study,
182 we observed no relationship between P-rich zones and the location of melt inclusions and/or
183 chromite inclusions.

184 **Pyroxene Phenocrysts**

185 Pyroxene is the most abundant phase in NWA 032, but the second most abundant
186 phenocryst. Groundmass pyroxenes formed during rapid cooling on the lunar surface are not
187 the focus of this study. Pyroxene phenocrysts in NWA 032 are euhedral crystals with sizes
188 ranging from 10's to 100's of microns in width. They sometimes form glomerocrysts with other

189 pyroxene phenocrysts or, less frequently, olivine phenocrysts. All the quantitative pyroxene EMP
190 analyses presented here can be found in the electronic supporting material for this study.
191 Pyroxene compositions span a narrow range from pigeonite to augite (Fig. 2) and have constant
192 Ti/Al of ~1:4, which is consistent with plagioclase undersaturation in the melt (i.e. Bence and
193 Papike, 1972). The narrow range in quadrilateral compositions suggests that the phenocrysts
194 represent a single population of pyroxenes. The arrows in Fig. 2 indicate the range in
195 groundmass pyroxene compositions and represent a reasonable extension of the phenocryst
196 compositions that would be expected had crystallization proceeded at pre-eruptive rates (Fagan
197 et al., 2002). Additional pyroxene analyses are available in the supplementary material of Elardo
198 et al. (In Review).

199 Oscillatory zoning in pyroxene phenocrysts in NWA 032 was noted by Burger et al.
200 (2009) and Elardo et al. (In Review). Pyroxenes show oscillatory zoning in Mg, Ca, Cr, Ti, Al,
201 and, less prominently, Fe and Mn. An example of this zoning is illustrated in Fig. 5 and an EMP
202 traverse of the same grain is shown in Fig. 6. Oscillatory zoning is sometimes visible in BSE
203 images (e.g. Figs. 5a, 6). Oscillatory bands of high Mg concentrations are antithetical to bands
204 with high Ca, Ti, Al, and Cr concentrations, consistent with the crystal chemical preferences of
205 pigeonite and augite (Bence and Papike, 1972; Papike et al., 1976; Papike and White, 1979;
206 Cameron and Papike, 1981). Most phenocrysts have relatively small cores (~25 μm) that are Mg-
207 rich. Most oscillatory bands are parallel to crystallographic planes (e.g. Fig. 5), indicating
208 constant euhedral growth throughout crystallization, and are easily traceable around the full
209 circumference of a crystal (when a crystal of interest is fully intact). Figure 7 shows WDS maps
210 of a pyroxene glomerocryst or multiple phenocrysts where bands are traceable around nearly the
211 full circumference of the individual grains. Occasionally, at contacts between phenocrysts where

212 contact with the melt was not maintained, zoning bands are discontinuous. An EMP traverse
213 through the grains in Fig. 7 is shown in Fig. 8. Figure 8 shows that although the short scale
214 zoning in pyroxene phenocrysts is oscillatory, this short scale zoning is overprinted on longer
215 scale zoning. Figure 9 shows the concentrations in atoms per formula unit (apfu) of Mg and the
216 sum of Ca, Ti, and Al^{total} along a 231 μm segment of the B – B' traverse from Fig. 8. This
217 segment represents a core to rim profile of a single phenocryst along the B – B' traverse. Linear
218 regressions through these compositional profiles show a longer scale decrease in Mg and
219 increase the sum of Ca, Ti, and Al from core to rim. This is characteristic of the typical pyroxene
220 crystallization sequence of pigeonite to augite in lunar basalts.

221 Oscillatory bands rich in Mg are sometimes less well defined than bands rich in Ti, Al,
222 Ca, and Cr. Among the pyroxene phenocrysts investigated in this study, WDS maps and EMP
223 traverses show at least 6 or more discernible Mg-rich oscillatory bands, and up to 22 discernible
224 Ti-rich bands in a single large grain. The gray scale WDS map of Ti in Fig. 10 clearly shows that
225 large grains often contain numerous oscillatory bands of varying width that are typically parallel
226 to crystallographic planes; however this is not always the case. Figure 10 shows a number of
227 pyroxene phenocrysts that contain concentric, well defined oscillatory zones with sharp, euhedral
228 edges in the interior/mantle portions of the grains. However, toward the edges of the
229 phenocrysts, a few oscillatory bands have rounded, diffuse edges and a subhedral to anhedral
230 form that are accompanied by slightly higher amplitude compositional changes (at least in the
231 grains mapped in Fig. 10). The widths of oscillatory bands in pyroxenes are highly variable
232 between phenocrysts and in single phenocrysts. Oscillatory bands range in width from $\sim 3\text{-}5\ \mu\text{m}$
233 to $\sim 60\ \mu\text{m}$ in the phenocrysts, and are frequently in the range of $10\text{-}20\ \mu\text{m}$ (Figs. 5, 7 and 10).

