Lithogeochemical exploration in a Hercynian Tin-Bearing Batholith in the Northwest of the Iberian Peninsula

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ABSTRACT

This work presents the results of a multi-element lithogeochemical study of the Hercynian Batholith of Ricobayo (Zamora, NW Spain). Several tin deposits are genetically associated with this batholith.

Probability plots have been used to prepare contour maps of SiO₂, Fe₂O₃, Na₂O, K₂O, CaO, MgO, Rb, Sr and Zr. The geochemical patterns of CaO reflects tin-bearing areas and may therefore indicate tin-target areas associated with this type of granite.

Key words: Lithogeochemical exploration. Tin, Calcium. Granite. Iberian Massif.

RESUMEN

El Batolito hercínico de Ricobayo, al que se encuentran asociadas genéticamente mineralizaciones de estaño, ha sido objeto de un estudio litogeoquímico con el fin de comprobar la efectividad de tales metodos en la exploración de áreas con mineralizaciones de estaño.

Tomando como referencia las rupturas de pendiente que muestran las distribuciones de SiO₂, Fe₂O₃, Na₂O, K₂O, CaO, MgO, Rb, Sr y Zr en los correspondientes gráficos probabilísticos, se ha procedido a determinar los mapas de isocontenidos de tales elementos en el Batolito de Ricobayo. La distribución de CaO es la única que refleja las áreas con mineralizaciones de estaño y puede utilizar-se como indicadora de las áreas de potencial interés asociadas a este tipo de granitos.

Palabras clave: Exploración litogeoquímica. Estaño. Calcio. Granito. Macizo Ibérico.

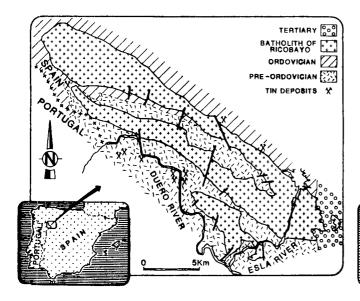
INTRODUCTION

The aim of this work was to ascertain whether the major and trace element distributions in a tin-bearing granite might indicate tin-target areas for more detailed prospecting surveys. In order to carry out this study lithogeochemical data of the Ricobayo Batholith (Zamora, NW Spain) were used.

The Ricobayo Batholith is located in the valley of Duero River to the west of the town of Zamora (Spain) in the northwest of the Iberian Peninsula. Geologically, this batholith is situated near the northern boundary of the Central Iberian Zone of the Hercynian Iberian Massif. The Ricobayo Batholith is rectangular in shape and 45 x 8 Km in extension (Fig. 1). The morphology is related to an emplacement that is conditioned by WNW-ESE Hercynian regional structures, especially by the Villadepera antiform and a regional shear zone.

The Ricobayo Batholith is composed of two mica granite, muscovite granite and biotite-cordierite granite. The third type only appears in a small area (about 1 $\rm Km^2$) in the central part of the batholith. These granites are essentially syntectonic with respect to the third phase of the Hercynian orogeny which resulted in a generalised orientation of their minerals and shear structures (especially in the northern part of the batholith). The age of these granites is 324 ± 12 m.y. (Toros, 1981).

These granites intruded materials of Pre-Ordovician Metamorphic Series of Duero and Ordovician



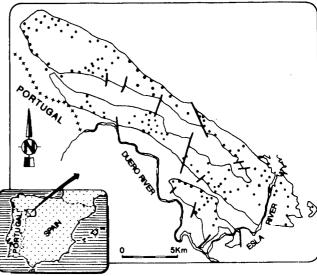


Figure 1. Geological map of the region studied in the province of Zamora (Spain).

Figura 1. Mapa geológico de la región estudiada en la provincia de Zamora (España).

Figure 2. Sample locations in the Ricobayo Batholith.

Figura 2. Localización de las muestras tomadas en el Batolito de Ricobayo.

Series of Cerezal de Aliste (Fig. 1). The Pre-Ordovician series consists of metasedimentary rocks (essentially schists) and materials with a volcano-sedimentary affinity, whereas the Ordovician series are composed of quartzite and schist.

SAMPLING AND ANALYTICAL METHODS

Granites from 139 locations in the Ricobayo Batholith were sampled (Fig. 2), which represented a mean sampling density close to 1 sample / 3 Km². Between 5 and 10 Kg of rock over an area of 100 m² were taken from each location.

