

A MULTI-SYSTEM APPROACH TO UNDERSTANDING THE CHRONOLOGY OF ENSTATITE CHONDRITES. P. Mc Ardle¹, R.H. Jones¹, R. Tartèse¹, R. Burgess¹, P.L. Clay², B. O'Driscoll², E.W.G. Hellebrand³ and O. Plümper³. ¹Department of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK (peter.mcardle@manchester.ac.uk). ²Department of Earth and Environmental Sciences, University of Ottawa, Ottawa, Canada. ³Department of Earth Science, Utrecht University, Utrecht, Netherlands.

Introduction: Enstatite chondrites (EC) are a rare class of meteorites which formed under extremely reducing conditions within the protoplanetary disk [1]. Their unusual mineralogy and chemistry are a result of these formation conditions: they contain lithophile-bearing metal and sulfides, and Mg-endmember silicates. ECs were likely a major contributing component during Earth's accretion, based on their similar chemical and isotopic compositions [2, 3]. However, even though they formed in the inner Solar System, they also contain significant quantities of volatiles, including halogen elements [4, 5]. We are conducting a correlated halogen and multi-system chronology analysis of type 3 ECs, using *in situ* methods.

Djerfisherite. $[(K,Na)_6(Fe,Cu,Ni)_{25}S_{26}Cl]$, is an excellent target for this study because it contains halogens and has a high K content, making it potentially suitable for Ar-Ar and Rb-Sr dating. Djerfisherite has been dated in previous studies, notably I-Xe dating has been successfully applied to djerfisherite in the EH3 Allan Hills A77295, giving an age of 4.56 Ga [6]. Using multi-system chronology we will further test whether djerfisherite is a primary nebular condensate, as suggested by [6, 7]. Djerfisherite appears to be sensitive to thermal metamorphism as it is rare in the equilibrated ECs [5]. This may cause a disturbance in isotopic systems and thereby affect chronologies. Also in some ECs, e.g. Sahara 97072 and Qingzhen, djerfisherite is associated with a texturally complex, fine grained (few μm to sub- μm) mineral assemblage, the "Qingzhen Reaction", which is thought to represent an alteration assemblage after djerfisherite [8]. These factors mean that it is important to understand the extent of metamorphism in each EC to help interpret djerfisherite chronology. We are assessing the extent of metamorphism within petrologic type 3 ECs through examining minor elements in silicates.

Enstatite Chondrite Chronology. The asteroid parent bodies of ECs and other chondrite groups formed broadly contemporaneously, within a few million years after the formation of CAIs [9]. Some ECs were subject to impact events and/or thermal metamorphism soon after their formation (4.50 Ga or older) [10, 11], while others may have been subjected to much later major shock event(s) (e.g. 2.10 Ga [10]). The oldest EC dates are recorded by the I-Xe (4.56 Ga) [6, 11] and Mn-Cr (4.55 Ga) [12] isotopic systems, corresponding to the

formation of EC parent bodies. Other chronometers such as Rb-Sr and Ar-Ar generally record younger ages (e.g. 4.41-4.53 Ga [13]). Different chronometers record different dates, this is predominantly controlled by closure temperatures and sensitivity to shock metamorphism. Amongst the ECs, the EH3s show the largest spread in dates. This is true even within individual meteorites, e.g. Qingzhen at 4.56 Ga (I-Xe) [14] to 2.15 Ga (Rb-Sr) [10], making interpretation challenging. Most dates in the literature were determined on bulk rock and/or mineral separates. Relatively few *in situ* measurements are available, particularly for the absolute chronometers Rb-Sr and Ar-Ar. In this study, the combination of *in situ* Rb-Sr dating via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and *in situ* Ar-Ar dating via neutron irradiation noble gas mass spectrometry (NI-NGMS), aims to directly address this knowledge gap and to unravel the chronological complexity observed in the EH3 meteorites.

Samples: *EH3 Chondrites.* EH3 meteorites are the primary target of this study due to their abundance of djerfisherite. Meteorites with a low shock stage and weathering grade were preferentially selected in order to avoid measuring impact resetting ages and the effects of terrestrial contamination. Seven EH3 meteorites were studied: Klein Glacier 98300 (KLE 98300), Dominion Range 14021 (DOM 14021), Larkman Nunatak 12252 (LAR 12252), Miller Range 07028 (MIL 07028), Sahara 97072 (SAH 97072), Allan Hills A77295 (ALHA77295) and Qingzhen. Because there are only limited studies of KLE 98300, DOM 14021, LAR 12252 and MIL 07028, the mineralogy and chemistry of these meteorites was characterized as part of this study.

Rb-Sr LA-ICP-MS Djerfisherite Standard. For the purposes of *in situ* Rb-Sr dating via LA-ICP-MS, samples of djerfisherite are required as a Rb/Sr standard to correct for elemental fractionation. Samples of terrestrial djerfisherite are available from the Khibina Massif (380-360Ma) of the Kola Peninsula [15]. Additionally, efforts to synthesize djerfisherite as per [16], spiked with both Rb and Sr, are underway.

