SIMULTANEOUS MEASUREMENT OF SIX HALOGEN ISOTOPES IN CHONDRULE MESOSTASIS FROM THE EH3 CHONDRITE QINGZHEN, USING NANOSIMS WITH AN O_2^+ PRIMARY BEAM.

J. A. Lewis[1], R. H. Jones[1,2], and I. C. Lyon[2], [1]Dept. of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131. jlewis11@unm.edu. [2]School of Earth and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK.

Introduction: The in-situ measurement of halogens is important for understanding the distribution of volatiles in a variety of geological materials. In chondrites, accurately characterized halogen abundances and distributions are vital for understanding the chemical distribution of volatiles in the solar system, the evolution of small bodies, and the initial volatile budgets of the planets [1].

NanoSIMS is an important tool for measuring isotopic distributions at nm resolutions. Typically, these measurements are made using a Cs^+ primary beam to analyze negative secondary ions. We have made new measurements using an O_2^+ source to explore its potential for measuring halogen abundances.

Bulk compositions of individual chondrules from the EH3 chondrite Qingzhen were measured for a number of elements, including Cl and Br, using instrumental neutron activation analysis by [2]. They showed that some of the chondrules were enriched in Cl and Br over the average for EH chondrite and inferred a Cl-, Br-rich nebular component. They also showed that the halogen abundance did not correlate with K, implying that djerfisherite ($K_6Na_9(Fe,Cu)_{24}S_{26}Cl$) is not likely the host for these elements and that they must be hosted in chondrule mesostasis. This inference was confirmed by [3]. We studied a Cl-, Br-rich chondrule from [2,3] using NanoSIMS in order to determine the distribution of all the halogen elements in chondrule mesostasis.

Methods: We used a petrographic thin section prepared by [2] and selected chondrule 3 because it had the highest bulk chondrule abundances of Cl (2450 ppm) and Br (36.1 ppm) in their study. We performed BSE imaging and EDS analysis on an FEI XL30 FEG-SEM at the University of Manchester in order to characterize the chondrule in preparation for NanoSIMS analysis.

Halogen abundance measurements were acquired using a CAMECA NanoSIMS 50L at the University of Manchester using the duoplasmatron source with an O_2^+ primary beam. The beam was rastered over a 60 x 60 µm region and 10 frames were collected with frame size of 512 x 512 px and dwell time of 5 ms/px. Collectors were positioned to measure ^{28}Si and the 6 stable halogen isotopes: ^{19}F, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, and ^{127}I. We used glass standards GL-D30-1 (Cl), GL-D52-5 (Cl), ALV-519-4-1 (F, Cl), and NIST 612 (F, Cl) from [4] and scapolite standards BB1 and BB2 from [5] for Cl, Br, and I.

Results: Chondrule 3 is a radiating pyroxene chondrule (Fig. 1a) with 10-15 µm wide laths of pyroxene and 5-10 µm wide patches of interstitial mesostasis (Fig. 1b). As noted by [3], the mesostasis has two distinct compositions (Fig. 1b), one Cl-rich and the other Si-rich and Cl-poor. [3] measured average compositions for the two mesostases using the electron microprobe and found the Cl-rich mesostasis has 64 wt.% SiO_2, 17 wt% Al_2O_3, 13 wt.% Na_2O, and 4.1 wt.% Cl and the Si-rich, Cl-poor mesostasis has 68 wt.% SiO_2, 19 wt.% Al_2O_3, 11 wt.% Na_2O and no detectable Cl.

NanoSIMS isotope maps (Figs. 1c-1h) show enrichments in Cl (Fig. 1d,1e) and Br (Fig. 1f,1g) in the Cl-rich mesostasis. F was detected (Fig. 1c) but shows significant contamination across the imaged area and no preferential enrichment in the Cl-rich mesostasis. I was detected in very minor amounts in the Cl-rich mesostasis (Fig. 1h) and no halogens were detected in the Si-rich, Cl-poor mesostasis.

Discussion: The O_2^+ primary beam successfully detected all 6 stable halogen isotopes in the Qingzhen sample. F showed extensive surface contamination which possibly masked any signal from the volatile-rich mesostasis. Both Cl isotopes were easily detected in the mesostasis and the O_2^+ primary beam significantly reduced interference from $^{34}S^1H$ on the ^{35}Cl signal. This interference is particularly troublesome in S-rich samples, such as enstatite chondrites, and the Cl-rich mesostasis in chondrule 3 has 1.4 wt.% SO_3 [3]. Both isotopes of Br were also detected in approximately equal abundances and correlate with Cl. If the Br/Cl ratio in the Cl-rich mesostasis is the same as that of the bulk chondrule, Br contents represented by the maps in the figure are around 600 ppm. Longer integration times are needed to adequately resolve the presence of iodine.

Overall, simultaneous measurement of all 6 stable halogen isotopes on the NanoSIMS using an O_2^+ primary beam shows considerable promise. Further development with elemental and isotopic standards will be needed to derive quantitative abundance and fractionation information.

As suggested by [2,3], the high abundances of both Cl and Br in Qingzhen's halogen-rich chondrules are concentrated in chondrule mesostasis and not in a crystalline phase such as djerfisherite. The I map also suggests that I is concentrated in chondrule mesostasis although it was not measured by [2]. Knowing the host phase of I is important for contextualizing the results of I-Xe chronology [e.g. 6].

