HYDROGEN ISOTOPE MAPPING IN CAI NOMINALLY ANHYDROUS MINERALS: DISENTANGLING NEBULAR FROM PARENT-BODY ALTERATION. D. Lévy\textsuperscript{1,2}, J. Aléon\textsuperscript{1}, A. Aléon-Toppiani\textsuperscript{1}, D. Troade\textsuperscript{1}, H. Bureau\textsuperscript{1}, H. Khodja\textsuperscript{1} and F. Brisset\textsuperscript{3}, \textsuperscript{1}IMPMC, Museum National d'Histoire Naturelle, Sorbonne Univ., CNRS, 61 rue Buffon, 75005 Paris, France (jerome.aleon@mnhn.fr), \textsuperscript{2}IAS, Univ. Paris-Saclay, CNRS, Orsay, France, \textsuperscript{3}ILEM, CNRS, Univ. Lille, Villeneuve-d'Ascq, France. \textsuperscript{4}LEEL, NIMBE, CEA, CNRS, Univ. Paris-Saclay, Gif sur Yvette, France, \textsuperscript{5}ICMMO, CNRS, Univ. Paris-Saclay, Orsay, France.

Introduction: Calcium, Aluminum-rich inclusions (CAIs) from chondritic meteorites are the first rocks formed at high temperature in the solar system. In many CAIs, primary minerals are replaced by secondary minerals, long assumed to have formed by gas-solid reactions in the nebular gas \[1,2\] but an asteroidal origin during fluid-assisted metamorphism is now favored \[3\]. Still, a parent-body origin is difficult to reconcile with the distribution of secondary minerals in some CAIs \[4,5\] and recent Fe isotopic data revived the possibility of nebular alteration \[6\]. Because secondary minerals are rich in FeO, whereas primary minerals are highly reduced, the existence of nebular alteration would have important implications for the redox conditions in the nebular gas.

A possible efficient tracer of nebular or asteroidal origin is the hydrogen isotopic composition. Indeed, H isotopes are extremely fractionated in astrophysical environments and can be either extremely enriched in deuterium in molecules formed in cold molecular clouds or depleted in D in H\textsubscript{2} gas due to D-burning in stars. Although asteroidal fractionations are possible \[7\], interactions and isotope exchange between extremely fractionated reservoirs tend to produce asteroidal/planetary H with homogenized intermediate D/H ratios.

However, measuring the H isotopic composition of CAIs is not a trivial task because CAIs are extremely depleted in H. Even their secondary minerals, mostly formed at several hundred degrees, are dominantly nominally anhydrous minerals (NAMs: garnets, feldspathoids, chlinoxyroxenes, olivines...). Here, we developed the D/H imaging of H-poor minerals at the \textasciitilde{}1 \textmu m scale and measured the H isotopic composition of secondary minerals in E101.1, a little-altered, compound ultra-refractory CAI from the reduced CV3 chondrite Efremovka \[4,8,9\]. FeO-rich minerals in E101.1 are restricted to the interior portion of xenolithic CAIs partially molten during capture by the main host. Their mineralogical study favors formation and oxidation in the nebula before capture of the xenoliths \[9\].

Sample and methods: Efremovka 101.1 is a melanite-rich (mel) compact type A CAI containing abundant metal grains with minimal evidence of secondary oxidation. Half of the host CAI contains xenolithic CAI sinuous fragments dominated by Al-diopside (Al-di) and partially rimmed by anorthite. FeO minerals are restricted to the xenoliths and consist of mm-sized kirschsteinite (~kip\textsubscript{0.80}), Fe-rich akermanite (Fe-\textalpha k) and a complex fine-grained (FG) assemblage of ~50 nm kir enriched in Mg relative to the \textalpha k-kir, minute Fe metal grains and sometimes porous di grains \[9\]. This FG-assemblage was interpreted as resulting from reduction of \textalpha k-kir \pm di \[9\]. Fe-\textalpha k probably formed by interaction with the host melt during capture of the xenoliths \[9\]. Xenoliths and the host CAI are crosscut by late alteration veins filled with a Ca-poor amorphous material attributed to parent-body alteration. Finally chemically heterogeneous melt pockets were attributed to partial melting of all these lithologies by a late impact \[4,9\]. Anorthite associated with metal grains outside xenoliths is partially replaced by a Na-rich phase of trinepheline composition.

NanoSIMS imaging. H isotope mapping of H-poor minerals was done using the IMPMC NanoSIMS 50 in the Museum National d'Histoire Naturelle, Paris, France. Terrestrial analogs of CAI minerals (nepheline, sodalite, grossular, andradite and hedenbergite) were analyzed for H content by Elastic Recoil Detection Analysis (ERDA) at LEEL, Gif-sur-Yvette, France.

