Geostandards - A New Approach to their Production and Use

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Selection, preparation, analysis for composition and for degree of homogeneity, certification and distribution of a useful geochemical reference sample is a long and complicated endeavour. Certain basic principles must be observed if this endeavour is to be successful. The material must be adequately uniform, its degree of homogeneity must be reported, certificate values must be reliable, and there must be enough left after certification to be useful. These principles have been followed in preparing and distributing a K-Ar dating standard, LP-6 Bio 40-60#, which may serve to illustrate them. Sources of error in preparation and utilization of geochemical reference samples have been investigated.

Geochemical analyses of all kinds depend on analyzed standards for calibration and control. These geostandards should be prepared with the needs of the user in mind: They should be provided with a certificate of analysis which reports degree of homogeneity for constituents of interest.

Biotite LP-6 Bio 40-60#, originally prepared as a geochronological standard, represents a first attempt to provide the geochemical community with a mineral standard of known composition and uniformity. LP-6 data show that failure to consider the sampling characteristics of geostandards can be devastating in all applications, and that a new approach to the production, certification, *and use* of such standards is imperative.

FACTORS TO CONSIDER DURING PREPARATION OF GEOSTANDARDS

APPLICATION

The uses for which the geostandard is intended must be a first consideration. For instance, many pure biotites would suffice as potassium standards, but if a biotite is also to be used as an argon standard, its absolute age becomes a consideration. Each additional application will make the problem of selecting a source material more difficult.

Even if a mineral contains all the elements of interest in the desired concentrations, chances are that an adequate degree of homogeneity cannot be achieved for all of them. A single investigator or institution may find it impossible to develop and analyze for composition and uniformity a geostandard suitable for all applications. Few organizations have the time and facilities to certify a material for all constituents of interest; most will have to be satisfied with reporting on an element or elements for which they have special competence. If, however, other investigating agencies are provided with sufficient material and with all available data, they may be able to determine sampling constants and concentrations for other constituents of interest.

It will be seen from data here presented that *USE OF A GEOSTANDARD AS A REFERENCE IN PROCEDURES FOR WHICH IT IS NOT INTENDED OR CERTIFIED MAY LEAD TO ERRONEOUS RESULTS AND TO ENORMOUS WASTE OF TIME AND EFFORT.*

AMOUNT

Before a preparation is begun, an estimate should be made of the number of potential users and their needs over a reasonable number of years. Enough must be produced to provide for extensive homogeneity tests and preliminary analyses, and still leave a useful supply for distribution. Geostandards which become exhausted at about the time they achieve usefulness should never have been prepared. Adequate preliminary information should be provided by the originator of the material so that it is not wasted on fruitless tests for inhomogeneously distributed elements. The geochemical community must be persuaded that expensively produced material intended for interlaboratory calibration ought not to be expended unnecessarily in routine work.

SEPARATION AND PURIFICATION

Choice of a field sample depends on projected application and intended methods of separation, purification, and packaging. The amount to be prepared may determine whether a mineral can be obtained from a single

crystal, or must be separated from crushed rock.

Sufficiently large crystals, in addition to being rare, may carry so many inclusions or be so zoned with respect to the element or elements of interest that the crushed material behaves virtually as a rock powder. If a single mineral phase is desired, extensive microscopic examination of thin sections and of rock powder is necessary to determine liberation size and to identify mineral phases which might render the final product poorly sampleable or otherwise undesirable.

Selection of methods of separation may be influenced by grain-size requirements, or by alteration of mineral structure during grinding and flotation or other processes. Oxidation of iron and loss of combined hydrogen may occur during grinding, washing, and drying. Heavy-liquid separations may be contraindicated if the product is to be used in mass spectrometry or if large amounts of crushed rock must be processed.

Packaging methods must avoid contamination of the material from equipment and containers; reagents used in separation and purification, and also in pretreatment of the packaging material, should be reported.

The amount and type of impurity should be carefully determined and reported to collaborating analysts, because impurities affect the sampleability of the product, especially when small subsamples are taken. Impurities can have several undesirable effects:

-a sampling effect (1-3);

-a gangue effect, which lowers the concentration of the constituent of interest;

-an interference effect, which depends on the method of analysis (as, for example, the effect of thallium from heavy liquids on some methods for determining alkali elements);

-and, in geochronology, the effect of a contaminant of different age from the bulk of the material (4).

It is our experience that unsampleability due to impurity in mineral separates has probably been the most important contributor to interlaboratory differences -- not analytical error or differences among methods.

INVESTIGATION OF INHOMOGENEITY

All geochemical materials are inhomogeneous at *some* sampling level for *each* constituent, due to impurities, zoning, or, in the case of rock powders, a general heterogeneity. Repetitive analysis of small subsamples, using precise analytical methods, will reveal the degree of inhomogeneity for each constituent, to discover if there is sufficient uniformity among subsamples. What is "sufficient uniformity" needs to be agreed upon in advance by potential users, and a statement of it should take the form "reproducibility using w-gram subsamples is X% of the amount present with Y% confidence". If the bulk sample exhibits satisfactory sampleability *at the lowest subsample weight used* by participating laboratories, it can be certified as a useful standard. If not, further purification or grinding or mixing is needed (this will, of course, reduce the total amount available for distribution), or investigators whose methods demand too-low subsample weights will have to seek another standard.

It should devolve on the producer of a geostandard to perform tests using smaller and smaller subsamples until the inevitable inhomogeneity appears and can be quantified. This should be done *before* numerous investigators donate time and effort to the project. If the primary producer cannot define the region of unsampleability, those working with subsample weights below those used by the primary producer should perform their own inhomogeneity tests before placing reliance on the certificate value or on their own results.

Attempts may be made to fractionate the prepared material by any appropriate means (e.g. using magnetic, chemical, density or shape properties). Analyses of the several fractions so obtained may be used to predict and quantify behaviour of the material at low subsample weights.

