Zircon and monazite texture and composition as fingerprints to establish their provenance in rare metal granite ore concentrates

Teresa Llorens González (1*), Teresa Sánchez García (2), Francisco Javier López Moro (1), Berta Ordóñez Casado (3), Susana Mª Timón-Sánchez (1), Alejandro Díez Montes (1)

(1) Centro Nacional Instituto Geológico y Minero de España (CN IGME-CSIC), 37001, Salamanca (España)
(2) Centro Nacional Instituto Geológico y Minero de España (CN IGME-CSIC), 28003, Madrid (España)
(3) Centro Nacional Instituto Geológico y Minero de España (CN IGME-CSIC), 28760, Tres Cantos(España)
* corresponding author: t.llorens@igme.es

Key Words: Monazite, Metamictic zircon, Greisen, Leucogranite, Acid fluids.

INTRODUCTION

The Penouta mine is currently the only active mine in Europe where Ta and Nb concentrates are obtained as a co-product of Sn concentrates. After several years reprocessing the old tailings dumps, the company Strategic Minerals Spain S.L. (SMS) obtained in 2022 the mining concession license of the primary deposit, consisting of an albitic leucogranite with Sn-Ta-Nb mineralization (Llorens González et al., 2017). The flowsheet of the processing plant mainly consists of classification, gravimetric concentration and high-intensity magnetic separation to obtain Sn and Ta-Nb concentrates (Nava et al., 2020). In addition to Sn and Ta-Nb oxides, other highly accessory heavy minerals are also concentrated, such as zircon and monazite, for which there is still little information. This contribution aims to show preliminary textural and compositional variations of these non-ore minerals, which can be useful to determine its granitic or mineralized metamorphic host provenance.

METHODS

The company SMS provided two samples of mineral concentrates from the leucogranite: (i) Sn concentrate and (ii) Ta-Nb concentrate, obtained in the Penouta processing plant. Both samples were studied under a stereoscopic microscope and zircon and monazite grains were handpicked, which were mounted in two different ways: 1/on glass slides and fixed with conductive carbon tape, and 2/ into an epoxy probe that was polished with diamond spray. Carbon coating of both preparations was performed to favor observation under high vacuum conditions. Textural and compositional study was carried out by a JEOL 6010 PLUS/LA scanning electron microscope (SEM) in the Applied Microscopy Unit of the Laboratories of the Geological and Mining Institute of Spain (IGME-CSIC), in Tres Cantos, Madrid. Operational conditions were 20 KV of acceleration voltage, magnification between x75 and x2300, 10-11 mm working distance and 50-60 spot size. Images of secondary electrons and backscattered electrons, as well as EDS analyzes and maps have been carried out. Semiquantitative analyzes were performed on them.

RESULTS AND DISCUSSION

Monazite grains were almost exclusively found in the Ta-Nb concentrate. They are generally less than 200 µm in size, rounded, yellow in color, with abundant dark microinclusions. SEM images show monomineralic grains, but also in association with xenotime and zircon. The vast majority of monazite grains show La-, Ce-rich compositions, with moderate LREE/HREE ratio, between 2.8 and 6.25, and HREE content between 14 and 26%. Only a few grains are enriched in Sm and Gd, with low LREE/HREE ratios, below 1.5, and up to 55% HREE. These findings are in agreement with López Moro et al. (2017), who discriminate two types of monazite depending on the host rock: (i) the monazite of the granite, with higher HREE contents, and (ii) the monazite typical of the greisenized metamorphic host rock (Ollo de Sapo augen gneiss), which is enriched in LREE. The great abundance of the latter suggests a strong influence of this type of alteration in the pit zone of the granite that was processed. Two types of zircon have been identified from the morphological, textural and compositional point of view: (i) elongated bipyramidal or acicular grains, typically needles up to 250 µm in length, generally colorless or with somewhat dirty

