

ABUNDANCES AND ISOTOPIC COMPOSITIONS OF VOLATILE H, N, C IN UNEQUILIBRATED ENSTATITE CHONDRITES AND THE VOLATILE INVENTORIES OF THE TERRESTRIAL PLANETS.

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Introduction: Enstatite chondrites (ECs) are primitive meteorites distinguished by stable (e.g., O, Cr, Ti, Ni, Zn) isotope chemistries that are similar to those of the Earth-Moon system [e.g., 1-4]. Recently, [5] showed that the H and N isotopic compositions of the ECs are similar to Earth's mantle. They [5] argued that ECs contain enough H to have delivered three times the amount of water currently in Earth's oceans.

To further understand the volatiles in ECs and test their relationship to Earth's volatile inventory, we present new H, N, and C abundances and isotopic compositions for five unequilibrated ECs: two EL3s [Northwest Africa (NWA) 8785, Asuka (A) 881314] and three EH3s [Yamato (Y) 691, Sahara 97096, Qingzhen]. Our goals are to explore the diversity of volatiles in solar system materials, understand the contribution of ECs to volatiles in the terrestrial planets and the implications for Earth.

Methods and Samples: The meteorites selected are among the least equilibrated ECs, with low to moderate weathering. Thin sections of each EC were studied with element maps and backscatter electron imaging. Matrix – where insoluble organic matter (IOM) is located – in E3s is generally less than 5 area% in regions dominated by FeO-poor silicates similar to the chondrules [6, 7]. NWA 8785 is anomalous; it contains >30 area% matrix, dominated by magnetite mixed with non-crystalline material [8]. Interior chips of each EC, ranging from 0.5g to 0.6g, were powdered and sieved to <106 μm . The magnetic component was removed, leaving non-magnetic portions with masses of 0.41g to 0.52g. Their H, N, and C bulk contents and isotopic compositions were measured using the analytical techniques in [9].

Results: The δD values of the five ECs range from -176‰ to -67‰ and overlap with previous ECs [5] and Earth's mantle (Fig. 1). CM chondrites overlap with this range but extend toward higher δD values. Most other carbonaceous chondrites (CCs) are also more enriched in D. Our samples have $\delta^{15}\text{N}$ values between -23.5‰ and -17.4‰, also similar to Earth's mantle (Fig. 2). The $\delta^{15}\text{N}$ values of the ECs are the closest match to Earth, with a few CM and CO chondrites overlapping the upper limit for the mantle.

Compared to other chondrite groups, ECs and aubrites display the lowest δD values and lowest bulk H content (Fig. 3). The two EL3 chondrites have relatively higher bulk H contents and lower δD values than the

three EH3 chondrites. Ordinary chondrites (OCs) have higher δD values, whereas heavily hydrated CCs display higher H contents but with a wide range of δD values (Fig. 3).

The E3 samples contain (wt.%) 0.075-0.321 H, 0.012-0.032 N, and 0.279-0.587 C. The bulk $\delta^{13}\text{C}$ values of our samples range from -14.5‰ to -3.2‰. The average C/N mass ratio of the samples is 18.7 ± 4.3 and the average H/C mass ratio is 0.47 ± 0.08 .

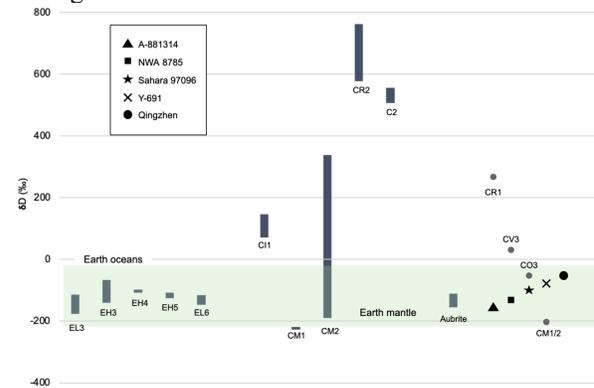


Figure 1. δD range and values of chondrite groups and aubrites [5, 9]. The green area represents Earth's mantle.

Discussion: Volatile carriers in ECs. Generally, organic material is the primary carrier of N and C in chondrites and the secondary carrier of H [10]. Based on previous results [11] ECs contain 0.16-0.27 wt.% IOM, which is in the same range as that of OCs (<0.36 wt.%). CCs can contain more IOM, ranging from 0.044-2.25 wt.%. In general, the H, N, and C abundances in ECs are lower than those of OCs and CCs [e.g., 5, 11, 12].

Analysis of the known carriers of H in the Sahara 97096 EH3 [5] gives a general idea of the carriers in ECs: Chondrule mesostases and IOM account for ~20% of the H. The remaining 80% may be in a combination of chondrule pyroxene and unknown carriers like sulfur-rich carbon-bearing porous amorphous silica [5]. ECs also contain graphite, nitrides and oxy-nitrides, carriers of C and N not significantly present in other chondrite groups [6].

Our data support previous findings that ECs have relatively low bulk $\delta^{15}\text{N}$; about -20‰ to -40‰ [13, 14]. This has partly been ascribed to isotopically light N condensates with a $\delta^{15}\text{N}$ value of -400‰ that contain 15% of the N in ECs [13]. The carriers of light N in ECs are

nitrides in refractory inclusions [14]. It is thought that the reducing conditions in which ECs formed resulted in N enrichment, but subsequently, some nitrides and oxy-nitrides may have been lost during parent-body processing, resulting in the relatively low N bulk content of ECs [13].