234

DISCUSSION

235 NWA 032 is an important sample for understanding the full extent of mare magmatism
236 on the Moon. Not only is it the youngest known igneous sample from the Moon, but its Fe- and
237 incompatible trace element-rich bulk composition, deep negative Eu anomaly, and depleted Sm-
238 Nd isotopic composition all demonstrate it represents a previously unsampled mare basalt
239 deposit (Fagan et al., 2002; Zeigler et al., 2005; Borg et al., 2009). Elardo et al. (In Review)
240 argued that NWA 032 (in addition to the compositionally similar lunar basaltic meteorites NWA
241 4734 and LAP 02205) is consistent with low-degree partial melting of Fe-rich cumulate source
242 regions formed relatively late in the crystallization sequence of the lunar magma ocean after
243 extensive flotation of plagioclase into the lunar crust (e.g. Warren, 1985; Snyder et al., 1992;
244 Elardo et al., 2011). These attributes give NWA 032 the potential to greatly expand our
245 understanding of the extent and diversity of mare magmas and source regions on the Moon.
246 Furthermore, oscillatory zoning in pyroxene and olivine is relatively understudied compared to
247 its occurrence in plagioclase, so its occurrence in pyroxene and olivine in NWA 032 offers an
248 opportunity to constrain oscillatory zoning formation processes in other magmatic minerals. In
249 the following discussion, we use our new data on complex zoning patterns in olivine and
250 especially pyroxene phenocrysts to address the cooling history of a young mare basalt.
251 Specifically, we will address what information these zoning patterns reveal about the
252 petrogenetic history of NWA 032. Furthermore, our new data on oscillatory zoning in pyroxene
253 and olivine phenocrysts complement the extensive existing literature for oscillatory zoning in
254 plagioclase (see Pearce, 1994). Lastly, we assess whether our new data can be used to constrain
255 the relationship (or lack thereof) between compositionally similar lunar basalts NWA 4734 and
256 LAP 02205.

257 **Oscillatory zoning in magmatic minerals**

258 Oscillatory zoning has received much attention in the literature due to its potential as a
259 recorder of physiochemical changes during magmatic crystallization and the dynamics of the
260 crystallization process (e.g. Pearce, 1994; Shore and Fowler, 1996; Milman-Barris et al., 2008;
261 Streck, 2008). The majority of the literature on oscillatory zoning in magmatic minerals has
262 focused on its occurrence in plagioclase. Oscillatory zoning is reported more frequently in
263 plagioclase than in other magmatic minerals (Pearce, 1994; Shore and Fowler, 1996) and is often
264 easily observed with a petrographic microscope. Crawford (1973) and Gotze et al. (1999)
265 documented the only occurrences, to our knowledge, in lunar plagioclase. The frequency of its
266 occurrence in terrestrial samples and the complexity of the zoning patterns that have been
267 observed (e.g. Pearce and Kolisnik, 1990) have generally resulted in conceptual and numerical
268 models focusing on explaining the form and features observed in volcanic and plutonic
269 plagioclase rather than other minerals. Reports of oscillatory zoning in pyroxene and olivine are
270 more rare (for examples, see: Smith and Carmichael, 1969; Boyd and Smith, 1971; Thompson,
271 1972; Downes, 1974; Barton et al., 1982; Eriksson, 1985; Clark et al., 1986; Shimizu, 1990;
272 Steele, 1995; Simonetti et al., 1996; Cioni et al., 1998; Reubi et al., 2003; Milman-Barris et al.,
273 2008; Shearer et al., 2013). In this section, we briefly review various aspects of oscillatory
274 zoning pertinent to our discussion before using the constraints they provide to discuss our data
275 for pyroxene and olivine phenocrysts in the sections below.

276 The use of high resolution imaging techniques such as Normarski interference contrast
277 imaging (e.g. Anderson, 1983; Anderson, 1984; Pearce and Kolisnik, 1990) and the
278 improvement of backscattered electron (BSE) imaging, including the use of accumulated BSE
279 images (e.g. Ginibre et al., 2002a; 2002b), over the past few decades has resulted in the ability to
280 resolve the fine micron-scale structure of oscillatory zoning in plagioclase. The recognition of

281 resorption surfaces at the interfaces of some oscillatory zones and correlations between zone
282 wavelength and the amplitude of zoning lead previous authors to divide oscillatory zoning in
283 plagioclase into (at least) two distinct types (Downes, 1974; Pearce and Kolisnik, 1990; Ginibre
284 et al., 2002a; Streck, 2008). The first type, referred to hereafter as fine banding (type I of Pearce
285 and Kolisnik, 1990), is typically characterized by short oscillation wavelengths with band
286 thicknesses of roughly 10 μm or less. Band thicknesses tend to be relatively consistent in a given
287 area of a crystal. Clear resorption surfaces are absent and the amplitude of the variation in An
288 content is low, typically about 0.5 - 2.0 % An (Pearce and Kolisnik, 1990; Ginibre et al., 2002a;
289 Streck, 2008). In contrast, the second type, referred to hereafter as coarse banding (type II of
290 Pearce and Kolisnik, 1990), is typically characterized by longer oscillation wavelengths with
291 band thickness up to many 10s of microns or even over 100 μm in width. The amplitude of the
292 change in An content is variable between adjacent coarse bands, but it can be as high as 10s of %
293 An, and is typically higher in amplitude than fine banding. When resolution of the imaging
294 method is high enough, jagged, rough, rounded, or uneven surfaces attributed to resorption are
295 sometimes observed (see Pearce and Kolisnik, 1990; Ginibre et al., 2002a).

