

## The Unrestrained Use of Python Libraries for Bridging the Gap Between Planetary and Material Sciences

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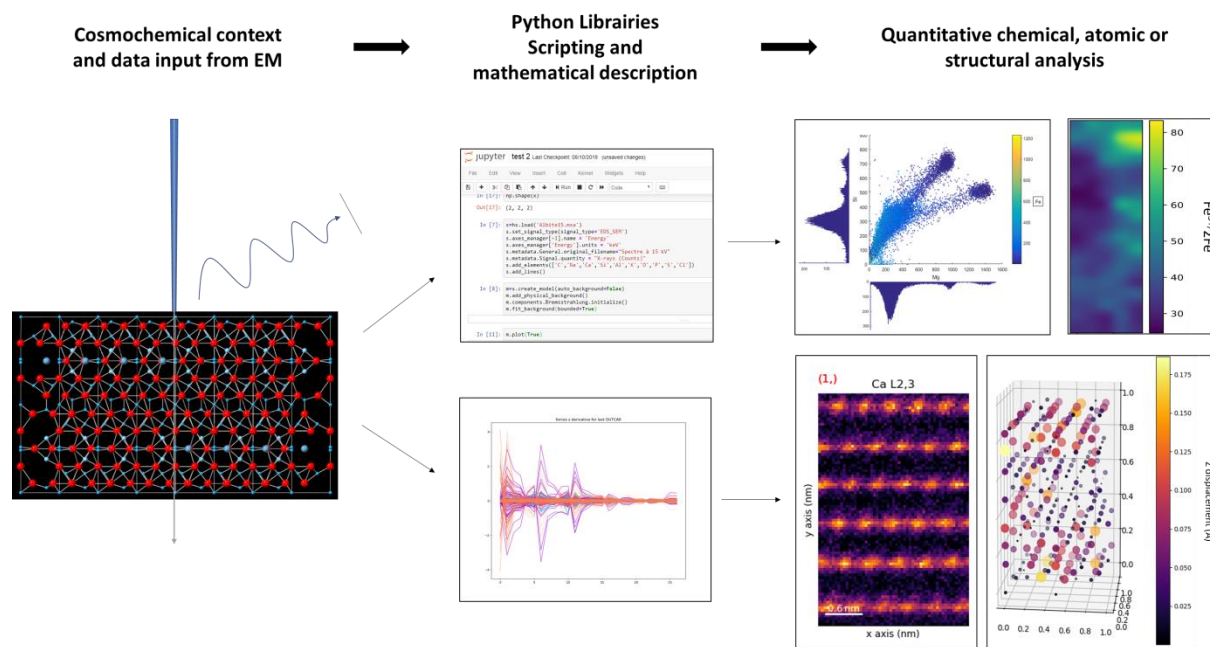
Our solar system was formed 4.5 billion years ago from a disk of gas and dust rotating around our protostar. A significant part of the mass constituting this solar nebula experienced high temperatures and evaporated [1]. The first stages of the gas cooling were marked by the condensation of the most refractory solid materials [2, 3]. This time-temperature sequence gave rise to the calcium aluminum rich inclusions (CAIs) found in primitive meteorites. Such CAIs mark time zero for our solar system [4, 5] and analysis of their detailed crystal structures and chemistry can provide new insights into the conditions of formation of our solar system [2]. Here I show how the use of python libraries has facilitated the manipulation and the processing of data at the interface between physical sciences and computational thermodynamics. I highlight three applications below that are part of one single long-term project.

The mineralogical and chemical diversity in the CAIs assemblages is fundamental to constrain since it must be compared iteratively to the predictions of thermodynamic models of condensation. The determination of the modal mineralogy constituted the first step in this project. Microscale images and EDS maps have been acquired using a Hitachi S-4800 cold-field emission gun at 30 keV. I will show how the use of phase mapping based on multiple least squares linear fitting of a spectral image acquired by energy dispersive spectroscopy (EDS) and processed via Hyperspy allowed us to establish the mineralogical context of the CAIs studied [6, 7].