The entire sample was crushed, split and ground using Ni-Cr steel equipment. After a HF - HNO₃ - HCl sample decomposition, SiO₂ and P₂O₅ were determined by colorimetry and Al₂O₃, Fe₂O₃, Na₂O, K₂O, CaO and MgO by atomic absorption spectrometry. Rb, Sr, Ba, Zr, Sn, W and TiO₂ were analysed by X-ray fluorescence spectrometry. Analytical methods are described in Garcia and Saavedra (1983).

RESULTS

The major and trace elements used in this study were selected on account of their significant petrogenetic variations in the Ricobayo Batholith (Fernández-Turiel, 1987). Ba, Sn and W were not used since most of their values were below the detection limits (10, 15 and 50 ppm respectively). Arithmetic mean, standard deviation, minimum and maximum concentrations of elements considered for the different granitic types of the batholith are shown in Tables I to III.

Their contour maps were made automatically using the optimal triangulation method (algorithm of Sheppard, 1968) which only uses measured locations.

The surface variations of geochemical parameters studied are displayed on the contour maps in Figs. 3 to 5. The value intervals were inferred from breaks in the slope of the respective probability plots (Sinclair, 1976, Cardoso-Fonseca and Santos-Oliveira, 1977, and Tuach et al., 1986). The major element cumulative frequency distributions suggest that they are normal and that the trace element distributions are lognormal.

Table I. Two mica granite (88 samples).

Table I. Granito de dos micas (88 muestras).

Table II. Muscovite granite (43 samples)

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Tabla II. Granito moscovítico (43 muestras)

	arithmetic mean	standard deviation	minimum	maximum
SiO,	74.46	2.06	67.09	79.52
Al,Ô,	12.94	1.70	9.48	19.67
Fe,O,	1.85	0.40	1.15	2.65
MgO	0.27	0.15	0.01	0.65
CaO	0.45	0.15	0.01	0.89
Na,O	3.80	0.59	1.85	5.10
K,Ô	4.63	0.62	2.44	6.46
TiO,	< 0.10		< 0.10	0.31
P,O,	0.24	0.07	0.01	0.43
MnÓ	0.02	0.01	0.01	0.06
LOI	1.25	0.24	0.68	1.79
Rb	327	59 .	238	480
Sr	52	24	16	114
Ba	126	170.	< 50	748
Sn	<10	_	<10	125
W	<15	_	<15	79
Zr	62	26	27	124

75.41 12.58 1.40	1.32 1.14	72.73	78.54
	1.14		
1.40		9.89	15.08
	0.39	0.85	2.36
0.19	0.07	0.07	0.36
0.28	0.11	0.01	0.53
4.27	0.54	2.80	5.30
4.29	0.61	3.46	6.06
< 0.10	_	< 0.10	0.16
0.20	0.06	0.01	0.31
0.02	0.01	0.01	0.04
1.30	0.25	0.90	2.01
10	100	257	702
37	19	14	91
50	_	<50	262
10	_	<10	66
15	_	<15	44
4.4	14.00	25	87
	0.02 1.30 10 37 50	0.02 0.01 1.30 0.25 10 100 37 19 50 - 10 - 15 -	0.02 0.01 0.01 1.30 0.25 0.90 10 100 257 37 19 14 50 - <50

Major oxides in %; trace concentrations in ppm.

Major oxides in %; trace concentrations in ppm.

The most striking features of the contour maps may be summarised as follows:

- a) Fe₂O₃, SiO₂, Na₂O, MgO, CaO, Sr y Zr (Fig. 3 to 5) present systematic variations but their patterns do not, in general, coincide exactly with one another. The highest values are in two areas in the inner part of the batholith, with the exceptions of SiO₂ and Na₂O which have the lowest values in this part.
- b) K₂O and, especially, Rb (Figs. 3 and 4) present relatively irregular and erratic surface distributions.
- c) Only the surface variation of CaO (Fig. 5) appears to be associated with the tin-bearing areas. The granites near the areas with tin deposits have amounts of CaO which do not exceed 0.30 %.