296 Oscillatory zoning in pyroxene phenocrysts is less commonly reported than in
297 plagioclase, but it has been identified by previous workers in magmas from various tectonic
298 settings (e.g. Downes, 1974; Barton et al., 1982; Eriksson, 1985; Shimizu, 1990; Simonetti et al.,
299 1996; Cioni et al., 1998; Reubi et al., 2003) and in Apollo 12 basalt 12021 (Boyd and Smith,
300 1971; Weill et al., 1971). Zoning has been observed in major (i.e. Mg and Ca more commonly
301 than Fe^{2+}), minor, and trace elements (i.e. Ti, Al, Cr, Na, Fe^{3+} , Sc, V, Zr, Sr). Downes (1974)
302 reported both fine banding and coarse banding ranging from 20 to 250 μm in width in augite
303 phenocrysts from Mt. Etna, Sicily; the distinction between band widths is similar to that of fine

304 vs. coarse banding in plagioclase. Oscillatory band width in pyroxene is commonly reported to
305 range from ~10 μm (sometimes less) to ~30 μm (Barton et al., 1982; Eriksson, 1985; Clark et al.,
306 1986; Simonetti et al., 1996; Streck, 2008). Compositional ranges between bands are variable,
307 however variations in the major divalent cations are typically on the order of a few mol%, with
308 the higher field strength cations such as Ti, Al, Cr, and Fe^{3+} showing variations up to 40 mol%
309 (e.g. Downes, 1974; Eriksson, 1985; Clark et al., 1986; Simonetti et al., 1996; Cioni et al., 1998).
310 Trace elements have been shown to vary greatly. For example, Shimizu (1990) reported
311 variations of a factor of 44 in Cr and 27 in Zr between oscillatory bands in an augite phenocryst
312 from an alkaline basalt from Lahir Island, Papua New Guinea.

313 Oscillatory zoning in olivine is reported less frequently than pyroxene. Clark et al. (1986)
314 reported olivine phenocrysts from Hawaii, Arizona, and Iceland that revealed ~30 μm wide
315 oscillatory banding in Normarski interference contrast images. However, in all cases the
316 oscillatory bands corresponded to small or non-existent compositional changes of <2% Fo
317 content and no correlation with Ni, Mn, and Ca contents. Steele (1995) reported oscillatory
318 zoning in Al and Ti in forsteritic olivine grains occurring in two chondritic meteorites. Shearer et
319 al. (2013) explored the relationship between P zoning in martian olivines and crystallization
320 history in basaltic martian meteorites Yamato 980459 and NWA 1183. Milman-Barris et al.
321 (2008) examined olivine phenocrysts in detail using high beam current EMP X-ray mapping and
322 found widespread oscillatory zoning of P in olivine from numerous terrestrial magmas and
323 martian basaltic meteorite ALHA 77005. Oscillatory zoning of P was correlated with Cr and Al
324 zoning in the olivines they studied that had short high temperature residence times in addition to
325 some experimentally grown olivine, which suggests a potential charge-coupling relationship.
326 However this was not ubiquitous in all olivine; natural phenocrysts with longer high temperature

327 residence times show weak or absent correlations with other elements (including potential charge
328 balancing elements like Al and Cr). The lack of zoning in Mg/Fe and in some cases Al and Cr
329 observed by Milman-Barris et al. (2008) is likely due to reequilibration with the magma as a
330 result of the fast diffusion rates of divalent and trivalent cations in olivine compared to P^{5+} (see
331 Chakraborty, 2010 and references therein). Milman-Barris et al. (2008) described multiple forms
332 of oscillatory zoning of P in olivines. Band widths ranged from 3-40 μm but most fell into the 5-
333 20 μm range. Oscillatory bands sometimes were traceable around the full circumference of a
334 crystal, but other terminated over short distances. Unlike oscillatory zoning in plagioclase, the P
335 zoning reported by Milman-Barris et al. (2008) was not continuous over the radius of a
336 phenocryst. Rather, broad P-poor zones were often times punctuated by more P-rich bands and
337 melt inclusions were often spatially associated with P-rich bands. The association of P-rich bands
338 and melt inclusions suggests that cooling rate plays a role in the formation P-rich zones in
339 olivine.

340 **The origin of oscillatory zoning in pyroxene phenocrysts in NWA 032**

341 Fagan et al. (2002) suggested that NWA 032 underwent a relatively simple cooling
342 history: crystallization of chromite and olivine followed by pyroxene, and subsequent rapid
343 cooling of the remaining liquid into a fine-grained groundmass upon eruption onto the lunar
344 surface. Our petrographic observations of NWA 032 support this crystallization sequence;
345 however, an examination of oscillatory zoning patterns of major and minor elements in pyroxene
346 phenocrysts argues for a more complex cooling history prior to eruption. Figures 5-10 show
347 examples and details of the form and compositional variations in the oscillatory zoning patterns
348 in pyroxene phenocryst in NWA 032. Oscillatory bands have widths ranging from $\sim 3\text{-}5\ \mu\text{m}$ up to
349 $\sim 60\ \mu\text{m}$ in the phenocrysts investigated here, and are typically in the range of 10-20 μm .

350 Oscillatory bands are usually well defined, with euhedral forms and sharp boundaries, but in
351 some cases uneven or rounded boundaries are observed (examples of both can be seen in Fig.
352 10). Compositional profiles indicate oscillations are overprinted on longer scale normal
353 magmatic zoning (Figs. 6, 8, 9).

