Unique zoned pyroxenes in basaltic shergottites meteorite: Implications for some open system process.
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Introduction: Mineral zoning is evidence for open system processes during magmatic evolution or impact events, and has always been the core of petrological research, providing some of the best evidence for changes in crystallization conditions [1]. Basaltic shergottites (e.g. Los Angeles, Zagami, Shergotty, QUE 94201) often present typical zoned pyroxenes, and the homogeneous magnesian pyroxene core is thought to be cumulates formed slowly at depth from melts followed by more rapid crystallization of the Fe-rich rims in a near-surface intrusive or extrusive setting [2-3]. Detailed TEM analysis has not been carried out for the occurrence state of iron in Fe-rich rims.

TEM foil located in the boundary between core and rim of unique zoned pyroxene within basaltic shergottite Northwest Africa (NWA) 12522 were extracted by FIB methods, as were prepared howardite and lunar meteorites for comparison.

Sample and analytical techniques: Here we conducted three meteorite studies: NWA 12522 (Martian shergottite), NWA 2727 (Lunar breccia), and NWA 8343 (Howardite). Petrographic and chemical mineralogy analysis of three polished thin sections were analyzed by FEI Scios field-emission scanning electron microscope (SEM) and JEOL JXA-8530F Plus electron microprobe (EPMA). FIB samples were characterized utilizing a FEI Talos F200X field-emission scanning transmission electron microscope (TEM).

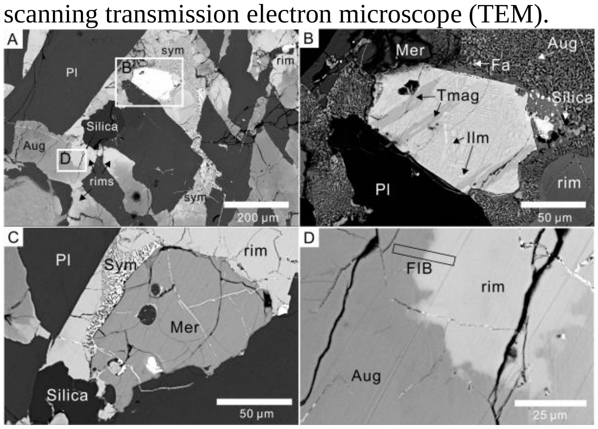

Fig 1. BSE images of NWA 12522. (A) Typical mineral assemblage. (B) Intergrowth of ilmenite (Ilm) - titanomagnetite (Tmag). (C) Symplectites (sym) occurred in the inner of rims and growth along the late-stage interstitial. (D) Close-up view of zoned pyroxene. Aug: augite; Fa: fayalite; Mer: merrillite; Pl: plagioclase.

Results: *Petrology and mineralogy of samples.* NWA 12522 is petrographically similar to QUE 94201 lithology [3], and primarily of strongly zoned pyroxene and maskelynite (converted from plagioclase by shock), with minor intergrowth of ilmenite-titanomagnetite (Fig 1B.), silica, and apatite (e.g. merrillite and chlorapatite). The zoned pyroxene is characterized by the irregular sharp chemical contrast between augite cores and Fe-rich rims (Fig 1D.). Symplectites of hedenbergite + fayalite + SiO_2 polymorph are commonly found within rims (Fig 1C.), which are contributed to the result of pyroxferroite breakdown under high temperature [4-5]. Narrow cracks are widely distributed in the pyroxene grains, and most of them are filled with troilite (Fig 1.).

Chemical composition analysis of zoned pyroxene in NWA 12522 indicates that it has heterogeneity cores ($Wo_{10.6\text{-}33.8}En_{31.6\text{-}52.3}Fs_{26.4\text{-}46.4}$) and extreme Fe-rich rim (FeO: 37.2-49.5 wt%). Based on 24 oxygen atoms, the calculated total cation (16.16-16.25) and Fe/Mn value of pyroxene rims significantly deviate from the pyroxene stoichiometry and the trend line of Mars [6]. Compared with the typical igneous and thermal metamorphism zoned pyroxene in NWA 2727 and NWA 8343, the radial concentration profiles of FeO from pyroxene rims to cores in NWA 12522 shows a sharply decrease (Fig 2.), which indicates a discontinuity trend, and could not reflect gradational condition changes or diffusive exchange [7]. We also performed the Raman spectrum of pyroxene cores and rims, and found no peaks of pyroxferroite.

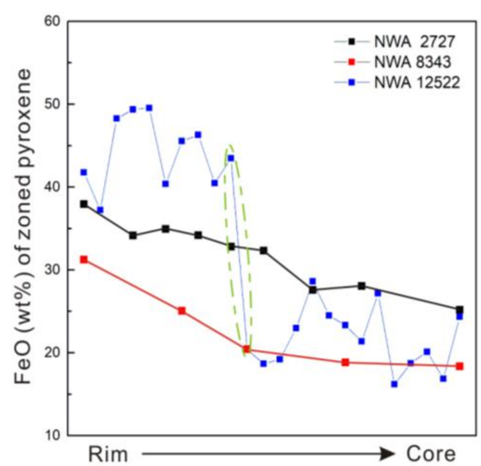

Fig 2. Profiles of FeO content from rim to core of zoned pyroxene in studied samples.

