

Proposal title: Geochemical and crystal-chemical processes forming world-class niobium (Nb) deposits revealed by micro-XAS and micro-XRD

Proposal number: ES-1036, **Beamline:** BM23, **Shifts:** 15, **Date(s) of experiment :** 27/10/2021-02/11/2021, **Date of report:** 2022

- **Objective & expected results :**

Niobium-enriched laterites are characterised by the physical accumulation of weathering resistant Nb-bearing minerals such as pyrochlores (type-1 laterite, e.g. Catalão-I deposit). However, Seis Lagos laterite is characterised by the large proportion of Nb minerals such as Nb-enriched Ti and Fe oxides formed at the expense of primary minerals (type-2 deposit). We investigated the elusive Nb speciation of these two types of laterites in order to decipher the crystal-chemical and geochemical processes favouring each type of Nb mineralisation.

- **Results and the conclusions of the study :**

1. *Micro-XAS spectra indicate various local structures of pyrochlore depending on its alteration*

Pyrochlores from Seis Lagos (SL) and Catalão-I (CI) laterites exhibit different spectral features (Fig. 1a). Three features of their K-edge XANES spectra (A,B,C) were compared with each other and with reference spectra (Fig. 1a). The A feature of CI pyrochlore is well-marked similarly to the hydroxyrochlore feature. It is also slightly shifted to lower energy compared to the other pyrochlore spectra. The A feature of SL pyrochlore (I) is shifted to high energy. The B feature is subject to smaller variations in energy. However, the B feature of fluorcalciopyrochlore is significantly wider. The C feature is only observed on CI pyrochlore, bariopyrochlore and hydroxyrochlore spectra. Comparison between micro-EXAFS and reference spectra also evidence similarities between SL pyrochlore with fluorcalciopyrochlore, and between CI pyrochlore with bariopyrochlore and hydroxyrochlore (Fig. 1b). There are slight differences in the intensity and the position of the pre-edge feature which varies in the range 19881-19883 eV.

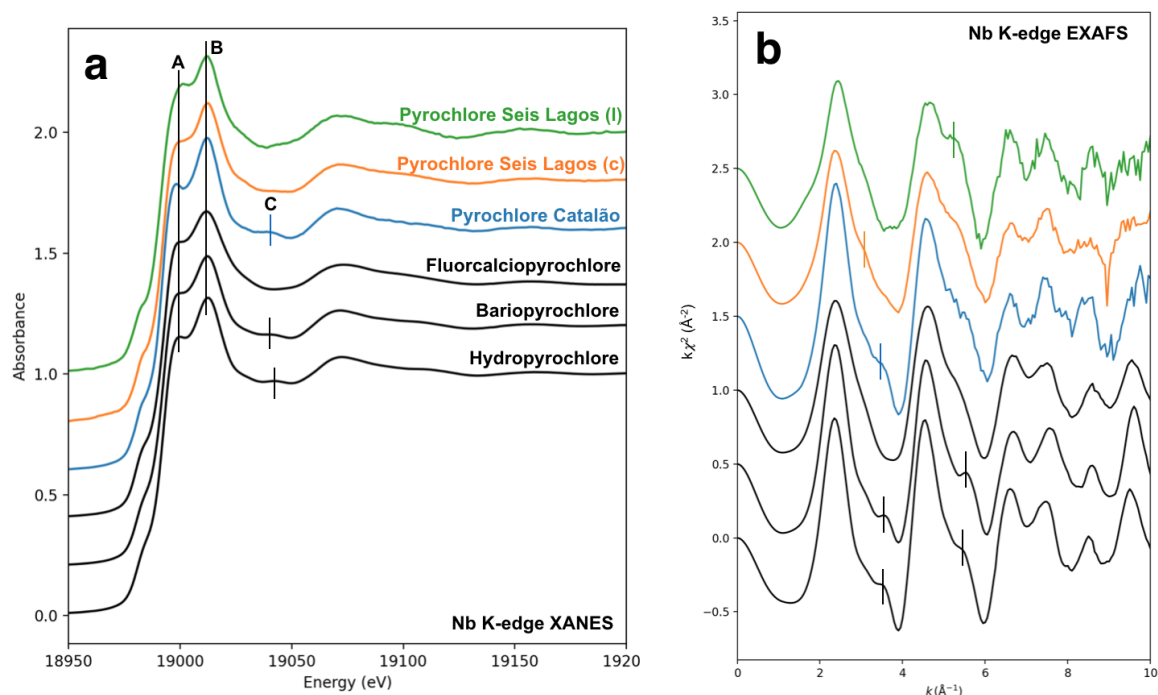


Figure 1: Niobium K-edge XANES and EXAFS spectra of pyrochlore references (black) and of micro-analysed pyrochlores from Seis Lagos (c: carbonatite, I: laterite) and Catalão-I laterites.

