HUNTING REFRACTORY INCLUSIONS IN CM2 AND CO3 CHONDRITES BY MID-INFRARED SPECTROSCOPY: A NON-DESTRUCTIVE APPROACH FOR RETURNED SPACE SAMPLES.

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Introduction: Refractory Inclusions (RIs) are the first objects to have formed in the primitive solar system by condensation of the nebular gas at high temperature 4.567 Gyr ago [1]. Therefore they are essential tracers of the early solar system processes. Their presence and characterization in samples returned from celestial bodies should bring multiple outcomes in terms of asteroid and solar system history e.g. bridge the gap between the early and the actual solar system physics and chemistry. It is therefore critical to be able to identify RIs in returned space samples as a prerequisite to detailed mineralogical and geochemical studies.

In this context, InfraRed (IR) reflectance spectroscopy is an ideal analytical tool (1) to develop a method for rapid detection of RIs in returned space samples, e.g. during advanced curation analyses (2) for non-destructive and non-invasive manipulation of priceless returned samples, and consequently giving the opportunity to study both mineralogy and organic matter in samples free of carbon coating, and (3) to compare between laboratory analyses and spatial observations.

Because the asteroid Bennu of the next sample return mission (OSIRIS-REx) is spectrally linked to CM carbonaceous chondrites [2,3], our study mostly focuses on these meteorites. To cover a range of variably altered objects of affinity with CM chondrites we studied sections from Colony CO3.05 [4], Paris CM2.9 [5] and Murchison CM2.5 [6].

Materials and Methods: The first step to develop our detection method was to build a database composed of Mid-InfraRed (MIR) reflectance spectra of terrestrial standards of typical Ca-Al-rich inclusions (CAIs) minerals (hibonite, perovskite, spinel, gehlenite, diopside). These spectra were acquired in spot mode with a ThermoFisher Continuum FT-IR microscope coupled to a mercury cadmium telluride detector installed at the SMIS beamline of the SOLEIL synchrotron. These spectra were taken with a x32 objective and a physical aperture of 60 x 60 μm and each measurement gathers only one spectrum in the mid-infrared range from 4000 to 400 cm^{-1} (2.5 to 25 μm) with a spectral resolution of 4 cm^{-1} with 512 coadded scans. We choose to work in the MIR range because CAI minerals have their characteristic features between 2000 and 400 cm^{-1} [7].

Secondly, we collected FT-IR hyperspectral reflectance maps of polished sections of Murchison, Paris and Colony, which were acquired with an Agilent Cary 670/620 microscope system coupled to a focal plane array (FPA) detector of 64x64 pixels, also installed at the SMIS beamline of the SOLEIL synchrotron. Each pixel gathers a spectrum in the range 4000 to 800 cm^{-1} (2.5 to 12.5 μm) with a spectral resolution of 4 cm^{-1} with 32 coadded scans.

For both IR measurements in reflectance, the internal globar source of the instruments was used and a spectrum was collected on a gold mirror for background calibration.
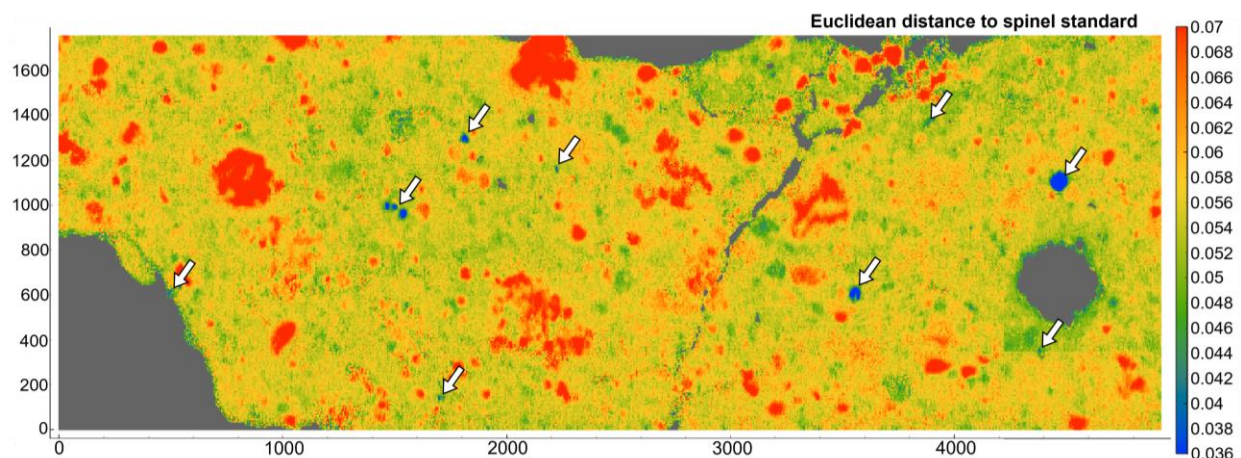