In addition to the large-scale analysis, I studied in detail the crystal chemistry of the phases that constitutes the CAIs. In particular, minerals in CAIs can host 3d transition metals in multiple oxidation states [8]. Measurement of their concentration and oxidation states by EDS and electron energy-loss spectroscopy (EELS) in the transmission electron microscope (TEM) can provide information on the thermodynamic conditions (temperature, composition of the gas, oxygen fugacity) under which they formed or last equilibrated and are used to precise the equilibrium thermodynamic predictions that are done on phase assemblages. In particular, meteoritic Hibonite ( $\text{CaAl}_{12}\text{O}_{19}$ ) contain significant amount of Ti in their structure as a mixture of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  [9–11]. To relate the relative amounts of these cations in the structure to the redox conditions of the system we acquired the nanoscale images and spectroscopic data (EDS and EELS) using a 200 keV aberration-corrected Hitachi HF5000 S/TEM equipped with an Oxford Instruments X-Max 100 TLE EDS system including twin, 100-mm<sup>2</sup> silicon-drift detectors and providing a large (up to 2 sr) solid angle for X-ray collection and a Gatan Quantum ER electron energy-loss spectrometer. Spectra were acquired in STEM mode using a 25  $\mu\text{m}$  condenser aperture (probe current  $\sim 105$  pA), a 2.5 mm spectrometer entrance aperture, and a dispersion of 0.25 eV/ch with a dwell time of 0.2 sec/pixel. To improve our understanding of spectral features, I consistently performed first-principle calculations using the Wien2k code and simulated the Ti-oxide spectra via TELNES 3 (Theoretical Electron Energy Loss Near Edge Spectra) on the High-Performance Computing resource (HPC) of the university of Arizona. I will describe the second step of this project which is a modified white-line approach (EELS) to quantify the Ti-oxidation states in meteoritic hibonite and how I processed the data via hyperspy and Atomap at the nanoscale [6, 12].

In order to develop a thermodynamic model that relates  $Ti_{4+}/\Sigma Ti$  to the  $fO_2$  of the gas and that sensitively reflects the chemistry and the details of the microscopic atomic arrangements, including small changes in atomic positions I used, as a third step, density functional theory (DFT), to determine ground state energy from first principles. The endmembers structure energies and enthalpy of mixing were obtained using the Vienna Ab ignition Simulation Package (VASP) [13]. To assess that the structure produced using the supercell software was not periodic (at microscopic length scales), the structures were characterized through multisite correlation functions as described by [14]. For the SQS calculations, a simple Gaussian smearing (width of 0.05 eV) was initially used during the first steps of relaxation but a final calculation was running with the tetrahedron method with Blöchl corrections. These spin polarized calculations were done with a 6x6x2 k-mesh a maximum of 200 ionic steps and plane wave energy cut off of 400 eV. The calculations threshold was attained for the energy difference of  $1.e^{-7}$  eV. The crystal structure relaxation of the selected endmembers chosen to be representative of the primitive meteorite hibonite compositions has also been handled using python libraries such as Spglib, VASPy and pymatgen [15–17]. The objective was to assess a criterion of convergence for the calculation and visualize structural deformations. From these ground state energies, the goal is to determine in the future a thermodynamic model by adding the entropy term to the enthalpy of mixing.

Coupling a quasi-quantitative description of the micro and nanoscale context with the characterization and simulation of the atomic-scale structure from electron microscopy and ab initio calculations allowed us to break down the barriers between planetary and materials science. The extensive use of python provided a consistent mathematical description of our data as well as an easy way to manipulate, visualize and process results from various packages. The latest version of the thermodynamic model that integrates the structure, composition, and oxidation state variations will be presented at the conference [18].



**Figure 1.** Schematic of the usage of various python libraries for processing planetary material data.

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