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# Petrology and geochemical modeling (Ba-W-Sn) of the Peña do Seo granitoids (West Asturian-Leonese Zone, León, Spain)

## *Petrología y modelización geoquímica (Ba-W-Sn) de los granitoides de Peña do Seo (Zona Asturoccidental-Leonesa, León, España)*

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## ABSTRACT

*The Cadafresnas granites and granitoid breccias (Peña do Seo, W of León) are small post-tectonic stocks of Variscan age related to W-Sn mineralizations. According to their mineralogical-geochemical characteristics, they are classified as granites-syenogranites, granodiorites and granitoids rich in quartz, of peraluminous/metaluminous composition. The Rb-Ba-Sr relationships allow assigning a metapelitic source for the granites and a metagreywacke source for the granitoid breccias. Using geochemical modeling (partial melting), the contribution of these sources to explain the Ba, W and Sn contents of the granites and granite breccias is investigated. The results indicate that the partial melting of these lithologies explains part of the content of these elements in the studied rocks, requiring additional processes of fractional crystallization and/or hydrothermal injections.*

**Key-words:** *Peña do Seo, granites, partial melting, geochemical modelling, dehydration.*

## RESUMEN

*Los granitos y brechas graníticas de Cadafresnas (Peña do Seo, O de León) son pequeños stocks post-tectónicos de edad Varisca relacionados con mineralizaciones de W-Sn. Por sus características mineralógico-geoquímicas se clasifican como granitos-sienogranitos, granodioritas y granitoides ricos en cuarzo, de composición peralumínica/metalumínica. Las relaciones de Rb-Ba-Sr permiten asignar una fuente metapelítica para los granitos y metagrauváquica para las brechas graníticas. Mediante modelización geoquímica (fusión parcial) se investiga la contribución de estas fuentes para explicar los contenidos de Ba, W y Sn de los granitos y brechas graníticas. Los resultados indican que la fusión parcial de estas litologías explica parte del contenido de estos elementos en las rocas estudiadas, siendo necesarios procesos adicionales de cristalización fraccionada y/o inyecciones hidrotermales.*

**Palabras clave:** *Peña do Seo, granitos, fusión parcial, modelización geoquímica, deshidratación.*

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## Introduction

Peña do Seo is a W-Sn vein-type ore deposit in the West-Asturian-Leonese Zone (WALZ, Fig. 1), associated with granites and granitoid breccias. These are late Variscan in age, and form part of the Boal-Los Ancares magmatic belt (289 ±3 Ma; Suárez, 1970a; Fernández-Suárez, 1994; Fernández-Suárez *et al*., 2000). Even though these igneous rocks are related to W-Sn ore deposits, recent detailed studies are lacking. In order to update their knowledge and study their origin and possible sources of its Ba, W and Sn, a petrological study and geochemical modeling were performed.

### *The granites and granitoid breccias*

The Cadafresnas post-Variscan granites are formed by K-feldspar (Kfs: 35 %), plagioclase (Pl: 25 %), quartz (Qtz: 20 %), muscovite (Ms: 10 %) ± biotite (Bt: 5-10 %) ± garnet (Grt: <2 %) ± altered cordierite (Crd: <2 %), with apatite and zircon as the main accessory minerals. Some of these granites are altered, with albite, sericite and pinnite.The granitoid breccias are composed of quartz (Qtz: 20%), K-feldspar (Kfs: 20%), muscovite (Ms: 25%), prehnite (Prh: 5%), fluorite (Fl: <5%) and cassiterite (Cst: <5%), with pyrite, a Pb-Bi-Ag sulfosalt, waylandite and native bismuth as accessories in the muscovite-sericite matrix. Sericite is found altering the K-feldspar. Both granites and granitoid breccias have a coarse-grained porphyritic texture (Caldevilla et al., 2023).

