Dating of gold-bearing skarns and intragranitic mineralizations in the Central Pyrenees. A new approach to thematic mapping.

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Introduction

The structure of the Pyrenees is built up around an "axial zone" of antiformal stacks that involve pre-hercynian basement rocks and that result from the superimposition of the Hercynian (late Carboniferous) and Alpine (Eocene - Oligocene) orogenic events. The Paleozoic rocks of the Central Pyrenees show several late- and post-kinematic Hercynian granites that intrude into Cambro-Ordovician to Devonian sediments (Fig. 1). The granites are locally associated with subeconomic gold-bearing skarn deposits (Soler, 1990; Soler et al., 1990; Delgado, 1993; Palau, 1995; Palau et al., 1995). Several intragranitic alterations, that can be classified by endogreissens (Kwack, 1987) are found spatially related with the gold-bearing skarns (Soler, 1990; Soler et al., 1990; Delgado, 1993; Espínola et al., 1996).

The purpose of the present work is to show the temporal relation between the gold-bearing skarns, the intragranitic alterations and the granitic rocks. The knowledge of this temporal relation is fundamental to point out the genetic relation between the different types of mineralizations enclosed or related to granites, and consequently is important in order to define a metallotec in the regional metallogenetic maps. Hence, we studied the ore deposits related to four late-hercynian granites from the Pyrenees (Maladeta, Marimanya, Sta. Coloma and Andorra-Mont Lluis) (Fig. 1).

Analytical procedure

The K content of mineral concentrates was measured by X-ray fluorescence and ICP-MS calibrated with eight International Standard rocks and minerals chosen specially for this purpose. Both standards and samples were mixed with lithium tetraborate at 1:120 ratio and fused in a platinum crucible. This high dilution ratio minimises greatly the matrix effects. All pearls were made by quadruplicate and measured with a Philips 6000 X-ray Spectrometer giving a precision and accuracy better than 2 %. Samples with low K content were measured using ICP-MS.

Isotopic analysis of argon was carried out by total fusion of approximately 30 mg of

sample in a high-vacuum electric furnace, using a molibdenum crucible. The resultant gas was mixed with pure ^{38}Ar spike, to apply the isotopic dilution technique. Measurements were done in static mode with an AEI MS-10S spectrometer fitted with a permanent magnet of 4.1 kG. Analytical precision on ^{40}Ar and ^{38}Ar peaks was near 0.05% and on ^{36}Ar was 1%. All the calculations were done using the constants recommended by Steiger and Jäger (1976). Age uncertainties were calculated from the analytical errors and assuming a 2% error in potassium determinations.

Geochronology

The radiometric database of the area consist of Rb/Sr whole rock (WR) and U/Pb from deep-seated, anatectic granites, charnockites and migmatites, and high level post- and late-kinematic granites. All the ages found span between 313±7 Ma (Majoor, 1988) and 277±7 Ma. Late kinematic granitoids, dated by Rb/Sr WR isochrons, that are geochemically very similar to the granites studied in the present work include the following intrusions (Fig. 1): Quérigut (303±10 Ma, Fourcade and Javoy, 1991; 304±5 Ma, Bickle, 1988), Ax les thermes (301±15 Ma, Majoor and Priem, 1987), Cauterets - Panticosa (298±0.5 Ma [WR orthoclase-biotite], Debon, 1975) and La Maladeta (277±7 Ma, Vitrac-Michard et al., 1980). These late-kinematic granites are dominantly calc-alkaline metaluminous granitoids, and are believed to represent crustal melts that formed in response to emplacement of significant amounts of mantle-derived material into the crust (Fourcade and Javoy, 1991).