354 Detailed reviews of models proposed for the origin of oscillatory zoning in plagioclase
355 and other minerals were provided by Pearce (1994) and Shore and Fowler (1996). The latter
356 authors divided the proposed models into two types based on formation conditions: intrinsic vs.
357 extrinsic. Intrinsic models are typically based in crystallization kinetics and the interplay
358 between diffusion rates of cations in the melt and the rate of crystallization. In a broad sense,
359 these models generally advocate a phenomenon called solute trapping, wherein the growth rate
360 of a crystal exceeds the rate at which cations in the liquid can diffuse toward or away from the
361 growing crystal, which results in non-equilibrium incorporation of chemical species into the
362 crystal (e.g. Sibley et al., 1976; Allegre et al., 1981; Aziz, 1982; Loomis, 1982; L'Heureux, 1993;
363 Pearce, 1994; Reitano et al., 1994; L'Heureux and Fowler, 1996; Lofgren et al., 2006; Schwandt
364 and McKay, 2006; Milman-Barris et al., 2008). The fast growth rate of the crystal is thought to
365 be a product of a high degree of undercooling of the magma. The crystal depletes compatible
366 growth components in the boundary layer surrounding it and incorporates a higher proportion of
367 incompatible components than equilibrium partitioning relationships would suggest because they
368 are enriched in the boundary layer and are “trapped” by the rapidly growing crystal. Crystal
369 growth then slows in response to a diminished degree of super-saturation in the boundary layer
370 which results from the depletion of compatible growth components. Eventually the boundary
371 layer is replenished by diffusion or destroyed by convection processes; either way the result is a
372 new stage of growth on the crystal-liquid interface. This intrinsic mechanism is thought to be

373 responsible for short-scale, low amplitude fine banding. It is thought that local depletion of a
374 boundary layer would prevent the growth of coarse bands $>15\ \mu\text{m}$ or so (Pearce and Kolisnik,
375 1990; Pearce, 1994; Ginibre et al., 2002a; 2002b). In contrast, extrinsic models produce
376 oscillatory zoning as a result of changes in liquid composition due to external forcing, which
377 may include processes such as magma chamber replenishment events and crystal convection.
378 The production of chemical oscillations by these mechanisms is not dependent (to a large extent)
379 on diffusion rates or local non-linear crystal growth, but rather on the composition of the magma
380 body in which the crystal is growing. Therefore, oscillatory bands with much greater width and
381 compositional amplitude (coarse bands) are permitted by these models. Additionally, the jagged,
382 rounded, uneven, or diffuse edges observed on many of these bands are attributed to resorption
383 when the crystal cycles to a less super-saturated zone of the chamber, or when a new batch of
384 more primitive magma is injected into the chamber (Pearce, 1994; Ginibre et al., 2002a).

385 The characteristics of oscillatory zoning patterns in pyroxene phenocrysts in NWA 032
386 make the task of distinguishing between fine banding and coarse banding difficult; the zoning
387 patterns observed have some characteristics of both. The widths of oscillatory bands fall into
388 both size ranges. Figures 5 and 10 show pyroxenes with some band widths of $\sim 10\ \mu\text{m}$ or less,
389 whereas Figs. 7 and 10 clearly show coarse bands with widths up to $\sim 60\ \mu\text{m}$. Additionally, the
390 interior portions of the phenocrysts in Fig. 10 show low amplitude oscillations, whereas the
391 exterior portions of the same grains, in addition to grains shown in Figs. 5 and 7, show higher
392 amplitude oscillations. Overall, however, the oscillations in NWA 032 pyroxenes more closely
393 resemble coarse banding as described by previous authors (Downes, 1974; Pearce and Kolisnik,
394 1990; Pearce, 1994; Ginibre et al., 2002a). Even though some bands show micron-scale widths,
395 the majority of bands are roughly $15\text{-}30\ \mu\text{m}$ in width and the presence of thick, $\sim 60\ \mu\text{m}$ bands

396 (e.g. Fig. 7) is indicative of coarse banding. Next, band widths are variable over short length
397 scales (e.g. Figs. 5, 10). A characteristic of fine banding is that it is fairly regular in width
398 throughout repeated oscillations (Pearce and Kolisnik, 1990; Ginibre et al., 2002a). Additionally,
399 the exterior portions of the phenocrysts indicated by the arrows in Fig. 10 show that some bands
400 have rounded or jagged forms which contrast the more euhedral forms in the interiors of the
401 same grains. We interpret this as evidence of resorption surfaces between zones, which is
402 characteristic of coarse bands and the processes that produce them (e.g. Pearce, 1994; Ginibre et
403 al., 2002a). It is also possible that more oscillatory zone boundaries than just those observed in
404 Fig. 10 represent resorption surfaces that are either not apparent in the images or maps in our
405 dataset due to the smaller scale of those features and/or the resolution of our imaging and
406 mapping techniques. Lastly, Fagan et al. (2002) suggested based on olivine morphologies, that
407 cooling rates in the magma chamber were $<2^{\circ}$ C/h. However, crystallization experiments
408 conducted by Lofgren et al. (2006) demonstrated that cooling rates of 5° C/h produced normal
409 magmatic zoning patterns in Mg, Fe, and Ca in CPX crystals with equant to euhedral
410 morphologies, similar to those in NWA 032. This suggests the $<2^{\circ}$ C/h estimate of Fagan et al.
411 (2002) would be too slow to produce oscillatory zoning in the pyroxene and that at rates up to at
412 least 5° C/h, solute trapping does not affect Mg, Fe, and Ca. Therefore, based on our data, the
413 oscillatory zoning in pyroxene phenocrysts in NWA 032 likely reflects large scale compositional
414 variations in the magma rather than the effects of crystallization kinetics (i.e. solute trapping;
415 although it is possible this mechanism may have operated locally in response a faster cooling
416 rate, see below).

