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Joana Cardoso-Fernandes, João Silva, Alexandre Lima, Ana Claudia C Teodoro, Monica Perrotta, et al.. Characterization of lithium (Li) minerals from the Fregeneda-Almendra region through laboratory spectral measurements: a comparative study. SPIE Remote Sensing, Sep 2020, Online Only, France. 10.1117/12.2573941 . hal-02969985

HAL Id: hal-02969985

<https://hal.science/hal-02969985>

Submitted on 17 Oct 2020

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Event: SPIE Remote Sensing, 2020, Online Only

Characterization of lithium (Li) minerals from the Fregeneda-Almendra region through laboratory spectral measurements: a comparative study

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ABSTRACT

Although several lithium (Li) bearing minerals have already been spectrally characterized, there are no current reference spectra for petalite in large and public access spectral libraries. This fact is aggravated by the difficulty in the identification of petalite's diagnostic features. The study area of this work is the Fregeneda (Spain) – Almendra (Portugal) region, where distinct Li bearing minerals occur in several types of enriched pegmatite dikes. Accordingly, the objectives delineated for this work were: (i) improve the existing knowledge on the spectral signatures of Li bearing minerals (lepidolite, spodumene, petalite); (ii) compare the spectra obtained for petalite and spodumene in the study area; (iii) and compare the spectra of the Li bearing minerals from the Fregeneda-Almendra area with the reference spectra from the United States Geological Survey (USGS), the ECOSTRESS and the Geological Survey of Brazil (CPRM) spectral libraries. For that, spectral measurements were conducted in the laboratory using the SR-6500A (Spectral Evolution, Inc.) spectrometer. The results only allowed to discriminate lepidolite, since that, both, petalite and spodumene, present absorption features typical of montmorillonite and illite, or a combination between these two minerals. This is also verified in samples of corresponding minerals in other spectral libraries. No diagnostic features of these two Li bearing minerals were identified, highlighting the difficulty to spectrally discriminate them from each other and from clay minerals.

Keywords: Geological exploration, remote sensing, reflectance spectroscopy, pegmatite, lithium

1. INTRODUCTION

Nowadays, satellite-based lithium (Li) exploration represents an emergent field with applications in Li brines and pegmatite-hosted hard rock Li deposits [1]. Most of the remote sensing data and techniques focus on the last type of deposit where the most common Li bearing minerals are spodumene (a Li bearing pyroxene), petalite (a Li bearing feldspathoid), and lepidolite (a Li bearing mica). However, there are no current reference spectra for petalite in large and public access spectral libraries such as the United States Geological Survey (USGS) [2] and ECOSTRESS [3] spectral libraries. Therefore, it is important to fill this gap and to develop new application studies. In the last decade, the Geological Survey of Brazil (CPRM) has been building a spectral library with a section specially dedicated to Li bearing minerals constantly updated and with more than 1500 reference spectra. However, they have experienced difficulties in the identification of petalite's diagnostic features [4].

The study area of this work corresponds to the Fregeneda (Spain) – Almendra (Portugal) region where distinct Li bearing minerals occur in rare-element enriched pegmatite dikes. In the region, several attempts to identify and map Li bearing pegmatites were made using several image processing techniques and employing different types of free satellite data [5-7].

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The results obtained are promising but can be improved through the acquisition of reference spectral data to use as a target. Taking this into consideration, the objectives of this work are: (i) improve the existing knowledge on the spectral signatures of Li bearing minerals; (ii) compare the spectra obtained for petalite and spodumene in the study area; (iii) and compare the spectral characteristics and diagnostic features of the Li bearing minerals from the Fregeneda-Almendra area with the reference spectra from the USGS, the ECOSTRESS and the CPRM spectral libraries.

1.1 The Fregeneda-Almendra area

The study area spreads from La Fregeneda in Spain to the Almendra parish in Portugal (Figure 1). In the region, both barren and rare-element pegmatite bodies were identified and classified into several types according to their distinct mineralogical, morphological, and structural properties [8, 9]. All the rare-element pegmatites were emplaced in pre-Ordovician metasediments of the Complexo Xisto-Grauváquico (CXG) [10] and show enrichment in Li, F, Sn, Rb, Nb>Ta, B, P and Be with increasing fractionation degree. The fractionation degree tends to increase with further distance to syn-Variscan Mêda-Penedono-Lumbrals granites of the Figueira de Castelo Rodrigo–Lumbrals Anatectic Complex [11]. Among the more evolved pegmatite dikes, there are four-types mineralized in Li [8, 9]: i) petalite-bearing dikes (exploited in the Bajoca mine), ii) spodumene-bearing dikes (exploited in the Alberto mine), iii) lepidolite-bearing dikes, and iv) lepidolite+spodumene-bearing dikes (exploited in the Feli mine) – Figure 1.