Calculated normative composition (Q: quartz, A: orthose, P: plagioclase) classifies the rocks as: monzogranites, syenogranites, alkali-feldspar granites and quartz-rich granitoids (Cadafresnas granites), and granodiorites, monzogranites and quartz-rich granitoids (granitoid breccias) (Fig. 2A).

According to the Rb/Sr vs Rb/Ba ratios of the studied rocks (Table I; Fig. 2B, after Sylvester, 1998), two different possible sources can be envisaged. The Cadafresnas granites, due to their elevated Rb/Sr, Rb/Ba and low CaO/Na$_2$O ratios, probably were derived from the melting of shales/metapelites. On the other hand, the lower Rb/Sr, Rb/Ba and elevated CaO/Na$_2$O ratios of the granitoid breccias are more compatible with compositionally intermediate metagreywackes as the most probable source (Caldevilla *et al*., 2023).

The Cadafresnas granites and the granitoid breccias show different contents in Ba (avg. 62 ppm in granites and 785 ppm

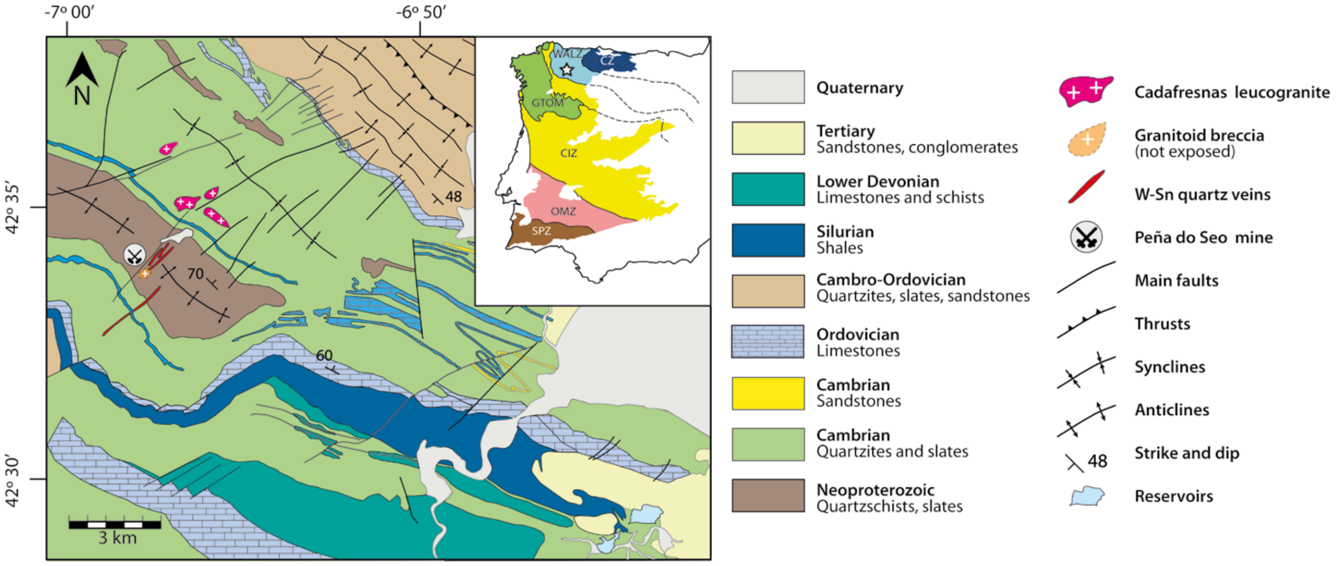

**Fig. 1. Simplified geological map of the Peña do Seo area, modified after Abril-Hurtado et al. (1981), and map of the different zones of the Iberian Variscan Massif, based on Julivert et al. (1972). WALZ: West Asturian-Leonese Zone; CZ: Cantabrian Zone; GTOM: Galicia-Trás-Os-Montes Zone; CIZ: Central-Iberian Zone; OMZ: Ossa Morena Zone; SPZ: South Portuguese Zone. The location of Peña do Seo mine is marked with a star, within the WALZ. Ver figura en color en versión web.**

