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Constraints on the Petrologic History of Gabbroic Shergottite Northwest Africa 6963 from Pyroxene Zoning Profiles and Electron Backscattered Diffraction.

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Abstract

Northwest Africa 6963 (NWA 6963) is a coarse grained, gabbroic Martian meteorite that further extends our Martian sample collection, both compositionally and texturally. Gabbroic shergottite NWA 6963 provides direct petrologic evidence of intrusive igneous conditions within the Martian crust. Here, we analyzed geochemical zoning profiles and microstructural-crystallographic information from electron-backscattered diffraction of augite and pigeonite to constrain the crystallization history of NWA 6963. Compositional zoning profiles reveal pyroxenes with augite or pigeonite cores mantled by Fe-rich pigeonite rims. Our results suggest complex pyroxene textures and zoning profiles observed in pyroxenes in NWA 6963 are due to pyroxene accumulation from a crystallizing magma in a large intrusive environment (sill or magma chamber); however, without geologic context or companion samples, it is currently impossible to rule out accumulation at the base of a very large (>>100 m) differentiated flow.

Keywords: NWA6963, Pyroxene, EBSD, Trace elements, Martian meteorite, Shergottite

Introduction

Martian meteorites provide unique and rare samples from unknown terrains on Mars, and are the only way, at present, to study the Martian crust directly (e.g., Udry et al. 2020). The number of Martian meteorites identified continuously increases and each new sample may answer previous questions about Mars, while also producing new inquiries. Martian meteorites are classified into three main groups: Shergottites, Nakhlites, and Chassignites (SNCs). Basaltic shergottites are further classified based on textures as basaltic, diabasic, or gabbroic (Stolper and McSween 1979; McSween and Treiman 1998; Filiberto et al. 2014; Udry et al. 2020). Pyroxenes in shergottites are often zoned and may have preferred grain orientation (McSween et al. 1996; Becker et al. 2011; Stephen et al. 2010; Filiberto et al. 2014).

While extrusive shergottites are invaluable for constraining surface lava conditions and can be used as a proxy for magmatic conditions at depth (Wadhwa et al. 2001; Goodrich 2003; Sarbadhikari et al. 2009), gabbroic shergottites provide direct evidence of subsurface magmatic conditions (Filiberto et al. 2014, 2018; Udry et al. 2017). NWA 6963 was recently described as an intrusive gabbroic shergottite containing cumulate pyroxene; however, the depth of the intrusion was not well constrained (Filiberto et al. 2014, 2018). In order to constrain the depth of crystallization and therefore the emplacement history, here we combine trace and major element zoning profiles from electron microprobe analyses (EMPA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), along with mineral microstructural-crystallographic information from electron backscatter diffraction of augite and pigeonite grains in NWA 6963.

Previous studies on Martian meteorite crystal zoning include work on basaltic shergottites (e.g., Mikouchi et al. 1999; McCoy and Lofgren 1999; Barrat et al. 2002a, 2002b; Hui et al. 2011; Udry et al. 2017), olivine-phyric shergottites (e.g., Sarbadhikari et al. 2009; First and Hammer 2016), and nakhlites (Treiman 1990, 2005). For example, recent investigations of the second classified gabbroic shergottite, NWA 7320, evaluated the petrogenetic history of the meteorite and provide insight into the Martian crust (Udry et al., 2017). X-ray compositional maps of NWA 7320 revealed complex pyroxene zoning and bulk rare earth element (REE) patterns depleted relative to other basaltic shergottites (Udry et al. 2017). The petrogenesis of NWA 732is proposed to have occurred in two main phases: pyroxene antecrysts crystallized at depths of 30-70 km, followed by magma ascent to shallow crustal depths, with plagioclase crystallization and accumulation to form the gabbroic shergottite (Udry et al. 2017). Previous work on basaltic shergottites (Shergotty, Zagami, EETA79001, and QUE94201) attribute dual pyroxene textures, chemical zoning trends, and exsolution features to be the result of magma undercooling (Mikouchi et al. 1999). Shergotty and Zagami experienced slight undercooling resulting in simultaneous cotectic growth of pigeonite and augite with plagioclase crystallizing later (Mikouchi et al. 1999). In contrast, EETA79001 and QUE94201 experienced significant undercooling of the parental magma and had a crystallization sequence of pigeonite, augite, plagioclase, and Fe-rich pigeonite. These melt conditions differ, with each metastable phase crystallizing alone because melt conditions did not follow equilibrium phase boundaries (Mikouchi et al. 1999). Additional evidence of undercooling is seen with pyroxene microstructures, such as exsolution lamellae, found in Shergotty and Zagami indicating faster subsolidus cooling rates (Mikouchi et al. 1999).