417 We have considered both magma chamber recharge events and convection as a means to
418 produce the variable magma compositions responsible for the oscillatory zoning in pyroxene;

419 however, these processes are not mutually exclusive. Ginibre et al. (2002b) argued that
420 oscillatory zoning, trace element variations, and resorption surfaces in plagioclase phenocrysts in
421 a dacite from Parinacota volcano, Chile, reflect both recharge and convection operating in the
422 same chamber. Magma mixing and recharge events have been suggested as an explanation for
423 oscillatory zoning in pyroxene phenocrysts in various terrestrial settings (e.g. Barton et al., 1982;
424 Cioni et al., 1998; Reubi et al., 2003). In the case of NWA 032, the magma chamber may have
425 experienced periodic replenishments of fresh magma followed by differentiation prior to
426 eruption. Injections of more primitive parental magma into the chamber would be reflected in
427 Mg-rich bands, whereas Ti-Al-Ca-rich bands reflect enrichments in the magma due to crystal
428 fractionation. If so, the amplitudes of compositional zoning bands should be generally equivalent
429 if new magma of the parental composition were added to the chamber (i.e. a semi-constant
430 baseline composition), or should at least be variable if the volume or composition of fresh
431 magma added to the chamber varied during each event. Figure 9 shows the concentrations of Mg
432 and the sum concentration of Ti, Ca, and Al^{total} in the B – B+231 μm core-rim segment of the
433 multi-phenocryst traverse B – B' in Fig. 8. Linear regressions through the concentration profiles
434 show that although the fine-scale zoning in pyroxene is oscillatory, it is overprinted on longer-
435 scale zoning. Mg decreases from 1.145 atoms per formula unit (apfu) in the core to 0.805 apfu in
436 the rim, and the sum of Ti, Ca, and Al^{total} increases from 0.245 apfu in the core to 0.844 apfu in
437 the rim. The long-scale decrease in Mg is the result of its replacement in the M2 site by Ca and
438 in the M1 site by Ti and Al (with some Al also going into the tetrahedral site), which is typical of
439 the non-tholeiitic pyroxene crystallization sequence from pigeonite to augite in lunar basalts.
440 This is indicative of a single, evolving magma, and argues against magma chamber
441 replenishment, unless the replenishment occurred in progressively smaller proportions in each

442 successive event. This variation on the recharge model would produce short-scale oscillatory
443 zoning the crystals, reflecting the changing magma composition due to each recharge event.
444 These oscillations should be overprinted on longer-scale zoning reflecting fractionation in the
445 chamber so long as the volume of parental magma decreased in each replenishment event. This
446 process would affect the entire magma chamber equally, and therefore one should expect to see
447 correlations in zoning patterns between crystals, which we do not observe here. However, based
448 on the limited amount of sample available to us, we cannot rule out this model. Recharge events
449 in progressively smaller proportions may have at least contributed to the formation of oscillatory
450 zoning.

451 Crystallization of a single magma with injections of a compositionally dissimilar magma,
452 however, is not supported by the narrow range of pyroxene composition. Pyroxenes vary
453 narrowly from $\text{En}_{60}\text{Wo}_9$ to $\text{En}_{42}\text{Wo}_{21}$ (Fig. 2) indicating an evolving, single magma composition.
454 Mixing of dissimilar magmas should produce a larger variation in pyroxene compositions.
455 Furthermore, the isotopic characteristics of NWA 032 argue for a closed system. After extensive
456 leaching procedures to remove terrestrial contamination, Borg et al. (2009) determined an
457 isochron age of 2931 ± 92 Ma that included a whole rock fraction and three magnetic mineral
458 fractions with a low mean square weighted deviation of 0.95. This suggests isotopic equilibrium
459 between the whole rock and individual mineral fractions that is indicative of closed system
460 crystallization. (2009)

461 Our preferred model is one in which oscillatory zoning in pyroxene preserves a record of
462 magma chamber convection before eruption. A schematic model for the growth of pyroxene
463 phenocrysts in NWA 032 is shown in Fig. 11. Pyroxene phenocrysts are cycled through warmer
464 and cooler regions of a cooling magma chamber by vigorous convection (Fig. 11a). Since solute

465 trapping is not likely to play a large role in development of the oscillatory zoning (see above), a
466 compositional gradient is required in the magma chamber. This is likely the result of a
467 temperature gradient imposed by differential cooling of the magma body: heat loss is most
468 efficient from the top of the chamber, inducing a greater degree of super-saturation in the upper
469 region, which would make it more crystal-rich. In the lower, warmer region of the chamber, the
470 stable pyroxene composition is more Mg-rich and Ca-Al-Ti-poor. Some resorption of higher-Ca
471 pyroxene growth zones occurs when crystals are carried to the lower, warm region from the
472 upper, cooler region, resulting in resorption surfaces like those in Fig. 10. However, if the
473 magma in the lower regions is saturated in pyroxene of a pigeonite composition, Mg-rich growth
474 zones will form on a crystal over higher-Ca growth zones (Fig. 11b). As the crystal is swept back
475 up into the upper, cooler region of the chamber, resorption will not occur. Rather, a growth zone
476 of a more evolved pyroxene composition (i.e. Ca-Al-Ti-rich) will form around the Mg-rich zone
477 (Fig. 11c). As the composition of the pyroxene growth zones is not dictated by the available
478 components in a boundary layer surrounding the crystal, but rather by the composition of the
479 magma, the thickness of the growth band is not limited as in the case of solute trapping from a
480 boundary layer. If the chamber experienced replenishments of the parental magma in
481 progressively smaller proportions, this may also result in chemical oscillations in the crystals like
482 those observed, and the addition of the hotter, more primitive parental magma may contribute to
483 inducing convection in the chamber.