*Fig. 1. Mapa geológico simplificado del área de Peña do Seo, modificado de Abril-Hurtado et al. (1981), y mapa de las distintas zonas del Macizo Varisco Ibérico, basado en Julivert et al. (1972). WALZ: Zona Asturoccidental-Leonesa; CZ: Zona Cantábrica; GTOM: Zona Galicia-Tras-Os-Montes; CIZ: Zona Centro-Ibérica; OMZ: Zona de Ossa Morena; SPZ: Zona Sudportuguesa. La ubicación de la mina Peña do Seo está marcada con una estrella, en la WALZ. See color figure on web.*

in granitoid breccias, Table I), W (avg. 43 ppm for granites and 25 ppm for granitoid breccias) and Sn (avg. 58 ppm for granites and 842 ppm for granitoid breccias). In order to investigate the possible role of these sources (metapelites, metagreywackes) for explaining such variable element contents, geochemical modeling with melting equations was performed.

## Geochemical Modeling

A non-modal batch melting equation is used to calculate the Ba, W and Sn contents in the melt: $C_L = C_0 / [D_0 + F(1-P)]$ (Zou, 2007 and references therein). $C_L$ is the concentration in the melt, $C_0$ is the initial element content, $D_0$ is the bulk distribution coefficient, P is the bulk dis-

|  | Ba | Rb | Sr | W | Sn |
|---|---|---|---|---|---|
| Granites (n=9) | 62 | 349 | 25 | 43 | 58 |
| Gr. Breccias (n=3) | 785 | 171 | 171 | 25 | 848 |

**Table I. Average contents (ppm) of Ba, Rb, Sr, W and Sn in the granites and granitoid breccias (Whole rock, Caldevilla et al., 2023).**

*Tabla I. Contenidos medios (ppm) de Ba, Rb, Sr, W y Sn de los granitos y las brechas graníticas. (Roca total, Caldevilla et al., 2023).*

