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Chemistry of biotites from a zoned granitic pluton in Morocco

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ABSTRACT. Chemical analyses and structural formulae of biotites from the Zaër pluton, a zoned granitic body in the Central Hercynian Massif of Morocco, are presented. The pluton grades from more mafic single-mica granodioritic facies near the margin to more felsic two-mica granitic facies in the central part. There is a relationship between the composition of the biotites and that of the host rocks. Biotite composition in the internal two-mica facies was influenced by a hydrothermal phase.

BIOTITE is present as an essential mineral in all the different rock types of the Zaër pluton. This Hercynian pluton is roughly oval in shape and is situated in the northwestern part of the structural unit called the 'Coastal Meseta of Morocco'. The highly folded sediments, composed of low-grade schists, quartzites, and calcareous rocks, which the granite intrudes, range from Ordovician to Devonian.

The stratigraphy and general geology of the area were discussed by Termier (1936), van Leckwijck *et al.* (1955), Vandenven (1969), Cailleux (1976), and Piqué (1979). The petrography and field aspects of various rock units of the pluton were studied by Mahmood (1979) and Mahmood and Couturié (1979). The pluton grades from a sub-porphyritic, dark coloured single-mica granodiorite along its margin through light coloured, equigranular, single-mica granodiorite to two-mica monzogranite in its central part. In the single-mica facies, the grain size increases roughly from margins inward, whereas textural variations in the two-mica facies are not regular. None the less, the latter facies exhibits more often than not finer-grained textures near its margin, in places oriented and sheared, particularly at the contact with country rocks.

Accessory minerals of the granitoid rocks of the pluton include iron ore, apatite, sphene, rutile, and zircon.

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Chemical and modal compositions of the rocks from which the analysed biotites were extracted are given in Table I. Nearly 100 % pure biotite fractions were recovered by electromagnetic means. Chemical analyses were made by atomic absorption.

Fresh biotite is pleochroic in the following scheme: α—colourless to pale brown; β, γ—deep reddish brown.

Major and trace element variations. As shown by figs. 1 and 2, the host rocks of the biotites constitute a continuous series ranging from basic to acidic. In order of increasing acidity, these types are: dark coloured single-mica granodiorite; light coloured single-mica granodiorite; two-mica monzogranite. In passing from the basic to the acidic types, variations in the amounts of major and trace elements of the biotites may be noted (Table II).

Variations in the concentrations of SiO_2 and TiO_2 are weak and unsystematic.

There is an increase in the amounts of MnO and Al_2O_3. As in the present case, Nockolds (1947) has also found that biotites co-existing with muscovite have high content of Al_2O_3 with respect to MgO and total iron as FeO.

Total iron does not show a systematic variation pattern from one facies to the other, though the highest value is recorded for the biotite sample of the two-mica monzogranite. In this sample, moreover, the iron is more oxidized than in biotite samples of the single-mica facies. This fact reflects on the conditions in which the two-mica facies was formed.

MgO and CaO show decreasing trends, their concentrations being higher in the more basic types.

The amount of alkalis remains more or less constant across the granitoid series.

Rubidium in the biotites increases generally with increase in acidity of the host rocks. A similar trend for Rb is reported by Albuquerque (1973) for biotites of the Hercynian granites of Portugal. The RB/K ratio also shows a sympathetic relationship with the host rock acidity, as is also the case with biotites of the Southern California Batholith (Sen *et al.*, 1959).

Concentrations of Cr and Ni fall in the above sequence. These trends conform to those observed in other granitic rocks (Nockolds and Mitchell, 1948). The Co content is fairly uniform in the single-mica facies, but falls markedly in the two-mica facies. Sr tends to be present in smaller amounts in the more acidic types. Ni/Fe^{2+}, Ni/Mg, and Cr/Fe^{3+} ratios are higher in biotites of the more basic granodioritic types. The ratio Co/Fe^{2+} does not vary systematically, whereas the ratio Co/Mg shows a tendency to rise toward the acidic end of the series.

