READING THE MICROSTRUCTURE OF APATITE IN THE MOON AND MARS TO CONSTRAIN THE PETROGENETIC EVOLUTION OF CHASSIGNITES AND NAKHLITES AND ASSESS THEIR VOLATILE SOURCES. Marina Martínez1, Adrian J. Brearley3, and Charles K. Shearer1, 1Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA (mmartinezjimenez@unm.edu).

Introduction: The Martian meteorites (Shergottites-Nakhites-Chassignites and several unique lithologies) represent a direct sampling of igneous processes on Mars. Their stable isotope ratios, noble gas signatures, and major and trace element contents distinguish them from other achondrite groups, and represent a range of different Martian mantle sources, processes, and emplacement environments [1-3]. Martian meteorites generally range from mafic to ultramafic in lithologies) represent a direct sampling of igneous processes on Mars. Their stable isotope ratios, noble gas signatures, and major and trace element contents distinguish them from other achondrite groups, and represent a range of different Martian mantle sources, processes, and emplacement environments [1-3]. Martian meteorites generally range from mafic to ultramafic in composition, and several petrogenetic models have been proposed to explain their petrologic and geochemical characteristics. However, aspects of their magmatic and subsolidus evolution, especially the role of volatiles have not been fully elucidated.

In the present work, we are evaluating the microstructures of apatite as potential recorders of petrogenetic processes in chassignites and nakhlites. The goal is to understand the behavior of volatiles on Mars, to ultimately constrain their potential reservoirs. However, the formation of apatite is very complex, and can result from a wide range of different processes (e.g., [4]). In this work, we have carried out a comparative study of apatite in Martian and lunar basalts, where apatite in lunar basalts represents the endmember of igneous crystallization from a relatively dry magma without the presence of fluids. Martian apatites, instead, may have experienced complex formational histories that could have involved subsolidus interaction with fluids [5]. Although there have been numerous mineralogical studies of Martian and lunar apatites, microstructural data are currently extremely limited [e.g., 6]. This study represents the first TEM study to understand the magmatic and subsolidus record of apatite in the nakhlites.

Methodology: Polished thin sections of two nakhlites (Northwest Africa (NWA) 998 and Nakhla) and two lunar basalt samples (15058,14 and 75035,78), have been studied using back-scattered electron (BSE) imaging on a FEI Quanta 3D FEG-SEM/FIB at the University of New Mexico. BSE imaging and EDS analysis imaging was used to locate apatite grains. Four FIB sections have been extracted, from one apatite grain in each sample, and studied with transmission electron microscopy (TEM) using a JEOL 2010F FEG-STEM instrument operating at 200 kV.

Results: Nakhlite NWA 998. Apatites are present as both cumulate phases and late-stage intercumulus phases in residual pockets. Cumulus apatites are coarse grained, randomly distributed, and subhedral to anhedral, ranging from ~50 to ~200 µm in size. Apatites in mesostasis regions are generally smaller (~5 to ~35 µm-size), euhedral to subhedral, and can be very acicular, typically embedded in K-rich glass. Apatite compositions typically have very low minor element contents and fairly constant F:Cl (~1:1 ratio) [5,7].

Nakhla. Apatite grains in Nakhla belong to a more evolved stage of the paragenetic sequence of the parental liquid compared to NWA 998 [7] and are only found as elongated inclusions in intercumulus residual mesostasis pockets, closely intergrown with K-rich maskelynite. They are much smaller (~1-5 µm thick and up to 50 µm long), acicular, subhedral to euhedral, randomly oriented, and notably more common compared to NWA 998. They are REE-rich and OH-poor, and have highly variable F:Cl ratios from Cl-rich to F-rich [5].

Pigeonite basalt 15058,14. Apatite grains are widespread and generally uniformly distributed throughout the thin section. They occur as inclusions in all of the minerals that crystallized in the sequence (pyroxene, anorthite, silica, and/or ilmenite), and preferentially associated with K-rich glass and troilite. Apatites range from ~10 to ~50 µm in size and display different habits, but are typically anhedral. Apatites are predominantly fluorapatite, with chlorapatite contents ranging from 1 to 7 mol% [8].