To achieve simultaneously (1) \textmu m-scale spatial resolution, (2) accurate and reproducible isotopic analysis and (3) minimal H contamination, H and D ions were measured simultaneously on two electron multipliers with a \textasciitilde{}1.5 \textmu m, 100 pA Cs\textsuperscript{+} beam rastered over 8 \textmu m on 2 \textmu m thick focused ion beam (FIB) sections using Au coating and electron flood gun for charge compensation \[10\]. After 3 weeks residence in the storage chamber of the NanoSIMS, the surface contamination on NAMs was \textasciitilde{}200 ppm equivalent H\textsubscript{2}O in these conditions. Using amphiboles \(\textasciitilde{}2 \text{wt}\% \text{H}_2\text{O}\), NAMs (\textlessthan{}500 ppm H\textsubscript{2}O) and the DR32 basaltic glass (3099 ppm H\textsubscript{2}O), we showed that over a large range of H concentration, the H intensity is broadly proportional to the water content and can be used to approximate the H content.

Five FIB sections extracted from E101.1 at IEMN, Lille, France, were mapped for D/H ratios. The instrumental fractionation was corrected using Fe-rich amphibole for FeO-rich minerals, Fe-poor amphibole for FeO-poor minerals and basaltic glass for amorphous and partial melt areas. We estimated a systematic un-
LH loss due to matrix effects between amphiboles and E101.1 minerals. The FIB sections were examined by scanning electron microscopy (SEM) before and after NanoSIMS analysis at IEMN, Lille, France, and ICMMO, Orsay, France, respectively, in order to identify the analyzed minerals. Image processing was done with LIMAGE software (© Nittrler, 1997) using regions of interest (ROIs) the size of the primary beam, i.e. 1 to 1.5 μm. Two types of ROIs were used: (1) square ROIs covering the whole surface of the analyzed areas and (2) ROIs corresponding to minerals identified by SEM, with the aim to provide the full range of D/H ratios and endmember compositions, respectively.

Results: While all terrestrial minerals, including those with the lowest H contents, consistently have terrestrial D/H ratios in both FIB and polished sections, a large range of D/H ratios and H content was observed in the E101.1 sections. When reported in δD notation, H isotopic composition range from δD values of -820 ± 140‰ to +1140 ± 250‰ and H intensities range from 10^4 to 3.4 × 10^5 counts/sec, corresponding to equivalent H2O content between ~500 ppm and 3.5 wt% (Fig. 1). All data plot in a mixing triangle indicating the contribution and mixing at the μm scale of three major components. Component 1 has both the lowest δD values at -820‰ and lowest H content at ~500 ppm. It corresponds to xenolithic anorthite and to some extent Al-di. Component 2 has the highest H content of ~3.5 wt%, a chondritic/terrestrial δD value of ~0 ± 200‰ and corresponds to trinepheline and alteration veins outside the xenoliths. Component 3 has the highest δD values at +1140‰, a H content of ~1000 ppm and was identified as the FG-assemblage.

Discussion: Component 1 has the lowest D/H ratio ever measured in meteorites and can be safely ascribed to H2 in isotopic equilibrium with nebular H2. It implies that not only Al-di but anorthite as well are primary minerals in the xenoliths, which retained the H isotopic composition of the environment where they condensed. Component 2 is most likely the result of parent-body alteration by an aqueous fluid of chondritic H isotopic composition. Mineralogical evidence of kir reduction suggests that component 3 results from D-enrichment and H loss from μm-kir during reduction. While the exact speciation of H in these phases remains to be determined, a similar D-enrichment is produced in a Rayleigh distillation by loss of ≥ 90% H2 from a precursor with chondritic δD and H content similar to or higher than that of the most H-rich FeO-rich minerals (≥5000 ppm). In light of the mineralogical relationships, this D-enrichment is best ascribed to H loss during capture of the oxidized xenoliths in the reduced partially molten host CAI, which implies in turn that kir must have formed in the nebula before accretion in the parent-body.

Conclusions: This work shows that NanoSIMS mapping of H isotopes in CAI primary and secondary minerals is a powerful tool to unravel the exposure of CAIs to volatile species. The effects of alteration can be heterogeneous at the CAI scale and both nebular and parent-body alteration can be recorded in individual CAIs. A nebular oxidizing environment not expected from thermodynamics alone and having a near chondritic D/H ratio has notably been evidenced in E101.1.

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Fig. 1. H isotope systematics in E101.1. Plain and dashed lines: terrestrial reference value ± 200‰ uncertainty due to matrix effects. Standards (black dots) plot in this interval. Grey dots: square ROIs coverage; colored diamonds: identified minerals. Dotted curves: mixing curves between the 3 endmembers. 1σ errors shown for clarity.