In order to show a relationship between chemical composition of the biotite and that of the host rock of the Zaër pluton the Fe/(Fe+Mg) ratio of the biotite is plotted against the same ratio for the host rock. The plot (fig. 3) shows a linear trend which confirms the relationship.

Structural formulae of the analysed biotites are also given in Table II. Two types of substitution in the atomic structure of biotite are generally considered important; these are replacement of bivalent ions by trivalent ions and Mg^{2+} by Fe^{2+} at the octahedral site. Foster (1960) classified trioctahedral micas on the basis of these substitutions. The biotites of the single-mica facies belong to that group of biotites which contain moderate quantities of octahedral R^{3+} and have Mg^{2+} as their predominant bivalent cation. On the other hand, the biotite of the two-mica facies has the properties of having a high amount of octahedral R^{3+} and Fe^{2+} instead of Mg^{2+} as its predominant bivalent cation.

Fig. 4 presents plots of biotites of the Zaër pluton on Foster's diagram. It is to be noted that the biotite sample obtained from the two-mica facies lies well outside the field of concentration of biotites. It also plots on the line along which Mg:Fe ratio is 1:1. This signifies that in this biotite the substitution was principally of Mg^{2+}, $Fe^{2+} \rightarrow R^{3+}$ type. Moreover, the biotites of the more acidic types, e.g. the two-mica monzogranite, compared with those of the more basic single-mica types, show a marked deficiency of atoms at the octahedral site. It may be recalled that in the two-mica facies, biotite is often intimately associated with muscovite, the latter having formed in hydrothermal conditions (Mahmood, 1981). Muscovite grows on biotite nuclei, and at times entire biotite grains are seen to give place to muscovite. Changes in the crystal chemistry of biotite yielding to muscovite in a hydrothermal, Fe-Mg-poor milieu

TABLE I. Composition of rocks of the Zaer pluton

	Single-mica dark coloured granodiorite				Single-mica light coloured granodiorite			Two-mica monzogranite
	AM 283	AM 329_A	AM 331	AM 334	AM 266	AM 330	AM 332	AM 295_A
SiO_2	67.30	66.50	67.20	67.30	67.80	69.50	71.50	74.00
TiO_2	0.55	0.70	0.65	0.50	0.60	0.45	0.30	tr
Al_2O_3	15.60	16.50	16.50	16.60	15.60	16.20	15.50	14.20
Fe_2O_3	1.22	1.37	1.55	1.55	1.42	1.04	1.16	1.10
FeO	2.05	2.82	2.17	2.03	2.05	1.59	0.94	tr
MnO	0.05	0.07	0.05	0.05	0.05	0.06	0.04	0.04
MgO	1.60	2.10	1.90	1.80	1.70	1.10	0.80	0.15
CaO	2.55	3.10	2.90	2.55	2.40	2.00	1.55	0.50
Na_2O	3.75	3.70	3.40	3.55	3.60	3.90	3.70	3.50
K_2O	3.35	3.10	2.80	3.45	3.10	3.50	4.30	4.80
H_2O^+	0.93	0.41	0.84	0.81	1.14	0.47	0.58	1.12
H_2O^-	0.20	0.12	n.d.	n.d.	0.30	0.05	0.12	0.16
Total	99.15	100.49	99.96	100.19	99.76	99.86	100.49	99.57
CIPW norms								
Q	24.0	21.9	27.0	25.3	26.6	26.9	28.6	34.2
or	19.8	18.3	16.6	19.2	18.9	20.6	25.6	28.3
ab	31.7	31.4	28.7	30.0	30.4	33.0	31.4	29.3
an	12.6	15.3	14.4	12.6	11.9	10.0	7.9	2.5
C	1.1	1.4	2.6	2.6	1.9	2.3	1.8	2.3
hy	5.9	8.2	6.4	6.2	5.9	4.3	2.3	0.5
mt	1.8	1.8	2.2	2.2	2.1	1.6	1.6	-
il	1.0	1.4	1.2	0.9	1.1	0.9	0.6	-
Modal analyses								
Quartz	27.8	23.7	28.8	28.7	29.6	21.3	26.2	36.6
K-feldspar	8.1	1.0	0.2	1.3	6.8	19.6	21.4	21.3
Plagioclase	54.3	52.5	49.5	47.7	46.2	48.0	44.5	29.6
Biotite	9.8	22.8	21.4	22.3	17.4	11.1	7.3	5.4
Muscovite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.1