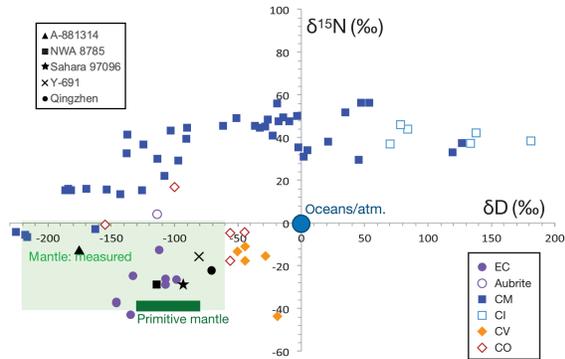


Figure 2. δD and $\delta^{15}N$ values of chondrite groups and aubrites. The green area represents Earth's mantle. Our data are in black. Modified from [5].

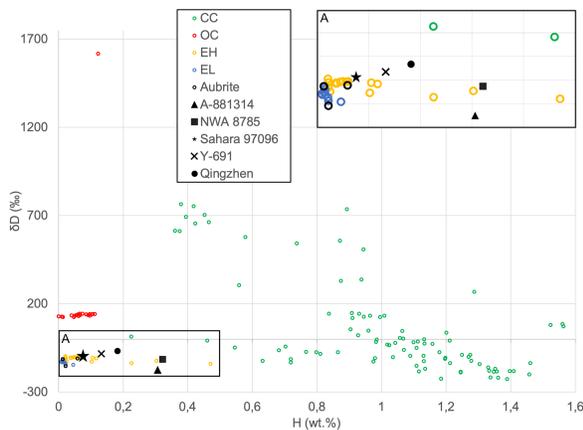


Figure 3. δD and H content of different chondrite groups and aubrites [5, 9, 15]. Our data are in black.

Comparisons to Earth. Among the chondrite groups, ECs are most like Earth in their δD and $\delta^{15}N$ values. The heterogeneity in the δD values suggest the data may not be due to atmospheric contamination [5]. However, it should be noted that some EC phases are unstable in air and their range of δD values are similar to the expected values for water vapor. Some CCs have comparable δD values, with some similar to Earth's oceans, making them potential sources for the delivery of water. However, they are more enriched in ^{15}N (Fig. 2), as are OCs [13].

The $\delta^{13}C$ values of Earth's mantle (-8‰ to -5‰ [16]) fall within the range of our E3 data, less primitive ECs (-28.5‰ to -4.1‰ [17]), and CCs (-23.7‰ to -0.4‰ [18]). OCs have relatively low bulk $\delta^{13}C$ values between -30‰ and -17‰ [18]. The assumed C/N mass

ratio of proto-Earth is 25 [19], more than double the ratio of comets [18]. Earth's value is somewhat similar to our samples and CCs (12.2-21.7 [19]). OCs have a higher ratio of 45.2-452.0 [19]. The H/C ratios of all chondrites are lower than the bulk silicate Earth (0.99 ± 0.42 [20]). However, the volatile abundances of the deep mantle and core are uncertain. The average H/C ratio of the E3 chondrites is similar to oceanic island basalt (0.5 ± 0.3 [20]), which is potentially representative of – but possibly more evolved than – Earth's mantle.

Conclusion: Our E3 data supports previous conclusions that ECs may have contributed to the volatile abundances in the solid Earth. Further work on equilibrated samples is also needed. With regard to the oceans and atmosphere – which are richer in D and ^{15}N – it has been suggested that other chondrite groups or cometary material may have also contributed to their accretion [5]. Comets are generally enriched in D, with 1 to 4 times the D/H ratio of the mantle [21, 22]. With regard to H, N, and C isotopes, ECs – consistent with other isotope systems – remain the best match for the material that accreted to form Earth.

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References: [1] Clayton R. N. and Mayeda T. K. (1984) *J. Geophys. Res.* 89, C245-C249. [2] Javoy M. (1995) *Geophys. Res. Lett.*, 22, 2219-2222. [3] Warren P. (2011) *Earth Planet. Sci. Lett.*, 311, 93-100. [4] Paniello R. C. (2012) *Nature*, 490, 376-379. [5] Piani L. et al. (2020) *Science*, 369, 1110-1113. [6] Weisberg M. K. and Kimura M. (2012) *Geochemistry*, 72, 101-115. [7] Rubin A. E. et al. (2009) *Meteorit. Planet. Sci.*, 44, 589-601. [8] Weisberg et al. (2013) *51st Lunar & Planetary Sci. Conf.* #1683. [9] Alexander C. M. O'D. et al. (2012) *Science*, 337, 721-723. [10] Alexander C. M. O'D. et al. (1998) *Meteorit. Planet. Sci.*, 33, 603-622. [11] Alexander C. M. O'D. et al. (2007) *Geochim. et Cosmochim. Acta*, 71, 4380-4403. [12] Pearson V. K. et al. (2006) *Meteoritics & Planetary Science*, 41, 1899-1918. [13] Rubin, A. E. and Choi B. G. (2009) *Earth, Moon, and Planets*, 105, 41-53. [14] Verchovsky A. B. (2017) *Geochemistry International*, 55, 957-970. [15] Robert F. (2003) *Space Sci. Rev.*, 106, 87-101. [16] Javoy M. et al. (1986) *Chemical Geology*, 57, 41-62. [17] Grady M. M. (1986) *Geochim. et Cosmochim. Acta*, 50, 2799-2813. [18] Ash R. D. and Pillinger C. T. (1995) *Meteoritics*, 30, 85-92. [19] Bergin E. A. et al. (2015) *PNAS*, 112, 8965-8970. [20] Hirschmann M. M. and Dasgupta R. (2009) *Chemical Geology*, 262, 4-16. [21] Hallis L. J. (2017) *Phil. Trans. R. Soc. A.*, 375, 20150390. [22] Lis D. C. et al. (2019) *Astronomy & Astrophysics*, 625, L5.