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CERTIFIED COMPOSITIONAL REFERENCE MATERIALS FOR THE EARTH SCIENCES

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ABSTRACT

There is growing evidence that many of the compositional reference ores, rocks and related materials issued by the Canadian Certified Reference Materials Project are of interest to workers in the earth sciences; therefore, descriptive information, recommended values and their confidence intervals are presented for 23 such materials. An insight into the philosophy and nature of the interlaboratory certification programs, for ores in particular, is given and it is shown how the quality of these materials can be assessed for particular applications.

SOMMAIRE

Il appert de plus en plus que de nombreux matériaux de référence de composition, minerais, roches et autres, émis par le Programme canadien des matériaux de référence certifiés intéressent tout ceux qui s'occupe des sciences de la terre. En conséquence, nous présentons ici, pour 23 de ces matériaux, outre leur description, les valeurs numériques recommandées avec intervalle de confiance. Le but et la nature des programmes de certification inter-laboratoires sont éclaircis, particulièrement en ce qui concerne les minerais; on indique aussi comment évaluer la qualité de ces matériaux en vue de leur application aux cas particuliers.

INTRODUCTION

Since 1971, the Canadian Certified Reference Materials Project (CCRMP), or its predecessor, has prepared a number of rocks, ores and concentrates as compositional reference materials. Although most of these materials are intended for use in the conventional analytical laboratory, they have proved to be in significant demand by workers in earth sciences laboratories. Their value to geochemists, mineralogists, and others, no doubt stems from the fact that they have been taken from known Canadian deposits and are not only certified for selected elements but, in many cases, are well-characterized mineralogically.

Despite the existing demand, the activities and products of the CCRMP are still not well-known, even in Canada, largely because of the difficulty of continuously disseminating information without a costly, large scale, advertising campaign. Because of the potential value of many of the reference ores and rocks to workers in the earth sciences, it is considered worthwhile to draw attention directly to these materials by describing them in this journal.* Also, it is felt that a description of, and the philosophy behind, the CCRMP certification schemes should be presented so that potential users of the reference materials are better able to appreciate their quality for particular applications.

Because the CCRMP must levy a charge for its reference materials, there is the danger that the intent of this article might be misconstrued as an attempt to promote a revenue-generating activity. However, it is to be realized that charges are made as a deterrent against unreasonably large or frivolous orders; moreover, the revenue from sales goes directly to the Receiver General for Canada and is not accessible to the CCRMP.

DESCRIPTION OF REFERENCE MATERIALS

The following is a description of the reference materials, including, where possible, information about sampling locations. In most cases, the materials are listed in chronological order of certification for each category. Tables 1 to 4 give the recommended value for selected elements in base metal ores, precious metals-bearing materials, radioactive ores, and rocks, respectively. The corresponding 95% confidence intervals are also given in Tables 1 to 3. The mineralogical composition of most of the ores listed below was determined by Dr. W. Petruk of CANMET.

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*To obtain CCRMP reference materials contact: Chairman, Canadian Certified Reference Materials Project, Mineral Sciences Laboratories, Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Ontario, Canada, K1A 0G1.

BASE-METAL ORES

Mo ore PR-1 (Faye *et al.* 1971)

PR-1 was obtained from the Preissac molybdenum mine near Cadillac, Quebec in 1970; the ore is from a vein-type deposit in a muscovite granite. The minerals present in PR-1, in decreasing order of abundance, are: quartz, K-feldspar, Na-feldspar, calcite, muscovite, chlorite, molybdenite, fluorite, pyrite, bismuthinite, bismuth, garnet, rutile, galena, and chalcopyrite. The approximate chemical composition of PR-1 has been determined and it has been certified for Mo, Bi, Fe, and S (Table 1).

Zn-Sn-Cu-Pb ore MP-1 (Faye *et al.* 1972)

MP-1 was obtained from the deposit of Brunswick Tin Mines Limited in southwestern New Brunswick in 1971; the material was chosen because of its mineralogical and chemical complexity. MP-1 consists of material from two sulfide veins blended with a small amount of mineralized wall rock. The minerals present in MP-1, in decreasing order of abundance, are: quartz, sphalerite, chlorite, fluorite, topaz, kaolinite, chalcopyrite, stannite-kesterite, galena, cassiterite, arsenopyrite, pyrite, feldspar, rutile, wolframite, bismuth, and molybdenite. The approximate chemical composition of MP-1 has been determined and it has been certified for Zn, Sn, Cu, Pb, Mo, In, Bi, As, and Ag (Table 1).

