# Ultra-Pristine Extra-Terrestrial Material with Unprecedented Nitrogen Isotopic Variation.

G. Briani[1,3], M. Gounelle[1], Y. Marrocchi[1], S. Mostefaoui[1], F. Robert[1], H. Leroux[2] and A. Meibom[1]. [1]Laboratoire d'Étude de la Matière Extraterrestre, Muséum National d'Histoire Naturelle, 57, rue Cuvier, 75005, Paris, France; [2]Laboratoire de Structure et Propriétés de l'Etat Solide, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France; [3]Dipartimento di Astronomia e Scienza dello Spazio, Università di Firenze, Largo Fermi 2, 50125, Firenze, Italy (briani@mnhn.fr).

**Introduction:** Physical and chemical conditions during the earliest stages of Solar System evolution can be studied in chondritic meteorites and Interplanetary Dust Particles (IDPs), believed to be among the most primordial objects left over from the formation of the Solar System. Here we describe the unaltered mineralogy and light element (i.e. H, C and N) isotopic composition of a primordial xenolith in the chondrite Isheyevo. Isheyevo is a highly primitive, metal-rich (~60 vol%) CH/CB chondrite that contains also chondrules, rare Ca-Al rich inclusions and hydrated matrix-lumps, but no fine-grained matrix [1-3]. We identified more than 100 matrix lumps in two polished sections of Isheyevo (~400 mm$^2$) [4]. These show a high degree of aqueous alteration, consistent with previous reports [2,3], indicating that they are not genetically related to the aforementioned high-temperature components in Isheyevo.

**Experimental procedures:** High resolution SEM images were acquired using a Zeiss Supra-55 VP field emission SEM. Quantitative analyses for the mineralogical composition of PXs are realized with a CAMECA SX-100 electron microprobe. Two thin sections have been extracted from PX-18 by focused ion beam technique and individual matrix grains have been analyzed by a Philips CM 30 TEM. Secondary ion mass spectrometry analyses have been performed with a NanoSIMS CAMECA N50. We used a $Cs^+$ primary beam in two sessions, the first one for the detection of $H^-$ and $D^-$ (sample current ~ 40 pA) and the second one for $^{12}C^-$, $^{13}C^-$, $^{12}C^{14}N^-$ and $^{12}C^{15}N^-$ (sample current ~4 pA). For H isotopes measurements the mass resolution was $\Delta M/M \geq 2000$, for C and N isotopes $\Delta M/M$ was between 7500 and 8000. We utilized as standard reference a type III kerogen. Measurements were made in scanning imaging mode on 40×40 µm$^2$ areas.

**Results:** Among the ~100 primordial xenoliths (PXs) studied here, PX-18 stood out by its distinct textural and mineralogical properties and for the extreme variation in N isotopic composition. PX-18 is a dark xenolith (~380×470 µm$^2$) dominated by a very fine-grained matrix, mainly composed of anhydrous Mg-rich silicates, and with tiny Fe-Ni sulphides grains and magnetite. A few, micrometer-sized Mg-rich olivine and pyroxene crystals (Fo% = 84–89; En% = 89–95, Wo% = 0–4), Fe-Ni metal inclusions, rare carbonates and magnetite grains are embedded in the matrix. TEM examination confirmed that PX-18 matrix is composed of crystalline, anhydrous, Mg-rich pyroxene, with a few, greater Mg-rich ($Fo_{99}$) olivine grains (Fig. 1). Low-Ca pyroxene grains ($Wo_0$ to $Wo_{14}$) show a wide compositional range, from $Fs_0$ to $Fs_{74}$, but enstatite clearly dominates. Small Fe-Ni metal and Fe-oxide grains are present as minor components between silicates. Importantly, phyllosilicates are totally absent from PX-18. These observations indicate that PX-18 is mineralogically similar to primordial objects, such as chondritic porous IDPs [5] and comet 81P/Wild2 samples returned by the Stardust mission [6]. Clearly, PX-18 has avoided the aqueous alteration that affected the other PXs in Isheyevo [1].

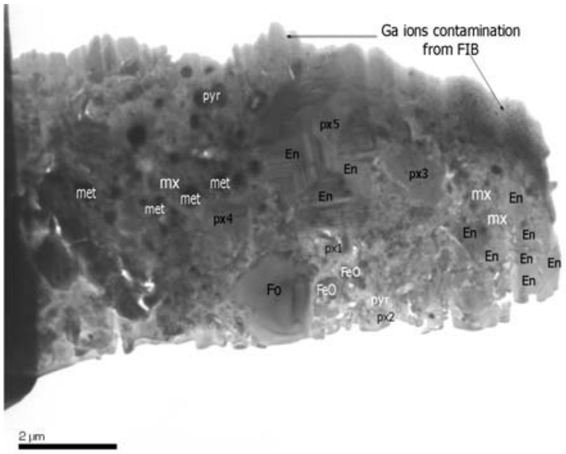

**Figure 1**. TEM bright-field micrograph of a thin section extracted from PX-18. A large olivine grain ($Fo_{100}$) is visible at the bottom of the section. "En" labels indicate pyroxene grains with En ≥ 98%. Other pyroxene grains range from $En_{63}Wo_1$ to $En_{95}Wo_1$. Metal grains (met), pyrrhotite (pyr) and a very fine-grained component (mx) are also present.

