THE ORIGIN OF OSCILLATORY ZONING OF MAJOR AND MINOR ELEMENTS IN PYROXENE PHENOCRYSTS IN LUNAR BASALTIC METEORITE NWA 032/479. S. M. Elardo and C. K. Shearer, Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. <u>selardo@unm.edu</u>

Introduction: Lunar basaltic meteorite Northwest Africa (NWA) 032/479 is currently the youngest known igneous sample from the Moon [2.93 Ga; see 1]. Previous workers have shown, based on compositional and isotopic constraints [1-4], that NWA 032/479 sampled a low-Ti basaltic flow that is distinct from those sampled during the Apollo and Luna missions. Texturally, NWA 032/479 contains ~17% chromite, olivine and pyroxene phenocrysts set in a fine-grained groundmass [3] that likely formed upon eruption on the lunar surface. Fagan et al. [3] argued based on this limited phenocryst assemblage and the fast cooling rate recorded by the groundmass that NWA 032/479 underwent a relatively simple cooling history: crystallization of chromite, olivine and then pyroxene followed by quench upon eruption. However, Burger et al. [5] initially studied the zoning patterns of olivine and pyroxene, and identified the presence of oscillatory zoning patterns in pyroxene phenocrysts, although the origin of this zoning was not determined.

Early studies of lunar mare basalts demonstrated the effects of cooling rate on mineral chemistry and the usefulness of zoning patterns, particularly in pyroxene, in unraveling the cooling history of a basalt [e.g. 6-8]. In this study, we present analyses of both olivine and pyroxene phenocrysts in NWA 032/479 to constrain the thermal history of a young mare basalt. Its young age indicates that it samples a basaltic flow erupted at the end of the main pulse of mare magmatism on the Moon. Not only do its bulk composition and isotopic compositions preserve a record of source regions and magmatic processes involved in young mare magmatism [see 4], 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 [9-11].

**Methods:** In this study, we examined two sections of NWA 032, which is paired with NWA 479. Quantitative wavelength dispersive spectrometry (WDS) analyses of olivines and pyroxenes were conducted at the University of New Mexico with a JEOL JXA 8200 electron microprobe using an accelerating current of 15 kV, a beam current of 30 nA, and a 1  $\mu$ m spot size. WDS analyses often consisted of core-rim or rim-rim traverses to investigate zoning patterns. Qualitative WDS maps of Mg, Ti, Ca, Al, and Cr in pyroxene were made using the same instrument operation at 15 kV with a beam current of 100 nA. Qualitative WDS maps of Mg, Fe, Cr, Ca, and P in olivine were made using the same instrument operation at 15 kV with a beam current of 400 nA, after the approach of [12].

**Results:** WDS maps and analyses show that olivine phenocrysts in NWA 032 are normally zoned in all major and minor elements measured here with the exception of faint oscillatory zoning of P. The mapped phenocryst has a high P core and periodic bands of high P within the mantling olivine. Single bands are not easily traced throughout the phenocryst; however bands have grown parallel to crystallographic planes, indicating constant euhedral crystal growth. Bands are typically thin, on the order of a few  $\mu$ m's in width.

All pyroxene phenocrysts investigated in this study exhibit oscillatory zoning of Mg, Fe, Ca, Ti, Al, Cr, and Mn. Bands with high concentrations of Mg are antithetical to bands richer in Ca, Ti, Al and Ca (Fig. 1), consistent with the crystal chemical preferences of augite versus pigeonite [6, 13]. Oscillatory bands have grown parallel to crystallographic planes, indicating constant euhedral growth. Unlike P-rich bands in olivine, oscillatory bands in pyroxenes are more easily discernible and traceable throughout the circumference of a phenocryst. In the largest pyroxenes studied here, up to six Mg-rich bands are discernible, and up to 22 Ti-rich bands are discernible. The some bands have sharp boundaries whereas some are more jagged or uneven. Bands are variable in width, ranging from ~1 µm to over 20 µm's in width. Pyroxenes often have a core of relatively constant composition, but whether the core is relatively Mg-rich or Ca-Ti-Al-Cr-rich is phenocryst dependent. Compositional core-rim profiles show that amplitude of compositional variations from band to band is not constant. Linear regressions though core-rim segments demonstrate that normal magmatic zoning (i.e. decreasing Mg, increasing Ca, Ti, Al and Cr) is overprinted on smaller scale oscillatory zoning.

