

The geochemistry of biotites from granites of northern Portugal with special reference to their tin content

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SUMMARY. Biotites from a number of granites have been analysed for major oxides and a wide range of trace elements. Their compositions are found to be typical of biotites from granite and to show element fractionation in presumed differentiation series. Estimates are made of the fugacity of oxygen and water during the crystallization of the granites. $P_{\text{H}_2\text{O}}$ is found to increase slightly through the differentiation series, and f_{O_2} for a temperature of 700 °C is estimated to be between 10^{-18} and 10^{-12} . Tin mineralization is connected with the igneous rocks and the relationship of tin in the micas to the rock compositions is described and the factors controlling the distribution of tin are discussed. The biotites have only up to 21 % of the tin of the granites. In general Sn increases in the biotites with decreasing temperature of equilibration and with increase in the degree of albitization of the granites. High Sn in biotites seems to be an indicator of potential mineralization.

BIOTITES from the various granites of Alijó-Sanfins, northern Portugal, have been analysed as part of a study of the geochemistry of the rocks. Some of the granites are associated with tin and tungsten mineralization and the present paper deals with the accumulation of tin in the biotite. In addition, the relationship between the tin content of the biotites and the modal and chemical composition of the granites is discussed as well as the more general chemistry and conditions of formation of the micas. Thirteen different types of granite, labelled G I to G XIII have been recognized (Neiva, 1971). They have been intruded into phyllites and metagreywackes, which show polyphase deformation. The main structural orientation is Hercynian. The rocks are all muscovite-biotite-albite-granites but they all also bear quartz, microperthitic microcline, apatite, zircon, ilmenite, and rutile. Some have tourmaline and in granite G XIII, delessite, sphene, pyrite, and zoisite were found.

G I is the oldest granite and is relatively fine-grained and gneissose. G II to G VII are concordant intrusions except for G V, which occurs as fine-grained gneissose inclusions in G IV and which may represent granitized phyllite. Granites G II to G VII are believed to be related to one another as a differentiation series. They do not have strong aureoles but effected muscovitization and tourmalinization. G IX cuts G IV and G VIII along faults. G X to G XIII are discordant and are all porphyritic. G X cuts G VIII, penetrates and surrounds G IV and G IX, and intruded between the phyllite and G VII; it is sometimes intruded along NE.-SW. faults. G XI is gneissose and pink and G XII and G XIII are pink and red granites respectively and all three occur as veins and small stocks. These last three granites form another presumed

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TABLE I. *Averages of the granites*

	Older Harmonic Hercynian granites										Veins and stocks of granite	Disharmonic Hercynian granite	Veins or small stocks of granites cutting the disharmonic Hercynian granite		
	G I	G II	G III	G IV	G V	G VI	G VII	G VIII	G IX	G X			G XI	G XII	G XIII
SiO ₂	72.65	71.88	71.98	72.25	73.28	73.44	71.37	70.22	72.33	70.92	71.69	71.80			
TiO ₂	0.19	0.26	0.22	0.11	0.07	0.16	0.29	0.35	0.23	0.34	0.38	0.37			
Al ₂ O ₃	14.36	15.33	15.58	15.61	15.27	14.44	15.56	15.33	15.22	15.31	14.95	14.71			
Fe ₂ O ₃	0.59	0.23	0.36	0.42	0.21	0.40	0.34	0.51	0.34	0.88	1.04	1.15			
FeO	0.70	1.19	0.99	0.68	0.58	0.73	1.16	1.60	1.08	0.93	0.70	0.57			
MnO	0.02	0.02	0.02	0.02	0.03	0.05	0.02	0.03	0.02	0.01	0.01	0.01			
MgO	0.23	0.13	0.14	0.05	0.04	0.04	0.08	0.18	0.12	0.27	0.08	0.13			
CaO	0.62	0.84	0.72	0.66	0.56	0.48	0.82	0.95	0.65	0.73	0.71	0.56			
Na ₂ O	3.47	3.84	3.89	3.64	3.84	3.81	3.74	3.51	3.73	2.99	2.95	3.35			
K ₂ O	5.23	5.13	4.62	4.84	4.61	4.78	5.15	5.69	4.94	5.81	5.48	5.86			
P ₂ O ₅	0.37	0.29	0.28	0.32	0.30	0.30	0.33	0.36	0.35	0.32	0.34	0.28			
B ₂ O ₃	0.08	—	0.12	0.07	0.04	0.08	0.07	n.d.	0.06	0.06	0.07	0.08			
H ₂ O ⁺	1.20	0.82	0.98	0.99	1.04	1.18	0.88	1.02	0.91	0.90	0.91	1.09			
H ₂ O ⁻	0.44	0.21	0.14	0.52	0.34	0.16	0.22	0.20	0.16	0.38	0.53	0.42			
Total	100.15	100.17	100.04	100.18	100.21	100.05	100.03	99.95	100.14	99.85	99.84	100.38			
<i>Norm</i>															
Q	31.86	28.62	29.94	31.68	32.70	32.22	27.90	25.86	30.90	30.24	32.22	28.56			
or	30.58	30.02	27.24	28.36	27.24	28.36	30.58	33.92	28.91	34.47	32.80	35.03			
ab	29.34	31.96	33.01	30.39	31.96	31.96	31.44	29.34	31.44	25.15	25.15	28.82			
an	0.56	2.22	1.95	1.95	1.39	0.83	3.06	2.50	0.83	1.11	1.95	1.39			
c	2.86	2.75	3.47	3.77	3.57	2.65	2.75	2.45	3.47	3.67	3.37	2.14			
hy	0.40	1.58	1.06	0.79	0.79	0.66	1.45	1.85	1.32	0.40	—	—			
{	0.60	0.30	0.40	0.20	—	0.10	0.20	0.50	0.30	0.70	0.20	0.30			
mt	0.93	0.23	0.70	0.70	0.23	0.70	0.46	0.70	0.46	1.39	1.16	0.70			
il	0.46	0.61	0.46	0.15	0.15	0.46	0.61	0.76	0.46	0.61	0.76	0.76			
ap	1.01	0.67	0.67	0.67	0.67	0.67	0.67	1.01	1.01	1.01	0.67	0.67			
B ₂ O ₃	0.08	—	0.12	0.07	0.04	0.08	0.07	n.d.	0.06	0.06	0.07	0.08			
H ₂ O ⁺	1.20	0.82	0.98	0.99	1.04	1.18	0.88	1.02	0.91	0.90	0.91	1.09			
H ₂ O ⁻	0.44	0.21	0.14	0.52	0.34	0.16	0.22	0.20	0.16	0.38	0.53	0.42			
Total	100.32	99.99	100.14	100.24	100.12	100.03	100.29	100.11	100.23	100.09	99.79	99.96			