NWA 6963

Northwest Africa (NWA) 6963 was found in 2011 in Guelmim-Es-Semara, Morocco near the river Oued Touflit (Ruzicka et al. 2014). NWA 6963 oxygen isotopes and bulk chemistry confirm it as a Martian

meteorite (Ruzicka et al. 2014). NWA 6963 is a coarse-grained Martian meteorite with large, oriented pyroxene crystals (up to 5 mm in length) (Filiberto et al. 2014, 2018). NWA 6963 is composed of 65 ± 5 % pyroxene (25 ± 5 % augite and 40 ± 5 % pigeonite), 30 ± 5 % maskelynite (shocked plagioclase), with minor amounts of ferroan olivine, spinel, ilmenite, merrillite, apatite, Fe-sulfides, and quartz-alkali feldspar intergrowths (Filiberto et al. 2014, 2018). Previous work showed that the augite and pigeonite cores are in equilibrium, as are augite and pigeonite rims, and, using two-pyroxene thermometry, give a calculated crystallization range for the pyroxenes of 1250 °C to 1000 °C (Filiberto et al. 2014; Filiberto et al. 2018). While the temperatures of crystallization were previously well constrained, the depth of the intrusion and style of emplacement were not. In fact, Filiberto et al. (2014) preferred a deeper plutonic emplacement history, while Filiberto et al. (2018) preferred a shallow emplacement history as a feeder dike for eruptive basaltic shergottites. Here we combine major element zoning profiles and trace element spot analyses, along with microstructural-crystallographic characterization from electron backscatter diffraction, to constrain the depth and style of emplacement.

Methods

A portion NWA 6963 was cut and polished into a thick section and thin section for analyses. Backscattered electron (BSE) images, X-ray element maps, and major element composition profiles were measured using a Cameca SX100 electron microprobe at the Open University, UK. Trace elements were measured using a laser ablation inductively coupled plasma mass spectrometer (ICP-MS) at the Open University, UK. Electron backscatter diffraction (EBSD) was completed using an Oxford Instruments Symmetry detector on the same thick section at the Plymouth Electron Microscopy Centre (PEMC) at the University of Plymouth, UK.

Major Elements

Zoning profiles were analyzed across eleven pyroxene grains and one maskelynite grain using standard measurement conditions for the SX100: 20 kV accelerating voltage with a 20 nA beam current; calibration against a set of standard phases, comprised of matrix matching minerals and synthetic standards (e.g., olivine (for-BM4), pyroxenes (jad-BM4, bustamite), feldspar (fspr-In5), apatite (ap-BM4), sulfates (barite) and oxides (hematite, rut-BM4, Cr2O3-JB4, Ni-JB4), and accuracy was checked against a set of in-house mineral standards. A 1 μm spot size was used and each measurement was spaced ~5 ± 1 μm apart. Lines were comprised of 40 to 120 measured points depending on grain size and line orientation. Data outliers were identified and were excluded; these include poor oxide weight totals (less than 98.0 and greater than 102.3 total weight percent), and thorough visual inspection of BSE images for cracks, pits, or alteration phases. Measurements taken close to the grain edges, melt inclusions, sulfides, fractures, exsolution, or

alteration were also removed from zoning profiles. X-ray element maps, using the same beam conditions and standardization procedures as for the lines, of three pyroxene grains were produced to better interpret zoning profiles and visualize the distribution of major element oxides.

