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PREPARATION, ANALYSIS, AND SAMPLING CONSTANTS FOR A BIOTITE

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A 99.9+ percent pure 40-60 mesh biotite, intended primarily as a K-Ar dating standard, but useful in other applications, has been exhaustively analyzed. About 8 kilograms have been prepared for distribution.

Sampling constants K_s (*i.e.* the weights of samples necessary for 1% sampling error) have been determined for potassium (0.005 g), for sodium (1 g), for total iron (0.005 g), for calcium (2 g), for aluminum (0.001 g), and for some other elements. Nonuniformity with respect to potassium, sodium, and calcium may be partly due to diadochic substitution: nonuniformity with respect to calcium may be caused in part by 0.02 percent of apatite impurity.

mineral standard of known composition and uniformity. While it was originally intended as a K-Ar dating reference sample, its usefulness in other applications has been demonstrated.

LP-6 is a biotite-pyroxenite from one of many biotite-rich zones in a pyroxenite mass peripheral to the Simalkameen composite pluton in the northern Okanogan Highlands of Washington State. It was found by C. D. Rinehart [1] during a geochronological study, and was chosen from among several other similar rocks for its richness in biotite, the quantity available, the predicted ease of mineral separation, and the approximate expected age. The biotite-pyroxenite is coarse-grained, xenomorphic granular, with grains up to 2 cm in linear dimension, and consists chiefly of augite and biotite. Minor amounts of microcline, albite, rutile, ferrohastingsite, apatite, calcite and magnetite are present. In thin section, the biotite is subhedral to anhedral and interstitial to augite, with local eutectic intergrowths in which augite encloses biotite grains poikilitically. Thus, the biotite is a primary constituent. Some bent cleavage traces show post-crystallization deformation in the biotite. Generally, the biotite is green, with minor brown biotite intergrown.

Determinations of CO_2 and P_2O_5, using large samples, showed 0.00 percent CO_2 and 0.00 – 0.03 percent P_2O_5, indicating the absence of calcite and a trace of apatite. A formal microscopic inspection of 1000 grains revealed no mineral other than biotite, and no visible inclusions. However, during numerous other examinations of LP-6 Bio grains, we have occasionally found inclusions of rutile, apatite, *etc.*

TABLE 4. *Analysis of fractions of LP-6 Biotite 40-60 #* [a]

Fraction Number	Weight (g)	Subsample (g)	$\%K_2O$	$\%Na_2O$	$\%CaO$	$\%Fe_2O_3$
1. Blocky	0.4	0.100	9.80	0.07	0.36	11.55
2.	.8	.100	9.90	.06	.31	11.95
3.	2.7	.100	9.78	.06	.28	11.69
4.	1.9	.100	9.95	.07	.24	11.51
5.	6.9	.100	10.03	.06	.16	11.81
6. Flaky	8.4	.100	10.08	.12	.11	11.76
1. Blocky (eight determinations)		.005			.34 to .38	

[a] Analyses by L. B. Schlocker and C. O. Ingamells.

The electron microprobe has been used to investigate the homogeneity of LP-6 Bio + 16 mesh. Two distinct biotites were found; these are individually homogeneous (except for calcium), as shown by the indices $\sigma/\sqrt{N}$ in table 7. The biotite PSU 5-110 [8] was used as a calibrating standard in these analyses; PSU 5-110 has never shown any measurable degree of inhomogeneity, even at the microprobe sampling level, and was analyzed by the most sophisticated primary methods available. The two LP-6 biotites are distinguishable visually in epoxy grain mounts, the high-Fe species occurring in more massive "blocky" grains. Some obvious anomalies in the data remain unexplained: while results on the +16 mesh material are not strictly comparable to those on the 40-60 mesh material, the need to consider the sampling characteristics of even the purest mineral separates is clearly demonstrated.

TABLE 7. *Microprobe analyses of LP-6 Biotite fractions*

	5–110[a]		LP–6 high Fe[b]		LP–6 low Fe[b]		LP–6 Bio 40–60#	
	wt %	$\sigma/\sqrt{N}$	wt %	$\sigma/\sqrt{N}$	wt %	$\sigma/\sqrt{N}$	wt %[c]	wt %[d]
SiO_2	38.63	1.2	37.67	1.5	39.08	1.2	37.83	38.33
Al_2O_3	13.10	1.5	15.58	1.7	15.48	1.2	15.21	15.30
TiO_2	1.58	1.7	1.80	2.5	1.60	0.9	1.52	1.67
FeO[e]	10.93	1.7	11.17	1.2	9.54	1.0	11.10	10.58
MnO	.14	1.1	0.10	1.5	0.06	2.2	0.16	0.11
MgO	19.90	2.4	18.63	2.3	20.03	1.1	19.66	19.35
CaO			0.05	8.0	0.03	6.4	0.04	0.21
K_2O	10.00	1.1	10.21	1.1	10.24	1.8	10.14	10.03
Na_2O	0.26	1.2	0.09	2.1	0.13	3.2	0.14	0.09

[a] Used as a calibrating standard. Chemical analysis by C. O. Ingamells.
[b] Microprobe analyses by G. K. Czamanske.
[c] Microprobe analysis by J. Gittins.
[d] Most probable values for LP–6 Bio 40–60# (see tables 8 and 9).
[e] Total iron calculated to FeO.