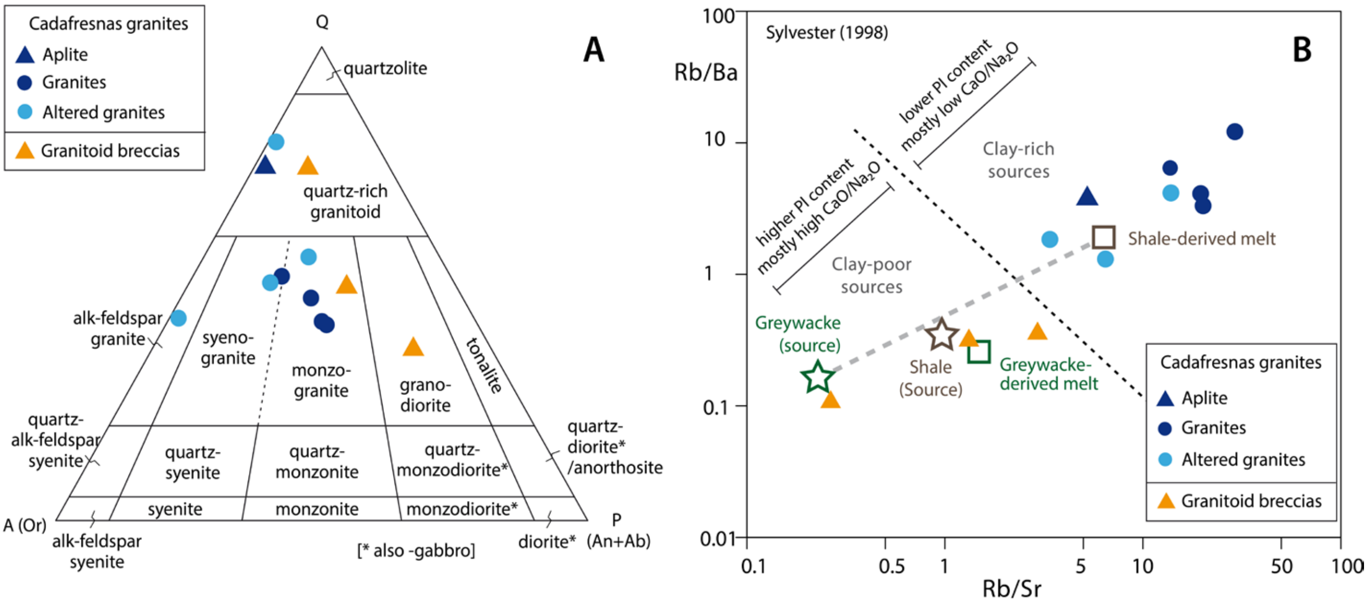

**Fig. 2. A) QAP (Q: Quartz, A: orthose, P: plagioclase) diagram of Streckeisen (1976). Most of the studied rocks have composition typical of granites and granodiorites. Some of them classify as quartz-rich granitoids due to their elevated content in SiO2. B) Rb/Ba vs. Rb/Sr diagram after Silvester (1998). Two magmatic pulses can be distinguished: i) Cadafresnas granites plot in the clay-rich source field and close to the pelite-derived melt. ii) The granitoid breccias are closer to clay poor rocks. See color figure on web.**

*Fig. 2. A) Clasificación QAP (Q: cuarzo, A: ortosa, P: albita+anortita) de Streckeisen (1976) para clasificar rocas ígneas saturadas en sílice. La mayoría muestran una composición Q-A-P típica de granitos y granodioritas. Algunas se clasifican como granitoides ricos en cuarzo dado su elevado contenido en SiO2.B) Diagrama Rb/Ba vs. Rb/Sr según Silvester (1998). Se pueden distinguir dos pulsos magmáticos: i) Los granitos de Cadafresnas se ubican en el campo de fuente rica en arcillas y cerca del fundido derivado de pelita. ii) Las brechas graníticas están más cerca de rocas pobres en arcilla. Ver figura en color en la versión web.*

| | $Kd_{Ms}$ | $Kd_{Bt}$ | $Kd_{Kfs}$ | $Kd_{Qtz}$ | $Kd_{Pl}$ | ppm in Ms | ppm in Bt | ppm in Kfs | ppm in Qtz | F | $X_{Ms}$ (melt) | $X_{Qtz}$ (melt) | $X_{Pl}$ (melt) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ba | 4.5 | 6 | 10 | 0 | 0 | 246.1 | 2133 | 9736 | 0.58 | 0.2 | 0.7 | 0.25 | 0.05 |
| W | 2 | 0.29 | 0.00255 | 0.0002 | 0 | 103.4 | 11.84 | 0.04 | 0 | 0.2 | 0.7 | 0.25 | 0.05 |
| Sn | 0.49 | 0.34 | 0.13 | 0.003 | 0 | 66.24 | 11.37 | 0.60 | 0.05 | 0.2 | 0.7 | 0.25 | 0.05 |

| Metapelite source | | | | Metagreywacke source | | | |
|---|---|---|---|---|---|---|---|
| $X_{Ms}$ | $X_{Bt}$ | $X_{Qtz}$ | $X_{Pl}$ | $X_{Ms}$ | $X_{Bt}$ | $X_{Qtz}$ | $X_{Pl}$ |
| 0.35 | 0.15 | 0.45 | 0.05 | 0 | 0.35 | 0.40 | 0.25 |

| Melt Fraction (F) | $C_0$ (Initial) | 0.01 | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.35 | 0.40 |
|---|---|---|---|---|---|---|---|---|---|
| MP Ba (ppm) | 406 | 166 | 172 | 180 | 189 | 199 | 210 | 222 | 236 |
| MG Ba (ppm) | 747 | 361 | 385 | 419 | 461 | 511 | 574 | 655 | 762 |
| MP W (ppm) | 38 | 51 | 52 | 54 | 56 | 57 | 59 | 61 | 63 |
| MG W (ppm) | 4 | 38 | 29 | 23 | 19 | 16 | 14 | 12 | 11 |
| MP Sn (ppm) | 25 | 108 | 97 | 86 | 77 | 70 | 64 | 59 | 55 |
| MG Sn (ppm) | 4 | 31 | 25 | 20 | 17 | 15 | 13 | 11 | 10 |