Trace Elements

Trace elements were analyzed by laser ablation-ICP-MS using a NewWave 213 nm Nd:YAG laser coupled to an Agilent 7500 quadrupole ICP-MS. Standards used for trace element analysis were NIST 612 (trace elements in glass) and BCR-2g (Columbia River basalt). Four pyroxenes were analyzed for trace elements with a spot size of 50 μm and 4-5 spots per grain. Spot measurements were chosen near edges and centers of grains to assess compositional differences between grain cores and rims while avoiding impurities. Trace element measurements were reduced using GLITTER!, a data reduction software for laser ablation microprobe (van Achterberg et al. 1999). Trace elements were calibrated using CaO and MgO weight oxide percent from major element analysis by EMPA.

Electron Backscattered Diffraction

Electron backscattered diffraction (EBSD) data were acquired using a Zeiss Crossbeam 550 FIB-SEM within the Plymouth Electron Microscopy Centre at the University of Plymouth, UK, operating at 20 kV and 15 nA. Simultaneous X-ray element mapping using energy dispersive spectroscopy (EDS) and EBSD data were generated using an Oxford Instruments Ultim Max 170 mm^2 energy dispersive spectrometer and Oxford Instruments Symmetry EBSD detector, on a polished and carbon-coated thick section mounted at 70˚. The area mapped was 2.21 mm by 1.66 mm with a 1.08 µm step size (2.16 µm EDS pixel size), producing 3.1 million electron backscatter patterns (EBSPs) with an 83.3 % hit rate over ~8 hours. All data were processed during acquisition in Oxford Instruments AZtec (version 4.2) software, and subsequently cleaned and reprocessed in AZtec Crystal.

Results

X-ray element maps show composite grains made of more than one phase within a single, defined grain of both pigeonite and augite in NWA 6963 (Fig. 1). Cores are identified from zoning profile line chemistry and interpreted using element maps. Some pyroxene element maps reveal small patches of thin, exsolution lamellae, which are discontinuous and appear slightly wavy throughout the pyroxene grains. Minor offset in lamellae is likely due to shock (Mikouchi et al. 1999) – see Filiberto et al. (2018) for a full description the lamellae and other shock textures in NWA 6963.

Pyroxene grains in NWA 6963 often have complex zoning profiles with step-function type patterns. Some grains have sharp steps, or abrupt changes, in composition while other grain zoning profiles are more regular. None of the zoning profiles follow a simple decreasing or parabolic pattern as would be expected

from continuous crystallization (Bowen, 1922). Zoning profiles of MgO, FeO, and CaO reveal abrupt jumps in pyroxene composition (within a few microns distance), but usually all three oxides vary independently of each other in the same mineral grain. Between jumps in composition are flat profiles or large portions of each grain with near constant composition, similar to a step-wise function shape.

Pyroxenes with zoning profiles measured in NWA 6963 can be split in two groups: (1) pyroxenes with pigeonite cores and Fe-rich pigeonite rims and (2) pyroxenes having augite cores with pigeonite rims. Cores may mimic the overall crystal shape, though irregular ribbon-like or anhedral cores exist in some grains. Pyroxenes 1-4 are pigeonites with increasing Fe content toward grain edges. Pigeonites exhibit the most changes between MgO and FeO, while CaO content remains constant across each grain (Figs. 2-4). Pyroxenes 5 – 11 have augite cores with pigeonite rims that were determined from zoning profiles with large jumps in CaO and FeO weight percent and semi-constant MgO across the grains (Fig. 5). Augite cores have higher MgO, Al_2O_3, and Cr_2O_3 contents than the pigeonite rims of each grain (Table 1). For pyroxenes with augite cores analyzed for this study, the cores are always touching other pyroxene grains, while the Fe-rich pigeonite rims are in contact with maskelynite.