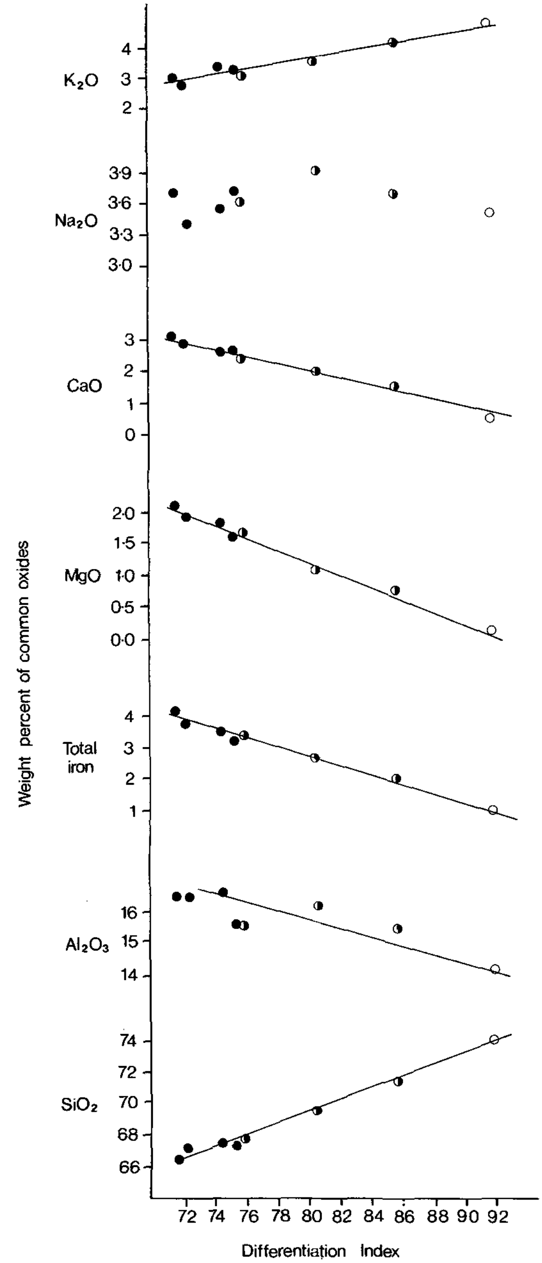

FIG. 1. Variation diagram for major oxides in rocks of the Zaër pluton, plotted against differentiation index (D.I.). Symbols (to be applied to the other figures also): solid circles, dark-coloured single-mica granodiorite; half-open circles, light coloured single-mica granodiorite; open circles, two-mica monzogranite.

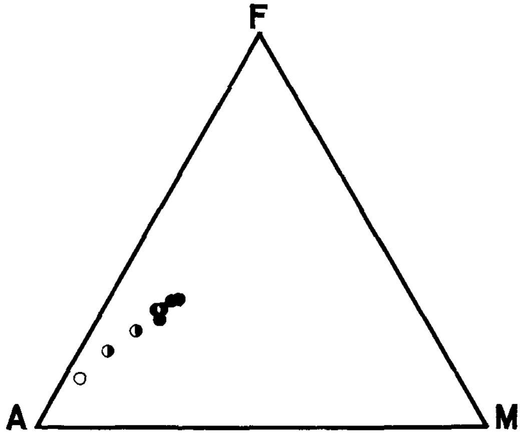

FIG. 2. AMF (total alkalis–MgO–total Fe) diagram of rocks of the Zaër pluton.