BIOTITES FROM PORTUGAL

	GI	GII	GIII	GIV	GVI	GVII	GVIII	GIX	GX	GXI	GXII	GXIII
<i>Modal composition</i>												
Quartz	44.2	35.7	34.3	37.7	36.9	38.1	33.1	27.0	38.3	33.1	33.4	33.8
Microcline { p. m.	—	19.6 17.4	11.4 23.0	— 29.2	2.0 24.4	1.9 20.0	13.6 22.1	4.6 27.6	14.5 12.1	6.8 31.4	9.5 28.2	12.3 18.3
Albite { p. m.	—	4.6	2.8	—	1.7	0.7	3.7	—	—	1.2	1.7	2.3
Muscovite	11.4	13.1	17.8	21.5	20.0	23.3	16.6	25.3	20.3	12.3	12.3	15.2
Biotite	13.4	5.9	7.4	9.1	12.9	15.7	7.0	9.8	11.3	11.4	12.4	13.0
Chlorite	2.5	2.9	2.7	1.5	1.0	—	3.1	5.2	1.9	2.4	1.5	—
Apatite	1.0	0.2	0.3	0.3	0.3	0.1	0.5	0.2	1.1	1.3	0.9	2.5†
Tourmaline	0.2	0.2	0.1	0.3	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.2
	—	0.3‡	0.2	0.2	0.7	0.1	0.1	0.1	0.3	—	—	—
<i>Trace elements (ppm)§</i>												
Be	13	14	28	26	77	13	20	16	25	*	*	13
Ga	28	33	25	23	20	30	29	23	28	36	28	28
Cr	*	10	7	6	4	4	11	14	11	14	12	7
V	*	17	14	9	6	5	12	22	11	26	13	9
Sn	33	36	32	36	41	46	18	25	18	20	8	20
Li	116	355	408	418	445	525	277	245	195	103	135	8
Ni	3	9	7	3	2	3	9	7	9	13	10	8
Zr	60	72	85	62	42	47	106	88	108	158	213	203
Yt	11	9	13	9	17	6	8	7	9	13	8	11
La	*	*	39	*	*	*	18	38	45	120	106	157
Sr	47	82	66	48	33	10	118	97	38	97	83	62
Pb	36	135	30	29	8	*	81	35	38	35	32	20
Ba	191	420	306	153	147	35	530	540	174	486	236	230
Rb	460	400	447	563	627	733	353	330	486	563	635	888
Cs	33	25	29	73	110	157	48	10	35	29	29	16

p. phenocrysts; m. matrix; — not determined; n.d., not detected; *, below the limit of sensitivity; † also 1.5 % delessite, 0.1 % sphene, and 0.8 % pyrite; ‡ also 0.1 % beryl. § Co and Sc were below the limit of sensitivity except for 5 p.p.m. Co in G XIII and 6 p.p.m. Sc in G IX.

differentiation series. They cut G X and were intruded in places along NE.-SW. faults between G X and the phyllite (Table I).

Biotites from all granites were analysed except for G VII (which has only 0.1 % chlorite after biotite), G XIII (because the biotite could not be separated from the chlorite), and G V. The biotites occur as subhedral grains pleochroic from γ and β brown to α pale yellow. They have apatite and zircon inclusions with pleochroic haloes and are sometimes partly altered to chlorite. X-ray powder photography showed them to be either 1M or 3T polymorphs and a Weissenberg photograph of the biotite from G X gave a 3T structure. The biotites were separated with a Frantz magnetic separator and purified by centrifuging in heavy liquids. A purity of about 99.8 % was estimated by optical and X-ray examination—zircon and apatite being the principal contaminants. Chlorite was removed satisfactorily.

SiO₂, TiO₂, Al₂O₃, total iron, MnO, MgO, and CaO were determined by XRF following the method of Norrish and Hutton (1969) using the C.S.I.R.O. standard FS 25. These oxides were also determined in two samples by standard wet chemical methods in order to check the results. Na₂O and K₂O were determined by flame photometry and FeO and water by classical methods. Trace elements Be, Ga, Cr, V, Sn, Li, Ni, Zr, Co, Sr, Pb, Ba, Rb, and Cs were determined by emission spectroscopy. A muscovite base was used and Pd was the internal standard. A large quartz-glass Hilger spectrograph was used and the intensities were measured on a Jarrell-Ash photodensitometer. A precision of ± 20 to 25 % is estimated. The limits of sensitivity are in (ppm): Be 5, Ga 2, Cr 4, V 4, Sn 5, Li 1, Ni 2, Co 5, Zr 5, Sr 3, Pb 5, Ba 5. An Associated Electrical Industries Ltd., MS 7 spark source mass spectrograph was used to determine Cl, F, Ge, W, Mo, Nb, Zn, In, Cu, Sc, Bi, Er, Yt, Dy, Tb, Gd, Sm, Nd, Pr, Ce, La, Au, Tl. The technique of Nicholls *et al.* (1967) was employed with rhenium as internal standard. The precision was estimated to be ± 7 % with a detection limit of 0.01 ppm.

Chemistry of the biotites. The major and trace element concentrations and structural formulae of the analysed biotites are given in Table II.

The major element chemistry of the micas shows them to be typical granite biotites. Plotted in the Al₂O₃ : total iron : MgO diagram the biotites fall in the field of coexistence with muscovite (Nockolds, 1947) and in the magmatic field defined by Gokhale (1968). In the (Fe₂O₃+TiO₂) : MgO : (FeO+MnO) triangle they correspond with plutonic biotites of igneous origin (Heinrich, 1946; Gokhale, 1968) and fall in the areas of granite biotites defined by Engel and Engel (1960). The minerals are all Fe²⁺ biotites and occupy the granite field in the triangle Mg : (Al+Fe³⁺+Ti) : (Fe²⁺+Mn) defined by Foster (1960). Several of them fall outside the field of coexistence with muscovite defined by Albuquerque (1973) in the diagram Ti : Al^{VI} : Fe³⁺ (fig. 1a). They show a decrease in Ti and increase in Fe³⁺ in the biotites of the presumed differentiation series. As Ti is normally thought to decrease with temperature of formation, this variation is in keeping with the notion of differentiation. The position of G XII mica on Albuquerque's figure suggests that the mineral has been oxidized.