CERTIFICATION

Certificate values should take the form :

XO ___ ± ___ weight %; K_s = ___ grams

where the ± is a measure of the uncertainty between bottles, including sampling weight base line and analytical uncertainty, and K_s is a sampling constant, used to estimate subsampling error for a given subsample weight. Although only one or two elements may be so certified, a complete analysis should be made by primary methods and reported. Reporting in this way can eliminate the common mistake of attempting calibration of an analytical method using unsuitable standards or using subsample weights too small to provide the desired precision.

Publication of data on geoanalytical standards should include *all* contributed information, including not only concentrations, but also effective subsample weights and methods of calibration (2). Since the reported value is a function of subsample weight, statistical treatment of reported values to obtain an average or a "consensus average" is invalid unless all subsample weights are taken into account. In the absence of information as to the subsample weight used to obtain a value, no statistical treatment should be attempted. In cases where the subsample weights used by a contributor are below that needed to ensure an adequately representative subsample, his average value may be erroneous. If many contributors use too-small subsample weights, an "outlier" may provide the only correct value.

It is a disappointment to us that most contributors of LP-6 data have not heeded our requests that they provide a statement

of their calibration procedure and of their effective subsample weights.

TIME AND COST

Most producers of geostandards are not in the business of simply preparing reference samples--this is often a necessary but unwelcome adjunct to their regular work. An estimate of the time required to prepare a viable geostandard may be useful to anyone who contemplates such an effort. In the case of LP-6 Bio 40-60#, we estimate that we and contributors have spent more than 4000 hours in the preparation, analysis, and distribution described here.

A vehicle such as this journal might in the future be instrumental in advertising an intent to produce a geostandard. Others could then contribute suggestions as to homogeneity needs, amounts required, elements of interest, possible field sources of starting material, suggestions for mineral separation techniques, and methods of analysis. In this way it might be possible to share the work leading to certification and avoid the duplication of effort which has characterised some efforts in the past. The more elements are involved, the less likely it is that a single investigator will have the necessary time, equipment, skill, and money to provide certification.

PREPARATION AND CERTIFICATION OF LP-6 Bio 40-60#

There follows a discussion of how each of the above factors applies to the preparation and certification of LP-6 Bio 40-60#.

SOURCE

LP-6 was chosen for preparation of a geochronological standard because of its fresh, unaltered (hence, high K_2O) biotite, and because of its expected K-Ar age (100-150 my). The field sample, found by C.D.Rinehart (5), is a biotite-pyroxenite from one of many biotite-rich zones in a pyroxenite rimming the Similkameen composite batholith in north-central Washington State. The field sample was selected from among about twenty possible sites after microscopic examination showed it to be best from the standpoint of richness in biotite, grain size, predicted ease of separation, and quantity available.

The biotite-pyroxenite is coarse-grained, xenomorphic-granular, with up to 2 cm grains, and consists of augite and biotite. Minor minerals include microcline, albite, rutile, ferrohastingsite, apatite, calcite, and magnetite. The biotite is generally a clear green, with very minor brown biotite intergrown. In thin section, the biotite is subhedral to anhedral and interstitial to augite; in some local areas there are eutectic intergrowths in which augite encloses biotite poikilitically. Some bent cleavage traces may indicate post-crystallization deformation of the biotite.

SEPARATION

About 400 kg of LP-6, containing about 20% biotite, were collected by Rinehart. A 10" Gy-roll reduction crusher was used to reduce the whole to about 20-mesh. Preliminary separation was accomplished in a 36" x 6" water column, using tap water. Material floated in the column was passed over a 30" square 105-mesh screen. The densities and grain sizes of the two major constituents, biotite and augite, were such that fine pyroxene washed through the screen, leaving a deposit of 95-98% pure biotite. The coarse gangue at the bottom of the column yielded additional biotite using a 14" x 4" water column and a 60- or 80-mesh screen. The wet biotite was washed with distilled water, dried, and screened. The 24-32, 32-40, and 40-60 mesh material was further purified using deionized water in the 14" x 4" column, with an additional distilled water rinse before drying. Each fraction was then passed through a Frantz Isodynamic Separator (setting: 15°,15°,0.56 amp.) at the rate of about 10 grams/hour.

YIELD

A total of 27 kg of biotite was recovered, of which 7.5 kg was 40-60#, 1 kg 32-40#, and 1.8 kg 24-32#. The 24-32# material was split into 320 2-gram portions and 256 5-gram portions. The 32-40# material was split into 172 5-gram portions. The 40-60# material was split into 960 8-gram portions. The +24-mesh fraction and the 60-100# fraction were not Frantzed and not split, because of lack of time and funds. Although the 24-32# and the 32-40# splits are 99.9% pure, little work has been done on them. Our efforts have concentrated on certification of the 40-60# material. After homogeneity tests, analyses and interlaboratory comparisons, about 4 kg of LP-6 Bio 40-60# remain available for distribution as a certified reference material, with about 1 kg in reserve. We regard this as a minimum supply of a sample of this kind; of a total of between 200 and 300 8-gram splits already distributed, about half have gone to geochronology laboratories.

PACKAGING

LP-6 Bio 40-60#, 32-40#, and 24-32# is distributed in glass vials which have been rigorously cleaned to remove the submicroscopic impurity always present on new glass (6,7).

SPLITTING SCHEME

LP-6 Bio 40-60# was split according to the scheme of Figure 1, by coning and quartering with a hard-rubber spatula on albanene paper. Metallic splitters were not used. Any tramp iron which might have been introduced during the initial crushing was removed during the magnetic separation. As far as possible, considering the mobility of the investigators, we are keeping records of which split belongs to which person or laboratory.