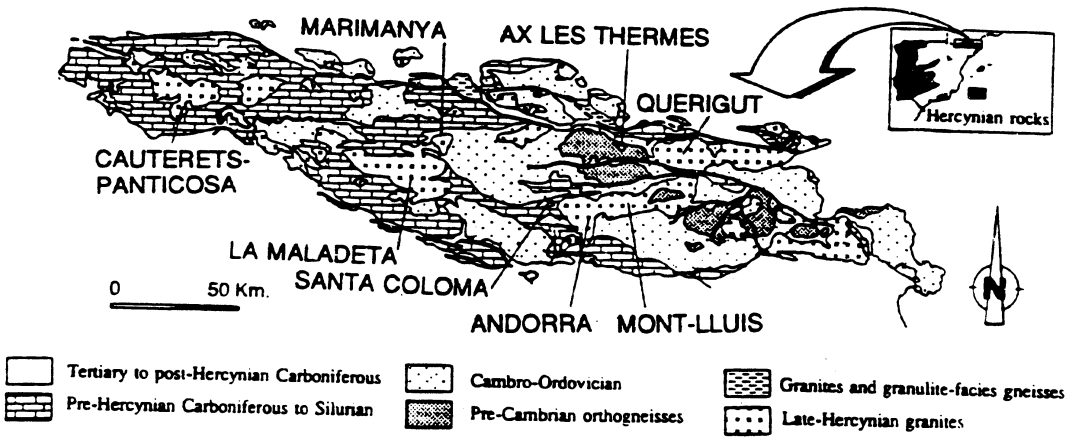

Fig. 1.- Geological map of the Pyrenees showing the location of the Hercynian granites in the Pyrenees (After Carreras & Santanach, 1983)

The Andorra-Mont Lluis granodiorite show several mineralized skarns and related intragranitic alterations (Soler, 1990; Soler et al., 1990; Soler y Delgado, 1991). We determined

the age of the Andorra granite at 307±12 and 309±12 Ma (±2σ) by K/Ar dating of two biotite concentrates from the granodiorite. These ages are identical, within error limits, with the age of 305±3 Ma obtained by Romer and Soler (1995) dating by U/Pb a titanite from a magmatic endoskarn from the same area. Although these ages are consistent with the geological data, K/Ar dating of two concentrates of K-feldspar coexisting with the dated biotites shows younger ages (182 ±7 and 199 ± 8 Ma). We interpret these younger ages as the result of a later opening of the K/Ar system, just as occurred in other Pyrenean sectors (Albarede, 1978). A separate of turmaline from the mineralized skarns gave an K/Ar age of 277±11 Ma whereas a separate of muscovite from an mineralized intragranitic greisen gave K/Ar age of 283±11 Ma (Table I). These ages are similar within error limits, suggesting that the skarns and the intragranitic alterations were formed at the same time.

Sample	Mineral	Rock type	wt %K	Radiogenic $40Ar^{*}$ (mol/g)	% radiogenic $40Ar^{*}/total^{40}Ar$	Age (M.a.±2σ)
Andorra-Mont Lluis						
449	Biotite	Granite	4.00	2.320×10^{-9}	70.6	307±12
449	K-feldspar	Granite	3.58	1.193×10^{-9}	73.5	182±7
538	Biotite	Granite	6.78	3.966×10^{-9}	98.3	309±12
538	K-feldspar	Granite	10.4	3.791×10^{-9}	89	199±8
693	Muscovite	Greisen	7.01	3.732×10^{-9}	97.8	283±11
855	Turmaline	Skarn	0.02	1.142×10^{-11}	27.3	277±11
Marimanya						
Mar114	Biotite	Granite	7.41	3.835×10^{-9}	97.4	276±11
Au20	Muscovite	Skarn	8.33	4.392×10^{-9}	97.7	281±11
Santa Coloma						
Gr2	Biotite	Granite	6.7	3.403×10^{-9}	98	271±11
Sch2	Muscovite	W-veins	7.09	3.516×10^{-9}	95.7	265±11
La Maladeta						
Mal-106	Flogopite	Marble	8.40	4.661×10^{-9}	98.2	295±11
Mal-107	Muscovite	Greisen	8.43	4.358×10^{-9}	98.5	276±11

Table I.- K-Ar age determinations.