Three pigeonites and one augite were chosen for LA-ICP-MS trace element analysis based on element maps and BSE images for having less visible fractures and terrestrial alteration. Both pyroxene cores and rims were analyzed for trace element abundances. NWA 6963 pyroxenes are enriched in heavy rare earth elements (HREEs) relative to depleted light rare earth elements (LREEs) (Fig. 6 shows chondrite normalized REE patterns; Table 2). All HREEs measured are within an order of magnitude, regardless of whether the measurement was taken on a grain core or rim. Light REEs abundances are more variable from pyroxene to pyroxene within two orders of magnitude of each other.

The region around pyroxene 1 was analyzed by EBSD to investigate the microstructure of the pyroxene grains to constrain if the pyroxene grains are oriented, as would be expected in a lava flow, or if they are not oriented, as would be more expected in a cumulate pile or intrusion (i.e. Paterson et al 1989; Weinberg et al. 2001; Žak, J. et al. 2008). Figure 7 shows the mapped region; holes in the crystal from prior LA-ICP-MS analyses are observed. Layered X-ray element maps reveal predominant core-to-rim zonation within large pyroxene grains, with Mg-rich cores zoning towards Fe-rich rims (Fig. 7A). Pyroxene 1 has a strong Mg-enrichment within the core, surrounded by terrestrial calcite fracturing. This region was also mapped using electron probe micro-analyzer (EPMA) (Fig. 7B) and therefore targeted specifically for LA-ICP-MS analysis. The 'maximum orientation spread' image (Fig. 7C) for the same region shows a 'hot spot' at the site of this LA-ICP-MS analysis, indicating that the analyses themselves may have affected pyroxene 1; primary strain within this laser-ablation site is increased relative to

the surrounding region. However, the 'kernel average misorientation' map, also known as local misorientation maps (Fig. 7D), reveals a relatively consistent misorientation (below a user defined maximum of 10°) throughout the region, indicating the low-angle grain boundaries observed throughout are unaffected by the laser ablation sites, and there is therefore no significant region of deformation within pyroxene 1.

Despite 10+ phases identified by routine EDS analysis, EBSD mapping focused on the two pyroxene phases, augite and pigeonite because they provide insight into magmatic crystallization orientation despite the shock event that is high enough to destroy such information in plagioclase (e.g., Fritz et al. 2005; Jaret et al. 2015). Further, both can be referenced from the American Mineralogist Crystal Structure Database, AMCSD (e.g., Downs and Hall-Wallace 2003). Both pyroxene phases successfully indexed and exhibited mean angular deviation (MAD) values, a measure of the agreement between the generated EBSP and the simulated solution, below 1°; augite = 0.94° and pigeonite = 0.91°. The band contrast, i.e., the quality of each EBSP, was significantly increased for both pyroxene phases compared to the interstitial amorphous plagioclase-glass/maskelynite and terrestrial calcite within fractures (Fig. 7E).

Electron backscatter diffraction data for the region surrounding pyroxene 1 indicate no distinct preferred orientation along any axis. Euler maps use RGB channels to show the three Euler angles that describe the orientation of a crystal lattice, where similar colors indicate similar crystallographic orientation. Both large and small pyroxene grains of augite and pigeonite in the region exhibit a random orientation distribution (Fig. 7F). This is reflected within the same data when plotted on a pole figure (equal area, upper hemisphere plot); clustering on all poles indicates a single-crystal fabric rather than preferential alignment (Fig. 8). The Euler map does, however, reveal simple twinning in several of the smaller pyroxene grains, typically along the long (001) crystallographic plane.