Bulk D/H ratios in PX-18 are slightly higher than the SMOW value ($60 \pm 20‰ < \delta D_{SMOW} < 240 \pm 30‰$), but no extreme D/H ratios were observed, neither in bulk nor as individual hotspots, compared to previous studies of IDPs [7] and insoluble organic matter (IOM) [8]. Carbon isotopic compositions ($-35 \pm 3‰ < \delta^{13}C_{PDB} < -14 \pm 2‰$) were also found to be comparable to bulk C isotopic composition of chondritic meteorites [9] and IOM [10]. For N isotopic distribution the main characteristics are: 1) surprisingly large areas with a diffuse enrichment in $^{15}N$ over the surrounding material (Fig. 2); 2) extremely $^{15}N$-enriched hotspots; 3) areas with negative $\delta^{15}N_{AIR}$ values. A total of 13 NanoSIMS images were obtained from PX-18, covering an area of ~ 12800 µm$^2$. They have mean $\delta^{15}N_{AIR}$ that range between 30 ± 20‰ and 700 ± 20‰, showing a heterogeneous distribution of the $^{15}N/^{14}N$ ratio in PX-18. Three images (each 40×40 µm$^2$) have very elevated bulk $\delta^{15}N_{AIR}$ values (630 ± 20‰, 640 ± 11‰ and 700 ± 17‰) due to the occurrence of a diffuse $^{15}N$-rich component, present in large fractions of the images. Hotspots with very high $\delta^{15}N_{AIR}$ were observed in PX-18. Two conditions are required to define hotspots in ratio images: 1) $\delta^{15}N_{AIR}$ such that $\delta^{15}N_{AIR} - 3\sigma > (\delta^{15}N_{AIR})_{mean} + 3\sigma_{mean}$ (mean refers to a whole image); 2) size greater than 250×250 nm$^2$ (the NanoSIMS spatial resolution is between 100 and 200 nm for C and N isotopes analyses). All the $^{15}$N hotspots have sizes greater than 300×300 nm$^2$, up to ~ 2×2 μm$^2$. The highest average $\delta^{15}N_{AIR}$ for a single hotspot is 3170 ± 150‰. However, several hotspots exhibit distinct internal structures, i.e. small internal regions with even higher $\delta^{15}N_{AIR}$. Four such cases have been identified, with $\delta^{15}N_{AIR}$ = 3000 ± 300‰, 3100 ± 500‰, 3700 ± 300‰ and 4900 ± 300‰. These two latter values are the highest ever measured in Solar System material. Moreover, in PX-18 also regions with negative $\delta^{15}N_{AIR}$ values were identified. In some case they represent up to 52% of the analysed surface. The minimum value measured for a single image is $\delta^{15}N_{AIR}$ = –310 ± 20‰, consistent with values inferred for the solar nebula [11-13].

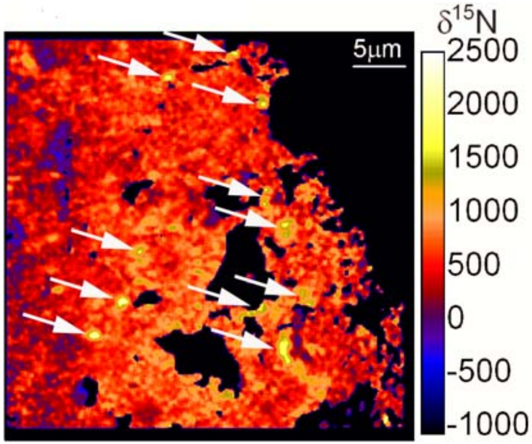

**Figure 2**. $\delta^{15}N_{AIR}$ distribution of a 40×40 μm$^2$ region in PX-18, with mean $\delta^{15}N_{AIR}$ = 640 ± 11‰. About 90% of this image is characterized by $\delta^{15}N_{AIR} \geq$ 250‰. Several hotspots are also visible (white arrows).

**Discussion:** The extremely large range of $\delta^{15}N_{AIR}$ values observed in PX-18 from Isheyevo is the widest ever measured for Solar System material (Fig. 3). This, combined with PX-18 unique mineralogy, is consistent with the notion that only highly unaltered material can preserve primordial isotopic compositions in the light elements.