Figure 1. Geological setting of the Fregeneda-Almendra area (Spain-Portugal), adapted from [8, 12, 13]. The location of Li-rich dikes is highlighted. Map projection: Universal Transverse Mercator zone 29N, WGS84 datum.

2. METHODS

A spectral database was built with 12 samples of Li bearing minerals (including petalite, spodumene, and lepidolite) collected in different types of mineralized dikes, accounting for a total of 49 analyzed spots. Most of the samples were acquired in Bajoca, Feli, and Alberto mines (Figure 1). The remaining samples were acquired in other unexploited pegmatite dikes. In the end, the spectra were averaged according to the respective Li bearing mineral.

All spectral studies were conducted in the laboratory in a controlled lighting environment using a halogen bulb (4.25 V, 1.06 A). The employed spectroradiometer was the SR-6500A (Spectral Evolution, Inc.) that acquires information in the visible and near-infrared (VNIR) to the shortwave infrared (SWIR) spectral range (350-2500 nm) with ultra-high-resolution (1.5 nm @ 700 nm, 3.0 nm @ 1500 nm, 3.8 nm @ 2100 nm) – Figure 2. Before performing the spectral measurements, a Spectralon reflectance standard (from Labsphere) was used to calibrate the equipment.

Figure 2. Laboratory equipment used for spectral measurements. Spectroradiometer model: SR-6500A.

The arithmetic operations between spectra were performed using the SpectraGryph software [14]. The mean spectra of each Li bearing mineral were then normalized through the continuum removal (hull quotient) process using the *pysptools* library [15] for the Python programming language (Figure 3-a). The analysis and identification of the absorption features were made using both the SpectraGryph software and the *pysptools* library (Figure 3-b, c, d).

Figure 3. The continuum removal (hull quotient) process (a) and the extraction of the main absorption features (b-d) using the *pysptools* library. crs – continuum removed spectra; pts – points; FWHM – full width at half maximum.

Afterward, the obtained mean spectra of each Li bearing mineral was compared with the USGS and ECOSTRESS spectral libraries using the “spectral similarity” algorithm of SpectraGryph [16]. This algorithm calculates the Pearson correlation coefficient for the full-spectrum and returns the highest-rating matching reference spectra [16]. Also, the mean spectra obtained in this work were visually compared with the corresponding minerals from the CPRM spectral library.

3. RESULTS AND DISCUSSION

The graphic presented in Figure 4 shows the lepidolite, petalite, and spodumene+quartz mean spectral signatures. It was not possible to acquire an isolated spectrum of spodumene because it is intergrown with quartz. However, the diagnostic features of quartz do not occur in the VNIR-SWIR range [17, 18] and, therefore, should not have great interference in the overall resultant spectrum. Comparing both the petalite and spodumene signatures (Figure 4-a), it is easily understandable that the percentage of reflectance has an identical evolutive trend throughout the spectra. Starting by rapidly increasing and getting to the maximum percentages of reflectance in the first third of the spectrum (350 to 850 nm), for then initiate a decrease for the remaining wavelengths. Although they might seem to have the same trend, spodumene has a slightly more continuous trend after the initial increase, staying longer in the top reflectance percentages, showing only a decrease in the second half of the spectrum (1350 to 2500 nm) – Figure 4-a. In the case of lepidolite, the reflectance values increase more slowly in the VNIR region, with two gentle absorptions around ~550 nm and ~950 nm that are caused by its the purple color. The reflectance also drops after the absorption around ~1900 nm (Figure 4-a), but showing more peaks and troughs than spodumene and petalite.

The main absorption features were identified in Figure 4-b, and, as can be seen, the three Li bearing minerals present coincident features around ~1410 nm, ~1910 nm, and ~2200 nm. These absorption features are related to OH+H₂O, H₂O, and Al-OH, respectively [17, 19]. Despite this, it is possible to distinguish lepidolite from spodumene and petalite: the first shows narrow, symmetric absorption features at 1410 nm and 2196 nm, while petalite and spodumene show broader, asymmetric features around ~1413 nm and ~2207 nm (Figure 4-b). Also, lepidolite presents features characteristic of white mica such as the absorption around 2346 nm and 2433 nm (Al-OH secondary features), as well as a deeper Al-OH absorption feature when compared to the H₂O one [18, 20, 21]. The location of the main Al-OH feature at 2196 nm may point to higher Al contents [20, 21].

Figure 4. Raw (a) and continuum removed (b) mean reflectance spectra of the three Li bearing minerals: lepidolite, petalite and spodumene. The main absorption features were identified in the continuum removed spectra.

