MINOR ELEMENT ABUNDANCES IN GEMS

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Introduction: Galactic cosmic rays (GCRs) are nuclei of our Milky Way galaxy most likely accelerated near the speed of light, by supernova remnants and roaming within the galaxy trapped by the galactic magnetic field. Previously attributed to newly processed supernova (SN) ejecta, they were re-assigned in 1970 to a GCR source (GCRS) which featured composition anomalies not controlled by nucleosynthesis, but rather by atomic parameters, such as the 1st ionization potential (FIP) or the element volatility. To single out one of these two hypotheses, we must compare abundances for both low FIP volatiles and high FIP refractories. "Markers" such as Ga, Ge, and possibly (Na, P, and Pb) as well as S, Zn, Se, featuring fairly different volatilities for similar FIPs could favor either FIP or volatility.

Scientific background: GCRS distributions have been rarely sampled by astrophysical exploration missions in GEMS, usually present in IDPs linked to cometary sources. GEMS are main cosmochemical building blocks of uncertain origin: either presolar grains exposed to ionizing radiation in the interstellar medium [1] or Solar System products, formed as late-stage non-equilibrium condensates [2]. GEMS are depleted in all major rock-forming elements with respect to Si, but the heavy trace elements, which may give clues to their origin, have not yet been measured. Our goal was to measure for the first time as many low abundance elements with Z>28 as possible, to look for excess/depletion patterns that may correlate with astrophysically-relevant atomic properties: first ionization FIP and volatility [3]. Given the jump in abundance at Z> 28, using abundances from Lodders *et al.* [4], it is a challenging task only up to a setup showing exceptional Minimal Detection Limits as low as 45 zg (10^{-21} g) absolute masses [5] with multi-element SDD detectors capable of high statistics acquisitions.

Methodology: Our experiments aim to measure the most dilute samples by XRF, and that is most challenging, as the whole sample environment behaves like an actual contaminating sample. A first experiment performed Oct-Nov 2016, used a 3 element SDD + 1 element SDD fast counting detectors aiming for ultratrace element estimation of all Z higher than Fe, up to the maximum element excited in K shell at E=29.6 keV which is Sn. We used 100 nm thick ultramicrotomed sections on spectroscopically clean Si_3N_4 100 nm windows. Samples were: an Allende spinel phase for calibration – pre-measured at ALS, Berkeley and by TEM, an Orgueil very fine (few µm) grain distribution and a GEMS sample of approximately Ø 500 nm. We used the high intensity PINK beam mode, energy resolution of $\Delta E/E \approx 1.5\%$, at fluxes < $\mathbf{37 \cdot 10^{10}}$ ph/s in a 50 x 50 nm^2 spot, down from the available $\mathbf{5\text{-}10 \cdot 10^{11}}$ ph/s because of detector saturation from : 1) Mo detector external collimators at E∈[17.5-19.6 keV], 2) or Zr internal collimator at E∈[15.7-17.6 keV] and **Sr** from the beamline sample holders made of PEEK plastic. Results of a second experiment in November 2017 will be shown, where we used a new 7 SDD element detector from Mirion/Canberra™, and Ta collimators to free-up the Mo spectral zone and decrease detector saturation. Also, new sample holders and sample alignment posts were machined out of Delrin with no high Z fluorescences. All the setup was optimized by means of Monte Carlo spectrum simulations [after careful scans of the sample environment and samples were mapped out at 50 nm resolution to identify hotspot zones. All in all, the best countrate obtained from fluorescence line impurities in the setup and sample environment and our samples were no higher than 150 kcps at detector deadtimes of 10-15%, which can reach concentrations of a few ppm for Ni, and hundreds of *ppb* for As, Br and Se. A current limitation is the pulse processing electronics which is upgraded from 150 kcps to 1-2 Mcps.

Furthermore, we will design and build new external collimators of specific metals (Co or Ni and Ta) allowing either the Ni-Cu-Zn-Ga-Ge free zone to be measured or the higher Rb-Sr-Br up to In.

We have secured a clean FIB Ni standard of variable thickness (30 - 100 nm), optimized for absolute fluorescence calibration [6] and we will produce a second one of higher Z, Ag or Cd. A continuation experiment after the ESRF upgrade in 2020 will benefit from 30-50 times more flux, and the Mcps capabilities of the Falcon/XIA™ fastest extant pulse processing electronics, thus allowing us to gain a few more steps towards our Z=50 goal.

References: [1] Bradley, J. P. (1994), *Science* 265, 925-929. [2] Keller & Messenger, GCA 75 (2011) 5336–5365. [3] Meyer, J. P., O'C. Drury, L., & Ellison, D. C, 1997, Astrophys. Jrnl. 487, 182-196, [4] Lodders K *et al.*, (2009), Landolt-Börnstein - Group VI Astronomy and Astrophysics Series, vol. 4B. Springer, 712-770. [5] Laforce B. *et al.*, , Anal. Chem. 86, 12369-12374, 2014. [6] L. Lemelle, A. Simionovici et al., Trends Anal. Chem. 91, 104–111, 2017. [7] T. Schoonjans et al., Spectrochim. Acta Part B 82, 36-41, 2013.