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

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ABSTRACT

Oscillatory zoning in silicate minerals, especially plagioclase, is a common feature found in volcanic rocks from various terrestrial tectonic settings, but is nearly absent in the lunar environment. Here we report backscattered electron images, quantitative wavelength dispersive spectrometry (WDS) analyses, and qualitative WDS elemental X-ray maps that reveal oscillatory zoning of Mg, Ca, Fe, Ti, Al, Cr, and Mn in euhedral pyroxene phenocrysts, and faint oscillatory zoning of P in olivine phenocrysts in basaltic lunar meteorite Northwest Africa (NWA) 032. This is only the third known occurrence of oscillatory zoning in lunar silicate minerals. Zoning bands in pyroxene range from ~3-5 μm up to ~60 μm in width, but are typically ~10-20 μm in width. Oscillatory bands are variable in width over short distances, often within a single grain. Most oscillatory bands preserve a euhedral form and have sharp edges; however some bands have jagged or uneven edges indicative of resorption surfaces. The short-scale oscillatory nature of the zoning in pyroxene is overprinted on longer-scale core to rim normal magmatic zoning from pigeonite to augite compositions. Oscillatory zoning of P in olivine is faint and only resolvable with high beam current (400 nA) mapping. Bands of higher P are typically only a few microns in width, and although they preserve a euhedral form, they are not traceable around the full circumference of a grain and have variable spacing.
Resorption surfaces, longer-scale normal magmatic zoning, and relatively thick oscillatory bands are indicative of the formation of these chemical oscillations as a result of variable magma composition. Pyroxenes likely experienced variable liquid compositions as a result of convection in a differentially cooling, chemically stratified magma chamber. Periodic replenishments of progressively decreasing volumes of primitive parental magma are also permissible and may have enabled convection. In a convection model, Mg-rich bands reflect growth in the lower, warmer, more crystal-poor regions of the chamber whereas Ca-Al-Ti-Cr-rich bands reflect growth in the upper, cooler, more crystal-rich regions of the chamber. The limited duration of crystallization in the magma chamber and the slow diffusion rates of multiple elements amongst multiple crystallographic sites in clinopyroxene, combined with fast cooling upon eruption, act to preserve the oscillatory zoning. Oscillatory zoning of P in olivine is a product of solute trapping resulting from the slow diffusion of P in silicate melts and minerals, and relatively fast magma cooling rates that may be related to magma chamber convection. Differential cooling of the chamber and the fast cooling rates within the chamber are likely a product of the thermal state of the lunar crust at 2.93 Ga when NWA 032, which is currently the youngest dated lunar igneous rock, erupted onto the surface of the Moon.

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

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

In the lunar literature, reports of oscillatory zoning in minerals are scarce. The apparent rarity of oscillatory zoning in lunar minerals may be due, at least in part, to the lower viscosities of lunar basalts compared to terrestrial counterparts (e.g. Murase and McBirney, 1970; Weill et al., 1971; Wilson and Head, 1981; Head and Wilson, 1992). The lower viscosities of mare basalts may act to increase cation diffusion rates in the melt and suppress the efficacy of solute
diffusion rate-based mechanisms for the development of oscillatory zoning. However, Boyd and Smith (1971) and Weill et al. (1971) reported oscillatory zoning of pyroxenes in low-Ti lunar basalt 12021, and Crawford (1973) reported oscillatory zoning of plagioclase in the same sample. Gotze et al. (1999) reported oscillatory zoning revealed by cathodoluminescence in plagioclase grains from the lunar regolith. Burger et al. (2009) first reported oscillatory zoning in both olivine and pyroxene in lunar meteorite Northwest Africa (NWA) 032, which is the focus of this study. The mare basaltic meteorite NWA 032 (and its pairing NWA 479) is particularly interesting, as it is currently the youngest dated lunar igneous rock (2.93 Ga; Borg et al., 2009). It is one of five mare basaltic meteorites (NWA 773, LaPaz Icefield 02205, Northeast Africa 003A, NWA 4734) with ages younger than the basaltic units sampled during the Apollo and Luna missions (Borg et al., 2004; Rankenburg et al., 2007; Borg et al., 2009; Haloda et al., 2009; Elardo et al., In Review). Previous workers have shown that NWA 032 sampled a low-Ti (1-6 wt. % TiO₂; Neal and Taylor, 1992) basaltic flow that is also compositionally and geochemically distinct from the Apollo 12 and 15 low-Ti basalt suites (Fagan et al., 2002; Barrat et al., 2005; Zeigler et al., 2005; Elardo et al., In Review). Its bulk composition and age are nearly identical to LaPaz Icefield (LAP) 02205 and NWA 4734, which has led to the suggestion that the three are source crater paired (Zeigler et al., 2005; Day et al., 2006; Joy et al., 2006; Day and Taylor, 2007; Elardo et al., In Review), despite their differing Nd isotopic compositions (Borg et al., 2009). Its young age indicates that NWA 032 samples a basaltic flow erupted at the end of the main pulse of mare magmatism on the Moon (Nyquist and Shih, 1992; Hiesinger et al., 2000; Shearer et al., 2006). Not only do its bulk composition and isotopic compositions preserve a record of source regions and magmatic processes involved in young mare magmatism (see Elardo et al., In Review), but the zoning patterns in its phenocrysts record the cooling history of
a basalt that passed through the lunar crust at a time when the elastic lithosphere had thickened significantly, to perhaps as much as 150 km, and mid-crustal temperatures had decreased to less than 400 °C (Solomon and Head, 1980; Parmentier and Hess, 1998; Hess, 2000; Wieczorek and Phillips, 2000; Hess and Parmentier, 2001; Spohn et al., 2001). In this study, we present major, minor, and trace element analyses of both olivine and pyroxene phenocrysts in NWA 032 combined with textural analysis from backscattered electron (BSE) images and WDS elemental X-ray maps. We discuss the possible roles of crystallization kinetics, specifically solute trapping, as well as magma recharge events and magma chamber convection to constrain the origin of oscillatory zoning in olivine and pyroxene, and the thermal history of a young lunar basalt. We also investigate whether these data can be used to constrain the relationship between NWA 032, NWA 4734, and LAP 02205.