In what concerns the petalite and spodumene, and similarly to what happened with the raw spectra, the continuum removed spectra of both minerals is very similar, with visible noise present between 1610 nm and 1670 nm (Figure 4-b). The Al-OH feature in these minerals is much less pronounced than in lepidolite and the very deep absorption features around ~1910 nm indicate the presence of free molecular H₂O [22]. These are diagnostic features of the smectite group, probably montmorillonite since it is the only smectite that readily absorbs water from the air [19, 22]. The only main difference, of these two minerals spectral signatures, is the existence of shallow Al-OH secondary absorption features at

2352 nm and 2438 nm in the spodumene spectrum (Figure 4-b). This shows that besides montmorillonite, illite is also present. It was not possible to identify any diagnostic feature of petalite or spodumene, and their spectral signal is mostly dominated by the alteration minerals.

When comparing the raw spectra of the Li bearing minerals with the reference spectra from the USGS and ECOSTRESS spectral libraries (Table 1), the existence of clay minerals diagnostic features clearly influenced the results. Table 1 shows for each mineral the top 5 highest-rating spectral matches (hit percentage above 96.82%).

Table 1. Highest-rating matching reference spectra from the USGS and ECOSTRESS spectral libraries for each Li bearing mineral raw spectrum. The matches are presented by decreasing hit percentage.

Mineral	Spectral match USGS	Spectral match ECOSTRESS
Lepidolite	Endellite; Kaolinite; Illite; Halloysite; Dickite	Muscovite; Microcline; Lepidolite
Petalite	Saponite; Montmorillonite	Scheelite; Montmorillonite; Illite/smectite
Spodumene (with quartz intergrowths)	Montmorillonite	Illite/smectite; Montmorillonite

Most of the matches correspond to clay minerals or to white micas. The match of petalite with the ECOSTRESS's scheelite (calcium tungstate) reference spectrum is unexpected. For petalite and spodumene, both spectral libraries returned matches of montmorillonite reference spectra. In the case of lepidolite, the best matches were obtained in the ECOSTRESS spectral library (Table 1). Figure 5 shows the reference spectra of the USGS spectral library that matched the raw spectrum of lepidolite (Figure 5-a), petalite (Figure 5-b, -c), and spodumene (Figure 5-b). In the future, it would be important to assess the influence of the chosen matching algorithm in the spectral match results. Perhaps, a Li-mineral dedicated method could be developed using machine learning techniques.

Finally, the mean spectra of each Li bearing mineral were visually compared with the correspondent spectra of the CPRM spectral library. The same diagnostic features of clay minerals are present in the petalite and spodumene samples of the CPRM database. However, the lepidolite from the Fregeneda-Almendra area presents deeper H₂O features, while the spodumene does not show any of the iron absorption features that seem to be very common in the CPRM samples.

Figure 5. Reference spectra extracted from the USGS spectral library [2]. These spectra represent the top 5 highest-rating spectral matches with the lepidolite (a), petalite (b and c) and spodumene (b) from the Fregeneda-Almendra area.

4. CONCLUSIONS

In this study, a characterization of three different Li bearing minerals (lepidolite, petalite, and spodumene) was made through laboratory spectral measurements. It was only possible to discriminate lepidolite based on its spectral signature since the spectra obtained for spodumene and petalite were very similar. The analysis and interpretation of the results indicate that both the petalite and spodumene from the Fregeneda-Almendra area present absorption features typical of clay minerals such as smectite (characteristically montmorillonite) and illite, or a combination between both. No diagnostic features of these two Li bearing minerals were identified at this stage. The presence of clays' diagnostic features is also verified in samples of corresponding minerals in other spectral libraries. Taking this into account, all the objectives delineated for this work were accomplished.

Although detailed geological studies are needed to fully understand the obtained results, namely petrographic and geochemical analysis, this work may represent a relevant contribution to the field of spectroscopy studies of Li bearing minerals. The results highlight the difficulty to spectrally discriminate petalite and spodumene because they constantly show signs of alteration minerals. This could also difficult the discrimination of Li bearing minerals from clays through satellite remote sensing. Future studies will include spectral measurements of Li bearing minerals' alteration products currently being characterized using X-ray diffraction (XRD).

ACKNOWLEDGEMENTS

The authors would like to thank the financial support provided by FCT– Fundação para a Ciência e a Tecnologia, I.P., with the ERA-MIN/0001/2017 – LIGHTS project. The work was also supported by National Funds through the FCT project UIDB/04683/2020 - ICT (Institute of Earth Sciences). Joana Cardoso-Fernandes is financially supported within the compass of a Ph.D. Thesis, ref. SFRH/BD/136108/2018, by national funds from MCTES through FCT, and co-financed by the European Social Fund (ESF) through POCH – Programa Operacional Capital Humano. The Spanish Ministerio de Ciencia, Innovación y Universidades (Project RTI2018-094097-B-100, with ERDF funds) and the University of the Basque Country (UPV/EHU) (grant GIU18/084) also contributed economically. Odile Barrès is thanked for the help handling the spectroradiometer at Université de Lorraine (France).

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