The Sta. Coloma intrusion located in the western margin of the Andorra - Mont Lluis granodiorite, and is characterized by a stock of granodioritic composition. Several tungsten-bearing skarns and veins are found spatially related with the granodiorite (Espínola et al., 1996). One separate of biotite was obtained from an apparently fresh granodiorite sample, the K/Ar age of this mineral is 271±11 Ma. The age of the tungsten mineralizations was determined at 265±11 Ma by K/Ar dating of muscovite from the greisen type mineralization related to the

tungsten bearing quartz veins (Table I).

Related to the Maladeta granodiorite two types of mineralizations are found: skarns and intragranitic greisens (Delgado, 1993; Delgado et al., 1993). We determined the age of the intrusion at 295±11 Ma, by K/Ar dating of flogopite grown up during the contact metamorphism related to the Maladeta granodiorite intrusion. One muscovite concentrate from the intragranitic greisens gave and age of 276±11 Ma (Table I). Vitrac-Michard et al. (1980) found younger ages by Rb/Sr dating of whole rock (277±7 Ma).

The Aurenere skarn is closed to the Marimanya intrusion, which is characterized by a small pluton of granodioritic-leucogranitic composition located at the NE part of the Maladeta granodiorite (Palau, 1995; Palau et al., 1995). We determined the age of the granodiorite at 276±11 Ma by K/Ar dating of biotite concentrate from the granodiorite. Palau (1995) found older ages by Rb/Sr dating of different terms of the magmatic series (315±6 to 293±21 Ma). One concentrate of muscovite from the skarn gave a K/Ar age of 281±11 Ma (Table I).

Discussion

The ages found are classified in four groups. The first group corresponds to the ages around 300 Ma found in the Andorra-Mont Lluis and Maladeta granitoids, that we consider as the age of intrusion. The second group corresponds to the ages clustered 275 to 285 Ma. These ages are similar to the ages found for the granitoids from the Catalan Coastal Ranges (Solé et al., 1994). The skarns and intragranitic alterations with these ages could be formed by hydrothermal fluid circulation related to younger intrusions. The third group of ages, between 265 to 275 Ma, could be related to a hydrothermal fluid circulation found in the Eastern Pyrenees by Briqueu and Inocenti (1994). In the case of Marimanya and Sta. Coloma granitoids, although the age found could be interpreted by the age of the intrusion, the Rb/Sr older ages found in the Marimanya granitoid by Palau (1995), points out that the K-Ar system was opened in later times. This hydrothermal fluid circulation would be related to the Permian volcanism that Briqueu and Innocenti (1993) dated in the Pyrenees by U/Pb at 278±5 and 272±3 Ma. The last group of ages corresponds to the younger ages found in the K-feldspar and could be related with a Mesozoic rifting episode, such as Solé et al. (1994) described in the Catalan Coastal Ranges and Albarède et al. (1978) in the Pyrenees.

Conclusions

Dating of the gold-bearing skarns and intragranitic mineralizations in the Pyrenees provide a valuable information to define the different metallotecs and their temporal and genetic relationships. It also prove that skarns and intragranitic mineralizations have the same metallotec. Thus this technique is a useful tool to improve the metallogenetic maps of this area.

Moreover these geocronological determinations also help to constrain the ages of the related structures and granitic bodies.

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References

Albarede, F.; Féraud, G.; Kaneoka, I. & Allègre, C.J. (1978).- ^{39}Ar-^{40}Ar dating: the importance of K-feldspars on multi-mineral data of polyorogenic areas. *J. Geol., 86,* 581-598.

Briqueu, L. and Innocenti, C. (1993).- Datation U-Pb sur zircon et géochimie isotopique du Sr et Nd du volcanisme Permien des Pyrenées occidentales (Ossau et Anayet). *C.R. Acad. Sci. Paris., sér. II,* 316, 623-628.

Briqueu, L. and Innocenti, C. (1994).- The origin of Pyrenean Hercynian volcanic rocks (France-Sapin): REE and Sm-Nd isotope constrains. *Chemical Geology, 121,* 295-297.

