Introduction: Pre-eruptive magmatic volatile ratios provide valuable information on the composition of the martian interior, indicating the presence of water and allowing comparison between the behavior of volatiles in different martian source regions and other planetary bodies. Apatite is a volatile-bearing mineral that records the volatile contents (OH, F, Cl) and the halogen and water fugacities of its parental magma at the time of its crystallization [1-7] and can be used to place constraints on the distribution and behavior of volatiles in martian magmas and the corresponding mantle [1-5]. This helps us place constraints on planetary properties such as mantle melting temperatures and melt production.

Meteorite Northwest Africa (NWA) 6963 is a gabbroic shergottite that presumably crystallized as part of an intrusion in the martian crust [8] and contains the phosphate minerals apatite and merrillite. In this study, we report apatite compositional data from NWA 6963 and calculate F2, Cl2, and H2O fugacity ratios for its parental magma. As an intrusive sample, apatites in NWA 6963 likely recorded pre-crystallization volatile ratios unaffected by degassing.

Sample: NWA 6963 is a gabbroic shergottite composed of pyroxene and maskelynite (shocked plagioclase) with minor ferroan olivine, spinel, ilmenite, merrillite, apatite, Fe-sulfides and quartz-alkali feldspar intergrowths (Figure 1). Textural properties suggest that it is an intrusive rock [8]. Apatite occurs much less frequently than the non-volatile-bearing phosphate mineral, merrillite. The two phosphate minerals occur both individually and as intergrowths with each other, with apatite often forming a rim around merrillite grains.

Methods: Apatite and merrillite compositions were obtained using the Cameca SX100 Electron Microprobe (EMPA) at the American Museum of Natural History (AMNH), following the procedures in [9]. All analyses of F, Na, and Cl were conducted with an accelerating voltage of 10kV, a beam current of 4nA, and a 5μm beam diameter. Peak times were 10s for F and Na and 20s for Cl. A second set of operating conditions was used for the remaining elements (Fe, S, Al, P, Mn, Y, Si, Ca, Ce, Mg): 15kV accelerating voltage, 20nA beam current, and 1μm beam diameter. The peak times were 30s for Fe, Al, Mn, Si, Mg, 60s for S, Y, Ce, and 20s for P, Ca. It is not possible to directly measure hydroxyl content using EMPA. Consequently, hydroxyl content in apatite was calculated as the missing X-site component by means of stoichiometry [2].

Volatile fugacity ratios were calculated using the methodology of [7] similar to [1]. This methodology allows for normalization of volatile fugacities to account for differences in oxygen fugacity and merrillite activity between different source regions or planetary bodies, therefore allowing comparison between volatile ratios in regions with differing fO2 values [3].

Results: Apatite composition in NWA 6963 ranges from fluorine- to chlorine-rich end members, and all apatite grains analyzed contain OH (Fig. 2).

OH occupancy of the X site (calculated assuming F+Cl+OH=1 structural formula units) ranges from 16.9% to 48.3%, Cl occupancy ranges from 3.0% to 74.1%, and F occupancy ranges from 5.0% to 54.9%. These values are largely consistent with the range of reported apatite compositions from other martian meteorites (NWA 6234, QUE 94201, and Shergotty).

The fluorine fugacities in NWA 6963 show a wider spread than the chlorine fugacities. Normalized to fluorine, the chlorine to water fugacities in NWA 6963 are similar to the trend of terrestrial basalts, NWA 6234, and QUE 94201 [1], but differ from Shergotty.
Discussion and Conclusions: Apatite records the volatile content (OH, F, Cl) of its parental magma and has been used in the past to evaluate the pre-eruptive volatile concentrations of martian magmas [e.g., 1,2,4,5]. The volatile ratios found in apatite grains in NWA 6963 are within the range of apatite volatile ratios reported for NWA 6234, QUE 94201, and Shergotty [1,2]. This provides further evidence for the presence of water in the martian interior. More importantly, calculated volatile fugacity ratios provide insight into the degassing history of the magma parental to NWA 6963.

Fig. 3: A: Fluorine fugacity vs Cl fugacity for NWA 6963, NWA 6234, QUE 94201, Shergotty, and terrestrial basalts - black x (other symbols as in Fig.1). B: Cl vs water fugacities, normalized to F to account for differences in fO2 and merrillite activity between different source regions. Data from [1-3].

Melts subjected to low pressures (including those at the martian surface or in shallow magma chambers) will likely have undergone magmatic degassing [10,11]. Magmatic degassing typically causes preferential chlorine and water loss, whereas fluorine tends to stay dissolved in the silicate melt [3,12]. A degassed magma presumably would show a wide spread in Cl-, and OH-fugacities. Chlorine fugacities in NWA 6963 show minimal spread, while the fluorine fugacities show a larger spread (Fig. 3a), implying that NWA 6963 experienced fractional crystallization rather than degassing.

The relative fluorine fugacity (normalizing water and chlorine fugacities to fluorine fugacity) ofapatites that crystallized in equilibrium with merrillite can be used as a reference to compare volatile fugacities among terrestrial planets or from different source regions with different oxygen fugacities [1,3]. Similar trends in the relationship of water and chlorine fugacities relative to fluorine indicate a similar volatile fugacity ratio [3]. The volatile fugacity ratios of NWA 6963 follow the same trend as terrestrial basalts, QUE 94201, and NWA 6234, but differ from the ratio of Shergotty (Fig. 3b). The different volatile fugacity ratio trend for Shergotty indicates that Shergotty may have come from a parent magma with a different melt composition, or it could have experienced degassing before the crystallization of apatite (see Fig. 3a). More importantly, the fugacity ratios in NWA 6963 (enriched) follow the same trend as intermediate olivinephyric shergottite NWA 6234 [1] and the depleted shergottite QUE 94201 [2,4,5]. This means that the source regions parental to intermediate, depleted, and enriched (NWA 6963) shergottites may have a similar volatile ratios.

The source regions of martian basalts, with the exception of Shergotty, seem to have ratios of F, Cl, and OH similar to terrestrial basalts, however, the actual content of fluorine, chlorine, and water of the martian mantle could be an order of magnitude lower and still show the same fugacity ratio relationship. The textural relationship of apatite and merrillite in NWA 6963 and other martian meteorites [e.g. 1] can be used to place further constraints on the volatile content of the parental melt. Typically merrillite in martian meteorites, including NWA 6963, formed before apatite. Thus, the volatile activity in martian basalts are lower compared to that on Earth, where apatite crystallization is common yet merrillite crystallization is rare [1,3]. Thus, the halogen and water activities (and thus concentrations) must be lower in NWA 6963 compared to terrestrial basalts, in order for apatite to crystallize after merrillite. Therefore, the volatile content of NWA 6963 cannot be higher than typical volatile contents of terrestrial mid-ocean-ridge basalts, consistent with recent estimates for martian magmas based on apatite analyses [1,2,4,5].