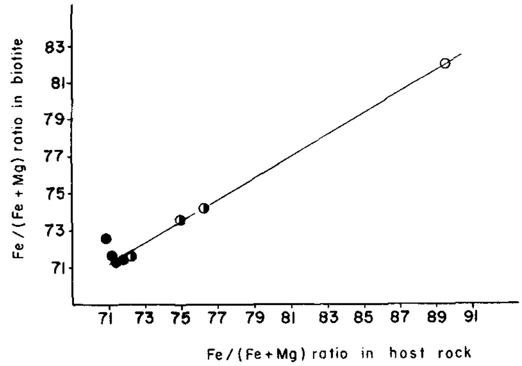

FIG. 3. Plot of Fe/(Fe + Mg) ratios of biotites against the same ratios of host rocks of the Zaër pluton.

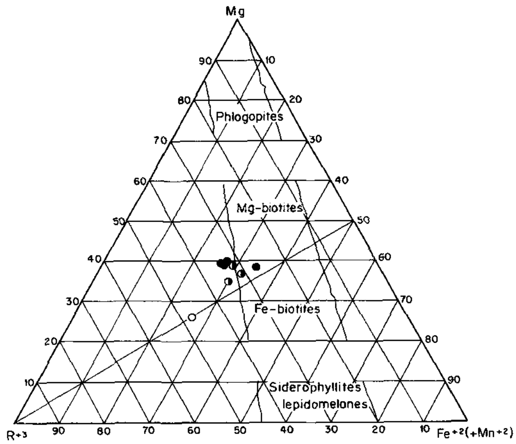

FIG. 4. Plot of biotites of the Zaër pluton on Foster's (1960) diagram.