VI. Chemical Analysis and Stoichiometry

Our best estimate of the gross chemical composition of LP-6 Bio 40-60 mesh is given in table 8. Data accumulated here comes from many sources: contributors are listed at the end of this article. Values for K and for Ar* are listed by contributor in table 2. Less complete analyses of certain fractions of LP-6 Bio are presented in table 9. Calculated gross stoichiometry appears in table 10. The mineral is best described as eastonite, a trioctahedral mica.

TABLE 8. *Composition and homogeneity of LP-6 Biotite 40-60 #*

	Sample weight (g)	Wt %	K_s (g)
SiO_2[a]	0.7	38.33	0.001
Al_2O_3[a]	.7	15.20	.001
TiO_2[a]	.7	1.67	.05
Fe_2O_3[b]	3.7[c]	2.25	.005 (total Fe)
FeO[a]	0.5	8.55	K_s for FeO probably high
Cr_2O_3		0.04 (?)	K_s probably high
V_2O_5		0.02 (?)	
MnO[a]		.11	0.01
NiO		.05 (?)	
CoO		.01 (?)	
ZnO		.01	
MgO[a]	0.7	19.32	.005
CaO[a]	.7	.21	2.
BaO		.22	0.01
Li_2O		.005	
Na_2O[b]		.09	1.
K_2O[b]	10.0[d]	10.03[d]	0.005
Rb_2O[b]		0.025	
Cs_2O		.0006	
H_2O+[a]	1.0	3.53	see text, table 6
H_2O-[a]	0.7	0.13	see text, table 6
F[a]		.26	
P_2O_5[a]		.01	(0.00, 0.03) K_s probably very high
CO_2[a]	2.0	.00	
less 0 = F		0.11	
Total		99.97	

TABLE 9. *Analyses of LP-6 Biotite 32-40#, 40-60#, + 16#*

	32–40# Split 20	40–60# 9–II–C–2	40–60# 8–II–B–1	40–60# Blocky	40–60# Flaky	+16#[a]
SiO_2	38.40	38.33		38.26	38.30	38.52
Al_2O_3	15.17[b]	15.30[b]	15.28[b]	15.26[b]	15.31[b]	15.52
TiO_2	1.66	1.67	1.67	1.54	1.69	1.68
Fe_2O_3	2.29	2.25	2.27	2.32	2.20	(2.16)
FeO	8.52	8.55	8.55		8.58	8.25
MnO	0.11	0.11	0.11	0.11	0.11	0.08
MgO	19.30[c]	19.35[c]	19.32[c]	19.28[c]	19.37[c]	19.47
CaO	0.41	0.21	0.19	0.34	0.14	0.04
BaO		.22	.22			
Na_2O	.09	.09	.09	.06	.12	.11
K_2O	10.03	10.03	10.03	9.85	10.08	10.23
Rb_2O	0.03	0.03	0.03	0.03	0.03	
H_2O+	3.45	3.66	3.50	3.75	3.48	
H_2O-	0.09	0.13	0.11	0.26	0.14	
F		.26	.26			

[a] Electron microprobe analysis by G. K. Czamanske.
[b] Uncorrected for Cr_2O_3, V_2O_5, etc.
[c] Uncorrected for NiO, ZnO, etc.

TABLE 10. *Gross stoichiometry of LP-6 Biotite 40-60#*

				Relative error
Na	0.026			
K	1.879			
Rb	0.004			
Ca	.033			
Ba	.011			
H_2O	.057			
		2.00	$(Na, K, Rb, Ca, Ba, H_2O)^{+2.00}_{\ 2.00}$	0.00
Mg	4.227			
Zn	0.001			
Mn	.014			
Ni	.006			
Co	.001			
Li	.004			
Fe″	.747			
		5.00	$(Mg, Zn, Mn, Ni, Co, Li, Fe^{++})^{+10.00}_{\ 5.00}$	0.00
Fe″	0.303			
Fe‴	.249			
Cr	.005			
V	.002			
Ti	.184			
Al	.257			
		1.00	$(Fe^{++}, Fe^{+++}, Cr, V, Ti, Al)^{+2.89}_{\ 1.00}$	−.11
Al	2.374			
Si	5.631			
		8.00	$(Al, Si)^{+29.65}_{\ 8.00}$	−.35
OH^-	3.399			
F	0.120			
		3.52	$(OH^-, F)^{-3.52}_{\ 3.52}$	+.48
O	20.48			
		20.48	$(O)^{-40.96}_{\ 20.48}$	
Total		40.00		−0.01

Note: There is a residual of 0.02 moles of H_2O, representing an uncertainty of about 0.02 percent in the dividing of total H_2O into H_2O+ and H_2O-. The inclusion of 0.057 moles of H_2O with the interlayer alkalies is arbitrary.