Cu-Mo ore HV-1 (Faye *et al.* 1973a)

HV-1 is an approximately equal mixture of materials taken, in 1971, from deposits of Highmont Mining Corporation and Valley Copper Mines Limited, both in the Highland Valley area of British Columbia. The minerals present in HV-1, in decreasing order of abundance, are: quartz, plagioclase, sericite, orthoclase, biotite, amphibole, calcite, clay minerals, hematite+magnetite, bornite, chalcopyrite, rutile, pyrite, molybdenite, and barite. The approximate chemical composition has been determined also and the recommended values for Cu and Mo are given in Table 1.

Ni-Cu-Co ore SU-1 (Faye *et al.* 1973b)

SU-1 is a composite of sample rejects collected, in 1958, at the Falconbridge Nickel Mines Limited, Falconbridge, Ontario (CAAS Report, 1961) and is, therefore, considered to be representative of the Sudbury nickel-copper ores. SU-1 was originally intended as a reference material primarily for use by spectroscopists (CAAS Report, 1961). It has been distributed widely to laboratories throughout the world, and numerous analytical results for minor and trace elements have been accumulated (Webber 1965; Sine *et al.* 1969). Most of the analytical results, however, were obtained by emission spectroscopy and only single values for each element were obtained from each laboratory. Because of the wide range in the results for most elements, recommended values were not assigned previously. However, in 1973, SU-1 was certified for Ni, Cu and Co by the CCRMP (Faye *et al.* 1973b) and the recommended values are given in Table 1.

Ni-Cu-Co ore (rock) UM-1
(Faye *et al.* 1973b; Faye 1975)

Although UM-1 is termed an ore because of its relatively high content of base-metal sulfides, it is an ultramafic rock from the Giant Mascot mine at Hope, British Columbia. UM-1 is one of a suite of three ultramafic rocks; the others are coded as UM-2 and UM-4 and have been

TABLE 1. RECOMMENDED VALUES AND THEIR 95% CONFIDENCE INTERVALS FOR BASE-METAL REFERENCE ORES

	PR-1	MP-1	HV-1	UM-1	SU-1	KC-1	SCH-1	CT-1	BH-1	TLG-1
					WT %					
Ag		59.5±3.2 (ppm)				0.114±0.002				
Al							0.509±0.009			
As		0.791±0.023								
Bi	0.111±0.003	0.025 0.002								
Ca							0.029±0.02			
Co				0.035±0.001	0.063±0.002					
Cu		2.15±0.03	0.522±0.004	0.43±0.01	0.87±0.01	0.114±0.002				
Fe	1.24±0.02						60.73±0.08			
In		0.071±0.003								
Mg							0.020±0.001			
Mo	0.594±0.016	0.014±0.001	0.058±0.002							
Mn							0.777±0.008			
Ni				0.88±0.01	1.51±0.01					
P							0.054±0.003			
Pb		1.93±0.03				6.98±0.04				
S	0.793±0.016						0.007±0.001			
Si							3.78±0.04			
Sn		2.50±0.11				0.68±0.01				
Ti							0.031±0.002			
W								1.04±0.02	0.42±0.01	0.083±0.004
Zn		16.33±0.13				20.37±0.06				

termed 'geochemical standards' for the determination of ascorbic acid/hydrogen peroxide-soluble nickel, copper and cobalt (Cameron 1972). Because UM-1 contains ore-grade concentrations of Ni, Cu and Co, and was available to the CCRMP in a comminuted condition, it was chosen, along with SU-1, for the certification of these three elements (Faye *et al.* 1973b). Details of the mineralogy of UM-1 have been given by Cameron (1972) and the approximate chemical analysis reported by Faye *et al.* 1973b). Table 1 gives recommended values for Ni, Cu and Co.

Zn-Pb-Sn-Ag ore KC-1 (Faye *et al.* 1974)

KC-1 was prepared from material hand-picked, in 1971, at the Kidd Creek deposit of Ecstall Mining Limited. It was chosen to represent a typical high-grade base-metal ore and to act as a complement to reference ore MP-1 (see above) which contains lower zinc, lead and silver values but higher copper and tin values than KC-1. The minerals present in KC-1, in decreasing order of abundance, are: sphalerite, pyrite, quartz, galena, cassiterite, chlorite, siderite, pyrrhotite, chalcopyrite, carbon, silver, and tetrahedrite+stephanite. The approximate chemical composition of KC-1 has been determined also, and it has been certified for Zn, Pb, Sn, Cu and Ag (Tables 1 and 6).