TABLE II. Composition of biotites from rocks of the Zaer pluton

	AM 283	AM 329_A	AM 331	AM 334	AM 266	AM 330	AM 332	AM 295_A
SiO_2	37.60	38.20	35.70	38.30	37.60	35.90	35.50	36.90
TiO_2	3.20	2.90	2.75	3.05	3.25	3.10	2.75	2.75
Al_2O_3	16.60	16.20	17.00	17.40	16.80	18.00	19.70	19.70
Fe_2O_3	3.82	7.88	9.32	6.68	7.04	6.61	6.98	11.46
FeO	15.93	12.45	11.87	12.45	13.03	14.77	12.45	11.30
MnO	0.34	0.34	0.33	0.32	0.34	0.44	0.55	0.55
MgO	10.00	10.10	9.85	9.50	10.00	9.50	8.50	6.00
Na_2O	0.30	0.37	0.29	0.43	0.23	0.29	0.26	0.24
K_2O	8.90	8.85	8.45	8.65	8.85	8.80	8.35	8.55
H_2O^+	1.98	1.98	2.78	2.64	1.96	2.30	3.44	2.64
H_2O^-	0.16	0.30	0.26	0.14	0.23	0.36	0.44	0.48
Total	99.53	100.37	99.20	100.11	100.03	100.67	99.32	100.77
Trace elements (ppm)								
Rb	500	420	500	525	515	790	900	820
Sr	20	35	25	30	15	15	15	20
Co	75	65	75	70	70	75	70	55
Cr	210	225	190	205	210	180	145	75
Ni	150	145	150	130	130	125	105	60
Chemical ratios (x1000)								
Cr/Fe^{3+}	8.7	4.5	3.2	4.9	4.7	4.3	3.3	1.0
Rb/K	6.7	5.7	7.1	7.3	7.0	10.8	13.0	11.5
Ni/Mg	2.5	2.4	2.5	2.3	2.2	2.2	2.1	1.7
Co/Mg	1.2	1.1	1.3	1.2	1.1	1.3	1.4	1.5
Ni/Fe^{2+}	1.2	1.5	1.6	1.3	1.3	1.1	1.1	0.7
Co/Fe^{2+}	0.60	0.67	0.81	0.72	0.69	0.65	0.72	0.62
Numbers of ions based on 24(O,OH)								
Si	5.801 } 8.000	5.826 } 8.000	5.460 } 8.000	5.756 } 8.000	5.745 } 8.000	5.497 } 8.000	5.353 } 8.000	5.561 } 8.000
Al	2.199	2.174	2.540	2.244	2.255	2.503	2.647	2.439
Al	0.817	0.734	0.562	0.824	0.769	0.732	0.843	1.052
Ti	0.370	0.329	0.312	0.342	0.376	0.358	0.307	0.307
Fe^{3+}	0.444 } 6.035	0.896 } 5.892	1.064 } 5.755	0.756 } 5.674	0.806 } 5.946	0.754 } 5.961	0.796 } 5.481	1.302 } 5.509
Fe^{2+}	2.045	1.582	1.514	1.560	1.659	1.884	1.564	1.420
Mg	2.313	2.305	2.258	2.147	2.290	2.178	1.917	1.356
Mn	0.046	0.046	0.045	0.045	0.046	0.055	0.054	0.072
Ca	0.120	0.128	0.100	0.090	0.119	0.101	0.063	0.036
Na	0.092 } 1.970	0.110 } 1.957	0.092 } 1.844	0.126 } 1.876	0.073 } 1.915	0.092 } 1.921	0.072 } 1.745	0.072 } 1.754
K	1.758	1.719	1.652	1.660	1.723	1.728	1.610	1.646
OH	2.035	2.012	2.827	2.652	1.998	2.353	3.454	2.659
$\frac{100Fe}{Fe+Mg}$	51.8	51.8	53.3	51.8	51.8	54.8	55.2	66.6
$\frac{Fe^{3+}}{Fe^{2+}+Fe^{3+}}$	0.18	0.36	0.41	0.32	0.32	0.28	0.33	0.77

may be considered as a possible explanation for the somewhat anomalous composition of the biotite of the two-mica facies. Such changes have been in fact discussed by some authors (see Deer *et al.*, 1965).

Discussion. As shown in fig. 3 variation in the Fe/(Fe + Mg) ratios for both the biotite and the host rock is much less strong within the single-mica facies than between the single and the two-mica facies. The relative uniformity of the Fe/(Fe + Mg) ratios in the single mica facies is also reflected in the atomic ratios Fe/(Fe + Mg) × 100 calculated for the analysed biotites and given in Table II. This latter ratio is 51.8 in four of the seven biotites of the single-mica facies. The maximum deviation, in the case of the three other biotites, is 6 %. Biotites with a ratio of 51.8 will define a constant oxygen fugacity of the order of 10^{-15} bar, using curves corresponding to biotite—K-feldspar—magnetite equilibria (Wones and Eugster, 1965). The atomic ratio 100 [Fe/(Fe + Mg)] of the biotite of the two-mica facies is considerably higher than the same ratios in the single-mica facies. The difference of atomic ratios of biotites of the two principal granitoid types is significant in terms of the history of solidification of the pluton.

In the internal two-mica facies, the primary magmatic trends were modified by an overprint of a later phase marked by H_2O and potassium enrichment in the melt (Mahmood, 1981). Muscovite and K-feldspar were formed in abundant quantities during this phase; the latter mineral also occurs as fissure-filling veins, alone or with sodic plagioclase and accessory amounts of muscovite and chlorite. The outer single-mica granodiorite had entirely solidified at the time of intrusion of the inner two-mica monzogranite, as is suggested by the observable contacts between the two facies and by the sharp compositional gradients which coincide with these contacts.

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[Note added in proof: in Table II the CaO values have been omitted; they are, reading from left to right, 0.70, 0.80, 0.60, 0.55, 0.70, 0.60, 0.40, and 0.20%.]