The F, Cl, OH, proportions of the micas shows a progressive increase in F and decrease in OH through the two series and biotites from G I and G VIII plot apart

from the series (fig. 1b). Variations in the micas in element proportions and certain ratios are shown in figs. 2 and 3. In general the variations for the series G II to G VI are typical for series of granites and broadly as would be expected from general principles. Similar sequences have been found, for example, by Nockolds and Mitchell (1948) for the elements Al, Fe^{3+} , Mn, Li, Cu, Ti, Mg, V, Ni, and Co; Sen, Nockolds and Allen (1959) for Mg, $\text{Fe}^{2+} + \text{Fe}^{3+}$, Li, V, Ni, and Co; Rub (1972) for Sn, Nb, Li,

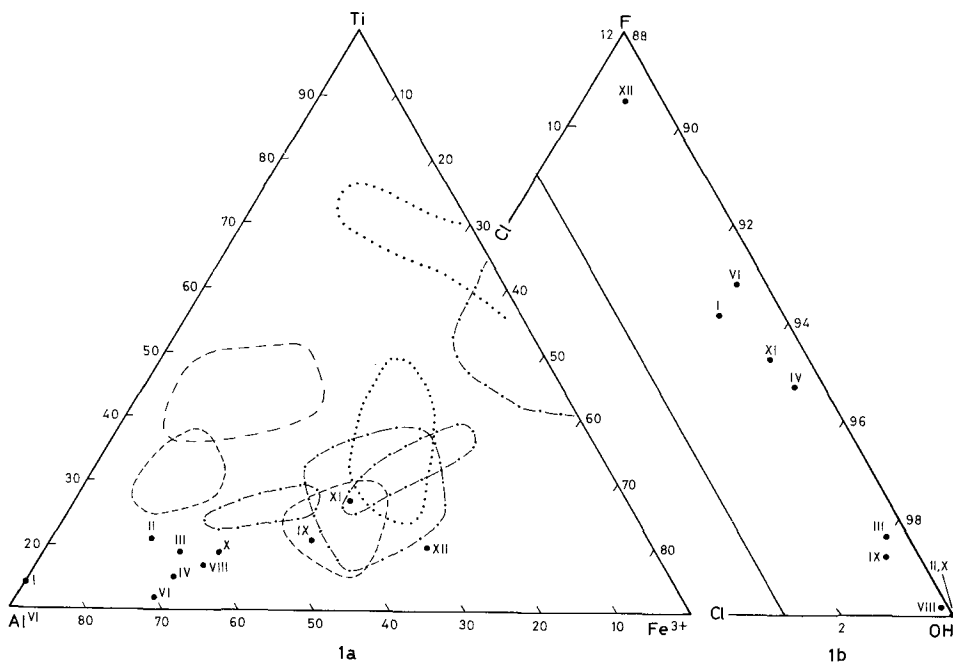


FIG. 1a: Ti-Al^{VI}-Fe³⁺ diagram after (Albuquerque, 1973). Dotted lines: fields of biotites coexisting with pyroxene. Dash-dot lines: fields of biotites coexisting with amphibole. Dashed lines: fields of biotites unaccompanied by other ferromagnesian minerals or coexisting with muscovite or aluminosilicates. • Alijó-Sanfins biotite. b: F-Cl-OH diagram of biotites from granites of northern Portugal.

and F; Kozlov (1969) for F; Lyakhovich (1970) and Mogarovskiy *et al.* (1968) for Nb; and by Ishikawa, Shibata, and Negishi (1963) for V, Ni, and Co. Also, as expected, the series of minerals show an increase in F/Li ratio though Tauson (1967) found this ratio to be constant in biotite from the different granitoid rocks of the main phases of the Verkhne Undisk mesabyssal batholith. Biotites from G I, G VIII, G IX, and G X differ from one another and from the two series. G I biotite for example contains more Al, Cl, Zn, Bi, and less Fe^{3+} , $\text{Fe}^{2+} + \text{Fe}^{3+}$, Mn, Mg, and Cr than any other and the ratios Fe^{2+}/Mg , Cs/K are greater and Mn/Fe^{2+} , Ga/Al, Cr/Fe^{3+} are lower than in any of the other biotites. G VIII biotite contains less Mn, Li, W, Nb, and Cs, and more Ti, Mg, Ni, In, Co, and Ce than those of G II to G VI. Similarly the ratios total FeO/MgO , Fe^{2+}/Mg , Mn/Fe^{2+} , Li/Mg are lower and Ni/Fe^{2+} , Ni/Mg , and Co/Mg