Discussion

Different types of mineral zoning patterns indicate distinct magmatic conditions at the time of crystallization (Ginibre et al. 2007). Compositional zoning patterns across a grain may be continuous or normal, oscillatory, step-function, or absent (Lofgren 1974). In mafic minerals, normal zoning is achieved from Mg-rich magma compositions that evolve to more Fe-rich (Bowen 1922). Normal zoning is assumed to be from magma differentiation or compositional changes in the magma over time with fractional crystallization (Costa et al. 2008). Oscillatory zoning, often seen in plagioclase phenocrysts, is a repeated sequence of composition patterns across a grain (Bottinga et al. 1966). This type of zoning forms from recurring changes in crystallization temperature, pressure, and/or magmatic composition (Bottinga et al. 1966). Step-function zoning is represented by rapid changes in crystal composition, followed by slower, more continuous crystallization. These step-like changes across a mineral grain are possibly due to magma mixing

or diffusion of elements over time (Costa et al. 2008). Sharp step-function zoning may occur in the original zoning profile with diffusion later smoothing these abrupt jumps in composition (Costa et al. 2008).

Pyroxenes in NWA 6963 have either an augite or pigeonite core. Augite cores are irregularly shaped and commonly have large pigeonite overgrowths. Pigeonite cores often make up an entire grain with relatively small rims of Fe-rich pigeonite (Figs. 1-5). Pigeonite and augite cores are identified based on homogeneous Mg#, compositionally consistent zonation profiles, and being located tangentially against other pyroxenes. Cores and rims within a single grain are distinguished by changes in atomic contrast (Z-contrast) viewed as gray scale variation in BSE images and by step-function chemical zoning patterns. Flat zoning profiles represent near constant compositions and indicate very slow cooling rates in the magma. Distinct changes recorded by pyroxene major element oxides occur within a few microns in each grin indicating rapid changes in magmatic conditions.

NWA 6963 pyroxenes have flat HREE patterns (Eu to Lu), slightly depleted LREE (Nd to Sm) and an increase in the lightest REE (La and Ce), while the bulk rock composition is relatively flat (Filiberto et al. 2018; Fig. 6). Pyroxenes have similar zoning patterns to gabbroic shergottite NWA 7320 (Udry et al. 2017), even though the bulk pattern of NWA 6963 is quite different. Minor enrichment of LREEs (specifically the increase in La and Ce) is likely from terrestrial contamination (Crozaz et al. 2003). While large cracks were avoided during analyses, small fractures could not be avoided and terrestrial weathering veins were found throughout the sample (Filiberto et al. 2018). In analyses free of terrestrial influence, there is no significant trend in REE concentrations between core and rim analyses or between augite and pigeonite, suggesting that there was not a significant change in magma composition (at least in terms of REE) from magma mixing between core and rim crystallization.

Crystallization Sequence

Comparing the Al content with Fe# (FeO / (FeO + MgO)) in pyroxene can help constrain the crystallization sequence of pyroxenes vs. plagioclase (Stolper and McSween 1979; Mikouchi et al. 1999; Barrat et al. 2002a, 2002b). In Shergotty pyroxenes, for example, Al decreases as Fe# increases toward the rim of the crystals, suggesting plagioclase began crystallizing with pigeonite and was followed by augite at a later stage (Mikouchi et al1999). In contrast, NWA 6963 augite and pigeonite cores have increasing Al content until an Fe# of 0.55-0.57 (Fig. 9). With increasing Fe# (>0.57), Al content decreases in pyroxene cores indicating the start of plagioclase crystallization from the melt. This indicates augite and pigeonite cores crystallized first followed by Fe-rich pigeonite rims and plagioclase, simultaneously. While no zoning is apparent in NWA 6963 plagioclase (now maskelynite; Filiberto et al. 2018), this shift in crystallization is apparent from Al content trends and decreases of Ca in pigeonite. There appears to be a small

overlap of pyroxene cores and plagioclase crystallizing concurrently, but the majority of pyroxene cores crystallized before the onset of plagioclase. Iron-rich pigeonite rims have decreasing Al content with increasing Fe# (>0.57). Pigeonite rims began to form in a separate stage of crystallization contemporaneous with plagioclase.

