ESRF	**Experiment title:** Cd and Y speciation in Moroccan sedimentary phosphate	**Experiment number**: ES-903
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Report:

Scientific stakes and aim of the study

Following the growth of global demography, economical forecasts for the next 30 years estimate a 100% increase in global demand for fertilizers. The latter are essentially produced from nitrogen (N), potassium (K) (P) and phosphorus (K). The latter is the more critical in terms of both amounts and availability and Morocco occupies a considerable position in this industry, the country holds more than 70% of the world reserves, and remains the world's largest exporter. However, sedimentary phosphate rocks, are known to contain significant quantities of cadmium (toxic metal; concerned by a limited content at import), and rare earth elements (REE; highly valuable metals). Such limits are expected to become stressful in the future agricultural economy, and therefore cannot be dissociated in an ore treatment/purification strategy a co-valorization of metals like REE. This opportunity enable the development of a clean phosphate resources and green technologies.

A perfect knowledge of such trace metals is today at the heart of exploitation strategies of mining companies, thus the characterization by XRF, XANES and EXAFS of the bulk distribution and speciation of Cd and Y in rock samples from moroccan appear essentials. Such information will help to understand what are the main Cd and Y bearing minerals in phosphate ores and what are the fixation mode. Answers to these questions may help to guide metallurgical beneficiation processes, as well as to understand the geochemistry at the origin of metal enrichments to better understand the phosphatogenesis.

Material and experimental techniques

We dispose of 50 rock powder samples compacted in 5mm diameter pellets. These samples come from the main Moroccan mining sites, two from the north (10 and 25 samples) and one from the south (15 samples).

We dedicate the first shift to calibrate the setup and plan the measurement strategy. Then 11 shifts were used to collect XANES and EXAFS at Cd *k-edge* (26.711 keV) with a Si(111) monochromator. Due to their very low content (20-70 ppm of Cd), only 22 samples were analyzed by XANES (7 in the south and 15 in the north) with a total of 44 scans of 14 min each. For the same reasons only 7 EXAFS samples were measured (3 southern and 4 northern) with an overall of 93 scans of 20 min each. Reference was collected at the same time with an identical configuration. The last 6 shifts were dedicated to the collection of XANES and EXFAS at Y *k-edge* (17.038 keV), the higher contents (80-250 ppm Y) and the use of the Si(311) allowed to reduce the number of scans by half compared to the previous shift.

Both *k-edges* were investigated with a Vortex silicon-drift detector located at 90° of the incident beam at room temperature. In both cases EXAFS were collected with an incremented integration time per point, which increase following a quadratic law to finally reach 4 second at the end of each EXAFS scan.

Results and discussion

Firstly, the XRF analyses show varying concentrations of Y and Cd. The northern sites are more concentrated in Y and more depleted in Cd than the southern site. The Cd K edge XANES are different between the sites and we denote that the southern samples have a greater post edge structuration than the northern ones, characterized by a bulge at 26.73 Kev and a trough at 26.74 (**Fig.1a**). Fourier transforms of the EXAFS spectra show that the southern samples are quite similar to the otavite one ($CdCo_3$), furthermore the intense second and third neighbors could suggest a significant clustering effect (**Fig.1c**). The northern samples are rather close to a cadmium enriched apatite (**Fig.1c**). In all cases the adsorbed cadmium that display a less intense second neighbors, is quite different from our samples thus ruling out the adsorption as the main process of fixation. So we proposed that the Cd exhibit a different speciation mode depending on the locality, either incorporated in the apatite structure like in the south or in the calcite like in the north.

