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SPECTROMETRY ANALYSIS TECHNIQUES FOR LCT PEGMATITE HALO IDENTIFICATION: THE ROLE OF EUROPEAN PROJECTS

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ABSTRACT

Lithium-Cesium-Tantalum (LCT) pegmatites are enriched in several raw materials. However, their small size and the limited penetration depth of the sensors, limits remote sensing approaches. This study evaluates the usefulness of hyperspectral data to identify geochemical halos related to LCT pegmatites by exploiting the information acquired in European projects. It was possible to identify key minerals and related mineralogical changes that can be due to hydrothermal alteration. Partial Least Squares Regression (PLSR) was used to model the abundance of Li, Rb and Cs. The most reliable results were obtained for Cs, with results being influenced by lithological and weathering factors. New outcomes are expected, namely mineral chemistry studies that will complement the hyperspectral results.

Index Terms— Reflectance spectroscopy, mineral exploration, PLSR, chemometrics, pegmatite

1. INTRODUCTION

Pegmatite rocks, including LCT (lithium-cesium-tantalum) pegmatites, are enriched in several raw materials critical for the energy transition [1, 2]. Therefore, it is essential to develop and improve less-invasive exploration techniques to target LCT pegmatites, namely based on remote sensing approaches. Previous works have employed multispectral satellite images to identify lithium (Li)-bearing pegmatites [3, 4]. However, the relatively small size of the pegmatite bodies and limited penetration depth of remote sensing are key constraints for their direct identification [5]. One possible strategy to increase the target size of pegmatites and detect buried bodies is detecting the associated geochemical halos in the host rocks instead.

The LIGHTS project (http://lights.univ-lorraine.fr/), finished in December 2021, allowed identifying target areas for Li-exploration through the integration of remote sensing data acquired at different scales with auxiliary geological and geochemical data [4]. In the scope of this project, a first characterization of the geochemical halos was conducted [6]. However, the ongoing GREENPEG project (https://www.greenpeg.eu/) goes further by linking geochemistry and remote sensing, i.e. by aiming to detect the pegmatite alteration halos using satellite data. Both projects cover the study area of this work, the Fregeneda-Almendra pegmatite field, spreading from Spain to Portugal, where several LCT pegmatites outcrop. This study tries to assess the usefulness of hyperspectral data (reflectance spectroscopy) for pegmatite halo detection through: (i) mineral identification and compositional changes; and (ii) distinct multivariate approaches. One strategy is Partial Least Squares Regression (PLSR) modeling, often used to estimate Rare Earth Elements (REE) or modal mineral abundances from hyperspectral data [7, 8]. PLSR can be useful when the spectral regions correlated with the target features are not clearly identified in the spectra, as is the case of important targets for LCT pegmatites such as Li, rubidium (Rb) and cesium (Cs).

2. DATA AND METHODS

2.1. Sampling and geochemical assays

A systematic sampling transverse to both mineralized and barren dykes was conducted in the Fregeneda-Almendra area (n = 106). Both surface and drill core samples of the pegmatite host rocks were collected. Moreover, samples were collected away from pegmatite influence to serve as a control group. The host rocks correspond to Neoproterozoic to lower Paleozoic alternating phyllites and metagreywackes [9]. All samples were analyzed at Activation Laboratories Ltd. (Actlabs), Ontario, Canada, through the 4LITHO(4B2), 8-Lithium Ore, 4F-B(2ppm), 4F-F, and 8-Peroxide ICP analytical packages, resulting in 58 major and trace elements, including Li, Rb and Cs, to model pegmatite halos.

2.2. Spectral measurements

Complementary reflectance spectroscopy studies were conducted in all 106 samples. The measurements were performed using an ASD FieldSpec 4 standard resolution

spectrometer (3.0 nm @ 700 nm, 10.0 nm @ 1400 nm, and 10.0 nm @ 2100 nm) with a Contact Probe with a halogen bulb. For calibration, a Spectralon (Labsphere) plate was measured every 30 to 45 minutes. Each final spectra represented an average of 5 measurements of 40 scans per point. For each sample, several spectra were acquired considering the different types of faces (naturally exposed, fractured, sawn, etc.). Each spectrum was individually inspected to select the most representative spectra in each sampling point, thus reducing the number of spectra for interpretation from 467 to 214.