TABLE II. *Biotites from granites. Anal. A. Neiva*

	G I	G II	G III	G IV	G VI	G VIII	G IX	G X	G XI	G XII
SiO ₂	33.80	34.63	34.99	35.45	35.17	33.87	34.54	33.66	33.12	33.50
TiO ₂	2.72	2.41	2.45	2.08	1.70	2.62	2.71	2.92	3.50	2.64
Al ₂ O ₃	27.22	19.69	20.62	20.34	21.49	21.66	18.31	21.08	19.05	19.22
Fe ₂ O ₃	n.d.	1.52	2.29	2.69	2.54	3.32	4.39	3.60	4.68	6.73
FeO	20.25	19.81	19.37	20.83	19.58	19.22	17.81	20.17	20.46	18.84
MnO	0.15	0.46	0.48	0.49	0.95	0.42	0.30	0.29	0.24	0.16
MgO	4.04	6.57	6.65	5.01	4.95	7.41	8.79	4.67	6.35	6.44
CaO	0.10	1.61	0.51	n.d.	n.d.	0.01	n.d.	1.29	n.d.	0.13
Na ₂ O	0.24	0.22	0.12	0.22	0.19	0.10	0.19	0.17	0.18	0.15
K ₂ O	8.03	8.73	9.04	9.10	8.97	8.49	9.44	8.21	8.64	7.45
Cl	0.17	—	0.06	0.09	0.11	0.01	0.07	—	0.10	0.13
F	0.46	—	0.14	0.37	0.60	0.01	0.08	—	0.42	1.09
H ₂ O +	3.33	3.89	3.99	3.61	3.95	3.21	3.01	3.35	3.57	4.35
H ₂ O —	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.13	n.d.	n.d.	0.10
O ≡ Cl	100.51	99.54	99.81	100.28	100.20	100.40	99.77	99.41	100.31	100.93
O ≡ F	0.04	—	0.01	0.02	0.02	0.00	0.02	—	0.02	0.03
O ≡ F	0.19	—	0.06	0.16	0.25	0.00	0.03	—	0.18	0.46
Total	100.28	99.54	99.74	100.10	99.93	100.40	99.72	99.41	100.11	100.44
Number of ions on basis of 24(O, OH, Cl, F)										
Si	5.059	5.306	5.197	5.417	5.327	5.163	5.342	5.209	5.109	5.043
Al ^{iv}	2.941	2.694	2.803	2.583	2.673	2.837	2.658	2.791	2.891	2.957
Al ^{vi}	1.861	0.862	0.902	1.081	1.164	1.055	0.680	1.054	0.573	0.454
Ti	0.306	0.278	0.281	0.239	0.194	0.300	0.315	0.340	0.406	0.299
Fe ³⁺	—	0.175	0.263	0.309	0.290	0.381	0.511	0.419	0.543	0.762
Fe ²⁺	2.535	2.538	2.470	2.662	2.480	2.450	2.304	2.611	2.639	2.372
Mn	0.019	0.060	0.062	0.063	0.122	0.054	0.039	0.038	0.031	0.020
Mg	0.901	1.500	1.511	1.141	1.118	1.684	1.684	1.077	1.460	1.445
Σ R ^{vi}	5.62	5.41	5.49	5.50	5.37	5.92	5.88	5.54	5.65	5.35
Ca	0.016	0.264	0.083	—	—	0.002	—	0.214	—	0.021
Na	0.070	0.065	0.035	0.065	0.056	0.030	0.057	0.051	0.054	0.044
K	1.533	1.706	1.753	1.774	1.734	1.651	1.863	1.621	1.700	1.431
Σ(Ca, Na, K)	1.62	2.04	1.88	1.84	1.79	1.68	1.92	1.89	1.75	1.50
Cl	0.043	—	0.016	0.023	0.028	0.003	0.018	—	0.026	0.033
F	0.218	—	0.067	0.179	0.287	0.005	0.039	—	0.205	0.519
OH	3.324	3.976	4.057	3.679	3.990	3.263	3.105	3.458	3.673	4.368
Σ(OH, F, Cl)	3.59	3.98	4.14	3.88	4.31	3.27	3.16	3.46	3.90	4.92

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	G I	G II	G III	G IV	G VI	G VIII	G IX	G X	G XI	G XII
<i>Trace elements (ppm)</i>										
Ge	1.2	0.20	0.7	2.2	2.7	1.6	2.8	3	3	3.5
Ga	90	110	90	90	92	110	110	90	75	110
W	12	7	9	12	184	5	11	7	13	15
Cr	*	37	48	23	17	100	100	75	60	48
V	*	48	48	*	*	48	100	28	48	48
Mo	0.11	0.30	0.41	0.6	0.30	0.40	0.40	0.30	0.5	0.40
Nb	118	71	91	133	362	47	76	42	24	168
Zn	972	242	250	359	543	386	163	609	259	405
Sn	100	100	100	140	100	100	100	68	45	*
Li	2150	3850	3900	4000	6000	3400	2150	3400	1200	1800
Ni	10	43	37	13	8	60	125	48	48	37
Zr	140	175	175	84	84	175	300	370	450	450
In	0.7	1.0	0.7	0.7	0.40	4	0.40	0.40	0.8	0.5
Co	28	30	30	*	*	37	60	28	37	37
Cu	18	9	16	25	55	15	57	30	37	193
Sc	3.4	7	6	1.5	1.2	1.8	0.40	0.01	3.5	1.6
Bi	25	1.4	2.1	3.4	3.3	2.2	1.9	2.0	3.7	3.9
Er	1.6	0.9	1.4	1.6	1.8	0.9	1.3	0.9	1.8	2.2
Yt	1.7	0.5	0.6	0.7	0.8	0.3	1.0	2.0	2.1	3.6
Dy	1.3	1.0	2.8	2.5	1.7	1.6	1.1	14	2.0	2.0
Tb	0.40	0.20	0.30	0.30	0.30	0.30	0.30	5	0.5	0.6
Gd	4	4.5	4	3.5	2.0	2.8	1.3	5	1.9	1.4
Sm	3.0	1.2	1.6	1.7	1.5	0.6	1.3	11	7	1.6
Nd	23	11	8	8	4.0	4.6	15	44	37	1.4
Pr	5	4	4	1.1	1.0	1.5	4	6	9	5.8
Ce	8	4	3	1.5	1.3	12	4	2.5	130	45
La	24	28	13	10	8	9	12	756	39	26
Sr	*	*	*	*	*	*	4	6	*	8
Pb	45	39	45	45	32	45	150	45	45	220
Au	37	21	33	142	152	108	143	2181	47	99
Ba	55	55	40	40	55	55	700	55	180	135
Rb	1500	2200	1360	2600	1800	1800	1500	1800	1600	1400
Tl	0.9	0.10	0.6	0.7	0.8	0.7	1.3	1.3	0.7	1.0
Cs	1000	1000	550	1000	1000	430	320	1000	320	320

* below the limit of sensitivity (Be * in all samples).