Methods: Meteorites and terrestrial djerfisherite samples were analyzed via optical microscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and electron probe microanalysis (EPMA). EPMA analyses of mineral grains were acquired on a JEOL JXA-8530F at Utrecht

University and a Cameca SX-100 at the University of Manchester. Sulfides and metal were analyzed with a beam current of 20nA, a beam energy of 20 kV and a 1 μm spot size. *In situ* Rb-Sr dating of djerfisherite via LA-ICP-MS, using a method similar to [17], is in progress. For Rb-Sr dating, NIST 610 glass was used as a standard, in addition to Khibina Massif djerfisherite. Whole rock meteorite samples are currently being irradiated for Ar-Ar dating and quantification of halogens via CO₂ laser stepped heating and noble gas mass spectrometry [18].

Results: *EH3 Chondrites.* Petrographic studies and mineral chemistry confirm that DOM 14021, LAR 12252 and MIL 07028 are EH3 chondrites. Amongst other features, this is evidenced by high (>1.9 wt%) Si content in kamacite and the presence of the sulfide niningerite rather than alabandite. MIL 07028 exhibits evidence of brecciation: the sample appears to be comprised of 2-3 clasts which are broadly similar to each other. Further work is required for a full classification of KLE 98300. In contrast to each of the other samples, KLE 98300 contains no djerfisherite. EPMA analysis of K-bearing phases indicate that djerfisherite has the highest K concentration in the EH3s (8.3 ± 0.4 wt%, n=529). Additional K-bearing phases, which could also be targets for *in situ* dating, such as roedderite (3.8 ± 0.2 wt%, n=33), chondrule mesostasis (albitic glass) (0.5 ± 0.5 wt%, n=63) and feldspar (0.3 ± 0.2 wt%, n=28) contain lower K concentrations. In enstatite, the most abundant phase in enstatite chondrites, K concentrations are generally below EPMA detection limits (<0.005-0.008 wt%).

Rb-Sr LA-ICP-MS Dating of Djerfisherite. Analysis of terrestrial djerfisherite (Khibina Massif) indicates it is a promising standard for Rb-Sr dating of meteoritical djerfisherite due to the homogeneity of K abundances. In our Khibina djerfisherite sample, abundances of K exhibit only minor variation (9.0 ± 0.2 wt%, n=182). Preliminary *in situ* dating of djerfisherite in MIL 07028 yielded a date of ca. 4.3 ± 0.1 Ga, falling within the range of other EH3 meteorites dated via the Rb-Sr system, e.g. [10].

Discussion: In this study, the classification of several EH3 meteorites has been confirmed. The unique mineralogy and histories of ECs are evident in their complicated chronologies; this is especially true for the EH3 meteorites. Djerfisherite is an important K carrier in EH3 meteorites, exerting a significant control on Rb-Sr and Ar-Ar dating. In addition, it is one of a few confirmed halogen carriers within ECs [5]. This study reports the first *in situ* dating of djerfisherite via Rb-Sr and brings much needed *in situ* chronology to bear upon the chronologically complex ECs. Combined with the

planned *in situ* halogen quantification, we aim to assess whether an important halogen carrier in primitive EC's, djerfisherite, is a nebular condensate. This study will further our understanding of volatile processes in the early inner Solar System, which is particularly relevant for determining the source of Earth's halogens.

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References:

- [1] Weisberg M.K. and Kimura M. (2012) *Chemie der Erde* 72:101-115. [2] Dauphas N. (2017) *Nature* 541:521-524. [3] Zhao C., et al. (2019) *Meteoritics & Planetary Science* 55:1404-1417. [4] Piani L., et al. (2020) *Science* 369:1110-1113. [5] Brearley A. and Jones R.H. In: D.E. Harlov and L. Aranovich. (2018). *The Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes Surface, Crust, and Mantle.* Springer Geochemistry. 871-958. [6] King A.J., et al. (2013) *44th Lunar and Planetary Science Conference* 2217. [7] Ebel D.S. and Sack R.O. (2013) *Contributions to Mineralogy and Petrology* 166:923-934. [8] El Goresy A., et al. (1988) *Proc. NIPR Symp. Antarct. Meteorites* 1:65-101. [9] Desch S.J., et al. (2018) *The Astrophysical Journal Supplement Series* 238. [10] Torigoye N. and Shima M. (1993) *Meteoritics* 28:515-527. [11] Hopp J., et al. (2016) *Geochimica et Cosmochimica Acta* 174:196-210. [12] Hopp J., et al. (2021) *Geochimica et Cosmochimica Acta* 310:79-94. [13] Minster J.F., et al. (1979) *Earth and Planetary Science Letters*. [14] Whitby J.A., et al. (2002) *Geochimica et Cosmochimica Acta* 66:347-359. [15] Kramm U., et al. (1993) *Lithos* 30:33-44. [16] Golovin A.V., et al. (2017) *Journal of Raman Spectroscopy* 48:1574-1582. [17] Gorojovsky L. and Alard O. (2020) *Journal of Analytical Atomic Spectrometry* 35:2322-2336. [18] Ruzié-Hamilton L., et al. (2016) *Chemical Geology* 437:77-87.