SAMPLE DESCRIPTION AND ANALYTICAL METHODS

Northwest Africa (NWA) 032

NWA 032 and NWA 479 are paired samples of an unbrecciated mare basaltic lunar meteorite found in the Saharan desert that have a combined weight of ~456 g. With a Sm-Nd age of 2931 ± 92 Ma, it is currently the youngest dated igneous rock from the Moon (Borg et al., 2009). The basalt consists of 11.3% olivine phenocrysts, 4.8% pyroxene phenocrysts, and 0.3% chromite phenocrysts set in a fine-grained groundmass of pyroxene, feldspar, ilmenite, troilite, and Fe-Ni metal (Fagan et al., 2002; Barrat et al., 2005; Zeigler et al., 2005; Day and Taylor, 2007; Elardo et al., In Review). BSE images showing representative textures in NWA 032 are shown in Fig. 1. Shock melt veins make up 3.2% of the sample. The sample has experienced terrestrial contamination from desert weathering that is apparent in the Rb-Sr and Sm-Nd isotopic systematics (Borg et al., 2009). NWA 032 is classified as a low-Ti, low-Al, low-K mare
basalt based on the scheme developed by Neal and Taylor (1992). The bulk rock composition reported by Fagan et al. (2002) and Zeigler et al. (2005) show it to be a relatively evolved, Fe-rich mare basalt with an Mg* (molar \([\text{Mg}/(\text{Mg}+\text{Fe})]*100\)) of 39. It is also enriched in incompatible trace elements (i.e. Th, Zr, LREEs) relative to mare basalt of similar TiO₂ content (Papike et al., 1998) and has a deep, negative Eu anomaly (Eu/Eu* = 0.46). It has been determined that NWA 032 is close to a magmatic liquid composition. Zeigler et al. (2005) recalculated the bulk composition to remove 4.8% accumulated olivine, 2.7% accumulated pigeonite, and 0.2% accumulated chromite to reconstruct the liquid composition. The compositions of phenocryst phases in NWA 032 span a narrow range (Fagan et al., 2002; Zeigler et al., 2005; Elardo et al., In Review). Olivine phenocrysts are normally zoned in Mg-Fe and vary in composition from Fo₆₅ in the most primitive cores to ~Fo₅₀ at the rim. They contain abundant poly-phase melt inclusions, as well as inclusions of primary chromite. Chromite compositions span a narrow range and sometimes have ülvospinel rims (Fagan et al., 2002). Pyroxenes span a narrow range from pigeonite to augite. The details of pyroxene compositions will be discussed in more detail below.

**Analytical Methods**

We examined two sections on NWA 032 that are part of the meteorite collection at the Institute of Meteoritics, University of New Mexico (UNM). The samples were documented via backscattered electron (BSE) imaging to understand textural relationships before analyses. Quantitative wavelength dispersive spectrometry (WDS) analyses were conducted on the pyroxene phenocrysts using the JEOL JXA 8200 electron microprobe (EMP) operated by the Institute of Meteoritics, UNM. Analyses of olivine were collected during a companion study and are available in the supplementary material of Elardo et al. (In Review). Quantitative WDS
analyses were conducted using an accelerating voltage of 15 kV, a beam current of 30 nA, a spot size of 1 µm. Standards were a mix of both natural and synthetic minerals and oxides, and the quality of analyses were assessed based on stoichiometric constraints. Multiple core to rim and multi-grain traverses were made to assess compositional profiles across grains.

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

RESULTS

Olivine Phenocrysts

Olivine is the most abundant phenocryst in NWA 032. It ranges in size from 10’s to 100’s of µm in length and sometimes form glomerocrysts with other olivine grains or, less frequently, pyroxene phenocrysts. We have observed no evidence for a reaction relationship existing between olivine and liquid. Olivine grains are typically euhedral and often contain euhedral chromite grains as inclusions in addition to polyphase melt inclusions (Fig. 1). Olivine
in NWA 032 in normally zoned in all elements measured in this study with the exception of faint oscillatory zoning of P. Their compositions are continuously zoned and range from ~Fo$_{65}$ in the cores to 1-3 μm Fe-rich rims of ~Fo$_{42}$ (Figs. 1, 2), the latter likely having formed during rapid cooling upon eruption (Fagan et al., 2002). All olivine analyses presented in Fig. 2 can be found in the supplementary data tables of a companion study by Elardo et al. (In Review).