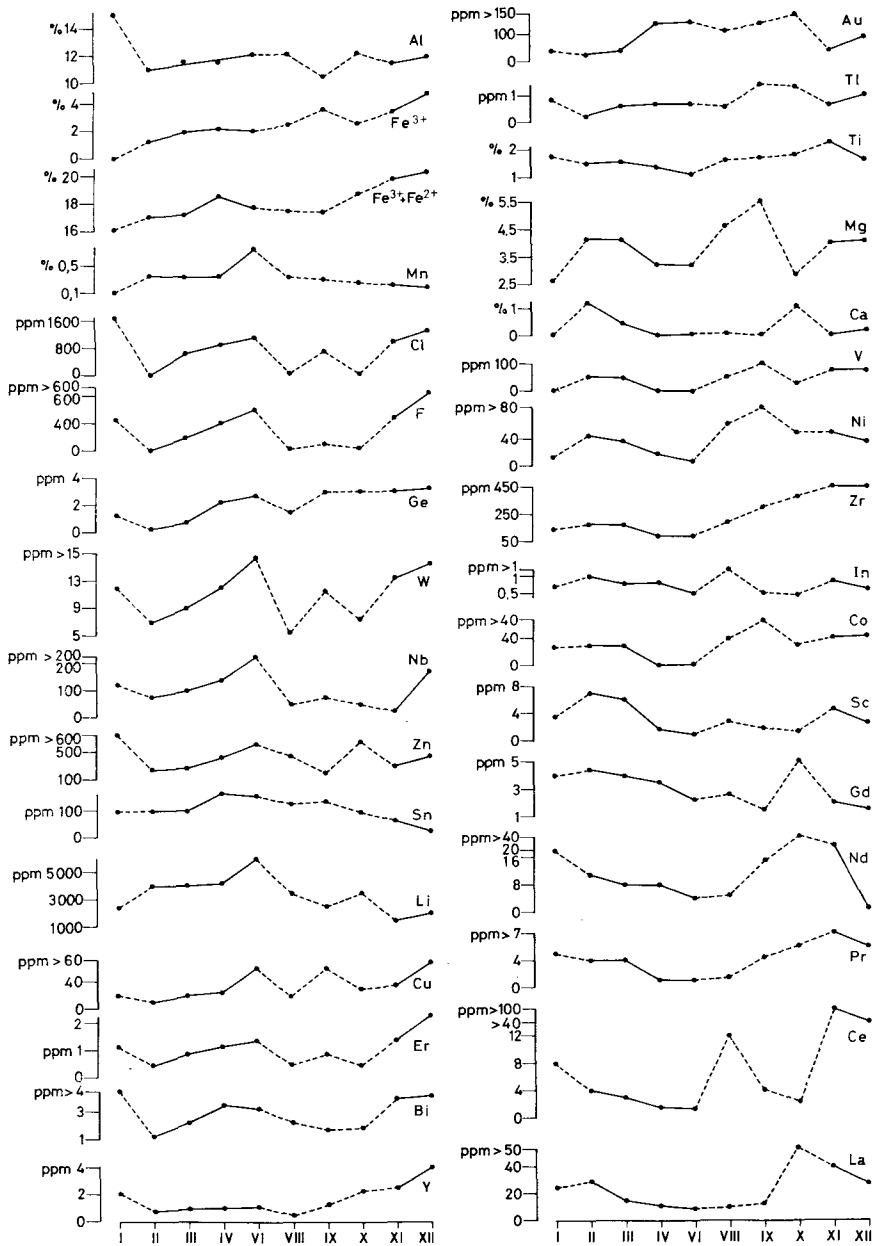


FIG. 2. Variation diagrams of the major and trace elements of the biotites from the granites of northern Portugal.

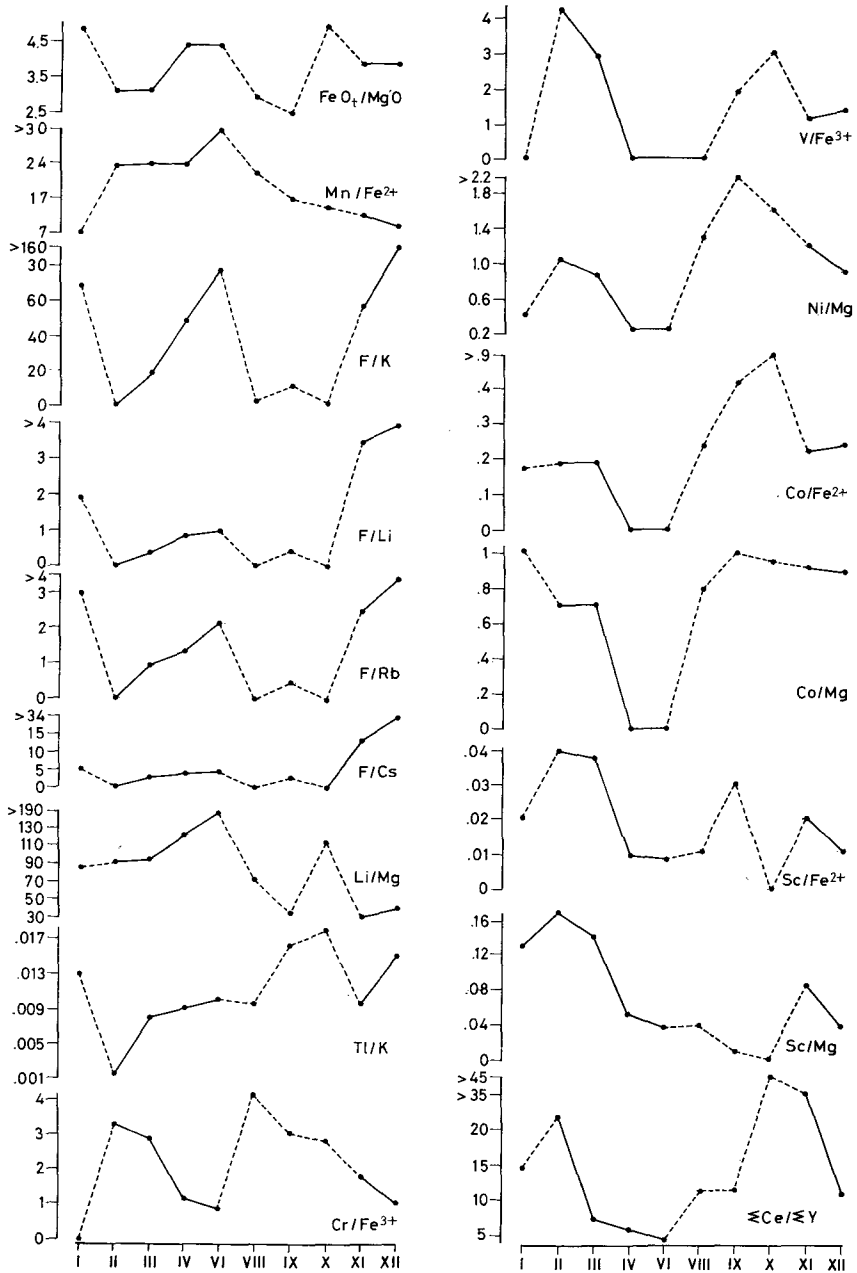


FIG. 3. Variation diagrams of the major/trace elements ratios of the biotites from the granites of northern Portugal.