Presolar grains can be excluded as the carrier phase of the N isotopic anomalies because *a*) they generally have smaller size than the diffuse $^{15}$N enrichments observed here, *b*) no presolar grains is observed at the hotspot locations comparing high resolution SEM and NanoSIMS images and *c*) most such grains would carry with them large anomalies in C, which are not observed [14]. These observations lead to the conclusion that $^{15}$N isotopic variation in PX-18 are due to the presence of diffuse organic matter with a range in $\delta^{15}N_{AIR}$ that greatly expands the range for a single extraterrestrial object or isolated IOM. Excluding a stellar nucleosynthesis origin (i.e. related to presolar grains) for the observed N isotopic anomalies, values of $\delta^{15}N_{AIR}$ as high as those observed in PX-18 can be produced only by low-temperature ion-molecule reactions. In the most recent model for N-containing molecules chemistry under dark molecular cloud conditions [15], values of $\delta^{15}N_{AIR}$ > 9000‰ are obtained for external layers of $NH_3$ ice accreted on dust grains. Transfer of fractionated N from $NH_3$ ice to organic matter is possible by UV-induced transformations in polycyclic aromatic hydrocarbons [16]. However, a fundamental problem is that low temperature ion-molecule reactions are also predicted to produce strong deuterium enrichments in organic matter [17], which are not found in Isheyevo PX-18 or any other xenolith in Isheyevo. These results call for a new theoretical and experimental approach, which must be able to provide an explanation for the decoupling of these light elements isotopic variations as well as for the high values measured in the hotspots.

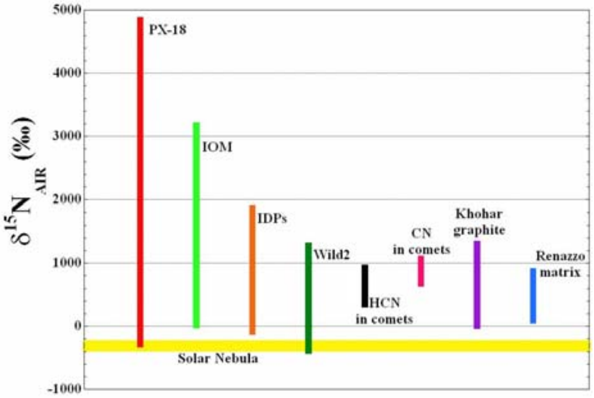

**Figure 3.** $\delta^{15}N_{AIR}$ values measured in PX-18, compared with previous measurements in other Solar System materials. Ranges reported in the figure comprise results from bulk measures as well as from hotspots (data from literature).

**Conclusions:** The primitive mineralogy of PX-18, in combination with the extreme range of N isotopic variation that it preserves, indicate that PX-18 represents a new class of extremely pristine extra-terrestrial material, which might sample little processed outer Solar System bodies. A Kuiper Belt parent body is a likely possibility. A full Solar System-scale event as the Late Heavy Bombardment (LHB) offers the explanation for the origin of PX-18 [5]. During the LHB collisions between fragile and/or unconsolidated objects, such as primordial chondritic asteroids (C-, D-type), cometary and Kuiper Belt objects, produced fragments that were scattered throughout the Solar System and embedded in meteorite parent bodies [18].

**References:** [1] Ivanova M. et al. (2008) *MAPS, 43*, 915. [2] Krot A. N. et al. (2007) *Chemie der Erde, 67*, 283. [3] Bonal L. et al. (2008) *LPSC, XXXIX*, 1506. [4] Briani G., Gounelle M. (2008) *Early Solar System Impact Bombardment Workshop*, 3013. [5] Bradley J. P. (2004) in *Meteorites, Planets and Comets* A. M. Davis, Ed. (Elsevier), 689. [6] Zolensky M. E. et al. (2006) *Science, 314*, 1735. [7] Floss C. et al. (2006) *GCA, 70*, 2371. [8] Busemann H. et al. (2006) *Science, 312*, 727. [9] Pearson V. K. et al. (2006) *MAPS, 41*, 1899. [10] Alexander C. M. O. D. et al. (2007) *GCA, 71*, 4380. [11] Meibom A. et al. (2007) *ApJL, 656*, 33. [12] Hashizume K. et al. (2000) *Science, 290*, 1142. [13] Owen T. et al. (2001) *ApJ, 553*, 77. [14] Nittler L. R. (2003) *EPSL, 209*, 259. [15] Rodgers S. D., Charnley S. B. (2008) *MNRAS, 385*, 48. [16] Bernstein M. P. et al. (2002) *ApJ, 576*, 1115. [17] Sandford S. A. et al. (2001) *MAPS, 36*, 1117. [18] Zolensky M. E. et al (2009) *LPSC, XL*.