The proposed sequence of crystallization for NWA 6963 is as follows: augite and pigeonite cores formed at high temperatures with minor plagioclase as the magma cooled, then at lower temperatures Fe-rich pigeonite rims and plagioclase grew concurrently followed by minor phases with further cooling of the magma. The sub-ophitic texture of NWA 6963 also supports this sequence of crystallization with euhedral-subhedral Fe-rich pigeonite rims partially surrounding laths of plagioclase.

Petrogenetic history

Basaltic shergottites with irregular pyroxene zoning have been reported in many Martian meteorites: e.g., QUE94201, Los Angeles, NWA 480, NWA 2800, NWA 5298, NWA 2975, and NWA 7320 (McSween et al. 1996; Mikouchi et al. 1999; Barrat et al. 2002a, 2002b; Warren et al. 2004; Bunch et al. 2008; Hui et al. 2011; He et al. 2015; Udry et al. 2017). Previous studies have discussed many possibilities for unusual pyroxene zoning in basaltic shergottites such as: single-stage crystallization with linear cooling rates (McSween et al. 1996; Barrat et al. 2002a), multi-stage crystallization (Hui et al. 2011; Udry et al. 2017), undercooling (Mikouchi et al. 1999), core dissolution or resorption (Hui et al. 2011; Udry et al. 2017), and diffusion (Udry et al. 2017). Modeling irregular or step-function zoning in igneous crystals also considers diffusion, magma mixing, and expulsion of volatiles as reasons for such zoning textures (Hort 1998; Costa et al. 2008). For NWA 6963, each mentioned possibility is evaluated in the context of the data and previous assumptions before discussing the most likely cause – crystal accumulation in an intrusive system at depth.

Previous studies used irregular pyroxene zoning to interpret crystallization histories of basaltic shergottites QUE94201 and NWA 480 (McSween et al. 1996; Barrat et al. 2002a). Pyroxenes from these meteorites are described as having pigeonite cores mantled incompletely by augite with Fe-rich pigeonite rims (McSween et al. 1996; Barrat et al. 2002a). Both studies suggest that this texture forms from continuous, single-stage crystallization in a closed system without pyroxene accumulation. These conclusions are based on linear, slow cooling-rate experiments of lunar basaltic melts (Lofgren et al. 1974; Grove and Bence 1977), where similar pyroxene textures formed (McSween et al. 1996; Barrat et al. 2002a). This is an unlikely scenario for NWA 6963 because it does not have pigeonite cores surrounded by augite like those seen in QUE94201 and NWA 480. Instead, NWA 6963 has both pigeonite and augite cores with rims of Fe-rich

pigeonite. Pyroxenes in NWA 6963 are also cumulate phases, which contrasts with single-stage crystallization conclusions made from non-cumulate pyroxenes in QUE94201 (McSween et al. 1996).

NWA 7320 and NWA 5298 are coarse-grained shergottites with augite or pigeonite cores with Fe-rich pigeonite rims (Udry et al. 2017; Hui et al. 2011). These textures match those identified in this study of NWA 6963. The patchy zoning in NWA 7320 and NWA 5298 pyroxenes is thought to be from core resorption during magma evolution. Core resorption or dissolution in a magma could occur if original phenocryst core edges began to interact with the melt in equilibrium with the crystals. This alternative reasoning may explain the gradual compositional changes between pigeonite and augite composite grains in gabbroic NWA 7320, but is unlikely for NWA 6963. Within NWA 6963, the compositional zoning between core and rim changes abruptly over a few microns. This sharp contact does not support grain edges interacting with surrounding melt.