Virtually all of the plagioclases in NWA 12522 have been converted by shock into maskelynite, and have a homogeneous composition ($An_{50.5-55.6}$).

TEM observations. The HAADF images of zoned pyroxenes within NWA 2727 and NWA 8343 showing that the rim and core have different proportion of Low-Ca and High-Ca pyroxene component formed by diffusive exchange (Fig 3C, 3D.).

A detailed view of zoned pyroxene in NWA 11592 shows that the core and rim have significantly different characteristics. Narrow exsolution lamellae (~40 nm) were observed in both the pyroxene rim and core of NWA 12522 by TEM analysis, indicating a faster cooling rate. High-Ca ($Fs_{36.8}Wo_{36.3}$) and Low-Ca ($Fs_{73.6}Wo_{4.4}$) lamellae are neatly arranged in the core of zoned pyroxene, with no other phases (Fig 3B.). Within the pyroxene rim, High-Ca ($Fs_{30.5}Wo_{35.5}$) and Low-Ca ($Fs_{55.3}Wo_{5.5}$) lamellae are crossed by the pigeonite ($Fs_{74.3}Wo_{18.6}$) in form of veinlets and fine grains, and abundant Nano-sized Fe-rich particles (~20 nm) were observed there (Fig 3A.). The EDS results show that those Fe-rich particles have extreme FeO enrichment (~ 49.3 wt%), and do not contain Ni and S content.

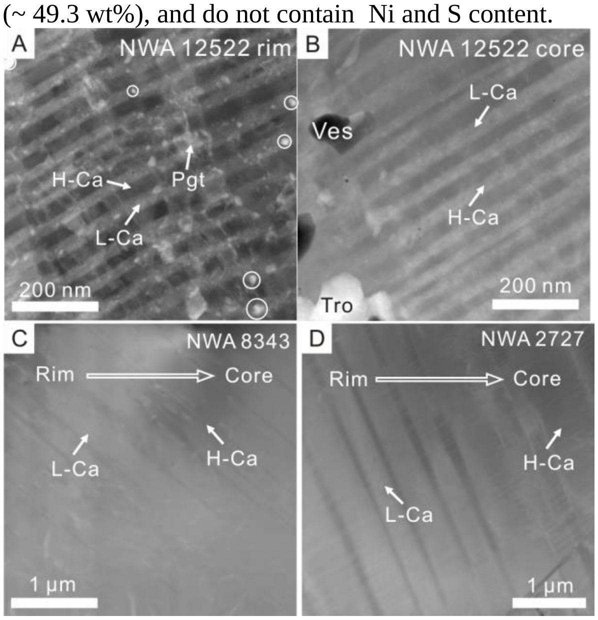

Fig 3. HAADF images of prepared TEM foils. Fe-rich particles were marked by white circles in Fig 3A. Pgt: pigeonite; L-Ca and H-Ca: Low-Ca pyroxene; H-Ca: High-Ca pyroxene.

Discussion: The mineral proportion assemblages and chemical composition (Fe/Mn value of pyroxene cores versus An of plagioclase) document the NWA 12522 is a basaltic shergottite [2, 6].

The uniqueness of zoned pyroxene in NWA 12522 is reflected in four aspects. (1) Exceed total chemical component of rim could not only be attributed to the Fe-rich pyroxene. (2) Raman spectrums of rim and core show the similar peaks, and no pyroxferroite peaks were found. (3) FeO content in NWA 12522 shows sharply decrease from rims to cores. (4) Pyroxene rim of NWA 12522 have complex phases in TEM observations.

The irregular sharp zoned pyroxenes in NWA 11592 indicates catastrophic changes in the environment during or after pyroxene crystallization. The randomly distributed pigeonite and Nano-sized Fe-rich particles could be the reason for the Fe enrichment in rims. Pigeonite veinlets cross-cut the exsolution lamella, indicating that it formed no early than the pyroxene crystallization. The highest Fe-rich feature means that the pigeonite in rims derived from the re-melting event, and the origin of Fe-rich particles need more analysis. The nanoscale and heterogeneity of the presence of pigeonite and Fe-rich particles suggest a rapid event for those unique assemblage formation, and impact would provide such a change.

The occurrence of symplectites was believed to be a result of slow cooling rather than reheating due to shock [8]. Symplectites in NWA 12522 often occurred in the inner of rims and growth along the late-stage interstitial, suggesting it formed after the residual melt solidified. The distinct cooling duration between the rim and symplectites contradicts their close spatial relationship in NWA 12522, so it might be a two-stage history.

Basaltic shergottites had experienced highest shock metamorphism effect in martian meteorite [9]. The extreme Fe-rich feature in the pyroxene rim of NWA 12522 could be the result of the formation of more evolving melt and nano-sized iron particles by shock event.

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