484 As the cycling of crystals via convection progresses and the chamber continues to cool,
485 the composition of magma throughout the chamber will evolve as a function of time and
486 crystallization. The oscillatory bands produced in each region of the chamber will therefore also
487 become more evolved with time. This is consistent with the linear regressions of core to rim

488 profiles that show that normal magmatic zoning is overprinted on the small scale oscillatory
489 nature of zoning in pyroxenes (e.g. Fig. 9), suggesting crystallization of a single magma. We
490 recognize that solute trapping may occur locally to form some of the thinner oscillatory bands if
491 at any point during pre-eruptive crystallization a phenocryst experiences a region of the chamber
492 where super-saturation is great and cooling rates are high. Based on our observations, however,
493 this is likely limited in occurrence and is not responsible for the great majority of chemical
494 oscillations in pyroxene.

495 Differential cooling of the NWA 032 magma chamber and the fast cooling rates within
496 the chamber are likely a product of the thermal state of the lunar crust at 2.93 Ga. Thermal
497 models of lunar evolution suggest that at this time the lunar elastic lithosphere has thickened
498 significantly, possibly up to ~150 km (Solomon and Head, 1980; Parmentier and Hess, 1998;
499 Hess, 2000; Wieczorek and Phillips, 2000; Hess and Parmentier, 2001; Spohn et al., 2001). This
500 indicates that the anorthositic lunar crust and mantle would have cooled significantly from its
501 relatively hot, post-magma ocean state (e.g. Elardo et al., 2011). Some thermal models indicate
502 that temperatures in the mid crust would be ~400° C at ~3 Ga, significantly cooler than the
503 >800° C at ~4.4 Ga (e.g. Parmentier and Hess, 1998). It is possible that the magma chamber
504 convection recorded by oscillatory zoning in NWA 032 is a product of rapid heat loss to the cold
505 lunar crust after the magma was emplaced.

506 **Origin of oscillatory zoning of P in olivine phenocrysts in NWA 032**

507 Even at the high beam currents used for WDS mapping in this study, oscillatory zoning
508 of P in olivine phenocrysts in NWA 032 is faint (Figs. 3, 4). P-rich zones do not correlate with
509 oscillations in any other elements and are typically euhedral, but irregularly spaced with broad P-
510 poor zones between them. These features are similar to many of the features observed in olivine

511 in the samples studied by Milman-Barris et al. (2008) and Shearer et al. (2013). Solute trapping
512 was invoked by Milman-Barris et al. (2008) to explain oscillatory zoning of P that is prevalent in
513 olivine phenocrysts in numerous terrestrial and martian magmas. In the case of NWA 032, we
514 envision two possibilities for the origin of P zoning in olivine. The first is that P zoning is the
515 result of the same magma chamber convection and melt composition gradient that resulted in the
516 oscillatory zoning in pyroxene. The lack of zoning in any other element in the olivine may be a
517 result of the faster diffusion rates of divalent and trivalent cations in olivine compare to
518 clinopyroxene (see section below), but slow diffusion rates of P^{5+} leads to the preservation of
519 remnant zoning. The second possibility is that the P zoning is a result of solute trapping during
520 olivine growth, as envisioned by Milman-Barris et al. (2008). Those authors demonstrated that
521 the process occurs frequently in olivine without invoking any extrinsic forcing like convection,
522 so long as cooling rates are fast enough, so it is not difficult to invoke its occurrence during the
523 formation of olivine in NWA 032. They were able to reproduce P oscillatory zoning features in
524 experimentally grown olivines at cooling rates of 15 – 30° C/h. Fagan et al. (2002) argued for a
525 cooling rate of <2° C/h for NWA 032 based on olivine morphologies. Therefore, P zoning in
526 olivine may be a product of transient fast cooling rates of 2 – 30° C/h, perhaps as a secondary
527 result of convection in the magma chamber and periodically resulted in solute trapping events
528 wherein P-rich zones were produced in olivine. This is the mechanism of origin we prefer for P
529 zoning in olivine.

530 **Preservation of oscillatory zoning**

531 The oscillatory zoning in NWA 032 pyroxene phenocrysts is preserved as the result of
532 two main factors: eruption onto the lunar surface and slow diffusion rates of cations in
533 clinopyroxenes. Fast cooling upon eruption is apparent from the fine grained crystalline