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

Pyroxene Phenocrysts

Pyroxene is the most abundant phase in NWA 032, but the second most abundant phenocryst. Groundmass pyroxenes formed during rapid cooling on the lunar surface are not are the focus of this study. Pyroxene phenocrysts in NWA 032 are euhedral crystals with sizes ranging from 10’s to 100’s of microns in width. They sometimes form glomerocrysts with other
pyroxene phenocrysts or, less frequently, olivine phenocrysts. All the quantitative pyroxene EMP analyses presented here can be found in the electronic supporting material for this study. Pyroxene compositions span a narrow range from pigeonite to augite (Fig. 2) and have constant Ti/Al of ~1:4, which is consistent with plagioclase undersaturation in the melt (i.e. Bence and Papike, 1972). The narrow range in quadrilateral compositions suggests that the phenocrysts represent a single population of pyroxenes. The arrows in Fig. 2 indicate the range in groundmass pyroxene compositions and represent a reasonable extension of the phenocryst compositions that would be expected had crystallization proceeded at pre-eruptive rates (Fagan et al., 2002). Additional pyroxene analyses are available in the supplementary material of Elardo et al. (In Review).

Oscillatory zoning in pyroxene phenocrysts in NWA 032 was noted by Burger et al. (2009) and Elardo et al. (In Review). Pyroxenes show oscillatory zoning in Mg, Ca, Cr, Ti, Al, and, less prominently, Fe and Mn. An example of this zoning is illustrated in Fig. 5 and an EMP traverse of the same grain is shown in Fig. 6. Oscillatory zoning is sometimes visible in BSE images (e.g. Figs. 5a, 6). Oscillatory bands of high Mg concentrations are antithetical to bands with high Ca, Ti, Al, and Cr concentrations, consistent with the crystal chemical preferences of pigeonite and augite (Bence and Papike, 1972; Papike et al., 1976; Papike and White, 1979; Cameron and Papike, 1981). Most phenocrysts have relatively small cores (~25 μm) that are Mg-rich. Most oscillatory bands are parallel to crystallographic planes (e.g. Fig. 5), indicating constant euhedral growth throughout crystallization, and are easily traceable around the full circumference of a crystal (when a crystal of interest is fully intact). Figure 7 shows WDS maps of a pyroxene glomerocryst or multiple phenocrysts where bands are traceable around nearly the full circumference of the individual grains. Occasionally, at contacts between phenocrysts where
contact with the melt was not maintained, zoning bands are discontinuous. An EMP traverse through the grains in Fig. 7 is shown in Fig. 8. Figure 8 shows that although the short scale zoning in pyroxene phenocrysts is oscillatory, this short scale zoning is overprinted on longer scale zoning. Figure 9 shows the concentrations in atoms per formula unit (apfu) of Mg and the sum of Ca, Ti, and Al\textsuperscript{total} along a 231 µm segment of the B – B’ traverse from Fig. 8. This segment represents a core to rim profile of a single phenocryst along the B – B’ traverse. Linear regressions through these compositional profiles show a longer scale decrease in Mg and increase the sum of Ca, Ti, and Al from core to rim. This is characteristic of the typical pyroxene crystallization sequence of pigeonite to augite in lunar basalts.

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

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

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

The use of high resolution imaging techniques such as Normarski interference contrast imaging (e.g. Anderson, 1983; Anderson, 1984; Pearce and Kolisnik, 1990) and the improvement of backscattered electron (BSE) imaging, including the use of accumulated BSE images (e.g. Ginibre et al., 2002a; 2002b), over the past few decades has resulted in the ability to resolve the fine micron-scale structure of oscillatory zoning in plagioclase. The recognition of
resorption surfaces at the interfaces of some oscillatory zones and correlations between zone
wavelength and the amplitude of zoning lead previous authors to divide oscillatory zoning in
plagioclase into (at least) two distinct types (Downes, 1974; Pearce and Kolisnik, 1990; Ginibre
et al., 2002a; Streck, 2008). The first type, referred to hereafter as fine banding (type I of Pearce
and Kolisnik, 1990), is typically characterized by short oscillation wavelengths with band
thicknesses of roughly 10 μm or less. Band thicknesses tend to be relatively consistent in a given
area of a crystal. Clear resorption surfaces are absent and the amplitude of the variation in An
content is low, typically about 0.5 - 2.0 % An (Pearce and Kolisnik, 1990; Ginibre et al., 2002a;
Streck, 2008). In contrast, the second type, referred to hereafter as coarse banding (type II of
Pearce and Kolisnik, 1990), is typically characterized by longer oscillation wavelengths with
band thickness up to many 10s of microns or even over 100 μm in width. The amplitude of the
change in An content is variable between adjacent coarse bands, but it can be as high as 10s of %
An, and is typically higher in amplitude than fine banding. When resolution of the imaging
method is high enough, jagged, rough, rounded, or uneven surfaces attributed to resorption are
sometimes observed (see Pearce and Kolisnik, 1990; Ginibre et al., 2002a).

