

U-PB DATING AND REE SYSTEMATICS OF PHOSPHATE MINERALS IN THE H4 AND H6 LITHOLOGIES OF THE ZAG CHONDRITE

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Introduction: The Zag meteorite is an H3-6 chondrite regolith breccia that fell in 1998. Together with the Mo-nahans (1998) H chondrite, Zag is unique in containing indigenous, extraterrestrial, halite that might have formed via evaporation of brines [1-4]. These brines may have originated from exogenous water delivered to the parent body by ice-rich cometary or asteroidal ice fragments [1,4], dehydration of the asteroid interior [2], or impact heating of phyllosilicates [3]. Alternatively, halite itself may be exogenous, derived from either a carbonaceous asteroid such as Ceres [5-6] or via cryovolcanism on a body such as the Saturnian satellite Enceladus [7]. Zag also contains OH-poor and Cl-rich apatite that records a complex fluid history: apatite composition is homogeneous and close to the Cl-apatite end-member in the porous dark H4 matrix (where halite is observed), while apatite composition is heterogeneous in H6 clasts, extending towards F-rich compositions [8]. It is thought that heterogeneous apatite compositions in Zag may record multiple stages of regolith processing and shock at the surface of the H chondrite parent body, with apatite recording circulation of fluids with variable compositions or interaction with a single fluid whose composition evolved as it interacted with the chondrite regolith [8]. To investigate this further, we have carried out *in situ* U-Pb dating and rare earth element (REE) abundance analysis of apatite and merrillite in the Zag H4 and H6 lithologies.

Methods: The U-Pb systematics and REE inventory of target apatite were analysed simultaneously by laser ablation – inductively coupled plasma mass spectrometry (LA-ICP-MS), using a Teledyne Excite+ 193 nm ArF excimer laser ablation system coupled to an Agilent 8900 triple quadrupole ICP-MS at The University of Manchester. We also analysed the merrillite REE abundances using the same setup.

Results: The apatite grains analyzed contain 0.8 to 15.2 $\mu\text{g}\cdot\text{g}^{-1}$ U. Apatite U-Pb dating for all grains including both lithologies yielded an intercept date of 4516 ± 10 Ma (95% confidence, MSWD=1.3, n=22). Interestingly, apatite U/Pb ratios are more discordant, thus, more disturbed, in the H4 lithology compared to the H6 lithology, although all analyses are consistent with the single date within error. Apatite contains *ca.* 20 to 100 times CI chondrite REE abundances, and display slightly fractionated REE patterns characterized by CI chondrite normalized (La/Yb) ratios of 1.6-3.3, and both negative and positive Eu anomalies. There is no obvious apatite REE abundance difference between H4 and H6 lithologies. Merrillite REE abundances are homogeneous across all analyzed grains, at *ca.* 300-400 times CI chondrite REE abundances, and display slight HREE enrichment (CI chondrite normalized (La/Yb) ratios of 0.7-0.8) and pronounced negative Eu anomalies.

Discussion: REE abundances in apatite and merrillite in Zag H4 and H6 lithologies are consistent with those obtained on Ca-phosphates in other H chondrites [9], suggesting similar formation conditions. The date of 4516 ± 10 Ma obtained on Zag apatite, in both the H4 and H6 lithologies, is consistent with U-Pb and Pb/Pb dates obtained on Ca-phosphates in H6 chondrites (e.g., ~4500-4520 Ma) [10]. This is younger than Ca-phosphate U-Pb and Pb/Pb dates obtained in H4 and H5 chondrites (>4550 Ma), except for the H4 Avanhandava in which Ca-phosphates record a date of *ca.* 4515 Ma [10]. It is likely that apatite U-Pb dates in the Zag H4 lithology were reset when they came into contact with hot H6 clasts at *ca.* 4516 Ma, a mechanism that has also been proposed to explain the young apparent Ca-phosphate date obtained on the H4 Avanhandava [10]. Therefore, the U-Pb system in Zag apatite probably dates the disruption of the H chondrite parent body and reaccretion into a rubble pile. The halogen-rich nature of apatite in Zag, coupled with the similar diffusivity of halogens and Pb in apatite [11], suggests that disruption and reaccretion of the H chondrite parent body at *ca.* 4515 Ma must have been accompanied by pervasive circulations of water-poor and halogen-rich fluids. With an I-Xe age of *ca.* 4559 Ma [2], halite in the Zag H4 lithology predates disruption of the H chondrite parent body. Dissolution of some of the pre-existing halite may have provided the F and Cl required for apatite formation; water-soluble halite extracts have $f_{\text{aq}}\text{HCl}/f_{\text{aq}}\text{HF}$ ratios of 35-101 [4], which could have first promoted formation of fluor-chlorapatite in some H6 clasts, evolving toward chlorapatite compositions as the fluids became progressively depleted in F because it is taken up by apatite [8,12]. This scenario would preclude halite formation from late-stage, concentrated, brines from which apatite had already crystallized.

References: [1] Zolensky M. E. et al. (1999) *Science* 285:1377-1379. [2] Whitby J. et al. (2000) *Science* 288:1819-1921. [3] Rubin A. E. et al. (2002) *Meteorit. Planet. Sci.* 37:125-141. [4] Bridges J. C. et al. (2004) *Meteorit. Planet. Sci.* 39:657-666. [5] Fries M. et al. (2013) *76th Meteoritical Society meeting*, Abstract #5266. [6] Yurimoto H. et al. (2014) *Geochem. J.* 48:549-560. [7] Zolensky M. E. et al. (2013) *76th Meteoritical Society meeting*, Abstract #5200. [8] Jones R. H. et al. (2016) *American Mineral.* 101:2452-2467. [9] Ward D. et al. (2017) *American Mineral.* 102:1856-1880. [10] Blackburn T. et al. (2017) *Geochim. Cosmochim. Acta* 200:201-217. [11] Li et al. (2020) *Earth Planet. Sci. Letters* 550:116545. [12] Shearer C. K. et al. (2011) *Meteorit. Planet. Sci.* 46:1345-1362.