2.3. Mineral identification

All 214 representative spectra were analyzed through AusSpec International Ltd.'s aiSIRIS software, a cloud-based artificial intelligence solution for spectral interpretation. The software provided complete mineralogy (up to eight minerals) identified in the Visible-Near Infrared (VNIR) to short-wavelength infrared (SWIR), as well as a quantitative measure of mineral spectral abundance and several spectral parameters automatically computed for alteration modeling. Moreover, the aiSIRIS software allowed performing a quality assessment of the spectra based on the reflectance, noise, and possible presence of water.

2.4. Exploratory analysis

Exploratory statistical techniques were employed to evaluate any possible correlation between: (i) the different spectra; (ii) the spectra and the Li, Rb and Cs contents; and (iii) the spectral parameters extracted for each spectrum and the respective metal contents. The statistical techniques included: (i) Pearson's and Spearman's correlation coefficient; (ii) cluster analysis through Ward hierarchical clustering (dendrograms) and K-means; and (iii) principal component analysis (PCA).

2.5. Partial Least Squares Regression (PLSR) analysis

The PLSR models were trained and evaluated in calibration (cal) and validation (val) datasets, respectively (75%-25%, obtained by random splitting). The VNIR-SWIR spectra served as independent variables (X) while the Li, Rb and Cs concentrations corresponded to the dependent variables (Y). The number of components was determined through leave-one-out cross-validation to minimize both the Root Mean Square Error (RMSE) and the number of components to avoid overfitting [7, 8]. Before training, anomalous Y values were removed (outliers identified in the boxplots and histograms; n = 148). The trained models were used to predict the Li, Rb and Cs concentrations of the val dataset, and model performance was assessed through the computation of the RMSE and coefficient of determination (R^2) on both cal and val datasets. The effect of different spectral pre-processing on model performance was also evaluated by training models on (i) raw data; (ii) continuum-removed (CR) spectra; (iii) first derivative (FD); and (iv) standard normal variate transformation (SNV). To improve model performance, additional data filtering was considered, namely: (i) remove spectra from weathered samples (Chemical Index of Alteration or CIA ≥ 70%; n = 80); and (ii) divide the original datasets considering SandClass classification [10] into Shale (n = 112) and Wacke (n =36).

3. RESULTS AND DISCUSSION

3.1. Mineral identification

The identification of diagnostic spectral features allowed the discrimination of one to five distinct minerals in each spectrum, with at least three minerals recognized in most spectra (68%). White mica was the most common mineral, being present in more than half of the spectra, followed by chlorite. Regarding the spectral contribution of minerals in each spectrum, white mica features are dominant in more than half of the spectra (53.74%). The second dominant features are those of montmorillonite (11.68%) followed by chlorite (7.94%), tourmaline (6.54%) and biotite (5.14%). Changes in the wavelength position of diagnostic features were investigated to detect possible changes in the mineral chemistry of white mica and chlorite (Fig. 1).

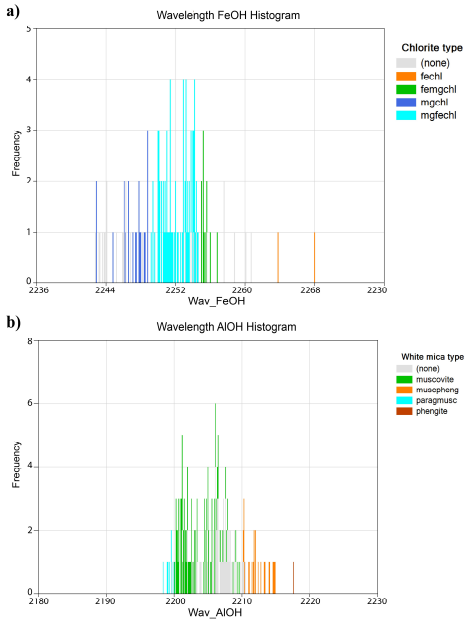

Fig. 1. Distribution of the wavelength (Wav) position of the FeOH absorption feature of chlorite (**a**) and the AlOH absorption feature of white mica (**b**), with respective inferred composition. Fe – iron, Mg – magnesium, chl – chlorite.