As a petrogenetic model for the Ricobayo Batholith, Fernández-Turiel (1987) suggested that the process of convective fractionation (Sparks et al., 1984) is the one that best suits the characteristics observed in these granites. This magmatic process produces a

crystal-liquid differentiation and induces an upwelling of lower density fluids rich in volatiles, K, Na and Sn towards the roof zone of the magmatic chamber. In such zones, these fluids give rise to deuteric phenomena that produce an alkali metasomatism and lixiviation of elements such as Ca and possibly Sn. Assisted by fracturation processes, these fluids migrate towards metasedimentary regional host rocks where changes of thermodynamic conditions originate the tin mineralization. The mineral parageneses observed in the Ricobayo granites (Fernández Turiel, 1987) suggest that the magma is formed at a pressure exceeding 7 Kb and that it reaches its emplacement in a relatively shallow cortical level (pressures of 1.5 to 1 Kb) where the magmatic processes finish and the deuteric alteration processes (microclinization, chloritization, albitization, muscovitization, tourmalinization and garnetization) start. It should be pointed out that the deuteric activity is especially pervasive in the granites studied due to the fact that the erosion level coincides with the roof of the batholith (Fernández-Turiel, 1987).

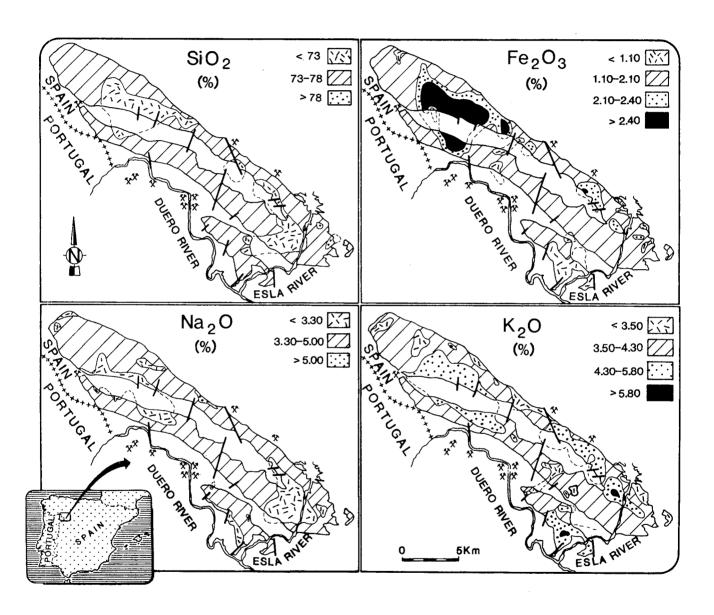


Figure 3. Distribution of SiO_2 , Fe_2O_3 , Na and K_2O in the Ricobayo Batholith.

Figura 3. Distribución de SiO₂, Fe₂O₃, Na y K₂O en el Batolito de Ricobayo.

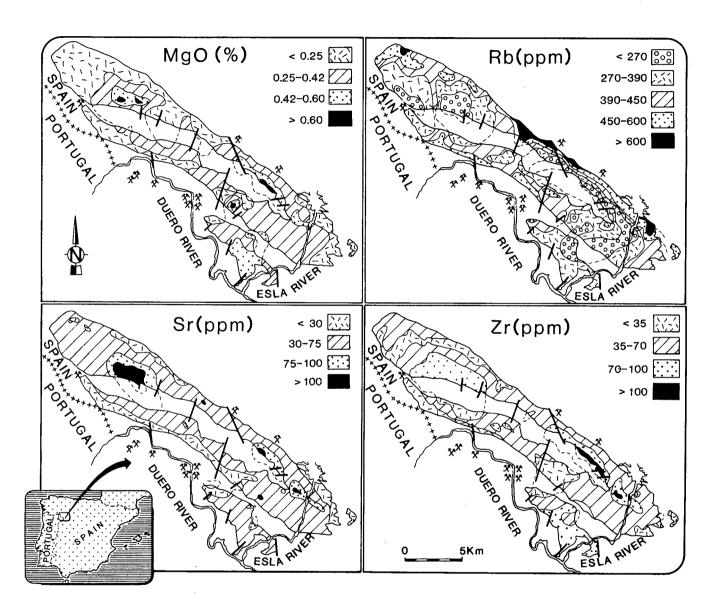


Figure 4. Distribution of MgO, Rb, Sr and Zr in the Ricobayo Batholith.

Figura 4. Distribución de MgO, Rb, Sr y Zr en el Batolito de Ricobayo.

Table III. Biotite-cordierite granite (8 samples).