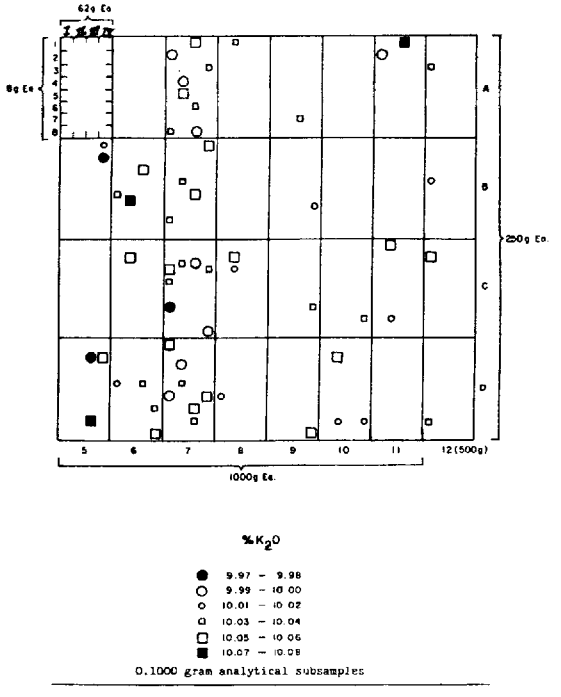

Figure 1. - Splitting scheme for LP-6 Bio 40-60#

The whole was first divided into seven 1000-g and one 500-g portions, designated 5 6 7 8 9 10 11 and 12. Each was then split into 250-g portions labelled A B C and D. Each of these was then split into four 62-g portions I II III and IV. Finally each of these was split into eight 8-g portions for distribution. Initial homogeneity tests for K_2O were performed in the manner indicated, and a sampling constant K_s = .005 gram was calculated.

IMPURITIES

Microscopic examination of 1000 grains of LP-6 Bio 40-60# revealed nothing other than biotite, and no inclusions. During other random examination of LP-6 Bio grains, however, we have found occasional rutile, apatite, etc.. A 1000-grain sample is insufficient to reveal the concentration of impurities; therefore, 100 grams were treated successively with 1:1 HNO_3, 6N NaOH, and then dilute HCl containing peroxide. Biotite dissolved completely, leaving 0.05 gram (0.05%) of unattacked pyroxene, amphibole, quartz, and feldspar. A few of the pyroxene grains were +60 mesh, but most of the residue was -60 mesh, indicating that most of the impurities existed as inclusions in the biotite grains. There were a few unidentified mineral grains; no zircons were detected.*Large samples were used to look for CO_2,(0.00%) and P_2O_5 (0.00-0.03%) indicating no calcite and a trace of apatite.

INHOMOGENEITY

Two types of tests were run on LP-6 Bio to check its homogeneity--one on the material as it is, and the other on deliberately fractionated material.

First, 59 0.1000-gram subsamples from different splits were analyzed for potassium; results are shown in Figure 1. The variance in these data is due to sample inhomogeneity, and not to analytical imprecision: this was demonstrated by repetitive determination of potassium on two mica samples which are completely homogeneous at the 0.1-gram subsampling level--PSU 5-110 and Nancy Mica-Mg(8). These data were used to calculate a sampling constant for potassium. Repetitive determinations on single bottles show essentially the same variance, indicating that there is no significant difference between bottles.

Table 1

SAMPLING CONSTANTS FOR POTASSIUM CALIBRATING STANDARDS

Sample	Weight % K_2O	Sampling constant** $\sqrt{K_s}$	K_s	w*
Nancy phlogopite Mica-Mg	10.18	.00 *	.000	.00
PSU biotite 5-110 [12]	10.00	.00 *	.000	.00
PSU orthoclase Or-1 [13]	14.92	.00 *	.000	.00
LP-6 Bio 40-60#	10.03	0.07	0.005	.045
Bern biotite 4B	9.47	0.11	0.012	.108
Nancy biotite Bio-R	8.80	0.11	0.012	.108
Nancy biotite Mica-Fe	8.84	0.1	0.01	.09
Nancy basalt BR	1.38	0.15	0.02	.18
Engels' amphibole	0.91	0.20	0.04	.36
USGS granite G-1	5.52	0.3	0.09	.81
USGS muscovite P-207	10.3	0.41	0.17	1.53
USGS basalt BCR-1	1.70	0.57	0.32	2.88
White mica	8.4(?)	2.1	4.4	39.6

* Even at the microprobe level of sampling, non-uniformity has not been detected in these materials.

** K_s is defined as the weight in grams which must be taken to ensure a sampling error no greater than 1% of the amount present, with 68% confidence. $\sqrt{K_s}$ is numerically equal to the coefficient of variation expected in a series of results on 1-gram subsamples using a precise analytical method. w* is the subsample weight required to diminish subsampling error to less than 1% of the amount present at the 98% confidence level.

Table 2

ARGON DATA FOR BIOTITE STANDARD LP-6 Bio 40-60# (7-II-D-1)*

Experiment Number	Sample wt. (grams)	$^{40}Ar^*$/gram (Moles x 10^{-9})	% $^{40}Ar^*$	$^{40}Ar^*/^{40}K$ (x 10^{-3})	Age (m.y.)
71036	.4263	1.934	78.9	7.635	126.2
37	.3987	1.930	89.2	7.620	126.0
38	.4107	1.926	84.2	7.603	125.7
42	.4209	1.923	91.8	7.589	125.5
73	.2032	1.926	93.0	7.602	125.7
74	.2046	1.946	93.7	7.682	126.9
75	.1993	1.948	74.4	7.689	127.0
76	.1973	1.935	93.7	7.651	126.4
77	.2019	1.937	95.2	7.644	126.3
79	.1964	1.938	79.9	7.651	126.4
80	.2120	1.963	95.7	7.747	128.0
82	.2224	1.926	96.3	7.643	126.3
72100	.2125	1.945	95.6	7.676	126.8
101	.2496	1.955	97.1	7.716	127.5
102	.2214	1.946	96.5	7.683	126.9

* Data of D. L. Turner, University of Alaska. A sampling constant was estimated from these data using the formula

$$K_s = \frac{10^4 \Sigma w_i (x_i - \bar{x})^2}{(N-1)\bar{x}^2}$$

where w_i are the subsample weights, x_i are the Ar* values, $\bar{x}$ is their arithmetic average. The formula yields $K_s \approx 0.09$ gram, which is too high because analytical error is not taken into account. Experience with homogeneous biotites indicates that analytical error is about 0.2% of the amount present (68% confidence), i.e. about half the relative error in Turner's data. We therefore estimate $K_s = 0.04$ gram. This value is supported by a calculation using the data of Turner and Kistler (Tables 3 and 4) in the general sampling constant equation (reference 10), which yield a sampling constant $K_s = 0.05$ gram.