Such changes have been employed as vectors towards metallic ore deposits [11, 12]. Muscovitic tending to phengitic compositions were observed in the contact samples of some mineralized pegmatite dykes. Similarly, in the same locations, magnesium-bearing chlorites were observed near

the contact with the mineralized dykes. Nonetheless, phengite has been reported to form as a consequence of either metamorphism or hydrothermal alteration processes [11]. These chemical changes and their potential use for pegmatite exploration need to be correlated and validated by ongoing detailed mineral chemistry studies.

3.2. Correlation and cluster analysis

No moderate or strong correlations were observed between the element concentrations and the automatically retrieved spectral parameters. Only weak correlations ($0.3 < r < 0.5$) were observed for parameters such as the wavelength of the white mica AlOH absorption or of the MgOH absorption. Moreover, hierarchical clustering allowed grouping the 214 spectra into three clusters based on their spectral similarities (Fig. 2). However, there is no relation between the clusters identified and the Li, Rb and Cs concentrations. Nonetheless, it could be valuable to evaluate in the future, which spectral properties contributed the most for clustering and if they can be used for mineral or lithological discrimination.

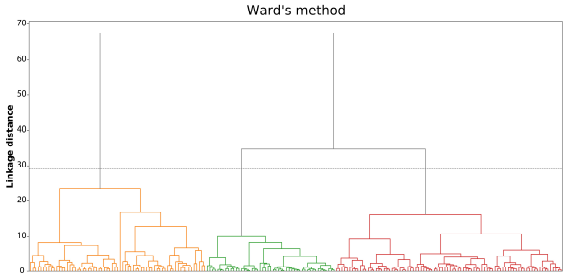

Fig. 2. Hierarchical clustering of the representative spectra.

3.3. PLSR modeling

It was not possible to obtain reliable predictions using the datasets without outliers. When removing samples with high CIA values, predictions improved all-around for Rb, and for Cs when considering SNV. The best results were obtained with the Shale dataset for Li and Rb, and with the Wacke dataset for Cs (Fig. 3). High overfitting, i.e., high R^2_{cal} but low R^2 in the prediction (R^2_{pred}), was observed for Li and Rb with the Wacke dataset, resulting in random predictions in some cases. This was also observed for Cs but in the Shale dataset instead. Since Li, Rb and Cs are expected to be incorporated in the same trap minerals (micas) of the host rocks, there is no current explanation for the distinct performances in the Wacke and Shale datasets. However, the results from the ongoing mineral chemistry studies should provide key insights on this matter. Regarding the type of spectral pre-processing (Fig. 3), the best results were obtained with the FD spectra considering the three Y variables (Fig. 4), since FD allows enhancing important absorptions while removing background noise. Comparing the measured and predicted compositions (Fig. 4), the most reliable results were obtained for Cs, being Li the most difficult element to model and predict based on spectral features. Plotting the regression coefficients as a function of the wavelength (Fig. 5) allowed identifying the most influential spectral regions for the PLSR models. In the case of Cs, spectral regions around 2200 nm and 1840 nm are positively related to predictions while the region around 2270 nm is negatively related. Such regions should be further investigated to evaluate if there is any absorption directly related to the presence of Cs. This information could also be used to develop satellite- or airborne-based remote sensing approaches for the detection of pegmatite halos. Li and Rb predictions are expected to improve with new geochemical data coming from the GREENPEG project, especially due to new sampling procedures of the host rocks.