ISSN 2659-9864

appearance, with occasional dark inclusions and marked zoning under CL. They are mostly found in the Sn concentrate. Their chemical composition is marked by low HfO_2 contents, between 3 and 4.5 %, and ZrO_2/HfO_2 ratios between 11 and 21; and (2) elongated prismatic grains, less than 250 µm in length, pinkish in color, normally opaque, although occasionally some grains show slight internal zoning, especially in the rims, where they show some transparency and colorless zones. These are widely found in the Ta-Nb concentrate. SEM images of these zircon grains show a metamictic structure, dissolution textures and high porosity with cracks and common inclusions of other minerals, such as cassiterite and baddeleyite. Their composition is strongly enriched in HfO_2 (between 10.6 and 20.6%, average 17%) and U_3O_8 (average 4%), with a very low ZrO_2/HfO_2 ratio, between 2.2 and 3.7. Light gray areas with clean appearance show the highest HfO_2 content, in contrast to darker areas with slightly lower HfO_2 contents but significant CaO, ThO_2 and U_3O_8 impurities. López-Moro et al., (2017) already mentioned the presence of cloudy and porous zircon crystals disseminated throughout the granite, containing up to 16.6 wt. % HfO_2 in the upper levels, average U_3O_8 contents of 1.14 wt. % and ZrO_2/HfO_2 ratios ranging between 3 and 6. This Hf-rich composition of zircon is a common feature of extremely evolved granites (e.g., Huang et al., 2002; Van Lichtervelde et al., 2009), while those separated from the Sn concentrate show different textures and compositions, thus suggesting provenance from the greisenized metamorphic host. The metamictic appearance of the granite zircon in contrast to the greisen-derived zircon would probably be the result of: (i) the higher U content of the granite zircon grains; (ii) the more acidic conditions of the granite fluids, with Cl, Sn, and Be (López Moro et al., 2017) compared to the greisen fluids that would be diluted with metamorphic/meteoric waters, which would then decrease the acidity and dissolution capacity of zircon; and (iii) a combination of both.

CONCLUSIONS

The presence of two different types of monazite and zircon in the Sn and Ta-Nb concentrates from the Penouta mine suggests the existence of an important influence of the greisenized metamorphic host-rock, the Ollo de Sapo augen gneiss, on the mineralogy of the material that feeds the processing plant. In addition, the metamictic Hf-rich zircon grains of the granite support the highly acidic nature of the granite fluids in the Penouta leucogranite.

ACKNOWLEDGEMENTS

This work was made possible by the projects: i) FRAME, which is part of the GeoERA project (https://geoera.eu/) co-funded through the European Union's H2020 research and innovative programme under grant agreement Nº 731166, ii) MINCE, Strategic Raw Materials for the Energy and Digital Transition in Spain, financed by the National Bureau of Mines (MITERD). The JEOL 6010 PLUS/LA SEM has been partially financed by the European Regional Development Funds (FEDER), (Ref. IGME13-4E-1518). The authors acknowledge the kind collaboration of Strategic Minerals Spain S.L. for providing the studied samples.

REFERENCES

Huang, X.L., Wang, R.C., Chen, X.M., Hu, H., Liu, C.S. (2002): Vertical variations in the mineralogy of the Yichun topaz-lepidolite granite, Jiangxi province, Southern China. Can. Mineral., **40**, 1047–1068. DOI: 10.2113/gscanmin.40.4.

Llorens González, T., García Polonio, F., López Moro, F. J., Fernández Fernández, A., Sanz Contreras, J. L., Moro Benito, M. C. (2017): Tin-tantalum-niobium mineralization in the Penouta deposit (NW Spain): Textural features and mineral chemistry to unravel the genesis and evolution of cassiterite and columbite group minerals in a peraluminous system. Ore Geol. Rev., **81**, 79-95. DOI: 10.1016/j.oregeorev.2016.10.034.

López-Moro, F.J., García Polonio, F., Llorens González, T., Sanz Contreras, J.L.; Fernández Fernández, A., Moro Benito, M.C. (2017): Ta and Sn concentration by muscovite fractionation and degassing in a lens-like granite body: The case study of the Penouta rare-metal albite granite (NW Spain). Ore Geol. Rev., **82**, 10-30. DOI: 10.1016/j.oregeorev.2016.11.027.

Nava, J., Llorens González, T., Menéndez-Aguado, J (2021): Characterization, Classification, Dry High-Intensity Magnetic Separation (DHIMS), and Re-Grinding Techniques to Improve the Mineral Performance of a Sn-Ta-Nb Mineral Concentrate. Environ. Sci. Proc., 2021, **6**, 10. DOI: 10.3390/iecms2021-09344.

Van Lichtervelde, M., Melcher, F., Wirth, R. (2009): Magmatic vs. hydrothermal origins for zircon associated with tantalum mineralization in the Tanco pegmatite, Manitoba, Canada. Am. Mineral., **94**, 439–450. DOI: 10.2138/am.2009.2952.

ISSN 2659-9864