**Table II. Mineral/melt partition coefficients (KdMs, KdBt, KdKfs, KdQtz, KdPl), Ba, W and Sn contents in the minerals (Michaud et al., 2021) and phases contributing to the melt (XMs, XQtz, XPl). Kd's for Ba, W and Ms from Icenhower and London (1995), Ewart and Griffin (1994), and Pichavant et al. (1988). Ba, W and Sn contents at different fractions of melting for the two models used. MP: metapelite protolith; MG: metagreywacke protolith. F: melt fraction, X: percentage contribution of mineral to melt.**

*Tabla II. Coeficientes de partición mineral/fundido (KdMs, KdBt, KdKfs, KdQtz, KdPl), contenido de Ba, W y Sn en los minerales (Michaud et al., 2021) y fases que contribuyen al fundido (XMs, XQtz, XPl). Kd para Ba, W y Ms de Icenhower y London (1995), Ewart y Griffin (1994) y Pichavant et al. (1988). Contenidos en Ba, W y Sn en las diferentes fracciones de fundido para los dos modelos. MP: protolito metapelítico; MG: protolito metagrauváquico. F: fracción de fundido, X: porcentaje contribución de cada mineral al fundido.*

tribution coefficient for the phases that contribute to the melt and F is the melt proportion (F = 1-40%) (Tables I and II). The value of the initial bulk partition coefficient, $D_0$, is given by $\Sigma(x_i \cdot Kd_i)$ where $x_i$ is the modal abundance of each mineral phase and Kd is the corresponding partition coefficient. We modeled two different sources; (1) metapelite (Fig. 3A), and (2) metagreywacke (Fig. 3B).

## Results

### *Metapelite source*

In this model we consider the Ms dehydration melting: Ms + Qtz + Pl = melt + Kfs + Sill, in a metapelite with 35% Ms + 15% Bt (+ 45% Qtz + 5% Pl). Ms dehydration can generate 20% of melt and its contribution to the melt can be about 70%. Qtz and Pl would contribute 25% and 5% respectively (Zhao *et al*. 2021). Contents of Ba, W and Sn for the different minerals, together with the mineral/melt partition coefficients (Kd) are shown in Table II. The calculated $C_L$ contents are: Ba 166-236 ppm, W 51-63 ppm and Sn 108-55 ppm with increasing melt fractions (Table II, Fig.3A).