are greater than in the biotites of G II to G VI. These findings show that the G VIII biotite does not belong to either series. G IX biotite contains less Al, Fe^{2+} and more Mg, K, V, Ni, Co, Gd, Ba and also lower total FeO/MgO , Fe^{2+}/Mg and greater Ni/Fe^{2+} and Ni/Mg ratios than the biotite of any other granite. This granite is slightly more basic than the others and according to Albuquerque (1973) it is normal for the biotites of more basic rocks to contain more V, Ni, Co, Ba and greater Ni/Fe^{2+} , Ni/Mg ratios than those of more acid. The biotite of G X is unique in containing more Dy, Tb, Gd, Sm, Nd, La, and Au and less Sc and greater $\Sigma \text{Ce}/\Sigma \text{Y}$ ratios than any other

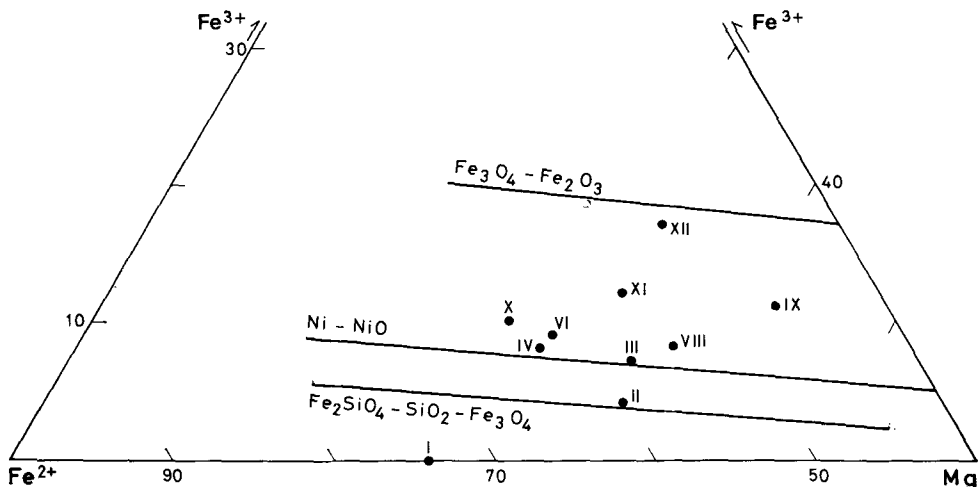


FIG. 4. Fe^{3+} - Fe^{2+} -Mg diagram of biotites from granites of northern Portugal. Lines: composition of biotites in the system $\text{KFe}^{3+}\text{AlSi}_3\text{O}_{12}(\text{H}_{-1})$ - $\text{KFe}^{2+}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ - $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ at constant f_{O_2} (after Wones and Eugster, 1965). • Alijó-Sanfins biotites.

biotite and there is a break in composition between G X biotite and the G XI and G XII biotites for some elements and ratios. There are also differences between the two presumed differentiation series. In particular, Mg, Ca, Mn, Sn, V, Co, and Zr vary in opposite ways in the two sets of micas.

Conditions of biotite formation. Wones and Eugster (1965) have studied the stability of biotite and given an 'educated guess' as to the biotite compositions likely under particular buffered conditions of f_{O_2} . The present biotite compositions have been plotted on this diagram and most fall close to either the Fe_2SiO_4 - SiO_2 - Fe_3O_4 or the Ni-NiO curve (fig. 4). If it is assumed that the biotites finally equilibrated at a temperature of about 700 °C, it is then possible to estimate roughly their f_{O_2} value. At this temperature and for the composition of these particular biotites the micas should be in equilibrium with potash-feldspar and iron oxides. Variations in total pressure will not greatly affect this equilibrium for the curves are not especially sensitive to pressure changes. From the molar composition of the biotites and the estimated f_{O_2} , the $f_{\text{H}_2\text{O}}$ can be calculated (these calculations are inevitably approximate and assume that the

activity of coexisting phases is unity). The $\log f_{O_2}$ values and P_{H_2O} values (from f_{H_2O}) obtained by these calculations are:

Biotite	G I	G II	G III	G IV	G VI	G VIII	G IX	G X	G XI	G XII
Log f_{O_2}	-19.7	-17.6	-16.3	-16.2	-16.2	-15.8	-14.2	-15.3	-14.2	-12.3
P_{H_2O} (bars)		178	819	2000	2000	935	4000	5000		

Taken at face value the results show that f_{O_2} increases slightly during the crystallization of both series of differentiates. This contrasts with results given by Albuquerque (1973), who found that f_{O_2} decreased during the crystallization of rocks varying from tonalite to granite. However, it seems reasonable to expect increase in P_{H_2O} to be equated with more oxidized minerals and if the later granites are residual from the earlier they might be expected to have a higher concentration of volatiles. The biotites from G I, G XI, and G XII give wild results for the calculation of P_{H_2O} . For G I the result is very low and the determined composition may not be sufficiently accurate. For G XI and G XII the P_{H_2O} value is very high and this may be attributed to post-solidification oxidation of the micas. The reddening of the feldspars may be an indication of this oxidation. The later granites show the highest P_{H_2O} and since $P_{total} > P_{H_2O}$, it seems that at least the later granites crystallized at a depth of more than 15 km. The total amount of mica increases through the series G II to G VI as the estimated P_{H_2O} increases. The calculated P_{H_2O} is lower in G VIII than in G VI and this is satisfactorily reflected in the reduced total quantity of mica in G VIII.

The role of tin in biotites has been widely discussed. Hesp (1971) noted a strong resemblance between the behaviour of Sn and Fe^{2+} , Fe^{3+} , and Ti^{4+} and considered that it would be diadochic with Ca^{2+} . Dmitriev *et al.* (1962) suggested that Fe^{3+} was more closely related than Fe^{2+} and Barsukov (1957), Barsukov and Durasova (1966), Hesp (1971), and Oliveira (1972) noted a positive correlation between Li and Sn. This was explained by Barsukov (1957) as the result of isomorphous replacement of $(Fe^{2+} + Mg^{2+})$ by $(Li^+ + Fe^{3+})$. Hesp (1971) and Levashev *et al.* (1971) found a negative correlation between Sn and Ti and attributed this to the greater degree of covalency of the Sn-O bond relative to the Ti-O and hence to the greater electronegativity of Sn. There are also negative correlations between total iron and Sn and between Fe^{2+}/Fe^{3+} and Sn (Rattingan, 1964, reported in Hesp, 1971). In the present micas Sn is positively correlated with Si and Li and negatively with Al^{IV} , Ti, and Fe^{3+} , total iron, and Fe^{2+}/Fe^{3+} . Li is therefore negatively correlated with Ti (fig. 5a). Thus support is found for the previous work and it seems likely that Sn substitutes in octahedral sites.