**Discussion:** Our observations indicate that the relatively simple cooling history inferred for NWA 032 [3] was more complicated, and that olivine and particularly pyroxene phenocrysts preserve a record of that cooling history. Oscillatory zoning of P in igneous olivine is not uncommon [12, 14], and is found in many terrestrial and martian olivine phenocrysts. Millman-Barris et al. [12] were able to reproduce many oscillatory features of P in olivine experimentally at cooling rates of 15-30° C. They attributed most such zoning to a kinetically controlled feedback mechanism called solute trapping, wherein the slowly diffusing P cannot "outrun" a rapidly growing crystal in

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the melt. P, being incompatible in olivine, builds up in the boundary layer surrounding the olivine and is enriched in the new growth layer. Repetition of this process results in oscillatory zoning. We infer from our observations that this mechanism is likely responsible for the oscillatory of P in olivine in NWA 032.

The oscillatory zoning of major and minor elements in the pyroxene, however, presents some challenges to a model of solely solute trapping during rapid cooling. Oscillatory bands in pyroxene phenocrysts are highly variable in width, ranging from ~1  $\mu$ m to over 20  $\mu$ m's. Studies of oscillatory zoning in natural pyroxenes and plagioclase have distinguished between fine (1-10  $\mu$ m) and coarse (>10  $\mu$ m) oscillatory zoning [e.g. 15-17]. Fine scale oscillatory zoning in magmatic minerals can be attributed to solute trapping, but the depletion of compatible elements in the boundary layer surrounding a crystal has the effect of slowing crystal growth as components become depleted, so the development of coarse bands may not be possible by this mechanism alone [see 17 and refs therein].

We favor a model similar to that of Pearce [17]. Convection of phenocrysts in a differentially cooling magma chamber leads to the crystals experiencing variable growth rates and possibly compositional gradients as well. The formation of boundary layers and solute trapping are important, and this may be responsible for fine zoning. Coarse zoning bands may be the result of the achievement of a steady state within either the warm or cool region of the chamber. As the crystal is cycled throughout the chamber, dissolution may act to decrease the width of the bands before the cycle repeats and forms new growth bands [i.e. 17]. The longer scale normal magmatic zoning overprinted on oscillatory zoning indicates that magma recharge events are not the cause of the oscillations. Further work is needed to refine this model; however these zoning patterns constrain the crystallization history of a lunar magma chamber at the end of the main pulse of mare magmatism.

**References:** [1] Borg et al. (2009) GCA 3963-3980. [2] Zeigler et al. (2006) MAPS 1073-1101. [3] Fagan et al. (2002) MAPS 371-394 [4] Elardo et al. (2013) LPSC, This conf. [5] Burger et al. (2009) LPSC #2043 [6] Bence and Papike (1972) GCA, 431-469. [7] Lofgren 1975 (1975) LSI contrib., 99-103, [8] Grove (1978) LPSC, 565-584. [9] Parmentier and Hess (1998) LPSC, #1182 [10] Hess (2000) JGR, 4347-4360 [11] Hess and Parmentier (2001) JGR-P, 28,023-28-032 [12] Millman-Barris et al. (2008) *Contrib. Min. Pet.*, 739-765. [13] Cameron and Papike (1981) *Am. Min*, 1-50. [14] Shore and Fowler (1996) *Can. Min.*, 1111-1126. [15] Downes (1974) *Contrib. Min. Pet.*, 187-196. [16] Streck (2008) *RiMG* **69**, 595-622. [17] Pearce (1994) *Feldspars &Their Reactions*, 313-349

Fig. 1: Qualitative WDS maps of two typical pyroxene phenocrysts in NWA 032. Warm colors correspond to higher concentrations whereas cooler colors are lower concentrations.