We also applied the model to an ini-

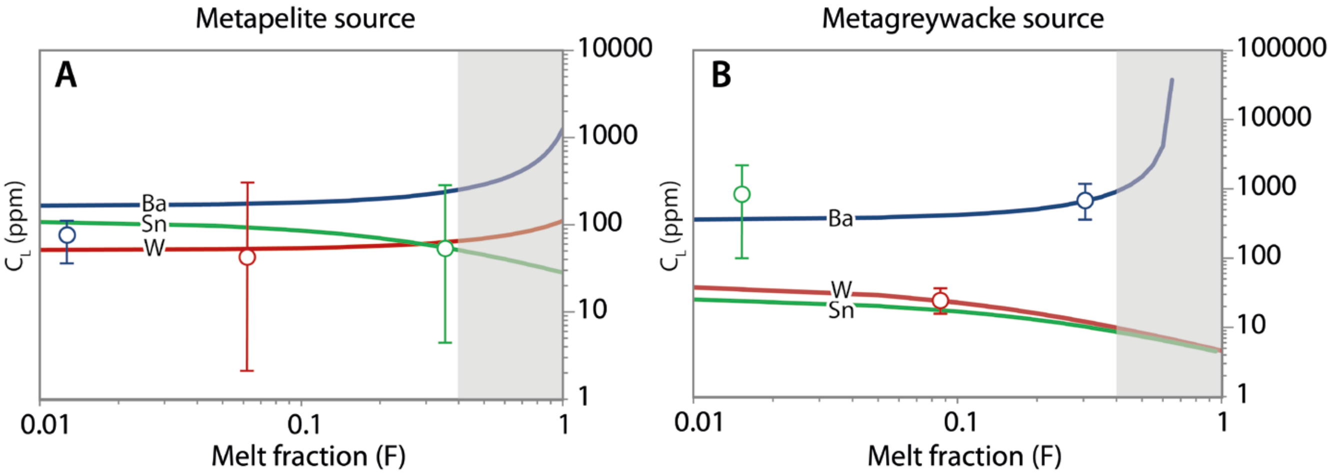

**Fig. 3. Results of the melting models (equilibrium batch non-modal) for Ba, W and Sn (lines). A) Model using a metapelite as source. B) Model using a metagreywacke as source. Gray area indicates melt fraction >40%, very rare in natural conditions. W,Sn and Ba contents observed in granites can be reached by melting of a metapelite (modeled contents of Ba are even higher than observed). W and Ba contents in granitoid breccias can be reached by melting of a metagreywacke, but Sn contents are higher than modeled, suggesting the involvement of other processes. Whiskers indicate the maximum, minimum and average (circles) Ba, W, and Sn contents in the granites (metapelite source, A), and granitoid breccias (metagreywacke source, B). See color figure on web.**

*Fig. 3.- Resultados de los modelos de fusión (batch en equilibrio no modal) para Ba, W y Sn (líneas). A) Modelo utilizando una fuente metapelítica. B) Modelo utilizando una fuente metagrauváquica. El área gris indica que fracciones de fundido >40% son muy poco frecuentes en condiciones naturales. Los contenidos de W, Sn y Ba observados en los granitos pueden alcanzarse mediante la fusión de una metapelita (los contenidos en Ba del modelo son incluso más altos que los observados) Los contenidos de W y Ba en las brechas graníticas se pueden alcanzar mediante la fusión de una metagrauvaca, pero los contenidos de Sn son extremadamente más altos que los obtenidos por el modelo, lo que sugiere la participación de otros procesos. Los whiskers indican el contenido máximo, mínimo y medio de Ba, W y Sn (círculos) en los granitos (fuente metapelítica, A) y las brechas graníticas (fuente metagrauváquica, B). Ver figura en color en la versión web..*

tial composition of the Villalba metapelitic schists, host of the W-Sn quartz veins, and obtained similar results to those described above.

*Metagreywacke source*

In this second model we consider the Bt dehydration melting: Bt ± Sill + Qtz = Opx/Grt/Crd + Kfs + melt, in a metagreywacke with ≈ 35% Bt (+ 40% Qtz + 25% Pl; Johnson *et al*., 2008; Devaraju *et al*., 2010). Bt dehydration can generate 25% of melt and its contribution to the melt can be about 70%. Qtz and Pl would contribute 25% and 5% respectively (approximations based on Johnson *et al*., 2008). Ba, W and Sn contents in Bt and Kd's are shown in Table II. The results of the modelling (calculated $C_L$ values) are: Ba 361-762 ppm, W 38-11 ppm and Sn 31-10 ppm with increasing melt fractions (Table II, Fig. 3B).

## Conclusions

The calculated melts derived from the metapelitic sources are similar to the Cadafresnas granites for W (2-306 ppm, avg. 43 ppm) and Sn (4-300 ppm, avg. 58 ppm), but not for Ba (14-112 ppm, avg. 76 ppm). The higher Ba contents calculated require either fractionation to reproduce the lower Ba content of the granites or a different initial Ba content; the latter being the favored option.