Tabla III. Granito biotítico con cordierita (8 muestras).

	arithmetic mean	standard deviation	minimum	maximum
SiO,	67.36	1.17	66.41	70.01
Al,Õ,	15.79	0.83	13.85	16.51
Fe ₂ O ₃	3.50	0.17	3.32	3.75
MgO	0.58	0.15	0.21	0.70
CaO	1.18	0.18	0.80	1.37
Na ₂ O	3.60	0.29	3.25	4.00
K,Ö	5.89	0.25	5.45	6.29
TiO ₂	0.14	0.09	< 0.10	0.25
P_2O_5	0.33	0.08	0.25	0.46
MnO	0.02	0.01	0.01	0.04
LOI	1.13	0.34	0.87	1.88
Rb	244	11	224	262
Sr	137	6.	127	146
Ba	1111	139	938	1405
Sn	<10	_	<10	<10
W	_	_	<15	80
Zr	141	11	126	160

Major oxides in %; trace concentrations in ppm.

The observed granitic variations towards less evolved terms from the outer to the inner part of the batholith (decrease in SiO₂ and Na₂O, increase in Fe₂O₃, MgO, Sr and Zr) must be related to the magmatic differentiation of the plutonic complex. Thus, it may be suggested that the circular patterns observed in the central part of te batholith for Fe₂O₃, MgO, SrO and Zr (Figs. 3 and 4) may reflect areas of magma upwelling (cf. eg., patterns of Ackley granite; Tuach et al., 1986).

Moreover, the geochemical surface variations (Figs. 3 and 4) of K_2O and Rb cannot be attributed solely to magmatic mechanisms and it is necessary to take into account the post-magmatic deuteric activity of a volatile phase rich in alkalis wich significantly changes the magmatic patterns. In this case, the distribution of K_2O and Rb has been essentially modified by the microclinization and the muscovitization which are the most marked alterations undergone by the Ricobayo granites.

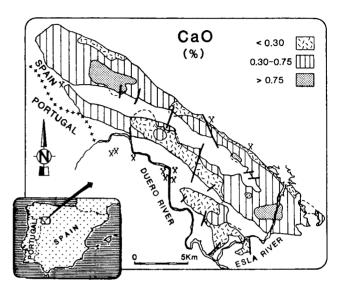


Figure 5. Distribution of CaO in the Ricobayo Batholith.

Figura 5. Distribución de CaO en el Batolito de Ricobayo.

CONCLUSIONS

The lithogeochemical exploration carried out in the Ricobayo Batholith using a sampling density of 1 sample / 3 Km² has proved to be of interest from the methodological point of view. The surface variations of CaO correlate with the tin-bearing areas in the zone studied. However, SiO₂, Fe₂O₃, Na₂O, K₂O, MgO, Rb, Sr and Zr define surface variations which do not display clear associations although they may be related to petrogenetic processes such as magmatic sensu stricto and post-magmatic deuteric alterations.

These results suggest that the lithogeochemical exploration may be considered in the definition of tintarget areas associated with the numerous tin-bearing granitic batholiths which have characteristics that are similar to the one studied.

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REFERENCES

- CARDOSO-FONSECA, E.M., SANTOS-OLIVEIRA, J.M., 1977: Aplicações da analise estatística univariada a prospecção litogeoquímica de mineralizações estanníferas. Comunic. Serv. Geol. Portugal, 62: 161 181.
- FERNÁNDEZ-TURIEL, J.L., 1987: Aspectos geológicos y metalogenéticos del Batolito de Ricobayo y del Complejo de Villaseco-Pereruela y sus mineralizaciones estanníferas asociadas. Tesis doctoral, Universidad de Barcelona, 307 pp.
- GARCÍA, A. and SAAVEDRA J., 1983: Datos analíticos sobre cuatro patrones geoquímicos de Salamanca (granitos s.l.) y técnicas utilizadas. An. CEBAS-IOATO, 9: 331-333.
- SHEPPARD, D., 1968: A two dimensional interpolation function for irregularly spaced data. *Proc. 23rd Nat. Conf. ACM*.
- SINCLAIR, A.J., 1976: Application of probability graphs in mineral exploration. Assoc. Explor. Geochem., Spec. Vol. 4, 95 pp.

- SPARKS, R.S.J., HUPPERT, H.E., TURNER, J.S., 1984: The fluid dynamics of evolving magma chambers. *Phil. Transact. R. Soc.* London, A 310: 511-534.
- TOROS, M., 1981. Les granitoïdes et les gîtes d'étain associés dans leur contexte lithostratigraphique et metamorphique a l'Ouest de Zamora (Massif Hespérique, Espagne). Thesis, University of Lausanne, 216 pp.
- TUACH, J., DAVENPORT, P.H., DICKSON, W.L., STRONG, D.F., 1986: Geochemical trends in the Ackley granite, southeast Newfoundland: their relevance to magmatic-metallogenic processes in high-silica granitoid systems. Can. J. Earth Sci., 23: 747-765.

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