Similarities between bariopyrochlore and Cl pyrochlore spectra can be explained by the Ba-enriched nature of pyrochlores. There are significant differences between SL pyrochlores found in the carbonatite and in the weathered horizons. These differences can be ascribed to the alteration of pyrochlore due to supergene weathering which lead to crystal-chemical evolution (in the weathered horizons, Pb is replacing Ba and Ce present in pyrochlores from the carbonatite). However, spectral differences between the altered pyrochlore of Catalão-I and Seis Lagos indicate that there is no unique spectral signature for altered pyrochlore.

2. Micro-XAS and micro-XRD analyses to constrain Nb speciation in fine-grained laterites

Niobium-Ti oxides are the main Nb carriers of the Seis Lagos deposit but the relative abundance of each Ti oxide polymorph is not known [1]. Several spectra collected on Nb-Ti oxide (10-15 wt% Nb₂O₅) are different from the reference spectra of Nb-anatase and Nb-rutile (Fig. 2a). The presence of the main peaks of brookite on the micro-XRD pattern testifies that these spectra are representative of Nb-brookite (Fig. 2b). As Nb-brookite is challenging to synthesize, micro-XANES spectra of Nb-brookite will be used as a reference spectrum in order to estimate the amount of Nb-brookite in the average Nb speciation.

Several spectra collected on Nb-enriched Ti oxide match the spectrum of Nb-rutile (Fig. 2d). Some of the Nb-rutile crystals occur as broken spherules within a goethite matrix (Fig. 2c). The determination of Nb-rutile is also evidenced by the presence of characteristic peaks on the micro-XRD pattern (Fig. 2d). The combination of micro-XAS and micro-XRD demonstrates that rutile and brookite are the main Nb carriers within the laterite (Fig. 2) confirming assumptions from bulk XRD analyses [1]. The presence of other phases in XRD patterns results from their presence in the depth of the sample along the X-ray beam path.