Since providing these values, Turner has asked for slight revisions, and has added some more values. These result in a slight change in the overall weighted average, but do not affect the estimation of the sampling constant.

Sampling constant information for this and other geostandards appears in Table 1. The sampling constant K_s is defined as the weight of material which must be taken to ensure a sampling error no greater than 1% of the amount present with 68% confidence. $\sqrt{K_s}$ is numerically equal to the coefficient of variation expected in a series of analytical results on 1-gram subsamples using a precise method. w* is the sample weight which must be taken to reduce the uncertainty in the result to less than 1% of the amount present with 98% confidence.

Fifteen subsamples from a single bottle of LP-6 Bio 40-60# were run for radiogenic argon by D.L.Turner at the University of Alaska (Table 2). Since sample weights were provided, we were able to calculate a sampling constant for radiogenic argon, $K_s \sim 0.04$ gram. This is ten times as great as the sampling constant for potassium, K_s = 0.005 gram, and the reason for this called for investigation.

A 21-gram portion of LP-6 Bio 40-60# was deliberately fractionated by passing over a vibrating mica table. This yielded six fractions which ranged from blocky to flaky in appearance. The blocky material consisted of thick books which almost resemble amphibole in their appearance under the microscope, while the flaky material consists of typical thin biotite flakes. 100-mg subsamples of each fraction were analyzed for K_2O, Na_2O, CaO, and Fe_2O_3. In addition, eight 5-mg subsamples of the blocky material were analyzed for CaO, a microscope count of 500 grains having shown no mineral other than biotite. Results are shown in Table 3. The increase in K_2O with concomitant decrease in CaO from "blocky" to "flaky" is surprising. The overall CaO content is about 0.2%, measured on large samples of the bulk material. Spectrographic analyses show about 0.13%, with poor precision, and microprobe analyses show about 0.04%. The low values are due to the small subsamples demanded by the latter techniques, and reflect the Ca inhomogeneity revealed in experiments on the fractionated material.

Table 3

ANALYSIS OF FRACTIONS OF LP-6 Bio 40-60#

Fraction number	Weight (grams)	Subsample (grams)	% K_2O	% Na_2O	% CaO	% Fe_2O_3
1. Blocky	.4	.100	9.80	.07	.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	

Analysts--L. B. Schlocker and C. O. Ingamells

It is clear that contributed values from methods utilizing anywhere from a few tenths of a gram down to a single biotite flake will yield an erroneous average.

The source of the Ca inhomogeneity is not clear. It could be due to diadochic substitution of calcium for potassium, or to minute inclusions of calcium mineral which behave like biotite in the chemical separation of impurities described above. Microprobe analyses (below) support the inclusion hypothesis. Submicroscopic inclusions may be thermodynamically stable in a two-phase system (9), but their effect on gross composition has previously been largely ignored by mineralogists.

Table 4

GEOCHRONOLOGICAL INHOMOGENEITY OF LP-6 Bio 40-60#

Fraction number	% K_2O	$^{40}Ar^*$, M/g	Atmospheric argon, M/g	
1 - 3 (blocky)	9.86	1.78×10^{-9}	6.48×10^{-11}	(a)
6 (flaky)	10.08	2.08×10^{-9}	6.14×10^{-11}	(a)
1 - 3 (blocky)	9.81	1.785×10^{-9} 1.795×10^{-9}	(b)	
4	9.95	1.830×10^{-9} 1.839×10^{-9}	(b)	
5	10.03	1.932×10^{-9} 1.931×10^{-9}	(b)	
6 (flaky)	10.08	2.029×10^{-9} 2.037×10^{-9}	(b)	

(a) R. W. Kistler, U. S. Geological Survey

(b) D. L. Turner, University of Alaska

The six fractions were analyzed for radiogenic argon by Turner, and R.W.Kistler of the U.S. Geological Survey independently analyzed the blocky and flaky fractions; results were startling, particularly from the point of view of geochronologists (Table 4). The apparent age of the fractions ranges from 116 to 132 million years. This should not impair the worth of the material as a K-Ar reference, provided it is carefully mixed and split, and provided adequate subsample weights are employed. Use of LP-6 Bio 40-60# as an Ar^{39}-Ar^{40} standard is contraindicated.

Table 5

DIFFERENCES IN TOTAL HYDROGEN CONTENT *[14]

Sample number	Subsample weight	Total H as H_2O, %			H_2O-, 108°
5-III-B-3	0.05 g	3.58	3.65	3.60	0.12
		3.65	3.61	3.74	
		3.75	3.66	3.66	
	1.00 g		3.66		
9-II-C-2	0.05 g	3.82	3.77	3.73	0.13
		3.87	3.85	3.80	
		3.74	3.74	3.79	
			3.82	3.73	
8-II-B-1	1.00 g		3.61		0.11

* Results on small samples by microcoulometry, on large samples by Penfield fusion. Reference 14.