The origin of the two different mesostasis compositions is ambiguous. [3] suggests sodalite as the precursor material for the Cl-rich mesostasis. Because Br can also be incorporated into sodalite [e.g. 7], it is a reasonable source for both Cl and Br as well as Na. The Si-rich, Cl-poor mesostasis is preferentially located in the outer rim of the chondrule. If the two compositions are primary features of the chondrule, the volatiles from the outer rim could have been lost during chondrule formation. Alternatively, because much of the mesostasis from the outer rim has been removed leaving open pore space, it is possible that the process that removed the mesostasis from the chondrule, possibly fluid related, also leached out the volatile elements.

Whatever processes operated, it appears that the halogens are not fractionated relative to each other either within chondrule precursor materials or during the secondary processes that have affected EH3 chondrites. This has important implications for the nature of the initial halogen-bearing condensate as well as the nature of secondary events.

References: [1] Brearley A. J. and Jones R. H. (2017) In *The Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes*, ed. D. Harlov, Springer. [2] Grossman J. N., et al. (1985) *GCA*, *49*, 1781–1795. [3] Mercer, J. A. and Jones R. H. (2010) *73rd Annu. Meet. Meteorit. Soc.*, Abstract #5268. [4] Clay P. L., et al. (2013) *Contrib. Mineral. Petrol.*, *165*, 373-395. [5] Kendrick M. A. (2012) *Chem. Geol.*, *292-293*, 116-126. [6] Whitby J. A., et al. (2002) *GCA*, *66*, 347-359. [7] Pan Y. and Dong P. (2003) *Can. Min.*, *41*, 529-540.

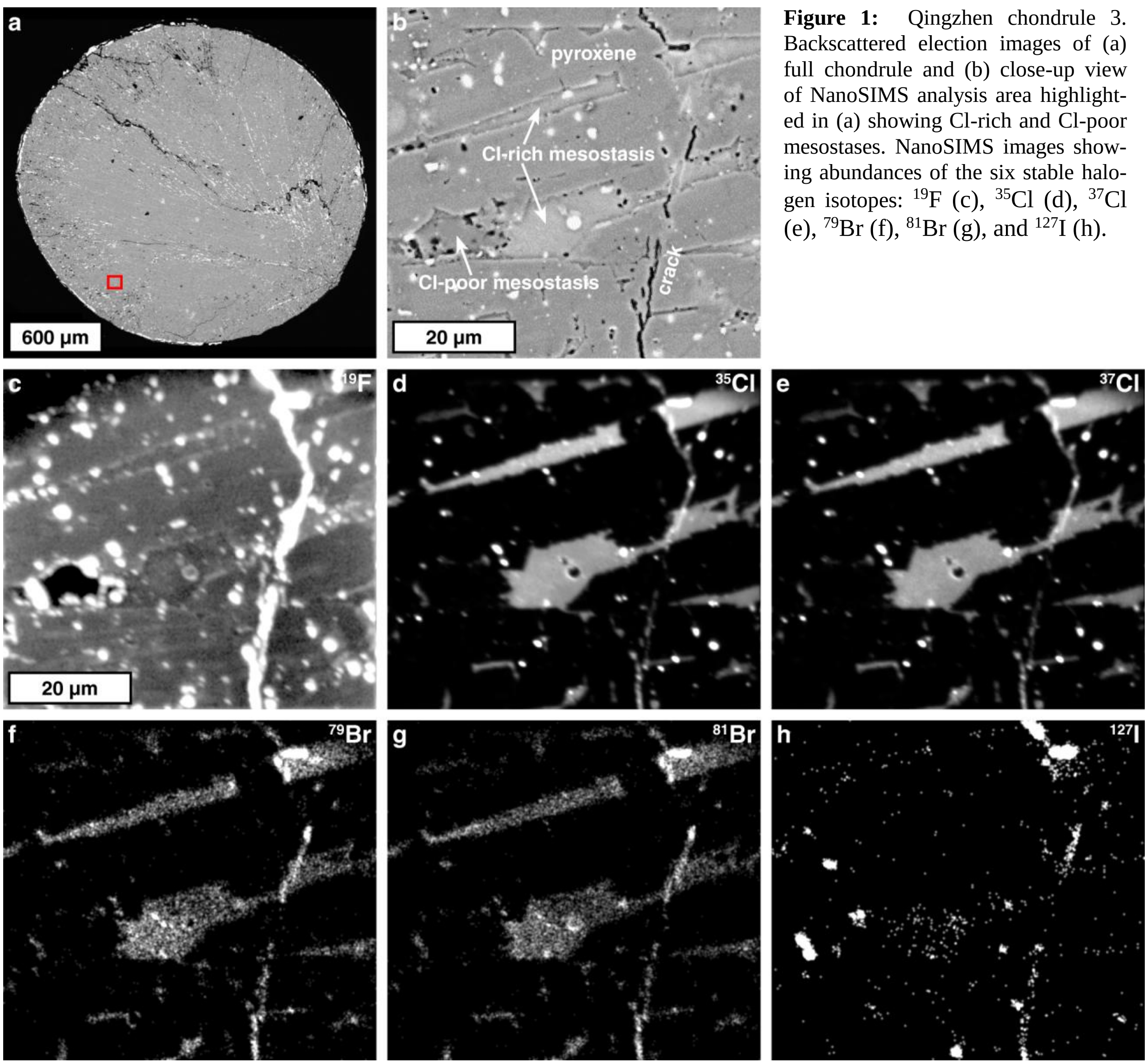

Figure 1: Qingzhen chondrule 3. Backscattered election images of (a) full chondrule and (b) close-up view of NanoSIMS analysis area highlighted in (a) showing Cl-rich and Cl-poor mesostases. NanoSIMS images showing abundances of the six stable halogen isotopes: ^{19}F (c), ^{35}Cl (d), ^{37}Cl (e), ^{79}Br (f), ^{81}Br (g), and ^{127}I (h).