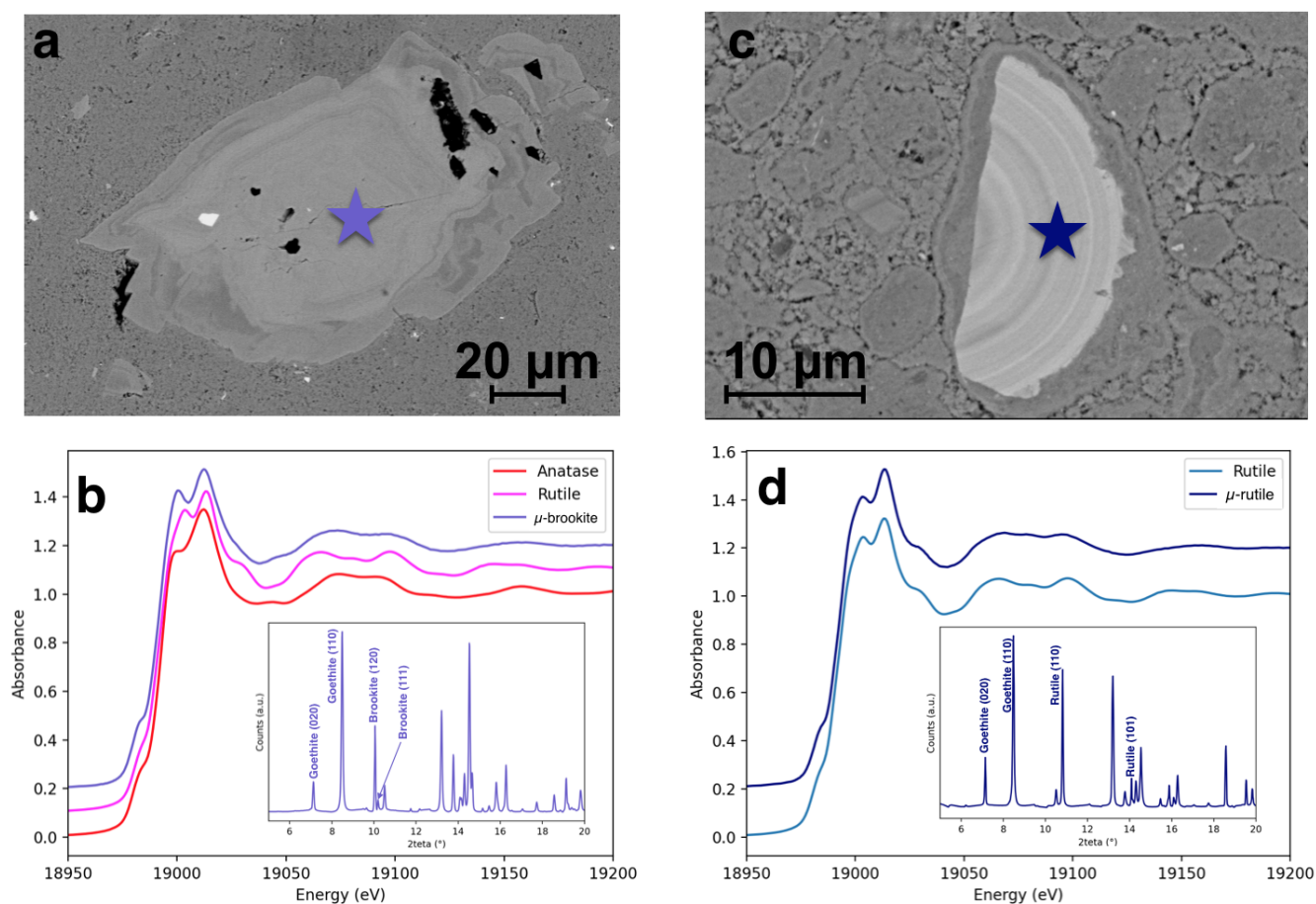


Fig 2: BSE images of the Seis Lagos laterite of (a) Nb-brookite and (c) Nb-rutile. (b) Micro-XANES spectra of Nb-anatase and Nb-rutile and another spectrum interpreted as Nb-brookite in light of XRD pattern. (d) Spectra of Nb-rutile reference and micro-focused rutile.

Micro-XRF maps reveal the presence of Fe-rich zones which also host Nb in relatively low concentration (Fig. 3a). Rather than micronic crystals, Nb seems dispersed in the Fe matrix as Nb-enriched goethite (Fig. 3b). Such observation was also made in the case of the Pitinga laterite [2]. Spectra of Nb-hematite were not recorded, thus implying either the absence or the minority of Nb-hematite in Seis Lagos laterite [1].

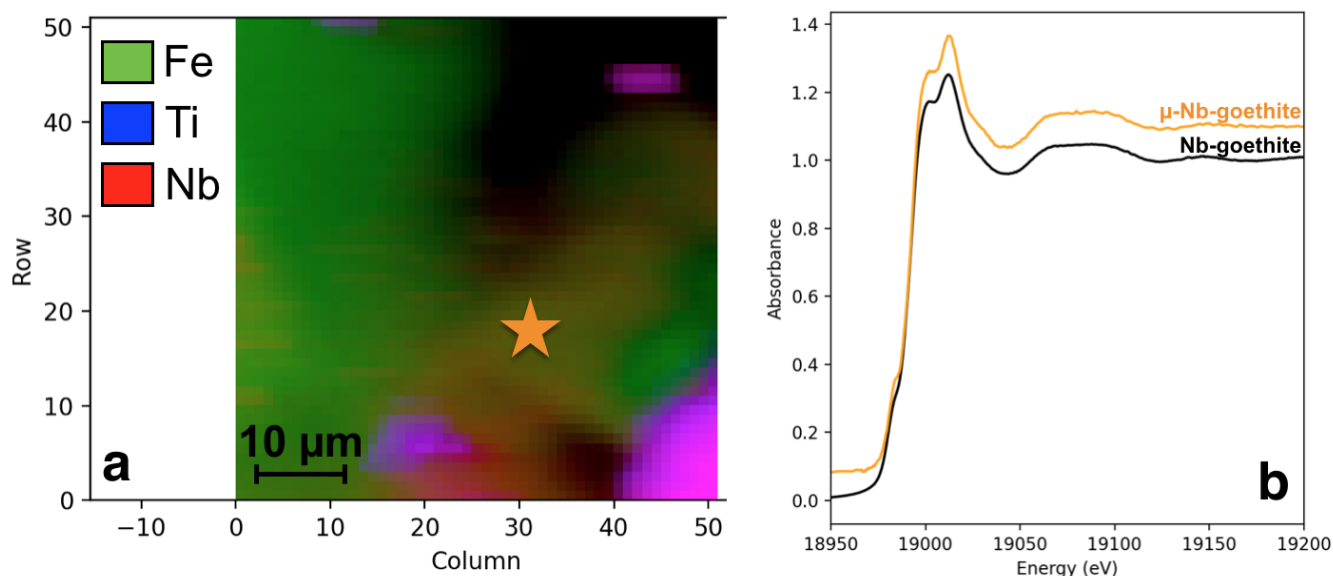


Fig 3: (a) Micro-XRF map of a lateritic horizon of the Seis Lagos laterite. (b) Spectra of Nb-goethite reference and micro-focused goethite in Seis Lagos.

Preliminary SEM-EDS studies conducted on the Catalão-I laterite evidence the presence of unusual Zr-Th-Nb-enriched zone. This zone does not match the composition of pyrochlore and is not associated with Ti (Fig. 4a). Micro-XANES spectrum exhibits similarities with that of fergusonite, though they do not have the same crystal-chemistry. These spectral similarities could be due to the metamict structure of these minerals, both of which are rich in radioactive Th and U.