Hesp (1971) proposed an empirical function based on these relationships that he called the tin-holding capacity (THC) of biotites. The expression given was $THC = [(Fe^{3+} + Li^+)/ (Fe^{2+} + Mg^{2+})] - [(Ti^{4+} + Mn^{2+})/10]$ and this was found to be correlated with the Sn content of the mica. Calculation of the function for the present biotites, however, shows no direct correlation with Sn though there is, as Hesp also showed, a negative correlation between THC and the modal amount of biotite and chlorite in the granites. It has also been found that another formula proposed by Hesp is obeyed

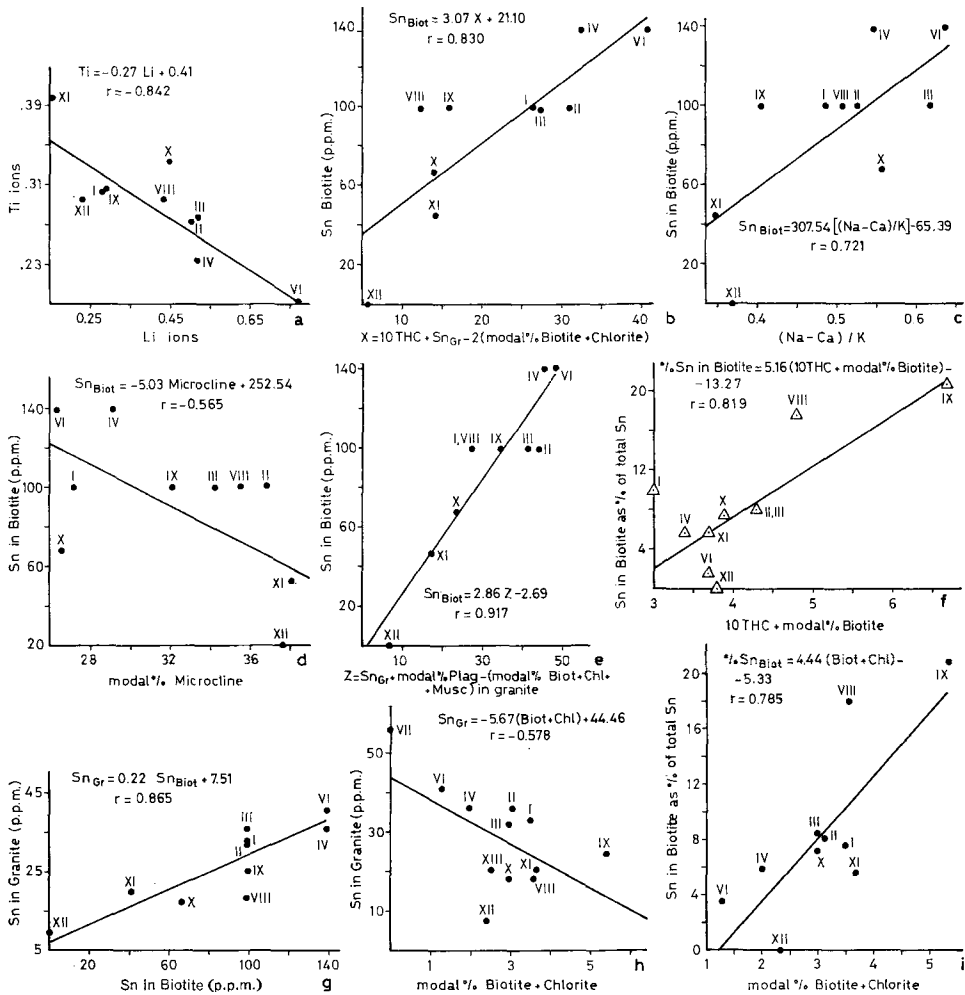


FIG. 5a: Correlation between Ti and Li ions of biotite from granites of northern Portugal. b: Tin in biotite as function of $[10THC + Sn_{Gr} - 2(modal\% biotite + chlorite)]$. THC = tin-holding capacity. Sn_{Gr} = tin content of granite (ppm). c: Correlation between Sn in biotite and the degree of albitization of the granites. d: Correlation between Sn in biotite and modal percentage of microcline in the granite. e: Correlation between Sn in biotite and $[Sn_{Gr} + modal\% plagioclase - (modal\% biotite + chlorite + muscovite)]$ in granite. f: Correlation between Sn in biotite as a percentage of total Sn and $10THC + modal\% biotite$. g: Correlation between Sn in granite and Sn in biotite. h: Correlation between Sn in granite and modal percentage of biotite + chlorite in the granite. i: Correlation between Sn in biotite as a percentage of total tin and modal percentage of biotite + chlorite in the granite.

by the present rocks, i.e. Sn (biotite) is proportional to $[10THC + Sn(\text{granite}) - 2(modal\% biotite + chlorite)]$ (fig. 5b).

The tin content of the biotites is related to several chemical and modal variations in the present granites and many of these relationships reflect the degree of albitization of the granites (fig. 5c). As albite increases at the expense of microcline so the tin

content of the biotite rises. This effect is shown by both differentiation series. The tin content of the granites themselves also rises as the amount of microcline falls (fig. 5d) so that the mineralization appears to be related to the albitization as Karaeva (1968) has suggested. It is therefore not surprising to find that the tin content of the granites is positively correlated with Na^+ , Li^+ , and Cs^+ and negatively correlated with Ti, Fe^{3+} , K^+ , Cr, Ni, Zr, and Sr of the granites. The tin content of the biotites can be correlated with numerous empirical formulae. For example the Sn(biotite) is proportional to $\text{Sn}(\text{granite}) + \text{modal } \% \text{ plagioclase} - (\text{modal } \% \text{ biotite} + \text{chlorite} + \text{muscovite})$ (fig. 5e); the percentage of tin in biotite is also proportional to $10\text{THC} + \text{modal } \% \text{ biotite}$ (fig. 5f) and $10\text{THC} + \text{modal } \% (\text{biotite} + \text{chlorite})$. The combination of positive correlation between tin in granite and biotite (fig. 5g) and negative correlation between tin in granite and the modal percentage biotite (fig. 5h) means that the higher quantities of tin are concentrated in smaller amounts of the mica. However, the amount of tin in the tin-rich granites is such that the tin-rich micas contain a smaller percentage of the total tin than does the mica of the tin-poor granites (fig. 5i). Hence high Sn content of biotites reflects possible mineralization. Barsukov (1957) indicated that the tin was held isomorphously in the biotite lattice, but Hesp (1971) found that some biotites held less than 45 % of the total rock tin and in high-tin granites this fell to 10 to 20 %. The present biotites hold less than at most 21 % of the available tin.