Sampling weight base line is a source of apparent inhomogeneity which is often ignored, so three bottles were checked for total hydrogen and "moisture" (reported as % H_2O, Table 5). The difference of 0.02 % H_2O between samples is large enough to have an appreciable effect on interlaboratory reproducibility for all major constituents when highly accurate methods are used; for example ±0.02 % K_2O and ±0.08 % SiO_2. In this case, drying the sample at 108°C does not remove the difficulty. While the H_2O (loss in weight at 108°C) in splits 5-III-B-3 and 9-II-C-2 does not differ appreciably, the total hydrogen values are quite different. Experiment with other biotites indicates that oxidation of iron and loss of combined hydrogen may be related. In using

LP-6 Bio 40-60# as a reference, sampling weight baseline effects will usually be negligible, but there may be a possibility of confusion and disagreement, especially for H_2O and Fe^{++}, if the cause of possible discrepancies is not recognized.

Table 6

SUBMITTED POTASSIUM AND ARGON DATA, LP-6 Bio 40-60#

Analyst	% K_2O	Analyst	Ar*, M/g x 10^{-9}
Armstrong	10.15	Armstrong	1.935
Baksi	10.06 10.09 10.01 10.09 10.14 10.04 10.07 10.14	Baksi	1.924
Gittins	10.14	Hebeda	1.956 1.933 1.933 1.902 1.941 1.936 1.910 1.922 1.900
Hebeda	10.09 10.12 10.09 10.07 10.08 10.01	Krueger	1.927 1.952 1.91 1.94
Schlocker (More than 100 determinations, of which 59 are plotted in Figure 1) Average, 10.03	9.97 to 10.08	MacIntyre	1.870 1.888 1.879
		McBride	1.921 1.903 1.914
Katsura	10.11	Rex	1.96 1.89 1.97
Krueger	10.06 10.07 10.19 10.20	Turner	1.934 1.930 1.926 1.923 1.926 1.946 1.948 1.938 1.937 1.938 1.963 1.936 1.945 1.955 1.946
MacIntyre	9.98 9.99		
McBride	10.17 10.10 10.13 10.16 10.08 10.18 10.02 10.05	Webb	1.926 1.922 1.918 1.918 1.942 1.930
Rex	9.84 9.92 9.89 10.01 9.95 10.07 9.98 9.97 9.94	Giuliani	1.92 1.87 1.85 1.85 1.90
Muysson	10.23 10.09	Radicati	1.92
Smith (gravimetric)	10.03	Other	2.024
Turner	10.03		
Webb	10.02 10.02 10.08 10.03 10.01 10.00 10.14 10.10		
Rice	10.02 10.07 10.07 10.05 10.08 10.09 10.04 10.00		
Other	9.31 9.30 9.45 9.42 9.67 9.62		

Table 6 shows K and Ar bulk sample results from several contributing laboratories. The scatter in these data is at least partially due to inhomogeneity, but without complete information on sample weights and methods of calibration, it is not possible to determine how much is due to analytical error, sampling error, or error in the calibrating standards.

Table 7

MICROPROBE ANALYSES OF LP-6 Bio +16# FRACTIONS **

	5-110[a]		LP-6 Bio +16# high-Fe		LP-6 Bio +16# low-Fe	
	wt. %	$\sigma/\sqrt{N}$	wt. %	$\sigma/\sqrt{N}$	wt. %	$\sigma/\sqrt{N}$
SiO_2	38.63	1.2	37.67	1.5	39.08	1.2
Al_2O_3	13.10	1.5	15.58	1.7	15.48	1.2
TiO_2	1.58	1.7	1.80	2.5	1.60	0.9
FeO*	10.93	1.7	11.17	1.2	9.54	1.0
MnO	.14	1.1	.10	1.5	.06	2.2
MgO	19.90	2.4	18.63	2.3	20.03	1.1
CaO			.05	8.0	.03	6.4
K_2O	10.00	1.1	10.21	1.1	10.24	1.8
Na_2O	.26	1.2	.09	2.1	.13	3.2

* Total iron calculated to FeO

[a] Used as a calibrating standard[12]

** Microprobe analyses by G. K. Czamanske, U. S. Geological Survey (values given are averages from many randomly selected grains)

The electron microprobe proved an invaluable aid in homogeneity investigations. The +16-mesh material shows two distinct biotites in epoxy grain mounts, a "blocky" high-Fe species and a "flaky" low-Fe species. Table 7 gives data for these two species, which are individually homogeneous (except for CaO), as indicated by the indices $\sigma/\sqrt{N}$ in the table.

Table 8 presents analyses of one split of 32-40#, two of 40-60#, one of 40-60# blocky, one of 40-60# flaky, and two microprobe analyses (+16# and 40-60#) for comparison. The +16# data from relatively few grains are not strictly comparable to the results from large samples of 40-60#.

Table 8

ANALYSES OF LP-6 Bio 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	40-60# (Note 1)	+16# (Note 2)
SiO_2	38.40	38.33		38.26	38.30	37.83	38.52
Al_2O_3	15.17*	15.30*	15.28*	15.26*	15.31*	15.21	15.52
TiO_2	1.66	1.67	1.67	1.54	1.69	1.67	1.68
Fe_2O_3	2.29	2.25	2.27		2.20		
FeO	8.52	8.55	8.55		8.58	11.10**	10.10**
MnO	.11	.11	.11	.11	.11	.11	.08
MgO	19.30#	19.35#	19.32#	19.28#	19.37#	19.35	19.47
CaO	.41	.21	.19	.34	.14	.04	.04
BaO		.22	.22				
Na_2O	.09	.09	.09	.06	.12	.14	.11
K_2O	10.03	10.03	10.03	9.85	10.08	10.14	10.23
Rb_2O	.03	.03	.03	.03	.03		
H_2O+	3.45	3.66	3.50	3.75	3.48		
H_2O-	.09	.13	.11	.26	.14		
F		.26	.26				

* Uncorrected for Cr_2O_3, V_2O_5, etc. ** Total Fe calculated to FeO

Uncorrected for NiO, ZnO, etc.