Step-function zoning is thought to be caused by diffusion or magma mixing (Costa et al. 2008). If diffusion had occurred in a mixed magma, the step between the two compositions would be smoothed out (Costa et al. 2008). In NWA 6963, diffusion does not explain composite pyroxene grains since the compositional zoning between cores and rims is very abrupt. Within some pigeonite rims, there are small changes in composition, but overall, the pigeonite rims have increasing Fe content towards grain edges (Figs. 2 -3). Small compositional steps in pigeonite grains are probably due to slight fluctuations in magmatic conditions and not diffusion. Further, trace element analyses of NWA 6963 are not consistent with magma mixing of magmas with significantly different REE compositions because all grains analyzed have similar REE patterns (Fig. 6).

The model for formation of stepped profiles that has been suggested the most often to explain pyroxene zoning in Martian meteorites is magma undercooling. Basaltic shergottites EETA79001 and QUE94201 both have composite grains of pigeonite and augite (Mikouchi et al. 1999). Complex zonation in pyroxenes in these meteorites often occurs as Mg-rich pigeonite cores, mantled by Mg-rich augite with rims of Fe-rich pigeonite (Mikouchi et al. 1999). Similar pyroxenes exist in NWA 6963 with pigeonite cores and Fe-rich rims (Figs. 1-3 and supplemental figures and data). Other grains in NWA 6963 have augite cores with pigeonite rims (Fig. 5 and supplemental figures and archived data; Wenzel et al. 2021; 10.6084/m9.figshare.15164658). Mikouchi et al. (1999) suggested composite pyroxene grains in EETA79001 and QUE94201 formed as each pyroxene phase crystallized metastably alone due to an undercooling event, as (1) crystallization did not follow expected equilibrium assemblages as predicted by phase diagrams, (2) pyroxene cores do not have exsolution lamellae suggesting fast cooling, and (3) plagioclase growth texture shows growth from the center and not from adjacent crystals. Magma undercooling

occurs when a magma transitions quickly from equilibrium to disequilibrium conditions. An example of undercooling conditions could involve pre-existing crystals that suddenly become metastable when the melt liquidus temperature abruptly changes (Hort 1998). The magma evolves to re-equilibrate by crystallizing phases while the melt keeps a constant temperature rather than continuing to cool (Hort 1998). However, each pyroxene phase in NWA 6963 could not have crystallized metastably alone because the crystallization sequence determined for NWA 6963 from Al vs. Fe# shows augite and pigeonite cores crystallized simultaneously and in equilibrium, followed by pigeonite rims and plagioclase (Fig. 9; Filiberto et al. 2014, 2018) and therefore did not crystallize during an undercooling event. Further, the EBSD results do not show evidence of a strong magmatic flow, which would be needed for undercooling as the magma containing crystals moved towards the surface.

The most likely explanation for the pyroxene textures and resultant EBSD data is pyroxene accumulation from a crystallizing magma. We previously suggested that NWA 6963 could represent the feeder dike system for other basaltic, extrusive, shergottites (Filiberto et al. 2018). However, if NWA 6963 represented the true feeder dike system, the EBSD results would show evidence for flow during emplacement. Instead, there are two options that, without geologic context, are nearly impossible to distinguish between: (1) crystal accumulation at the base of a large > 100 m differentiated flow or (2) crystal accumulation in large intrusive environment (sill or magma chamber).

As shown by Arndt (1977), two large, thick (120 m) lava flows (Fred's flow) with komatiite and tholeiite compositions, in Munro Township, Ontario, fractionally crystallized to form gabbroic and pyroxenitic layers, among others. Specifically, the gabbroic layers have a range in pyroxene sizes and compositions similar to what is seen in NWA 6963 and even have similar bulk Al_2O_3 contents to NWA 6963; however, the pyroxenes in Fred's flow are not aligned and EBSD was not available at that time to confirm these observations. Therefore, further work on Fred's flow would be needed to confirm if this process could produce all of the textures seen in NWA 6963. Further, previous estimates for pyroxene core crystallization pressures (> 5 kb; Filiberto et al. 2018) would require lava flow thicknesses of ~ 40 - 50 km, an order of magnitude more than the Fred's flow (Arndt 1977), which is likely not plausible on Mars, even for more viscous flows (e.g., Warner and Greg 2003) .