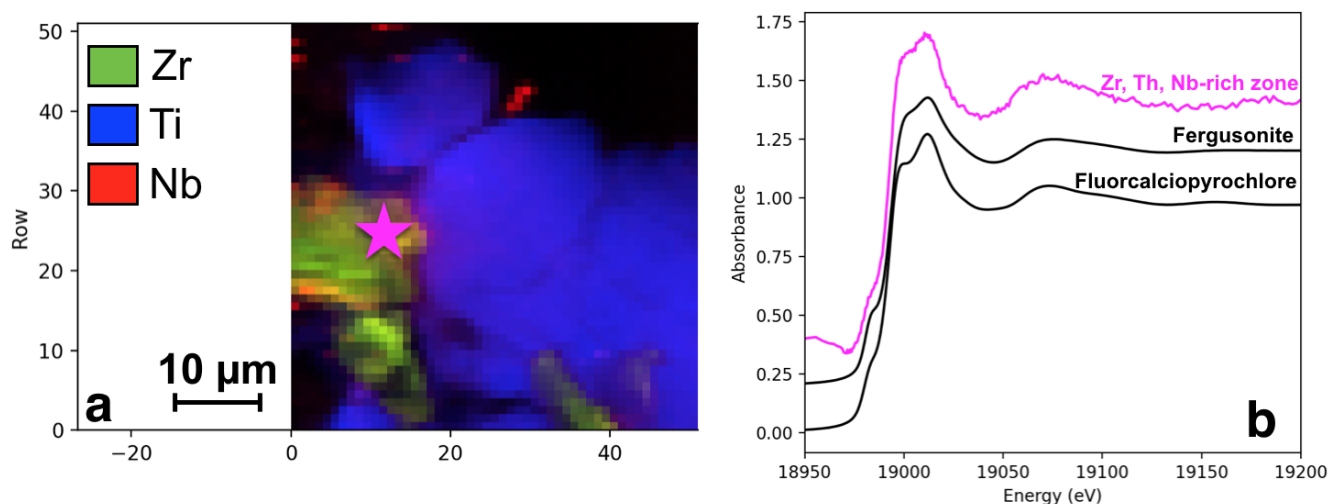


Fig 4: (a) Micro-XRF map of a lateritic horizon of the Catalão-I laterite. (b) Comparison of the spectra of fergusonite, fluorcalciopyrochlore and micro-focused Zr-Th-Nb-enriched zone.

3. Processes of formation of type-1 and type-2 laterites revealed by micro-XAS and micro-XRD

The first two most intense peaks of the XRD pattern of Nb brookite exhibits a significant shift of ca 0.5° compared to that of pure brookite. Such shift is ascribed to the slight distortion of the crystal cells, in particular, the shortening of c crystal-cell parameter due to substitution of Ti^{4+} by Nb^{5+} ions [3]. Micro-diffraction data will be further analysed in order to identify pyrochlore and unknown Nb carriers.

We noted variations in the position and intensity of the pre-edge between micro-focused spectra with their reference spectra analogues. For example, the pre-edge of rutile spectrum of Seis Lagos does not have the same shape and is more intense than the pre-edge of rutile reference spectrum (Fig. 2d). Similarly, the pre-edge of micro-focused goethite is of higher intensity than the spectrum of its reference counterpart (Fig. 3b). As the pre-edge intensity is a marker of the degree of distortion of the NbO₆ octahedra [4], the local environment of Nb in the Fe and Ti oxides of Seis Lagos is more distorted than in our references. This could be due to the higher proportion of Nb they host.

After processing the EXAFS spectra, we will carry shell-by-shell calculations on pyrochlore, Nb-bearing Ti and Fe oxide spectra which will give access to Nb bond lengths with its first oxygen and second cation neighbours. The study of the local structure of pyrochlore in Seis Lagos and Catalão-I laterites obtained by μ -XANES and μ -EXAFS combined with information retrieved from L₃-edge micro XANES spectroscopy will allow the determination of the crystal-chemical factors responsible for the alteration of pyrochlore. Moreover, the study of Nb incorporation into secondary oxides shed light on the relative affinity of Nb for Fe oxides and TiO₂ polymorphs.

- **References :**

[1] Giovannini et al. (2017), *Ore Geol. Rev.* [2] Bollaert et al., *in prep.* [3] Liu et al. (2017), *Journal of Materials Chemistry A*. [4] Piilonen et al. (2016), *The Canadian Mineralogist*.

- **Future publication using the data of this proposal:**

Weathering of niobium minerals in a world-class Nb lateritic deposit (Morro dos Seis Lagos, Brazil). *in prep.*