Oscillatory zoning in pyroxene phenocrysts is less commonly reported than in
plagioclase, but it has been identified by previous workers in magmas from various tectonic
settings (e.g. Downes, 1974; Barton et al., 1982; Eriksson, 1985; Shimizu, 1990; Simonetti et al.,
1996; Cioni et al., 1998; Reubi et al., 2003) and in Apollo 12 basalt 12021 (Boyd and Smith,
1971; Weill et al., 1971). Zoning has been observed in major (i.e. Mg and Ca more commonly
than Fe^{2+}), minor, and trace elements (i.e. Ti, Al, Cr, Na, Fe^{3+}, Sc, V, Zr, Sr). Downes (1974)
reported both finebanding and coarse banding ranging from 20 to 250 μm in width in augite
phenocrysts from Mt. Etna, Sicily; the distinction between band widths is similar to that of fine
Oscillatory band width in pyroxene is commonly reported to range from ~10 μm (sometimes less) to ~30 μm (Barton et al., 1982; Eriksson, 1985; Clark et al., 1986; Simonetti et al., 1996; Streck, 2008). Compositional ranges between bands are variable, however variations in the major divalent cations are typically on the order of a few mol%, with the higher field strength cations such as Ti, Al, Cr, and Fe$^{3+}$ showing variations up to 40 mol% (e.g. Downes, 1974; Eriksson, 1985; Clark et al., 1986; Simonetti et al., 1996; Cioni et al., 1998).

Trace elements have been shown to vary greatly. For example, Shimizu (1990) reported variations of a factor of 44 in Cr and 27 in Zr between oscillatory bands in an augite phenocryst from an alkaline basalt from Lahir Island, Papua New Guinea.

Oscillatory zoning in olivine is reported less frequently than pyroxene. Clark et al. (1986) reported olivine phenocrysts from Hawaii, Arizona, and Iceland that revealed ~30 μm wide oscillatory banding in Normarski interference contrast images. However, in all cases the oscillatory bands corresponded to small or non-existent compositional changes of <2% Fo content and no correlation with Ni, Mn, and Ca contents. Steele (1995) reported oscillatory zoning in Al and Ti in forsteritic olivine grains occurring in two chondritic meteorites. Shearer et al. (2013) explored the relationship between P zoning in martian olivines and crystallization history in basaltic martian meteorites Yamato 980459 and NWA 1183. Milman-Barris et al. (2008) examined olivine phenocrysts in detail using high beam current EMP X-ray mapping and found widespread oscillatory zoning of P in olivine from numerous terrestrial magmas and martian basaltic meteorite ALHA 77005. Oscillatory zoning of P was correlated with Cr and Al zoning in the olivines they studied that had short high temperature residence times in addition to some experimentally grown olivine, which suggests a potential charge-coupling relationship. However this was not ubiquitous in all olivine; natural phenocrysts with longer high temperature
residence times show weak or absent correlations with other elements (including potential charge balancing elements like Al and Cr). The lack of zoning in Mg/Fe and in some cases Al and Cr observed by Milman-Barris et al. (2008) is likely due to reequilibration with the magma as a result of the fast diffusion rates of divalent and trivalent cations in olivine compared to P\(^{5+}\) (see Chakraborty, 2010 and references therein). Milman-Barris et al. (2008) described multiple forms of oscillatory zoning of P in olivines. Band widths ranged from 3-40 µm but most fell into the 5-20 µm range. Oscillatory bands sometimes were traceable around the full circumference of a crystal, but other terminated over short distances. Unlike oscillatory zoning in plagioclase, the P zoning reported by Milman-Barris et al. (2008) was not continuous over the radius of a phenocryst. Rather, broad P-poor zones were often times punctuated by more P-rich bands and melt inclusions were often spatially associated with P-rich bands. The association of P-rich bands and melt inclusions suggests that cooling rate plays a role in the formation P-rich zones in olivine.

The origin of oscillatory zoning in pyroxene phenocrysts in NWA 032

Fagan et al. (2002) suggested that NWA 032 underwent a relatively simple cooling history: crystallization of chromite and olivine followed by pyroxene, and subsequent rapid cooling of the remaining liquid into a fine-grained groundmass upon eruption onto the lunar surface. Our petrographic observations of NWA 032 support this crystallization sequence; however, an examination of oscillatory zoning patterns of major and minor elements in pyroxene phenocrysts argues for a more complex cooling history prior to eruption. Figures 5-10 show examples and details of the form and compositional variations in the oscillatory zoning patterns in pyroxene phenocryst in NWA 032. Oscillatory bands have widths ranging from ~3-5 µm up to ~60 µm in the phenocrysts investigated here, and are typically in the range of 10-20 µm.
Oscillatory bands are usually well defined, with euhedral forms and sharp boundaries, but in some cases uneven or rounded boundaries are observed (examples of both can be seen in Fig. 10). Compositional profiles indicate oscillations are overprinted on longer scale normal magmatic zoning (Figs. 6, 8, 9).