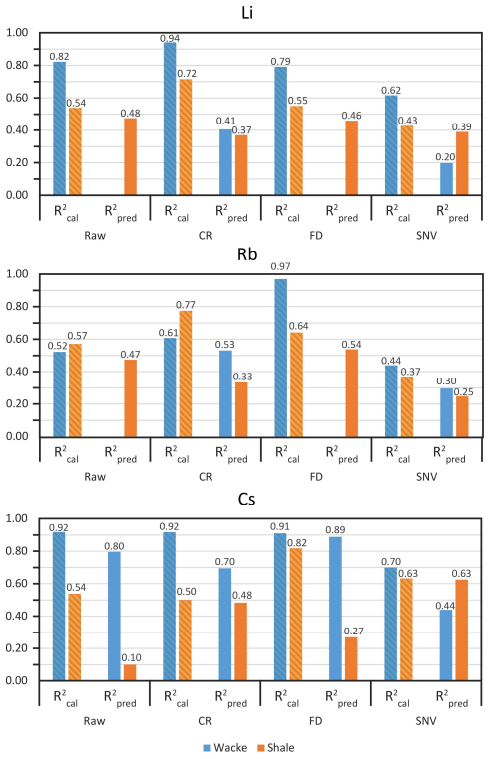

Fig. 3. Comparison of R^2_{cal} and R^2_{pred} values for Li, Rb and Cs with different spectral pre-processing for both datasets.

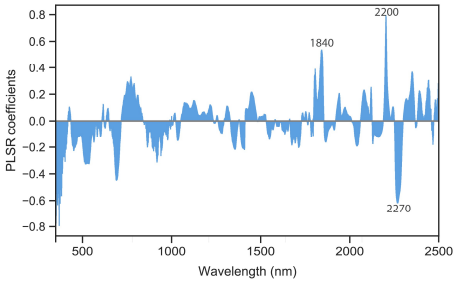

Fig. 5. PLSR coefficients of the Cs model (built on the Wacke dataset) as functions of wavelength.

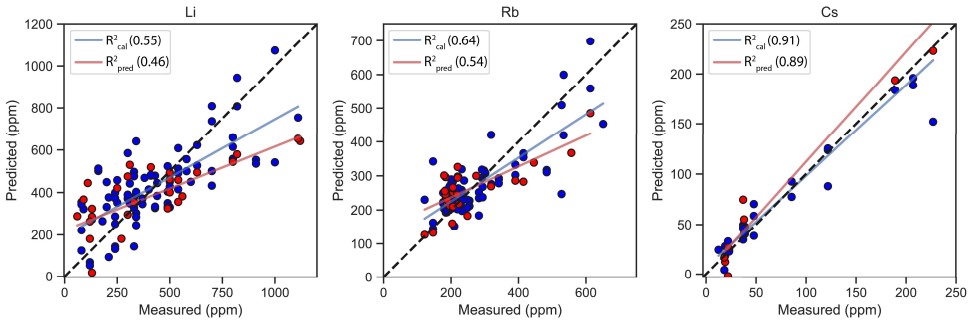

Fig. 4. PLSR models constructed using the Shale dataset for Li and Rb, and the Wacke dataset for Cs, while excluding outliers**.**

4. CONCLUSIONS

This study evaluates for the first time the potential use of hyperspectral data for the detection of chemical halos related to LCT pegmatites by exploiting data acquired under recent European projects. VNIR-SWIR spectra of the host rocks allowed to identify key minerals and respective mineralogical changes that can be further exploited to model and map hydrothermal alteration related to pegmatite emplacement. The understanding of these chemical changes will be improved with future integration of mineral chemistry. Clustering of the spectra based on similar properties could be useful for lithological or mineralogical discrimination. Finally, a first chemometric approach was employed with the PLSR, showing that lithological and weathering factors influenced the results. The correct spectral pre-processing was also determinant in the prediction, with the most reliable results obtained for Cs. The results will be improved in the future through newly acquired geochemical data. The GREENPEG project will build on the obtained results by proposing improved algorithms for LCT pegmatite halo detection. The results indicate that similar approaches could be attempted using AUV/airborne or satellite borne hyperspectral sensors, such as Mjolnir or PRISMA.

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