Fig. 1 *: Euclidean spectral distance map of Murchison (1760 x 4928 μm) to spinel standard between 800 and 940 cm^{-1}. The detected CAIs are pointed with white arrows. Grey areas are either metal grains or pixels out of the section.*

Back-Scattered Electron images and spot Energy-Dispersive X-ray Spectroscopy (EDS) analyses were systematically carried out on all the CAIs present in the IR map of Murchison to determine their characteristics, using the Clara TESCAN Field Emission Gun Scanning Electron Microscope (FEG-SEM) of the Museum National d'Histoire Naturelle electron microscopy facility in Paris operating at 15 keV and 3 nA. We localized all the CAIs using false colors MgCaAl X-ray maps of the Murchison section. The properties of the CAIs present in Murchison were used to assess the accuracy and the limits of our detection method in IR.

The detection of CAI minerals in IR maps is based on supervised machine learning using our standards database. The detection method was developed on Murchison for spinel and diopside and Colony was used for hibonite and gehlenite because of the absence of secondary processes. The Paris section was subsequently used as an unknown sample for validation of the detection method. We used the nearest neighbors method of the open-source software Quasar using the Orange spectroscopy toolbox [8] to detect typical CAI minerals. For each pixel in the hyperspectral maps, nearest neighbors calculates a spectral distance between the sample spectrum and that of the given reference. In this method, we used euclidean distances to our standard reference spectra to plot maps for the detection of CAI minerals (e.g. spinel in Fig. 1). On these maps, pixels having the smallest distance (blue spots) are those with spectral features most similar to the CAI mineral used as reference.

Results and Discussion: Using the developed method, we detected (1) 19 RIs for an area of 8.04 mm² in Murchison, accounting for 2.36 RIs/mm², (2) 16 RIs for an area of 8.18 mm² in Paris, i.e. 1.96 RIs/mm², (3) 15 RIs for an area of 8.67 mm² in Colony, i.e. 1.73 RIs/mm². On average we detected about 2 RIs/mm². To evaluate the amount of RI material detected and the efficiency of detection, we calculated the area of the detected RIs relative to all the RIs present in Murchison. We find an area ratio of detected RIs to overall RIs of 0.9088 (Amoeboid Olivine Aggregates, AOAs excluded) and 0.9657 (AOA included) on Murchison. It means that we detect approximately 91% (or 96,5% AOAs included) of the total RI surface, which is a satisfactory proxy for the total volume or mass of refractory material in the sample.

SEM examination shows that the RIs that were not detected in Murchison by IR are either phyllosilicate-rich (extensively altered) CAIs or CAI fragments that are smaller than the IR diffraction limit. RIs are efficiently detected when the extent of either hibonite or spinel is larger than 8-10 microns. For diopside and gehlenite this detection limit is closer to 4-5 microns. This limit of detection varies because diopside and gehlenite have lots of characteristic features above 800 cm^{-1} in contrast with hibonite and spinel that have their main features close to or below the range of the FPA detector (i.e. under 800 cm^{-1}).

We also acquired spectra of different CAI types and AOAs in Murchison in order to characterize their mineralogy in the whole MIR range and their extent of alteration through OH stretching absorption band. Performing these analyses after detection allows the selection of CAIs that could be interesting for further studies.

Conclusion: The non-destructive and non-invasive method we developed allows the detection of more than 95% of the refractory inclusion content in CM-like materials. Undetected CAIs are either extensively altered or highly fragmented. Regardless of the sample type, all refractory inclusions with individual refractory minerals/mineral aggregates larger than 10 μm should be detected. Most CAI studies and analysis methods focused on such objects, therefore the method we developed is very useful for the rapid selection of CAI-bearing returned space samples for further mineralogical or geochemical studies and linking the first solar system objects with present-day asteroids. Interestingly, our detection method can be easily applied to any other mineral in any kind of sample.

References: [1] Amelin, Y. et al. (2002). *Science*, *297*(5587), 1678-1683. [2] Clark, B. E. et al. (2011). *Icarus*, *216*(2), 462-475. [3] Hamilton, V. E. et al. (2019). *Nature Astronomy*, *3*(4), 332-340. [4] Davidson J. et al. (2014). *LPS XLV*, Abstract #1384. [5] Hewins, R. H. et al. (2014). *Geochimica et Cosmochimica Acta*, *124*, 190-222. [6] Rubin, A. E. et al. (2007). *Geochimica et Cosmochimica Acta*, *71*(9), 2361-2382. [7] Beck, P. et al. (2018). *Icarus*, *313*, 124-138. [8] Toplak, M. et al. (2021). *Cells*, *10,* 2300.