VII. Discussion

Although LP-6 Bio 40-60 mesh is better than 99.9 percent pure biotite, and contains far fewer impurities than most widely distributed mineral standards, it shows perceptible nonuniformity at the analytical subsampling level.

Figure 2 is a sampling diagram [9] for potassium in LP-6 Bio 40-60 mesh. The expected variability due to subsampling error in analytical results for potassium is found [6] from $R = \sqrt{K_s/w}$ percent, where R is the relative deviation due to subsampling error, K_s is the sampling constant for potassium (0.005 g for LP–6 Bio 40–60 mesh), and w is the analytical subsample weight in grams. Table 11 shows some corresponding values of R and w for potassium in LP–6 Bio 40–60 mesh.

Table 12 gives similar data for radiogenic argon. It is evident that subsample weight is an important parameter which must not be ignored in data evaluation, especially in standards programs. For example, if LP–6 Bio 40–60 mesh is used as a calibrating standard in ^{39}Ar–^{40}Ar dating, where small subsamples (≈ 10 mg) are the rule, a large variance may be expected: in conventional K–Ar dating, where larger subsamples of up to 500 mg are taken for argon analysis, variance due to sampling

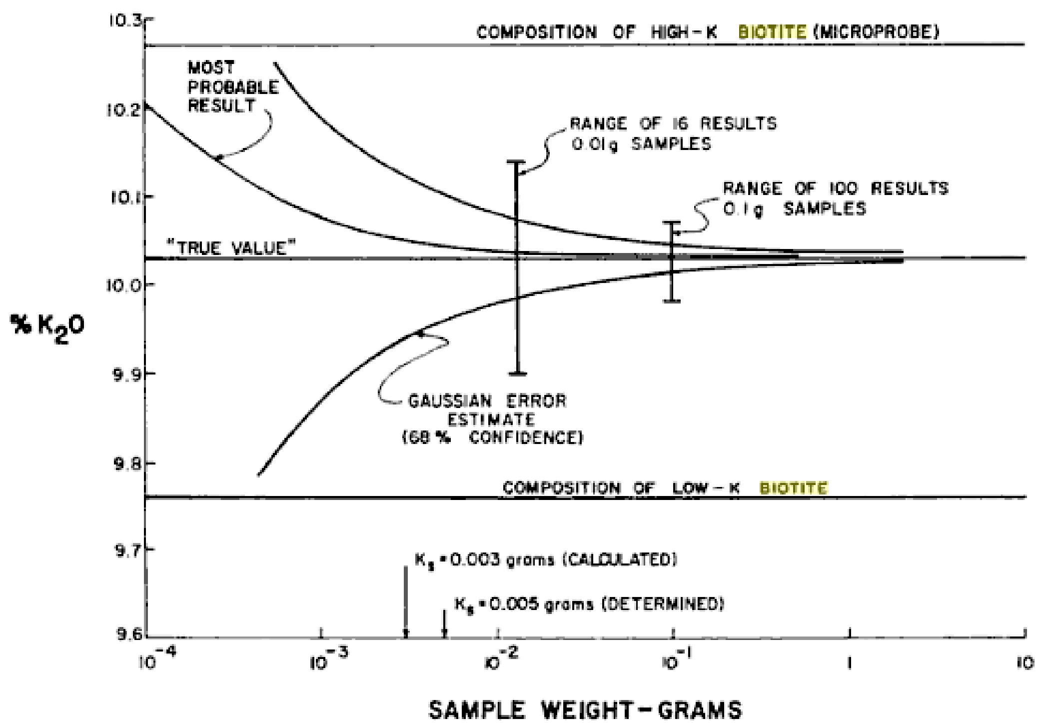

Figure 2. Sampling diagram for potassium in LP-6 Bio 40-60 mesh.

LP-6 Bio 40-60 mesh may be used as a microprobe standard for potassium if high-K grains are selected and they are taken as having 10.27 percent K_2O. It will probably be useful as a microprobe standard for iron, aluminum, silicon, and magnesium; this has not been thoroughly confirmed. Its worth as an emission spectrometric standard for major elements has been established. It is probably not desirable as a ^{39}Ar-^{40}Ar dating standard; in fact, its deficiency in this respect may draw attention to a hitherto unrecognized weakness of the ^{39}Ar-^{40}Ar method.