Note 1 - Microprobe analysis by J. Gittins, University of Toronto

Note 2 - Microprobe analysis by G. K. Czamanske, U. S. Geological Survey

Columns 1-5 are classical analyses of single 0.7-gram subsamples: the microprobe analyses represent averages over many randomly selected grains.

CERTIFICATION

Table 9 gives our best estimate of the gross chemical composition of LP-6 Bio 40-60#, together with as many sampling constants as could be estimated from the data at hand. Data accumulated here comes from many sources : contributors are listed in the acknowledgements.

LP-6 Bio 40-60# should be used "as-received"; oven drying may lead to oxidation of iron and loss of combined hydrogen. No subsample should be removed from any bottle before thorough mixing, preferably hand-rolling on albanene paper. Shaking or rolling the bottle could lead to segregation of blocky and flaky grains. Sampling constants can be used to predict relative subsampling error (68 % confidence) :

Relative subsampling error = $\sqrt{K_s / w}$ % of amount present, where K_s is sampling constant and w is subsample weight.

Analytical error may be calculated from a series of determinations :

Analytical error (%) = $\sqrt{Orv - (K_s/w)}$, where Orv is observed relative variance.

Calculated gross stoichiometry of LP-6 Bio 40--60# is $(Na,K,Rb,Ca,Ba,H_2O)_{2.00}^{+2.00}(Mg,Zn,Mn,Ni,Co,Li,Fe^{++})_{5.00}^{+10.00}(Fe^{++},Fe^{+++},Cr,V,Ti,Al)_{1.00}^{+2.89}(Al,Si)_{8.00}^{+29.65}(OH^-,F)_{3.52}^{-3.52}(O)_{20.48}^{-40.96}$. There is a residual of 0.02 moles of H_2O, representing an uncertainty of about 0.02% in the dividing of total H_2O into H_2O^+ and H_2O^-. Inclusion of 0.057 moles of H_2O with the interlayer alka-

lies is arbitrary.

Table 9

COMPOSITION AND HOMOGENEITY OF LP-6 Bio 40-60#

	Weight % (Note 1)	K_s (grams)
SiO_2	38.33 ± 0.1	.001
Al_2O_3	15.18 ± 0.05	.001
TiO_2	1.67 ± 0.01	.05
Fe_2O_3	2.25	Note 2
FeO	8.55	Note 2
total Fe_2O_3	11.75 ± 0.02	.005
Cr_2O_3	.06 ± 0.02	
V_2O_5	.02	
MnO	.11 ± 0.01	.01
NiO	.05 ± 0.01	
CoO	.01	
ZnO	.01	
MgO	19.32 ± 0.05	.005
CaO	.21 ± 0.04	2.
BaO	.22	
Li_2O	.005	
Na_2O	.09 ± 0.02	1.
K_2O	10.03 ± 0.02	.005
Rb_2O	.025	
Cs_2O	.0006	
H_2O+	3.53 ± 0.2 (Note 2)	.1
H_2O-	.13	
F	.26	
P_2O_5	.01 ± 0.02	
CO_2	.00	
Radiogenic argon	$1.93 \pm 0.01 \times 10^{-9}$ M/gram	.05 (Note 3)
Air argon	less than 2% of the total argon	(Note 4)

Note 1 - The ± is the maximum range expected between bottles

Note 2 - The Fe(II)/Fe(III) ratio and the H_2O+ may vary between bottles

Note 3 - K_s for Ar^{*} is 0.04 gram by repetitive determination, and 0.05 gram using the data of Kistler and Turner (Table 4) in the general sampling constant equation (reference 10)

Note 4 - Established by plotting submitted values against sample weight and drawing a cut-off line

USE OF ANALYZED GEOSTANDARDS IN CALIBRATION

The above considerations show that geostandards should only be used to calibrate an analytical method if sampling constants are available in addition to concentration values. The sampling constants are used to construct error bars on the readout value for each standard, as shown in Fig. 2, which is a plot of instrument readout for 50-mg subsamples of geostandards listed in Table 1. The calibration curve passes through each of the error bars, which are computed from

$$\pm E = 6s = 6\,\frac{R\,y}{100} = \frac{6}{100}\,.\,y\,.\,\sqrt{K_s/w},$$

where E is the half-length of an error bar which contains 99+ % of a large number of readout values from w-gram subsamples, y is a single readout value, R is the relative subsampling error in % of the amount present, and s is the standard deviation expected due to sample inhomogeneity. In the example, the slope of the calibration curve is determined by the three most homogeneous standards, LP-6 Bio 40-60#, Nancy BR, and Engels' amphibole. The USGS granite G-1, despite relatively poor sampleability, contributes an upper limit to the slope because it fortuitously gave a low-probability readout value. Uncertainty in the slope corresponds to the lower half of the LP-6 Bio error bar.

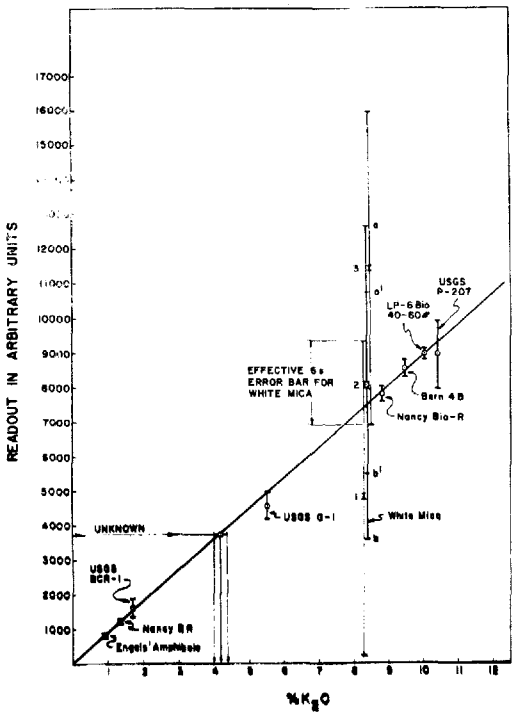

Figure 2. - Calibration of a flame method for potassium using 50-mg subsamples.