Ilmenite basalt 75035,78. Apatite grains occur in late-stage pockets ~100 µm in size, although they can be as large as ~800 µm, and are usually associated with or included within large, embayed, anhedral silica crystals. Apatites are more abundant and bigger than in 15058,14, ranging from ~1 to ~50 µm, and are closely associated with K-rich feldspar, REE-rich zirconolite, and troilite. Unlike in 15058,14, apatites in this sample are most commonly found as euhedral to subhedral grains, with notable zonation in BSE images (Fig. 1b).

Figure 1. Examples of BSE images of apatite grains in a) nakhlite NWA 998 and b) lunar basalt 75035,78.
TEM studies. Apatites in both lunar and Martian samples are single crystals with a few slightly misoriented subgrains. Dislocations and sets of parallel fractures are also present in the four FIB sections. HRTEM images of apatite in NWA 998 reveal a distinct domain structure at the 5-10 nm scale (Fig. 2), each domain being slightly misoriented relative to one another. Distinct, but slight curvature of lattice fringes is apparent around the domains and narrow diffuse boundaries also appear to distinguish one domain from another. The lattice planes are continuous, despite showing curvature, indicative of localized strain within the structure. Electron diffraction patterns of NWA 998 apatite also show a diffuse streaking parallel to the [111] direction. In comparison, apatite in 75035,78 lacks any observable nanostructure with no evidence of strain. STEM/EDS reveals that rare-earth elements (REEs) and silica are causing the zonation in 75035,78, where REEs increase in content towards the rim (e.g., Y$_2$O$_3$ ranges from ~1 wt% in the core to ~4 wt% at the rim).

Figure 2. HRTEM image from Nakhlite NWA 998 apatite with inset Fast Fourier Transform (FFT) showing apparent domain structure and evidence of strain.

Discussion: Based on HRTEM observations from NWA 998 and 75035,78, it appears that the domain texture is only seen in the nakhlite apatite (Fig. 2, with F:Cl ~ 1) in contrast to lunar apatite, which is predominantly fluorapatite and displays a more uniform nanostructure (Fig. 3). We infer this phenomenon as the result of nanoscale segregation into distinct F- and Cl-rich domains, which have different unit cell parameters ($a$=9.598Å; vol. 543Å$^3$ Cl-apatite, c.f. 9.3973Å; vol. 523Å$^3$ F-apatite [9]). Although the volume difference between the endmembers is only ~1%, it may be sufficient to cause lattice strain between F- and Cl-rich domains. This assumption seems reasonable given that Cl is 36% larger than F, resulting in Cl disordered 1.2 Å above and below the mirror plane [9]. Diffraction patterns from NWA 998 apatite show diffuse streaking parallel to the [111] direction. The $c$ or $a$ directions (affected by the halogen column) are the crystallographic directions with significant lattice mismatches. Therefore, the optimal phase boundaries for different compositional domains form between lattice planes in F- and Cl-apatite domains with the lowest lattice mismatch, (111) being one of them. More FIB sections in NWA 998 apatite with different orientations are needed to further investigate if indeed the halogen column is causing the observed domain strain.

Conclusions: This study aims for the first time to understand how the microstructure of apatite relates to its composition and petrogenetic histories. The microstructure of nakhlite apatite is characterized by a domain structure resulting from strain in the lattice, which we suggest may be the result of the unit cell mismatch between Cl- and F-rich domains. Following [9], we argue that the accommodation of both halogens in the apatite structure at high temperature produces the possibility of a miscibility gap along the F-Cl join at low temperature and thus, the domains in NWA 998 apatite may represent exsolution during slow subsolidus cooling. This is especially favorable inapatites with a F:Cl ratio ~ 1:1. Later interaction with an aqueous fluid could also have promoted the unmixing process.

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