Detailed reviews of models proposed for the origin of oscillatory zoning in plagioclase and other minerals were provided by Pearce (1994) and Shore and Fowler (1996). The latter authors divided the proposed models into two types based on formation conditions: intrinsic vs. extrinsic. Intrinsic models are typically based in crystallization kinetics and the interplay between diffusion rates of cations in the melt and the rate of crystallization. In a broad sense, these models generally advocate a phenomenon called solute trapping, wherein the growth rate of a crystal exceeds the rate at which cations in the liquid can diffuse toward or away from the growing crystal, which results in non-equilibrium incorporation of chemical species into the crystal (e.g. Sibley et al., 1976; Allegre et al., 1981; Aziz, 1982; Loomis, 1982; L’Heureux, 1993; Pearce, 1994; Reitano et al., 1994; L’Heureux and Fowler, 1996; Lofgren et al., 2006; Schwandt and McKay, 2006; Milman-Barris et al., 2008). The fast growth rate of the crystal is thought to be a product of a high degree of undercooling of the magma. The crystal depletes compatible growth components in the boundary layer surrounding it and incorporates a higher proportion of incompatible components than equilibrium partitioning relationships would suggest because they are enriched in the boundary layer and are “trapped” by the rapidly growing crystal. Crystal growth then slows in response to a diminished degree of super-saturation in the boundary layer which results from the depletion of compatible growth components. Eventually the boundary layer is replenished by diffusion or destroyed by convection processes; either way the result is a new stage of growth on the crystal-liquid interface. This intrinsic mechanism is thought to be
responsible for short-scale, low amplitude fine banding. It is thought that local depletion of a
boundary layer would prevent the growth of coarse bands >15 μm or so (Pearce and Kolisnik,
1990; Pearce, 1994; Ginibre et al., 2002a; 2002b). In contrast, extrinsic models produce
oscillatory zoning as a result of changes in liquid composition due to external forcing, which
may include processes such as magma chamber replenishment events and crystal convection.
The production of chemical oscillations by these mechanisms is not dependent (to a large extent)
on diffusion rates or local non-linear crystal growth, but rather on the composition of the magma
body in which the crystal is growing. Therefore, oscillatory bands with much greater width and
compositional amplitude (coarse bands) are permitted by these models. Additionally, the jagged,
rounded, uneven, or diffuse edges observed on many of these bands are attributed to resorption
when the crystal cycles to a less super-saturated zone of the chamber, or when a new batch of
more primitive magma is injected into the chamber (Pearce, 1994; Ginibre et al., 2002a).

The characteristics of oscillatory zoning patterns in pyroxene phenocrysts in NWA 032
make the task of distinguishing between fine banding and coarse banding difficult; the zoning
patterns observed have some characteristics of both. The widths of oscillatory bands fall into
both size ranges. Figures 5 and 10 show pyroxenes with some band widths of ~10 μm or less,
whereas Figs. 7 and 10 clearly show coarse bands with widths up to ~60 μm. Additionally, the
interior portions of the phenocrysts in Fig. 10 show low amplitude oscillations, whereas the
exterior portions of the same grains, in addition to grains shown in Figs. 5 and 7, show higher
amplitude oscillations. Overall, however, the oscillations in NWA 032 pyroxenes more closely
resemble coarse banding as described by previous authors (Downes, 1974; Pearce and Kolisnik,
1990; Pearce, 1994; Ginibre et al., 2002a). Even though some bands show micron-scale widths,
the majority of bands are roughly 15-30 μm in width and the presence of thick, ~60 μm bands
(e.g. Fig. 7) is indicative of coarse banding. Next, band widths are variable over short length scales (e.g. Figs. 5, 10). A characteristic of fine banding is that it is fairly regular in width throughout repeated oscillations (Pearce and Kolisnik, 1990; Ginibre et al., 2002a). Additionally, the exterior portions of the phenocrysts indicated by the arrows in Fig. 10 show that some bands have rounded or jagged forms which contrast the more euhedral forms in the interiors of the same grains. We interpret this as evidence of resorption surfaces between zones, which is characteristic of coarse bands and the processes that produce them (e.g. Pearce, 1994; Ginibre et al., 2002a). It is also possible that more oscillatory zone boundaries than just those observed in Fig. 10 represent resorption surfaces that are either not apparent in the images or maps in our dataset due to the smaller scale of those features and/or the resolution of our imaging and mapping techniques. Lastly, Fagan et al. (2002) suggested based on olivine morphologies, that cooling rates in the magma chamber were <2° C/h. However, crystallization experiments conducted by Lofgren et al. (2006) demonstrated that cooling rates of 5° C/h produced normal magmatic zoning patterns in Mg, Fe, and Ca in CPX crystals with equant to euhedral morphologies, similar to those in NWA 032. This suggests the <2° C/h estimate of Fagan et al. (2002) would be too slow to produce oscillatory zoning in the pyroxene and that at rates up to at least 5° C/h, solute trapping does not affect Mg, Fe, and Ca. Therefore, based on our data, the oscillatory zoning in pyroxene phenocrysts in NWA 032 likely reflects large scale compositional variations in the magma rather than the effects of crystallization kinetics (i.e. solute trapping; although it is possible this mechanism may have operated locally in response a faster cooling rate, see below).