Carreras, J. & Santanach, P. (1983).- El hercínico de los Pirineos. In: J.M. Comba (ed.) Geología de España. Libro Jubilar de J.M. Rios, 2, IGME publ., 356-550.

Delgado, J. (1993).- Caracterización mineralógica, físico-química y geoquímica de los skarns del contacto N del batolito de la Maladeta, Vall d'Aran (Lleida). Ph. D. Thesis, Barcelona Univ. 418 pp.

Delgado, J.; Soler, A., Arcos, D. & Ayora, C. (1993).- Geochemical constraints of formation of Au-bearing and barren skarns along the northern contact of the Maladeta batholith (Central Pyrenees, Spain). In P. Fenoll Hach-Alí; P. Torres-Ruiz & F. Gervilla (eds). Univ. Granada, 81-84.

Debon, F. (1975).- Les massifs granitöids à structure concentrique de Cauterets-Panticosa (Pyrenees occidentales) et leur enclaves. Un étude pétrographique et géochimique. Mém. Sci. Terre. 33, 420 pp. Nancy.

Espínola, M.R.; Soler, A. & Arcos, D. (1996).- Las mineralizaciones de wolframio asociadas a la granodiorita de Santa Coloma (Andorra). *Geogaceta, 20(7),* 1586-1589.

Fourcade, S. and Javoy, M. (1991).- Sr-Nd-O isotopic features of mafic microgranular enclaves and host granitoids from the Pyrenees, France: evidence for their hybrid nature and inference on their origin. In J. Didier; B. Barbarin (eds) Enclaves and granite petrology, Elsevier, Amsterdam, 435-364.

Kwak, T.A.P. (1987).- W-Sn skarn deposits and related metamorphic skarns and granitoids. Developments in Economic geology, 24, 451 pp.

Majoor, F.J.M. (1988).- On the age and origin of the Aston Gneiss Massif Central Pyrenees, *Hercynica IV,* 57-62.

Majoor, F.J.M. and Priem, N.A. (1987).- Rb-Sr whole rock investigations in the Aston massif (Central Pyrenees). *Geol., Rundsch, 75,* 787-794.

Palau, J. (1995).- El pluto de MArimanya i el seu encaixant. Ph. D. Thesis, Barcelona Univ. 436 pp.

Palau, J.; Arcos, D.; Delgado, J. & Soler, A. (1995).- Gold-bearing bodies related to the Hercynian plutonism in the Marimanya area (Central Pyrenees, Spain). In: B. Kribek & K. Zák (eds). Mineral Deposits: from their significance to their enviromental impacts. 493-496. Balkema Publications.

Romer R.L. y Soler, A. (1995).- U-Pb age and lead isotopic characterization of Au-bearing skarn related to the Andorra granite, *Mineralium Deposita, 30,* 374-383.

Solé, J.; Delaloye, M. & Enrique, P. (1994).- Edades aparentes K-Ar de las biotitas y feldespatos potásicos del batolito granítico hercínico del Montnegre (Cadenas Costero Catalanas). Evidencias de un calentamiento regional durante el límite Tríasico-Jurásico. *Bol. Soc. Esp. Mineral., 17-1,* 68.

Soler, A. (1990).- Geologia i Metal.logenia de la terminació sud del granit d'Andorra (Pirineu Central). Ph. D. Thesis, Barcelona Univ. 886 pp.

Soler, A.; Ayora, C.; Cardellach, E. & Delgado, J. (1990).- Gold bearing hedembergite skarns from the SW contact of the Andorra granite (Central Pyrenees, Spain). *Mineralium Deposita, 25S,* 59-68.

Steiger, R. and Jäger, E. (1977).- Subcomission on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett., 36,* 359-362.

Vitrac-Michard, A.; Albarede, F.; Dupuis, C. & Taylor H.P. (1980).- The genesis of Variscan (Hercynian) Plutonic Rocks: Interferences from Sr, Pb, and O studies on the Maladeta Igneous Complex, Central Pyrenees (Spain). *Contrib. Mineral. Petrol., 72,* 57-72