The calculated melts from the metagreywacke source are similar to the granitoid breccias in W (15-39 ppm, avg. 25 ppm, Table I) and Ba (381-1140 ppm, avg. 785 ppm, Table I). Regarding Sn, its content in the granitoid breccias is highly variable (97-2320 ppm, avg. 848 ppm, Table I), and much higher than values obtained from this model (31-10 ppm, Table II). The measured Sn and the highest Ba contents need an external hydrothermal fluid input to reach such elevated amounts.

## Author contributions

Paper structure: PC, LGM; methodology: PC, LGM, AL; data acquisition: PC, LGM, FGF; editing: PC, LGM, AL; figures: PC, LFM; manuscript review: LGM, FGF, AL, AMC, research/analysis: PC, LGM, FGF, coordination and supervision: LGM, FGF, AMC.

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## References

Abril-Hurtado, J., Matte, P. and Rodríguez-Fernández, L.R. (1981). *Memoria de la Hoja nº 157 (Oencia). Mapa Geológico de España E 1:50.000. Segunda Serie (MAGNA), Primera Edición*. IGME, Marid, 48 p.

Caldevilla, P., González- Menéndez, L., Martín-Crespo, T., Vindel, E., Guedes, A., Berrezueta, E., Castañón-García, A.M. and Gómez-Fernández, F. (2023). *Ore Geology Reviews*, 155, 105361. https://doi.org/10.1016/j.oregeorev.2023.105361

Devaraju, T. C., Sudhakara, T. L., Kaukonen, R.J., Viljoen R. P., Alapieti T. T., Ahmed, S. A. and Sivakumar, S. (2010). *J. Geol. Soc. India*, 75, 465-487. https://doi.org/10.1007/s12594-010-0050-8

Fernández-Suárez, J. (1994). *Petrología de los granitos peralumínicos y metamorfismo de la banda Boal-Los Ancares*. PhD thesis, Departamento de Geología, Univ. of Oviedo, 418 p.

Fernández-Suárez, J., Dunning, G., Jenner, G.A. and Gutierrez-Alonso, G. (2000). *Journal of the Geological Society*, 157, 565-576. https://doi.org/10.1144/jgs.157.3.56

Ewart, A. and Griffin, W.L. (1994). *Chemical Geology*, 117, 251-284. https://doi.org/10.1016/0009-2541(94)90131-7

Icenhower, J. and London, D. (1995). *American Mineralogist*, 80, 1229-1251. https://doi.org/10.2138/am-1995-11-1213

Johnson, T.E., White, R.W. and Powell, R. (2008). *J. Met. Geol.*, 26, 837-853. https://doi.org/10.1111/j.1525-1314.2008.00790.x

Michaud, J.A-S., Pichavant, M. and Villaros, A. (2021). *Contributions to Mineralogy and Petrology*, 176, 96. https://doi.org/10.1007/s00410-021-01855-9

Pichavant, M., Kontak, D., Briqueu, L., Valencia Herrera, J. and Clark, A. H. (1988). *Contrib. Miner. Petrol*. 100:325–338. https://doi.org/10.1007/BF00379742

Streckeisen, A. (1976). *Earth Sci. Rev.* 12, 1-33.

Suárez, O. (1970). *Studia geologica salmanticensia*, ISSN 0211-8327, Vol. 2, pp. 93-113.

Sylvester, P.J. (1998). *Lithos*, 45, 29-44. https://doi.org/10.1016/S0024-4937(98)00024-3Zhao

P., Chu, X., Williams-Jones, A.E., Mao, J. and Yuan, S. (2021). *Geology*, 50, 1, 121-125. https://doi.org/10.1130/G49248.1

Zou, H. (2007). *Quantitative Geochemistry*. Imperial College Press, London, 287 p.