We have considered both magma chamber recharge events and convection as a means to produce the variable magma compositions responsible for the oscillatory zoning in pyroxene;
however, these processes are not mutually exclusive. Ginibre et al. (2002b) argued that oscillatory zoning, trace element variations, and resorption surfaces in plagioclase phenocrysts in a dacite from Parinacota volcano, Chile, reflect both recharge and convection operating in the same chamber. Magma mixing and recharge events have been suggested as an explanation for oscillatory zoning in pyroxene phenocrysts in various terrestrial settings (e.g. Barton et al., 1982; Cioni et al., 1998; Reubi et al., 2003). In the case of NWA 032, the magma chamber may have experienced periodic replenishments of fresh magma followed by differentiation prior to eruption. Injections of more primitive parental magma into the chamber would be reflected in Mg-rich bands, whereas Ti-Al-Ca-rich bands reflect enrichments in the magma due to crystal fractionation. If so, the amplitudes of compositional zoning bands should be generally equivalent if new magma of the parental composition were added to the chamber (i.e. a semi-constant baseline composition), or should at least be variable if the volume or composition of fresh magma added to the chamber varied during each event. Figure 9 shows the concentrations of Mg and the sum concentration of Ti, Ca, and Al\(_\text{total}\) in the B – B+231 μm core-rim segment of the multi-phenocryst traverse B – B’ in Fig. 8. Linear regressions through the concentration profiles show that although the fine-scale zoning in pyroxene is oscillatory, it is overprinted on longer-scale zoning. Mg decreases from 1.145 atoms per formula unit (apfu) in the core to 0.805 apfu in the rim, and the sum of Ti, Ca, and Al\(_\text{total}\) increases from 0.245 apfu in the core to 0.844 apfu in the rim. The long-scale decrease in Mg is the result of its replacement in the M2 site by Ca and in the M1 site by Ti and Al (with some Al also going into the tetrahedral site), which is typical of the non-tholeiitic pyroxene crystallization sequence from pigeonite to augite in lunar basalts. This is indicative of a single, evolving magma, and argues against magma chamber replenishment, unless the replenishment occurred in progressively smaller proportions in each
successive event. This variation on the recharge model would produce short-scale oscillatory zoning the crystals, reflecting the changing magma composition due to each recharge event. These oscillations should be overprinted on longer-scale zoning reflecting fractionation in the chamber so long as the volume of parental magma decreased in each replenishment event. This process would affect the entire magma chamber equally, and therefore one should expect to see correlations in zoning patterns between crystals, which we do not observe here. However, based on the limited amount of sample available to us, we cannot rule out this model. Recharge events in progressively smaller proportions may have at least contributed to the formation of oscillatory zoning.

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

Our preferred model is one in which oscillatory zoning in pyroxene preserves a record of magma chamber convection before eruption. A schematic model for the growth of pyroxene phenocrysts in NWA 032 is shown in Fig. 11. Pyroxene phenocrysts are cycled through warmer and cooler regions of a cooling magma chamber by vigorous convection (Fig. 11a). Since solute
trapping is not likely to play a large role in development of the oscillatory zoning (see above), a compositional gradient is required in the magma chamber. This is likely the result of a temperature gradient imposed by differential cooling of the magma body: heat loss is most efficient from the top of the chamber, inducing a greater degree of super-saturation in the upper region, which would make it more crystal-rich. In the lower, warmer region of the chamber, the stable pyroxene composition is more Mg-rich and Ca-Al-Ti-poor. Some resorption of higher-Ca pyroxene growth zones occurs when crystals are carried to the lower, warm region from the upper, cooler region, resulting in resorption surfaces like those in Fig. 10. However, if the magma in the lower regions is saturated in pyroxene of a pigeonite composition, Mg-rich growth zones will form on a crystal over higher-Ca growth zones (Fig. 11b). As the crystal is swept back up into the upper, cooler region of the chamber, resorption will not occur. Rather, a growth zone of a more evolved pyroxene composition (i.e. Ca-Al-Ti-rich) will form around the Mg-rich zone (Fig. 11c). As the composition of the pyroxene growth zones is not dictated by the available components in a boundary layer surrounding the crystal, but rather by the composition of the magma, the thickness of the growth band is not limited as in the case of solute trapping from a boundary layer. If the chamber experienced replenishments of the parental magma in progressively smaller proportions, this may also result in chemical oscillations in the crystals like those observed, and the addition of the hotter, more primitive parental magma may contribute to inducing convection in the chamber.

As the cycling of crystals via convection progresses and the chamber continues to cool, the composition of magma throughout the chamber will evolve as a function of time and crystallization. The oscillatory bands produced in each region of the chamber will therefore also become more evolved with time. This is consistent with the linear regressions of core to rim
profiles that show that normal magmatic zoning is overprinted on the small scale oscillatory nature of zoning in pyroxenes (e.g. Fig. 9), suggesting crystallization of a single magma. We recognize that solute trapping may occur locally to form some of the thinner oscillatory bands if at any point during pre-eruptive crystallization a phenocryst experiences a region of the chamber where super-saturation is great and cooling rates are high. Based on our observations, however, this is likely limited in occurrence and is not responsible for the great majority of chemical oscillations in pyroxene.

