Large-scale hydrothermal processes in the Hercynian massives of Eastern Pyrenees (France)

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Metasomatic processes, resulting in massive feldspar rocks (either albite, oligoclase or K-feldspar) or muscovite $\pm$ biotite rocks, have affected several palaeozoic massives in Eastern Pyrénées, including mainly: (1) the Agly massif, composed of metasedimentary (granulite facies) precambrian gneisses overlain by meso- and epizonal schists of ordovician to silurian age; hercynian granodiorites are intrusive in these formations (2) the Millas massif, situated south of the Agly massif from which it is separated by the North-Pyrenean fault, and composed of hercynian granodiorite intruding a series of metapelites, partly preserved as schlieren in the southermost part of the massive. All granitoids exhibit at some places numerous dioritic to gabbroïc enclaves, up to several hundred meters large.

General features of metasomatic rocks

All host rock types, granodiorites, pegmatites, diorites, gneisses, metapelites and metagraywackes, show intense transformations forming discontinuous patches a few hundreds of meters large, along two major alignments of general direction N 110°, with a E–W extension of about 20 km (Pascal, 1979; Clavières, 1990). In the Agly massif and eastern part of Millas granite, the dominant metasomatic rock is a monomineralic feldspar, either albite or oligoclase, exceptionnally microcline, and is exploited for ceramic industry due to its high purity. In central part of the Millas massif, the granite is mainly transformed into a massive muscovite or muscovite-biotite rock with remnants of the original K-feldspar phenocrysts. Locally this micaceous rock is intensely foliated, due to a later mylonitization which affected the Millas granite, either metasomatized or unaltered, at cretaceous times (Monié *et al.*, 1994).

The transformation of the host rock usually shows a spectacular metasomatic zoning, with sharp fronts separating homogeneous zones up to more than 10 meters wide. The sequences of mineralogical associations differ from one place to another and depend also on the protolith; as an example, in the case of albitization of granite, one of the observed sequences is given in Table 1.

The replacement of all minerals by albite occurs with a perfect preservation of the original texture, visible under the microscope as well as on hand specimen.

A most important observation is a sequence granite/feldspathic rock/muscovite rock, which suggests that in spite of their contrasting mineralogical and geochemical characters, feldspathic and muscovitic alterations belong to a unique hydrothermal event and represent different zones of a large-scale metasomatic process. A late hercynian age (266 M.Y.) for this process is indicated by the $^{40}Ar/^{39}Ar$ geochronological study of the hydrothermal muscovites (Monié *et al.*, 1994).

The pressure and temperature conditions are roughly estimated at 350–450°C, 3 kbars from the coexistence of biotite, chlorite, muscovite, K-feldspar and quartz, and the composition of the phengitic muscovite (3.2 to 3.3 atoms Si per unit formula).

Geochemistry

Typical examples of major-element compositions of unaltered, muscovitized and albitized dioritic enclaves are indicated in Table 2. The compositions of the

TABLE 1. Albitization sequence of the Millas granodiorite

Plag An_{30}	Plag An_{10}	Plag An_{10}	Albite	Albite
Biotite	Muscovite	Muscovite	Muscovite	
Kspar	Kspar	Kspar		
Quartz	Quartz			

TABLE 2. Selected chemical compositions of unaltered and modified diorite, recalculated to constant wt percent for inert elements

	Diorite	Albitized	Muscovitiz.
SiO_2	63.05	77.03	25.36
TiO_2	0.69	0.69	0.69
Al_2O_3	15.82	25.97	15.02
Fe_2O_3	5.95	2.52	6.48
MgO	3.46	3.55	1.73
CaO	3.38	1.72	0.23
K_2O	3.19	0.36	5.52
Na_2O	2.92	11.01	0.09
P_2O_5	0.19	0.16	0.23
H_2O	1.10	2.18	2.69
Total	99.75	125.19	58.04

transformed rocks have been recalculated so that the inert elements (Zr, Nb, Ti, P, Sc, V,.., determined from their constant ratios throughout the alteration processes, have unchanged weight percent contents.

Whereas albitization involves important Na and appreciable Al inputs, muscovitization is mostly characterized by a drastic Si leaching which results in a weight loss up to 50%.

Interpretation: simplified model

Due to the presence of quartz in all host rocks, the leaching out of SiO_2 through muscovitization implies an increase in quartz solubility along the fluid pathways which suggests that the fluid underwent a temperature raise. This is the most likely process leading to an appreciable increase of quartz solubility under the considered temperature and pressure conditions, since the dominant aqueous silica-bearing species is the neutral complex, insensitive to pH and weakly sensitive to salinity. Increasing temperatures are expected if fluid circulation is promoted by heat sources related to late magmatic activity. A quantitative geochemical modelling of this process would require, in particular, the precise knowledge of aqueous Al behaviour in complex fluids, not available yet. A first insight on the mineralogical consequences of a fluid temperature increase can be obtained by considering an aqueous fluid initially equilibrated with a quartz-muscovite-K-felsdpar rock at 300°C, percolating this rock while the temperature is raised to 400°C (Fig. 1).

At 400°C, the initial composition of the fluid (point A) is located within the muscovite field, implying the fluid-rock reactions:

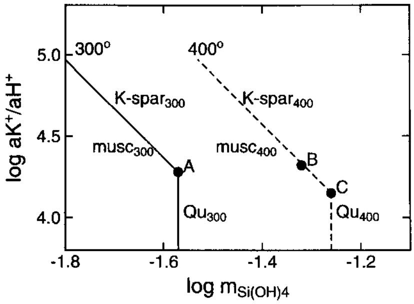

FIG. 1. Fluid-mineral equilibrium relationships in the system K_2O-Al_2O_3-SiO_2-H_2O-HCl at 300 and 400°C, 3 kbar.

$$\text{Quartz} + 2H_2O \rightarrow Si(OH)_4^0$$

$$1.5\ \text{K} - \text{Feldspar} + H^+ \rightarrow 0.5\ \text{Muscovite} + 3Si(OH)_4^0 + K^+$$

The fluid composition is shifted by these reactions towards higher K^+/H^+ ratios and silica concentrations until the muscovite/feldspar boundary (point B) is reached, whereas equilibrium with the quartz-muscovite-feldspar assemblage (point C) would require a lower K^+/H^+ ratio. Fluid-rock equilibration thus implies the appearance of a intermediate feldspathic, quartz-free zone, between the muscovite zone and the three-mineral rock.

This schematic pattern will not be much changed by adding Na_2O to the considered system, and should be applicable to those hydrothermal zones where CaO, FeO and MgO are virtually competely leached out. Indeed, the conclusions are consistent with the observed zonation in biotite-free albitization/muscovitisation.

Conclusions

Late Hercynian fluid circulations in several hercynian massives of Eastern Pyrenees resulted in deep transformation of granitic and metamorphic quartzo-feldspathic and pelitic formations, into mono- or bi-mineralic muscovite, muscovite-biotite, albite, oligoclase or K-feldspar rocks. These transformations exhibit remarkable metasomatic zoning which indicate that they basically belong to a unique hydrothermal event, chemically characterized by silica leaching out and interpreted by convective circulation of a metamorphic fluid. A large-scale zonation, with predominance of muscovite ± biotite rocks in the western part of the system and of albite/oligoclase rocks in the East, may represent the crosscut of palaeoisotherms.