Fe ore SCH-1 (Steger *et al.* 1975)

The material for SCH-1 was obtained from the Iron Ore Company of Canada in 1973. The ore is from the Schefferville area, Quebec, and is hematite with a mixture of unidentified hydrous oxides of iron, minor magnetite, and trace pyrolusite. The gangue consists mainly of quartz with minor amounts of feldspar and traces of biotite, chlorite, and amphibole. SCH-1 has been certified for Fe, Si, Al, Ca, Mg, Mn, Ti, S and P (Table 1) and provisional values have been determined for Na, K, moisture, and loss on ignition.

W ores CT-1, BH-1 and TLG-1
(Faye *et al.* 1975a)

CT-1 is a sample of a scheelite ore obtained in 1973 from Canada Tungsten Mining Corporation, Tungsten, N.W.T. In decreasing order of abundance, the minerals present in CT-1 are: pyroxene, quartz, pyrrhotite, amphibole, calcite, mica, dolomite, feldspar, scheelite, chalcopyrite, and clay minerals.

BH-1 is a sample of a wolframite ore, hand-picked in 1973 from a stockpile at the Burnt Hill deposit near Fredericton, New Brunswick; the deposit is owned by the International Paper Company Limited. The minerals present in BH-1, in decreasing order of abundance, are: quartz, biotite, chlorite, muscovite, feldspar, pyrrhotite, beryl + topaz, wolframite, cassiterite + rutile, pyrite, molybdenite, bismuth, bismuthinite, galena, and chalcopyrite.

TLG-1 is a sample of a low-grade scheelite ore from Browne's Lake mine, Beaverhead County, Montana, and was donated by the General Electric Company, Cleveland, Ohio. In decreasing order of abundance, the minerals present in TLG-1 are: quartz, calcite, hydrogarnet, amphibole, dolomite, chlorite, feldspar, mica, clay minerals, scheelite, hematite, magnetite sphalerite and chalcopyrite.

The approximate chemical composition of the three samples has been determined (Faye *et al.* 1975a) and each has been certified for tungsten (Table 1).

ORES WITH PRECIOUS METALS

Platiniferous black sand PTA-1
(McAdam *et al.* 1971)

The material used to prepare PTA-1 was obtained from B. H. Levelton and Associates, Vancouver, British Columbia. It is essentially a magnetite concentrate from alluvial material from the Tulameen River area of British Columbia. Careful mineralogical examination of material similar to PTA-1 has revealed at least ten minerals known to contain platinum-group elements, with an iron-platinum alloy being predominant (Cabri *et al.* 1973). PTA-1 has been certified for platinum only (Table 2). It was chosen as a reference material because experience over many years has shown that the determination of platinum in such material is difficult.

TABLE 2. RECOMMENDED VALUES AND THEIR 95% CONFIDENCE INTERVALS FOR PRECIOUS-METALS-BEARING MATERIALS

	MA-1	PTA-1 (ppm)	PTC-1	PTM-1
Pt		3.05±0.13	3.0 ±0.2	5.8±0.3
Pd			12.6 ±0.7	8.1±0.7
Rh			0.62±0.07	0.9±0.1
Au	17.8±0.2		0.65±0.07	1.8±0.2
Ag			5.8 ±0.3	66 ±7

Sulfide concentrate PTC-1
(McAdam *et al.* 1973a)

PTC-1 is an Fe-Cu-Ni flotation concentrate typical of those produced from the Sudbury ore; some of its principal and minor constituents are: Fe 24.2%, S 24.1%, Cu 5.0%, Ni 0.6%, and Co 0.3%. In contrast to the alluvial material PTA-1, in which platinum predominates, PTC-1 contains every member of the platinum group and gold and silver in detectable concentrations. The bulk of platinum and palladium occur as the minerals michenerite (PbBiTe), moncheite ($PtTe_2$), and sperrylite ($PtAs_2$), as well as in solid solution in arsenides and sulfarsenides; however, little is known about the mode of occurrence of the less-abundant platinum-group metals (Cabri & Laflamme 1975). PTC-1 has been certified for Pt, Pd, Rh, Au and Ag (Table 2) and provisional values are available for ruthenium and iridium (McAdam *et al.* 1973).

Ni-Cu matte PTM-1 (McAdam *et al.* 1973b)

PTM-1 is a matte produced from Sudbury ore and was obtained from Falconbridge Nickel Mines Limited. This material was chosen as a reference material mainly because it contains appreciably higher concentrations of some of the precious metals than do PTA-1 and PTC-1, and because they occur in a matrix rich in nickel, copper and sulfur (44.8%, 30.2% and 21.6% respectively). PTM-1 has been certified for Pt, Pd, Rh, Au and Ag (Table 2) and provisional values are available for ruthenium and iridium.