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

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

Even at the high beam currents used for WDS mapping in this study, oscillatory zoning of P in olivine phenocrysts in NWA 032 is faint (Figs. 3, 4). P-rich zones do not correlate with oscillations in any other elements and are typically euhedral, but irregularly spaced with broad P-poor zones between them. These features are similar to many of the features observed in olivine.
in the samples studied by Milman-Barris et al. (2008) and Shearer et al. (2013). Solute trapping was invoked by Milman-Barris et al. (2008) to explain oscillatory zoning of P that is prevalent in olivine phenocrysts in numerous terrestrial and martian magmas. In the case of NWA 032, we envision two possibilities for the origin of P zoning in olivine. The first is that P zoning is the result of the same magma chamber convection and melt composition gradient that resulted in the oscillatory zoning in pyroxene. The lack of zoning in any other element in the olivine may be a result of the faster diffusion rates of divalent and trivalent cations in olivine compare to clinopyroxene (see section below), but slow diffusion rates of $P^{5+}$ leads to the preservation of remnant zoning. The second possibility is that the P zoning is a result of solute trapping during olivine growth, as envisioned by Milman-Barris et al. (2008). Those authors demonstrated that the process occurs frequently in olivine without invoking any extrinsic forcing like convection, so long as cooling rates are fast enough, so it is not difficult to invoke its occurrence during the formation of olivine in NWA 032. They were able to reproduce P oscillatory zoning features in experimentally grown olivines at cooling rates of 15 – 30° C/h. Fagan et al. (2002) argued for a cooling rate of <2° C/h for NWA 032 based on olivine morphologies. Therefore, P zoning in olivine may be a product of transient fast cooling rates of 2 – 30° C/h, perhaps as a secondary result of convection in the magma chamber and periodically resulted in solute trapping events wherein P-rich zones were produced in olivine. This is the mechanism of origin we prefer for P zoning in olivine.

**Preservation of oscillatory zoning**

The oscillatory zoning in NWA 032 pyroxene phenocrysts is preserved as the result of two main factors: eruption onto the lunar surface and slow diffusion rates of cations in clinopyroxenes. Fast cooling upon eruption is apparent from the fine grained crystalline
groundmass in NWA 032, and this reduces time available for diffusive reequilibration. Additionally, studies of cation diffusion in clinopyroxene suggest that diffusive reequilibration of oscillatory bands is not favorable in the estimated residence time of the phenocrysts in the magma before eruption (~3.5 - 35 days; Fagan et al., 2002), even at the pyroxene crystallization/near-eruption temperature of ~1180°C estimated by crystallization modeling of Fagan et al. (2002) and suggested by Cr contents of olivine (Fig. 10 of Elardo et al., 2012). Both Al and Ti are slow diffusing cations in clinopyroxene. For example, Al diffusion coefficients at 1180°C are on the order of 2.7-3.7 x 10^{-21} m^2/s (Sneeringer et al., 1984; Sautter et al., 1988; Cherniak and Dimanov, 2010; Cherniak and Liang, 2012). Self- and inter-diffusion rates of Mg and Fe in clinopyroxene are unusually slow compared to other Mg-Fe silicates (e.g. olivine, garnet; Dimanov and Sautter, 2000; Dimanov and Wiedenbeck, 2006; Cherniak and Dimanov, 2010; Zhang et al., 2010). Calcium has been shown to be the slowest diffusing octahedrally-coordinated major cation (e.g. Dimanov et al., 1996; Dimanov and Jaoul, 1998; Zhang et al., 2010), and therefore is likely to be the kinetically-limiting species (Cherniak and Dimanov, 2010). Furthermore, diffusive reequilibration of the oscillatory bands requires the simultaneous diffusion of multiple species exchanging with multiple crystallographic sites in order to maintain local charge balance. For example, Al occupies both the octahedral M1-site and the tetrahedral-site, and is charge balanced by Ti^{4+}, Cr^{3+}, or a second Al in octahedral coordination (Bence and Papike, 1972; Cameron and Papike, 1981). All three of these couples can be significant in lunar pyroxenes (Bence and Papike, 1972), so diffusion of these three species in addition to Mg, Fe, Ca and Si must all occur simultaneously for reequilibration to occur. Given that NWA 032 consists of only ~17% modal of phenocryst phases, crystallization in the magma chamber was
likely not a long duration process before eruption, and therefore provided insufficient time for reequilibration of oscillatory bands.