Conclusions. The biotites can be distinguished from one another by both major and trace elements and they show sequential change through the presumed differentiation series. Their chemistry also indicates differing f_{O_2} values. At 700 °C, f_{O_2} can have values ranging from 10^{-18} to 10^{-12} and tends to increase slightly through the differentiation series. $P_{\text{H}_2\text{O}}$ calculated from the f_{O_2} and mica composition also increases through both series, reflecting increase in the modal quantity of mica. It is inferred that at least two of the granites formed at a depth greater than 15 kilometres, though the calculations have to be used with caution for there is the possibility of subsequent change in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of the micas. The tin content of the biotites is probably not dependent of f_{O_2} or total pressure but on temperature. It increases with decrease of temperature and varies inversely with Ti in the Y group in the differentiation older to younger rocks, suggesting that the mechanism of concentration is fractional crystallization. Tin probably substitutes isomorphously for some of the octahedral cations and is not influenced by the presence of fluorine.

Various empirical formulae relate the tin content of the micas to the granite chemical and modal composition. The biotites contain less than 21 % of the tin content of the granites and the amount is directly related to the granite composition. A high tin content of the granite corresponds with a high tin content of biotite, a low modal percentage of biotite and a low percentage of the total tin held in the biotite. The development of the high tin content of the granites is directly related to the degree of albitization and hence high tin (and lithium) contents of biotites seem to reflect possible mineralization.

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REFERENCES

- ALBUQUERQUE (C. A. R.), 1973. *Geochimica Acta*, **37**, 1779–802.
- BARBUKOV (V. L.) [Барсуков (В. Л.)], 1957. *Geochemistry*, 41–51 (transl. of Геохимия).
- and DURASOVA (N. A.) [— и Дурасова (Н. А.)], 1968. *Geochemistry Int.* **3**, 97–107 (transl. of Геохимия, 168–79).
- DMITRIYEV (= DMITRIEV) (L. V.), KOTINA (R. P.), and MOISEYeva (= MOISEEVA) (R. P.) [Дмитриев (Л. В.), Котина (Р. П.) и (Мойсеева (Р. П.)], 1962. *Geochemistry*, 248–65 (transl. of Геохимия, 220–35).
- ENGEL (A. E. J.) and ENGEL (C. G.), 1960. *Geol. Soc. Amer. Bull.* **71**, 1–58.
- FOSTER (M. D.), 1960. *Geol. Surv. Prof. Paper* **354B**, 1–49.
- FYFE (W. S.), 1970. *Geol. Journ. Special Issues*, **15**, 187–216.
- GOKHALE (N. W.), 1968. *Bull. Comm. Géol. Finlande*, **40**, 107–11.
- HEINRICH (E. W.), 1946. *Amer. Journ. Sci.* **244**, 836–48.
- HESP (W. R.), 1971. *Geochemical Exploration. Canadian Inst. Mining Metallurgy Spec.*, **11**, 341–53.
- ISHIKAWA (H.), SHIBATA (H.), and NEGISHI (R.), 1963. *Japanese Journ. Geol. Geogr.* **34**, 67–80.
- KARAYEVA (= KARAEVA) (Z. G.) [Караева (З. Г.)], 1968. *Dokl. Akad. Nauk S.S.S.R., Earth Science Sect.*, **179**, 164–6 (transl. of Докл. акад. наук СССР).
- KOZLOV (V.) [Козлов (В.)], 1969. *Geochemistry Int.* **6**, 269–80 (transl. of Геохимия, 309–21).
- LEVASHEV (G. B.), STRIZHKOVA (A. A.), and GOLUBEVA (E. D.) [Левашев (Г. Б.), Стрижкова (А. А.), и Голубева (Е. Д.)], 1971. *Doklady. Akad. Nauk S.S.S.R.*, **202**, 207–10 (transl. of Докл. акад. наук СССР).
- LYAKHOVICH (V. V.) [Ляхович (В. В.)], 1970. *Geochemistry Int.* **7**, 824–34 (transl. of Геохимия, 1215–24).
- MOGAROVSKIY (V. V.) and MEL'NICHENKO (A. K.) [Могаровский (В. В.) и Мельниченко (А. К.)], 1968. *Ibid.* **5**, 893–99 (transl. of Геохимия, 1088–96).
- NEIVA (A. M. R.), 1971. Unpublished Ph.D. dissertation, University of Cambridge, England.
- NICHOLLS (G. D.), GRAHAM (A. L.), WILLIAMS (E.), and WOOD (M.), 1967. *Anal. Chem.* **39**, 584–90.
- NOCKOLDS (S. R.), 1947. *Amer. Journ. Sci.* **245**, 401–20.
- and MITCHELL (R. L.), 1948. *Trans. Roy. Soc. Edin.* **61**, 533–75.
- NORRISH (K.) and HUTTON (J. L.), 1969. *Geochimica Acta*, **33**, 431–53.
- RUB (M. G.), 1972. *Chem. Geology*, **10**, 89–98.
- OLIVEIRA (J. M. S.), 1972. *Estudos, Notas e Trabalhos do S. F. M., Portugal*, **19**, 227–75.
- SEN (N.), NOCKOLDS (S. R.), and ALLEN (R.), 1959. *Geochimica Acta*, **16**, 58–78.
- TAUSON (L. V.) [Таусон (Л. В.)]. 1967. *Geochemistry Int.* **4**, 1067–75 (transl. of Геохимия, 1310–9).
- WONES (D. R.) and EUGSTER (H. P.), 1965. *Amer. Min.* **50**, 1228–72.

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