The error bars are calculated from ±E = 6s. The poorly-sampleable white mica is included for demonstration purposes. Three readout values are shown (1,2,3), with associated error bars. The length of the error bars is a function of subsample weight: for example, if white mica sample n°. 2 was derived from a 150-mg subsample, or the average of three 50-mg subsamples, the error bar would be shorter by a factor $\sqrt{50/150} = 1/\sqrt{3}$, i.e. a'b' instead of ab. If two subsamples (e.g. n°. 1 and n°. 3) give widely different values, the overlap of the two error bars gives a much shorter effective error bar, because the chances of any value falling outside a 6s error bar are vanishingly small. In such circumstances, an "outlying" value is very useful: this is also demonstrated by the low-probability value obtained for USGS G-1, which established an upper limit for the slope of the calibration curve.

The figure shows the fallacy in the common device of drawing a linear regression line through calibration points. Disregarding the white mica, a linear regression line will pass outside the LP-6 Bio error bar, because the poorly-sampleable P-207 and G-1 both happened to yield low readout values.

The white mica, with extremely poor subsampling characteristics, is included here for demonstration purposes. Three readout values, with associated 6s error bars, are shown. If, during a calibration, readout value no. 1 had been obtained, a linear regression line would be in gross error, with too low a slope. Analyses of unknowns would all come out too high.

When calibrations are performed using a single standard of unknown sampling characteristics, as is frequently done, the calibration curve may pass through any part of the error bar belonging to the standard. To be sure, it is most likely to pass through the middle of the error bar: this has led some investigators into the deplorable practice of repeating the calibration until they get an intuitively satisfying slope for their calibration curve. Should the unknown to be analyzed have good sampling characteristics, repetitive results will show high precision: the temptation to equate this precision to accuracy, and forget the trouble experienced during calibration, has sometimes proven to be great.

Having established a calibration curve, signals from unknowns should be interpolated into concentrations as indicated in Figure 2, and an uncertainty corresponding to the horizontal error bar reported with the result. The length of the horizontal error bar depends on the sampling constant of the unknown, which may be estimated by repetitive determination or from one or another version of the sampling constant equation (8,10), e.g.

$$K_s = 10^4(K - H)(B - H)u^3d/K^2$$

where K is the overall K_2O content, H is the K_2O content of a major low-K mineral, B is the K_2O content of a minor high-K mineral, u is the effective grain size in cm, and d is the density of the minor high-K mineral.

ROCK STANDARDS

Sampling constants are of great importance in analyzing for trace elements in rocks, and lack of attention to this has produced much confusion in the literature. As a specific example, G-1 is unsampleable with respect to Cr; this has been extensively investigated (8). In the case of small concentrations of heavy minerals in rock powders, error bars may be asymmetrical; distribution of results may be Poissonian, and not Gaussian (8,11).

Spectacular examples are found in analysis of precious metal ores: a gold ore with 3 ppm Au in the form of 74 x 74 x 10 micron flakes has a sampling constant (10)

$$K_s = 10^4(K - H)(B - H)u^3d/K^2 = 10^4(.0003)(100)(5.5 \times 10^{-8})(19.3)/(.0003)^2 = 3500 \text{ grams}$$

If one-gram samples are taken, subsampling error is $R = \sqrt{K_s/w} = 59\%$ with 68% confidence. One flake of gold of this size weighs about a microgram, and contributes 1 ppm to a 1-gram sample. Assays of 1-gram samples will show a Poisson distribution, and will vary from 0 to 8 or 9 ppm Au. If assay-ton (29.2--gram) subsamples are taken, sampling error will be

$$R = \sqrt{K_s/w} = \sqrt{3500/29} = 11\%(68\% \text{ confidence}),$$

or 33% with 98% confidence.

Evidently the establishment of precious-metal geostandards which may be confidently used to calibrate methods reaching into the ppm and ppb range is very difficult: since complete homogeneity is probably impossible to achieve, a report on the degree of homogeneity must be made an essential part of a certificate of analysis, if users are to avoid unnecessary work and frustration.

DISCUSSION

Although LP-6 Bio 40-60# is 99.9+ % pure, purer than most widely-distributed mineral standards, it exhibits perceptible non-uniformity at the analytical level of subsampling. Sampling constants (.005 for K_2O, .05 for Ar*) can be used to calculate the expected variability in analytical results due to subsampling error for any given subsample weight. Table 10 shows relative error, most probable result (8), and expected range of results for different subsample weights used in potassium determination. Table 11 gives similar data for radiogenic argon.

Table 10

RELATIVE SAMPLING ERROR FOR POTASSIUM (K_s = 0.005 g)

Subsample weight w (grams)	Relative error (%) R (68% confidence)	Most probable result*	Error**	Expected range in 100 results (% K_2O)
1.	.07	10.03	± 0.007	10.01 - 10.05
.1	.22	10.03	± 0.02	9.96 - 10.10
.01	.71	10.04	± 0.07	9.82 - 10.21
.001	2.2	10.08	± 0.2	(9.76 - 10.27)#

* Reference 8. ** Absolute error due to inhomogeneity, 68% confidence level
# The range of results should not exceed these limits with smaller samples

Table 11

RELATIVE SAMPLING ERROR FOR RADIOGENIC ARGON (K_s = 0.05 g)

Subsample weight w (grams)	Relative error (%) R (68% confidence)	Absolute error (68% confidence)	Range expected in 100 results (Moles/gram x 10^{-9})
10.	.07	± 0.0013	1.926 - 1.934
1.	.22	± 0.0042	1.917 - 1.943
.1	.71	± 0.013	1.894 - 1.966

Such data can be graphically presented in sampling diagrams (1) (Figure 3). Sampling diagrams provide a quick overview of a sampling or subsampling problem, and illustrate exactly where in a continuum of possible subsample weights a geostandard loses its usefulness.