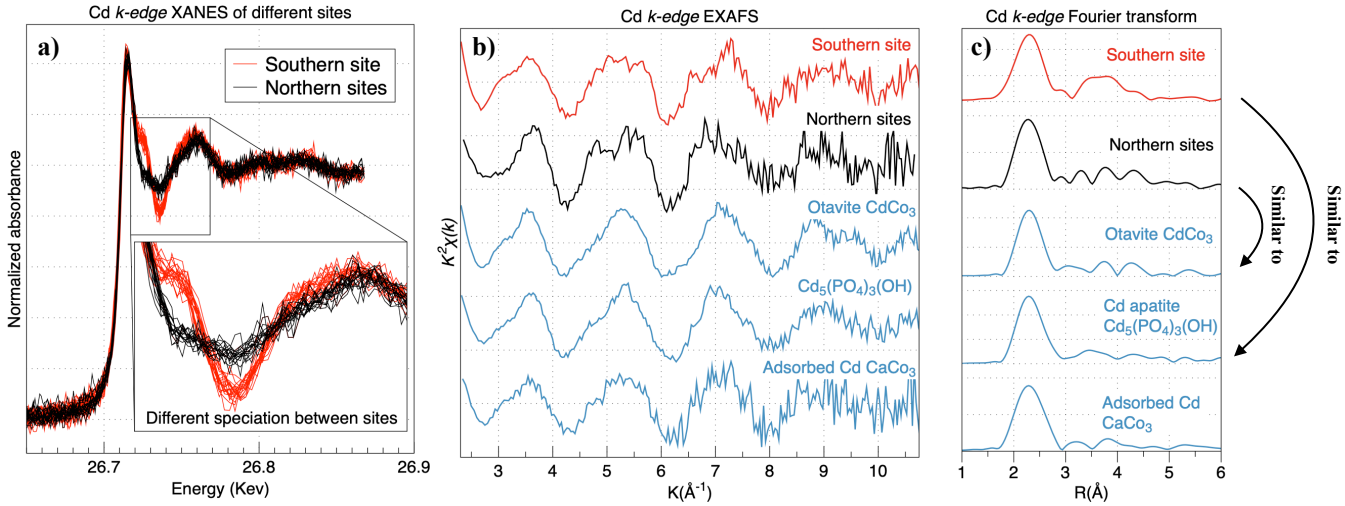

Fig. 1 a) Comparison of Cd k-edge XANES spectra of different sites b) Cd k-edge EXAFS spectra of different sites and references c) Fourier transform of Cd k-edge EXAFS.

Unlike Cd, Y K edge XANES spectra are identical regardless of their sampling site. The EXAFS and corresponding Fourie transforms illustrate that the signature of all samples is very close to that measured in natural fluorapatite (durango). Furthermore, the high intensity of the second neighbours is more in favour of an incorporation process of Y into the apatite lattice.

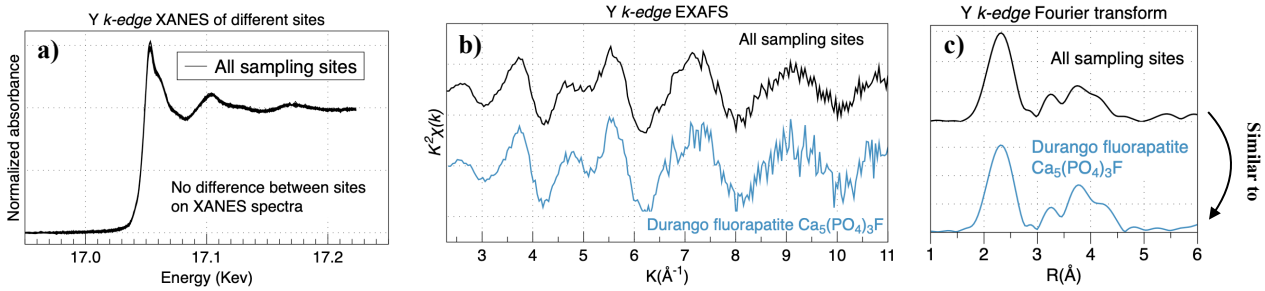

Fig. 2 a) Comparison of Y k-edge XANES spectra of different sites (all are similar) b) Y k-edge EXAFS spectra of all the sites and references c) Fourier transform of Y k-edge EXAFS

Nevertheless a more in depth study that include Fourier transform, needs to be undertaken to highlight clustering effects as well as preferential occupancy sites in fluorapatite lattice. Moreover, the analysis remains global, therefore it would be relevant to continue the study by characterizing the in-situ distribution and speciation of Cd and Y. Such analysis would enable us to i) evaluate in a smaller scale if the main Cd and Y bearing minerals are the same, ii) to what extent Cd and Y are homogeneously distributed at what concentration, iii) how other elements such as U and Th are distributed in relation to Cd and Y.