534 groundmass in NWA 032, and this reduces time available for diffusive reequilibration.
535 Additionally, studies of cation diffusion in clinopyroxene suggest that diffusive reequilibration of
536 oscillatory bands is not favorable in the estimated residence time of the phenocrysts in the
537 magma before eruption (~3.5 - 35 days; Fagan et al., 2002), even at the pyroxene
538 crystallization/near-eruption temperature of ~1180°C estimated by crystallization modeling of
539 Fagan et al. (2002) and suggested by Cr contents of olivine (Fig. 10 of Elardo et al., 2012). Both
540 Al and Ti are slow diffusing cations in clinopyroxene. For example, Al diffusion coefficients at
541 1180°C are on the order of $2.7\text{-}3.7 \times 10^{-21} \text{ m}^2/\text{s}$ (Sneeringer et al., 1984; Sautter et al., 1988;
542 Cherniak and Dimanov, 2010; Cherniak and Liang, 2012). Self- and inter-diffusion rates of Mg
543 and Fe in clinopyroxene are unusually slow compared to other Mg-Fe silicates (e.g. olivine,
544 garnet; Dimanov and Sautter, 2000; Dimanov and Wiedenbeck, 2006; Cherniak and Dimanov,
545 2010; Zhang et al., 2010). Calcium has been shown to be the slowest diffusing octahedrally-
546 coordinated major cation (e.g. Dimanov et al., 1996; Dimanov and Jaoul, 1998; Zhang et al.,
547 2010), and therefore is likely to be the kinetically-limiting species (Cherniak and Dimanov,
548 2010). Furthermore, diffusive reequilibration of the oscillatory bands requires the simultaneous
549 diffusion of multiple species exchanging with multiple crystallographic sites in order to maintain
550 local charge balance. For example, Al occupies both the octahedral M1-site and the tetrahedral-
551 site, and is charge balanced by Ti^{4+} , Cr^{3+} , or a second Al in octahedral coordination (Bence and
552 Papike, 1972; Cameron and Papike, 1981). All three of these couples can be significant in lunar
553 pyroxenes (Bence and Papike, 1972), so diffusion of these three species in addition to Mg, Fe,
554 Ca and Si must all occur simultaneously for reequilibration to occur. Given that NWA 032
555 consists of only ~17% modal of phenocryst phases, crystallization in the magma chamber was

556 likely not a long duration process before eruption, and therefore provided insufficient time for
557 reequilibration of oscillatory bands.

558 **Constraints of the petrogenetic relationship between NWA 032, NWA 4734, and LAP**
559 **02205**

560 A number of studies have focused on the origin of basaltic lunar meteorites NWA 032,
561 NWA 4734, and LAP 02205, not only because they are three of the five youngest known igneous
562 rocks from the Moon and sample geologic units unlike those sampled by the Apollo and Luna
563 missions, but also because the three basalts have very similar bulk compositions, mineralogy,
564 and ages, yet very different Nd isotopic compositions (Fagan et al., 2002; Barrat et al., 2005;
565 Righter et al., 2005; Zeigler et al., 2005; Anand et al., 2006; Day et al., 2006; Joy et al., 2006;
566 Day and Taylor, 2007; Borg et al., 2009; Wang et al., 2012; Elardo et al., In Review). We
567 examined pyroxene zoning patterns in a companion study of all three meteorites and found that
568 pyroxenes in NWA 4734 and LAP have normal magmatic zoning patterns (Elardo et al., In
569 Review). Our data on oscillatory zoning in pyroxenes in NWA 032 places a number of
570 constraints on its relationship to NWA 4734 and LAP. First, the data presented above argues
571 against mixing of a compositionally dissimilar magma during the pre-eruptive magma chamber
572 phase of crystallization. Additionally, the high degree of similarity in the bulk rock trace element
573 compositions suggests that assimilation cannot have played a large role in their origins.
574 Therefore, the oscillatory zoning in pyroxene in NWA 032 does not record a chemical change in
575 the magmatic system that could be used to argue against a pairing with NWA 4734 and LAP or
576 be used to explain their different Nd isotopic compositions. Next, the lack of oscillatory zoning
577 in pyroxene in NWA 4734 and LAP does not rule out a pairing relationship. It may indicate that
578 the NWA 4734 and LAP parental magmas had more time to diffusively re-equilibrate oscillatory

579 bands, either in the magma chamber or during cooling in the interior of a thick lava flow, which
580 is consistent with their coarser-grained subophitic textures. Alternatively, they may be derived
581 from a different magmatic system or a different eruptive episode in the same magmatic system,
582 and never underwent the convection processes that formed oscillatory zoning in the NWA 032
583 phenocrysts. The available data cannot distinguish between these possibilities. Therefore, the
584 conclusion of Elardo et al. (In Review) that NWA 032, NWA 4734, and LAP are source crater
585 paired and are likely derived from the same volcanic province remains the most likely
586 explanation for the origin of these basalts.

587 **IMPLICATIONS**

588 Although oscillatory zoning is common in terrestrial silicate minerals, the zoning patterns
589 reported here are only the third known instance of oscillatory zoning in lunar silicates. The
590 interpretation that these zoning patterns record processes operating within the magma chamber
591 allows for a more detailed reconstruction of the petrogenetic history of NWA 032, which is an
592 important lunar sample as it is not only the youngest lunar igneous sample currently known, but it
593 is also geochemically distinct from Apollo low-Ti basalts. Firstly, oscillatory zoning in pyroxene
594 and olivine in NWA 032 preserve a record of vigorous convection and possibly magma
595 replenishment within a cooling crustal magma chamber prior to eruption. Insight into magma
596 chamber dynamics in the lunar environment is rarely preserved by crystal zoning patterns in
597 lunar basalts and NWA 032 offers constraints on those processes. Secondly, the zoning patterns
598 and mineral compositions in NWA 032, combined with previous isotopic studies (e.g., Borg et
599 al., 2009), allow us to exclude assimilation of exogenous material during crystallization from the
600 petrogenetic history of the basalt. This is an important constraint when using the trace element
601 and isotopic compositions of NWA 032 to make inferences in regards to its source region

602 composition and mantle melting at 3 Ga. Finally, oscillatory zoning in pyroxene and olivine is
603 rare compared to plagioclase, so these observations provide important constraints for oscillatory
604 formation models that are primarily based on constraints from zoning patterns in plagioclase.