We would suggest in this regard that the geochemical community agree on what is meant by adequate sampleability. Our suggestion is that standard materials should have a subsampling error of not more than 1 % with 98 % confidence, when they are used in methods commonly applied--i.e. in methods using a generally accepted subsample weight. For example, assay for gold is commonly accomplished using an assay-ton subsample (∿ 29 grams): a gold geostandard should carry a certificate assuring the user of assay-ton subsamples that subsampling error will not exceed 1% with 98% confidence.

If we apply this criterion to LP-6

Bio 40-60#, it is adequately sampleable for potassium if subsamples of 50-mg or more are taken, and for radiogenic argon if subsamples are at 500 mg. If a 1% error with 68% confidence is acceptable, as little as 50 mg and 5 mg may be taken for K and for Ar* respectively.

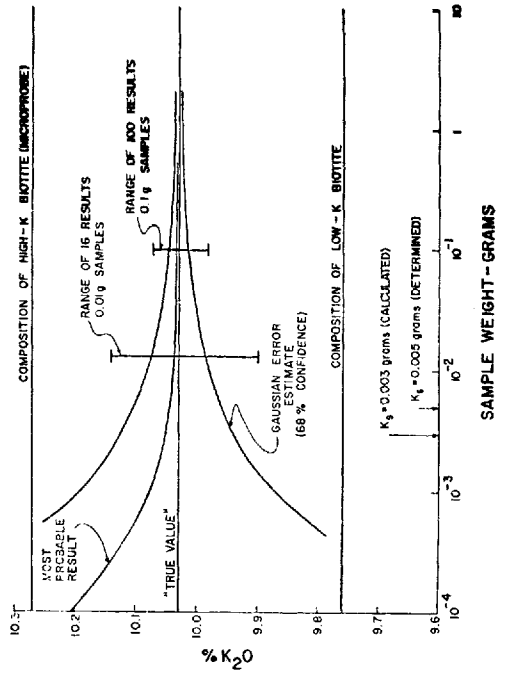

Figure 3. - Sampling diagram for LP-6 Bio 40--60# (Reference 1)

The diagram shows how uncertainty in K_2O determination increases with decreasing subsample weight, and that with very small subsamples (i.e. in microprobe analysis) results may vary from 9.76 to 10.27 % K_2O with no analytical error. The several parameters of the diagram are estimates compatible with experimental data reported in this paper. The error bars shown determine the general shape of the diagram. The calculated value K_s = 0.003 gram depends on certain approximations which are not strictly valid for this material.

CONCLUSIONS

First and foremost, those willing and able to undertake the lengthy and difficult task of preparing a viable geostandard need input from potential users regarding methods of preparation, amounts required, and desired degree of homogeneity.

Suppliers should finally certify geostandards by element, and should provide sampling information along with concentration values.

Users should take into account the sampling characteristics of the material, as reported by the supplier, when splitting out subsamples. They should *never* operate in a subsample weight range which will produce a Poissonian distribution of results, unless they do so deliberately on behalf of the supplier in efforts to further establish sampling constants.

Some methods require fairly large subsamples (common methods for radiogenic argon; assays for precious metals). Preparation of large amounts of material almost always involves accepting some non-uniformity and diminished sampleablity. It is unreasonable to expect anyone to prepare a mineral standard suitable for microprobe work, for example, in which each grain has exactly the same composition, and at the same time expect to have many kilograms of the same material available for methods using large subsamples. very occasionally (e.g. the Nancy Mica-Mg) Very such a material become available. LP-6 Bio 40-60# only marginally approaches this ideal.

Rapid secondary methods, while often highly precise, and useful for determining sampling constants, should not be used to establish certificate values for geostandards. Certificate values should be based on primary methods which do not depend on analyzed standards for calibration. Thereby systematic errors are minimized, and transfer of analytical error from old to new standards is avoided. The use of old standards to calibrate the new leads to accumulation of analytical inaccuracy.

In reporting data on geostandards, *all* data is important. Among "outliers" there are those which are due to undetected systematic error, but there are also those which reflect sampling problems in the material being examined. Gaussian and log-normal models may not apply, and the average of all values for a constituent may be meaningless. Users should be aware that non-replication of results does not necessarily indicate analytical error, that the "anomalous" value may be the only true value, or may at least be an invaluable clue to the solution of inhomogeneity problems. All participants in a collaborative effort to establish a geostandard should therefore report all relevant information, including a description of calibrating standards and procedures, subsampling procedures, subsample weights, and *all* analytical results, including those which appear anomalous.

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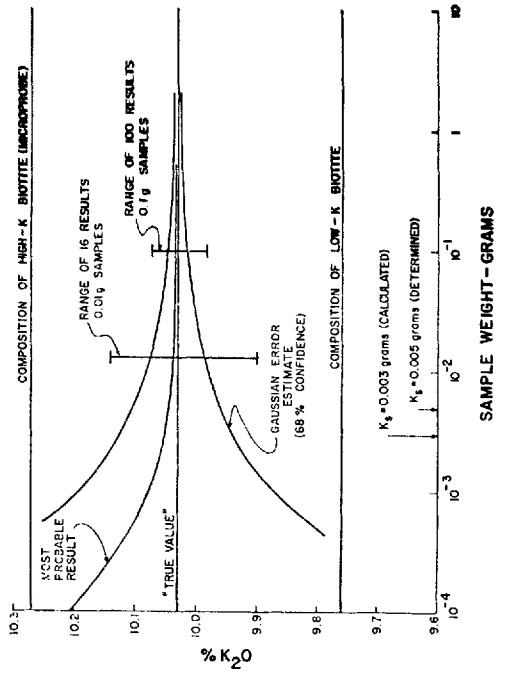

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