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

A number of studies have focused on the origin of basaltic lunar meteorites NWA 032, NWA 4734, and LAP 02205, not only because they are three of the five youngest known igneous rocks from the Moon and sample geologic units unlike those sampled by the Apollo and Luna missions, but also because the three basalts have very similar bulk compositions, mineralogy, and ages, yet very different Nd isotopic compositions (Fagan et al., 2002; Barrat et al., 2005; Righter et al., 2005; Zeigler et al., 2005; Anand et al., 2006; Day et al., 2006; Joy et al., 2006; Day and Taylor, 2007; Borg et al., 2009; Wang et al., 2012; Elardo et al., In Review). We examined pyroxene zoning patterns in a companion study of all three meteorites and found that pyroxenes in NWA 4734 and LAP have normal magmatic zoning patterns (Elardo et al., In Review). Our data on oscillatory zoning in pyroxenes in NWA 032 places a number of constraints on its relationship to NWA 4734 and LAP. First, the data presented above argues against mixing of a compositionally dissimilar magma during the pre-eruptive magma chamber phase of crystallization. Additionally, the high degree of similarity in the bulk rock trace element compositions suggests that assimilation cannot have played a large role in their origins. Therefore, the oscillatory zoning in pyroxene in NWA 032 does not record a chemical change in the magmatic system that could be used to argue against a pairing with NWA 4734 and LAP or be used to explain their different Nd isotopic compositions. Next, the lack of oscillatory zoning in pyroxene in NWA 4734 and LAP does not rule out a pairing relationship. It may indicate that the NWA 4734 and LAP parental magmas had more time to diffusively re-equilibrate oscillatory
bands, either in the magma chamber or during cooling in the interior of a thick lava flow, which is consistent with their coarser-grained subophitic textures. Alternatively, they may be derived from a different magmatic system or a different eruptive episode in the same magmatic system, and never underwent the convection processes that formed oscillatory zoning in the NWA 032 phenocrysts. The available data cannot distinguish between these possibilities. Therefore, the conclusion of Elardo et al. (In Review) that NWA 032, NWA 4734, and LAP are source crater paired and are likely derived from the same volcanic province remains the most likely explanation for the origin of these basalts.

**IMPLICATIONS**

Although oscillatory zoning is common in terrestrial silicate minerals, the zoning patterns reported here are only the third known instance of oscillatory zoning in lunar silicates. The interpretation that these zoning patterns record processes operating within the magma chamber allows for a more detailed reconstruction of the petrogenetic history of NWA 032, which is an important lunar sample as it is not only the youngest lunar igneous sample currently know, but it is also geochemically distinct from Apollo low-Ti basalts. Firstly, oscillatory zoning in pyroxene and olivine in NWA 032 preserve a record of vigorous convection and possibly magma replenishment within a cooling crustal magma chamber prior to eruption. Insight into magma chamber dynamics in the lunar environment is rarely preserved by crystal zoning patterns in lunar basalts and NWA 032 offers constraints on those processes. Secondly, the zoning patterns and mineral compositions in NWA 032, combined with previous isotopic studies (e.g., Borg et al., 2009), allow us to exclude assimilation of exogenous material during crystallization from the petrogenetic history of the basalt. This is an important constraint when using the trace element and isotopic compositions of NWA 032 to make inferences in regards to its source region.
composition and mantle melting at 3 Ga. Finally, oscillatory zoning in pyroxene and olivine is rare compared to plagioclase, so these observations provide important constraints for oscillatory formation models that are primarily based on constraints from zoning patterns in plagioclase.

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REFERENCES


FIGURE CAPTIONS

**Figure 1:** Backscattered electron (BSE) images of representative textures and phenocryst assemblages in NWA 032. Ol = olivine, Pyx = pyroxene, Chr = chromite, MI = melt inclusion, GM = groundmass.

**Figure 2:** A pyroxene quadrilateral showing the range in compositions for pyroxene phenocrysts from NWA 032. Arrows indicate the approximate range in groundmass pyroxene compositions from Fagan et al. (2002). The range in composition of olivine phenocrysts is show below. This figure is adapted from a companion study (Elardo et al., In Review) and the complete olivine EMP dataset can be found there.

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

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

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

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

**Figure 7:** Qualitative WDS X-ray maps of Ti, Mg, and Cr in a large pyroxene that represents either a broken phenocryst or a glomerocryst consisting of two phenocrysts. The coarse nature of many oscillatory bands is visible here, with band widths of ~60 μm in some cases. The color contrast of the maps have been adjusted to better show zoning patterns and therefore colors are not necessarily comparable between maps and with pyroxene maps in other figures. Hot colors
represent higher concentrations whereas cooler colors represent lower concentrations. Dark patches prominent in the Ti map are SIMS spots from previous analyses.

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

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

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

**Figure 11:** A schematic magma chamber model for the origin of oscillatory zoning in pyroxene phenocrysts in NWA 032. (a) Differential cooling of a magma chamber in the lunar crust produces a compositional gradient in the chamber, which drives convection that carries phenocrysts through the different regions of the chamber. Periodic replenishments of parental magma may occur, but only insofar as they are in progressively smaller proportions. (b) In the lower, warmer, more crystal-poor regions of the chamber, phenocrysts transported from the upper regions may undergo some resorption of growth zones richer in Ca. However, the lower
region is still pyroxene saturated and this results in a growth band that is Mg-rich. (c) Phenocrysts carried into the upper, cooler, more crystal-rich portions of the chamber do not undergo resorption. Growth bands richer in Ca, Ti, and Al form over more Mg-rich bands. Repetition of this process results in oscillatory zoning of pyroxene phenocrysts.
Diagram showing the groundmass compositions of NWA 032 meteorite with eruption points.

- Di: Diopside
- Hd: Hornblende
- En: Enstatite
- Fs: Fs (Forsterite)

Mole % Forsterite:

- 100
- 90
- 80
- 70
- 60
- 50
- 40
- 30
- 20
- 10
- 0