605

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840

841 FIGURE CAPTIONS

- 842 **Figure 1:** Backscattered electron (BSE) images of representative textures and phenocryst
843 assemblages in NWA 032. Ol = olivine, Pyx = pyroxene, Chr = chromite, MI = melt inclusion,
844 GM = groundmass.
- 845 **Figure 2:** A pyroxene quadrilateral showing the range in compositions for pyroxene phenocrysts
846 from NWA 032. Arrows indicate the approximate range in groundmass pyroxene compositions
847 from Fagan et al. (2002). The range in composition of olivine phenocrysts is show below. This
848 figure is adapted from a companion study (Elardo et al., In Review) and the complete olivine
849 EMP dataset can be found there.
- 850 **Figure 3:** A BSE image and qualitative WDS X-ray maps of Mg, Cr, and P in an olivine
851 phenocryst in NWA 032. Arrows in the P map indicate some of the oscillatory zones of high P

852 concentrations. The color contrast of the maps have been adjusted to better show zoning patterns
853 and therefore colors are not necessarily comparable between maps and with the maps in Fig. 4.
854 Hot colors represent higher concentrations whereas cooler colors represent lower concentrations.

855 **Figure 4:** A BSE image and qualitative WDS X-ray maps of Mg, Cr, and P in an olivine
856 phenocryst in NWA 032. Arrows in the P map indicate the oscillatory zones of high P. The color
857 contrast of the maps have been adjusted to better show zoning patterns and therefore colors are
858 not necessarily comparable between maps and with the maps in Fig. 3. Hot colors represent
859 higher concentrations whereas cooler colors represent lower concentrations.

860 **Figure 5:** A BSE image and qualitative WDS X-ray maps of Mg, Ti, and Cr in a small euhedral
861 pyroxene phenocryst in NWA 032. This phenocryst displays multiple oscillatory bands of
862 varying thickness with sharp boundaries. The color contrast of the maps have been adjusted to
863 better show zoning patterns and therefore colors are not necessarily comparable between maps
864 and with pyroxene maps in other figures. Hot colors represent higher concentrations whereas
865 cooler colors represent lower concentrations.

866 **Figure 6:** Compositional profiles from EMP traverse across the pyroxene phenocryst show in
867 Fig. 5 to quantitatively show oscillatory zoning. Traverse A - A' is shown in the BSE image.
868 Compositions are shown in atoms per formula unit (apfu). Step size between analyses is 3.4 μm .
869 Individual analyses can be found in the supplementary data table.

870 **Figure 7:** Qualitative WDS X-ray maps of Ti, Mg, and Cr in a large pyroxene that represents
871 either a broken phenocryst or a glomerocryst consisting of two phenocrysts. The coarse nature of
872 many oscillatory bands is visible here, with band widths of $\sim 60 \mu\text{m}$ in some cases. The color
873 contrast of the maps have been adjusted to better show zoning patterns and therefore colors are
874 not necessarily comparable between maps and with pyroxene maps in other figures. Hot colors

875 represent higher concentrations whereas cooler colors represent lower concentrations. Dark
876 patches prominent in the Ti map are SIMS spots from previous analyses.

877 **Figure 8:** Compositional profiles from EMP traverse across the pyroxene phenocryst show in
878 Fig. 7 to quantitatively show oscillatory zoning. Traverse B - B' is shown in the Ti map.
879 Compositions are shown in atoms per formula unit (apfu). Step size between analyses is 4 μm .
880 Individual analyses can be found in the supplementary data table. Dark patches are SIMS spots
881 from previous analyses.

882 **Figure 9:** The EMP segment from 0 - 231 μm of the B - B' traverse in Fig. 8, which is
883 equivalent to a core to rim traverse. Concentration profiles for Mg and Ti + Al^{total} + Ca in apfu
884 are shown with linear regressions of the data (black lines).

885 **Figure 10:** A grayscale qualitative WDS Ti X-ray map of pyroxene phenocrysts in NWA 032.
886 The interior portions of the grains show oscillatory banding with euhedral forms and sharp
887 edges. The exterior portions of the grains show oscillatory zones with rounded or jagged
888 boundaries, as indicated by arrows. These are interpreted as resorption surfaces. The contrast of
889 the map has been adjusted to better show zoning patterns. Bright shades represent higher
890 concentrations whereas darker shades represent lower concentrations.

891 **Figure 11:** A schematic magma chamber model for the origin of oscillatory zoning in pyroxene
892 phenocrysts in NWA 032. (a) Differential cooling of a magma chamber in the lunar crust
893 produces a compositional gradient in the chamber, which drives convection that carries
894 phenocrysts through the different regions of the chamber. Periodic replenishments of parental
895 magma may occur, but only insofar as they are in progressively smaller proportions. (b) In the
896 lower, warmer, more crystal-poor regions of the chamber, phenocrysts transported from the
897 upper regions may undergo some resorption of growth zones richer in Ca. However, the lower

898 region is still pyroxene saturated and this results in a growth band that is Mg-rich. (c)
899 Phenocrysts carried into the upper, cooler, more crystal-rich portions of the chamber do not
900 undergo resorption. Growth bands richer in Ca, Ti, and Al form over more Mg-rich bands.
901 Repetition of this process results in oscillatory zoning of pyroxene phenocrysts.
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