A further possible explanation would be crystal accumulation from a mafic magma in a large intrusion similar to a large mafic intrusion (LMI) on Earth (e.g., Winter 2013). Large mafic intrusions on Earth typically have a cumulate pyroxene layer (or layers) along with a layered gabbroic layer, which can be layered or have preferred orientation of crystals, similar to the preferred orientation seen in pyroxenes in NWA 6963 (Filiberto et al. 2018), and would not show strong flow direction, consistent with our EBSD results. In

LMIs, pyroxenes (and other mafic minerals) have a range of Mg# preserved throughout the entire sequence with each layer recording smaller variations (~20 Mg#; e.g., Fig. 12.12 Winter 2013). Pyroxenes in NWA 6963 have a range of ~30 in Mg# within one rock, but each pyroxene typically has little variation; however, previous estimaes for pyroxene core crystallization pressures (> 5 kb; Filiberto et al. 2018) are consistent with terrestrial LMI crystallization conditions.

Conclusions

Due to the intrusive nature of NWA 6963, a new petrogenetic interpretation is needed to explain its conditions of formation. NWA 6963 has complexly zoned, composite pyroxenes with augite and pigeonite cores mantled by Fe-rich pigeonite rims, which provide evidence for changing magmatic conditions for NWA 6963 at the time of formation. Augite and pigeonite cores are in equilibrium as shown by matching Mg# and homogenous, flat zoning profiles. The most likely explanation for the pyroxene chemistry, textures, and microstructural-crystallographic information is pyroxene accumulation from a crystallizing magma in a large intrusive environment (sill or magma chamber).

Figure Captions:

Fig. 1: Large area map of polished thick section of NWA 6963; Layered X-ray element map (red=Mg, green=Ca, blue=Fe, turquoise=Ti, yellow=phosphorus). Numbers are analyzed pyroxenes with zoning profile outlines represented by white arrows.

Fig. 2: Pyroxene 1 X-ray element maps (CaO, MgO, FeO) and backscattered electron (BSE) image. The black arrow represents the zoning profile line measured across the grain and is plotted on the chart. The black dashed line outlines the interpreted pigeonite core. Colored circles and letters correlate with LA-ICP-MS trace element measurements.

Fig. 3: Pyroxene 3 X-ray element maps (CaO, MgO, FeO) and backscattered electron (BSE) image. The black arrow represents the zoning profile line measured across the grain and is plotted on the chart. The black dashed line outlines the interpreted pigeonite core. Colored circles and letters correlate with LA-ICP-MS trace element measurements.

Fig. 4: Pyroxene 4 X-ray element maps (CaO, MgO, FeO) and backscattered electron (BSE) image. The black arrows represent the zoning profile lines measured across the grain and are plotted on the charts. The black dashed line outlines the interpreted pigeonite core. Colored circles and letters correlate with LA-ICP-MS trace element measurements.

Fig. 5: Pyroxene 5 backscattered electron (BSE) image. The black arrows represent the zoning profile lines measured across the grain and are plotted on the charts. The black dashed line outlines the interpreted pigeonite core. Colored circles and letters correlate with LA-ICP-MS trace element measurements.

Fig. 6: Trace element abundances for NWA 6963 pyroxenes normalized to CI chondrite values from Anders & Grevesse, 1989. NWA 6963 bulk trace elements from Filiberto et al., 2018.

Fig. 7: Various maps around pyroxene 1. (A) Layered X-ray element map (red=Mg, green=Ca, blue=Fe). (B) EPMA map. (C) Maximum orientation spread (MOS) map. (D) Kernel average misorientation (KAM) map. (E) Band contrast map. (F) Euler map.

Fig. 8: Pole figures (PFs) for pigeonite and augite. Contoured plot (above) set at 10˚.

Fig. 9: Aluminum content plotted against Fe# for pigeonite rims, pigeonite cores, and augite rims.

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