Au ore MA-1 (Faye *et al.* 1975b)

MA-1 was prepared from head ore obtained from Wilroy Mines Limited, Macassa Division, Kirkland Lake, Ontario. It was chosen because a demand exists for a relatively simple siliceous ore containing elemental gold. Although the CCRMP has issued several certified gold-bearing materials (see PTC-1 and PTM-1 above), these are rich in one or more of copper, nickel, and iron, and contain platinum-group metals; consequently they may not be satisfactory for laboratories wanting a simple gold ore as a reference material. MA-1 has been certified for gold (Table 2) and its approximate chemical composition has also been determined (Faye *et al.* 1975b).

RADIOACTIVE ORES

Six radioactive ore samples, DH-1, DL-1, BL-1, BL-2, BL-3 and BL-4 were prepared in 1971 to replace the previous reference materials of the Canadian Uranium Producers Analytical Subcommittee, the major supply of which is now exhausted. Materials from both of the uranium-producing areas of Canada were selected. Two of the samples, DH-1 and DL-1, consist of ore-grade and waste-grade material, respectively, from the Elliot Lake area of Ontario and both contain thorium and uranium. Four samples designated BL-1, BL-2, BL-3, and BL-4, from the Beaverlodge area of northwestern Saskatchewan, are relatively free of thorium, are in radioactive equilibrium, and cover a range of concentrations that should make them useful as reference materials for radiometric methods of analysis. The recommended values for uranium and thorium and their 95% confidence intervals are given in Table 3.

TABLE 3. RECOMMENDED VALUES AND 95% CONFIDENCE INTERVALS FOR Th AND U IN RADIOACTIVE ORES

Designation	Description	Thorium as Th wt %	Uranium as U wt %
DH-1	Brannerite, Elliot Lake, Ont. Ore-grade Material	0.104±0.005	0.177 ±0.003
DL-1	Brannerite, Elliot Lake, Ont. Waste Rock Material	ppm 83±5	0.0041±0.0002
BL-1	Pitchblende, Beaverlodge, Sask. Radiometric Reference Material	15±1	0.022 ±0.001
BL-2	Pitchblende, Beaverlodge, Sask. Radiometric Reference Material	(16±4)*	0.453 ±0.005
BL-3	Pitchblende, Beaverlodge, Sask. Radiometric Reference Material	(15±6)*	1.02 ±0.01

*Because of excessive between-laboratory variation, these values are for information only.

ROCKS

Syenites SY-2 and SY-3 (Abbey *et al.* 1975)

SY-2 is a syenite from the Bancroft area of eastern Ontario. At the time of its preparation, in 1968, it was known that SY-2 contained 'minor to trace' amounts of uranium, thorium, and rare earths. However, analyses showed subsequently that the concentrations of these constituents was lower than desired. Therefore, to produce a material having concentrations closer to the target values, a batch of syenite from the same source as SY-2 was ground autogenously with lumps of a 'concentrate' containing uraninite, allanite and betafite; subsequently this material was coded as SY-3.

Although SY-2 and SY-3 were prepared several years ago, and samples that were distributed internationally were analyzed on a rather casual basis to provide provisional values for a number of constituents (Gillieson 1969), only recently were they analyzed in a systematic round-robin program to certify them as compositional reference materials (Abbey *et al.* 1975) (Tables 4 and 5).

Gabbro MRG-1 (Abbey *et al.* 1975)

MRG-1 is a sample of an augite-olivine gabbro from Mount Royal (Montreal, Quebec) that was intruded into sedimentary rocks of the Lower Paleozic (Perrault *et al.* 1974). MRG-1 is compositionally different from other certified reference rock samples and the recommended values given in Tables 4 and 5 should be of interest to rock analysts.

TABLE 4. RECOMMENDED VALUES FOR MAJOR AND MINOR CONSTITUENTS IN SYENITES AND GABBRO*

	SY-2 wt %	SY-3 wt %	MRG-1 wt %
SiO_2	60.07	59.71	39.22
Al_2O_3	12.15	11.70	8.51
Fe_2O_3	2.31	2.46	8.36
FeO	3.61	3.61	8.61
MgO	2.66	2.63	13.49
CaO	8.03	8.30	14.68
Na_2O	4.37	4.17	0.72
K_2O	4.52	4.20	0.18
H_2O^+	0.41?	0.49?	1.02
CO_2	0.49?	0.36?	1.04
TiO_2	0.15	0.15	3.69
ZrO_2	0.04	0.04	0.01?
ThO_2	0.04?	0.11?	
RE_2O_3(T)†	0.09?	0.75?	0.01?
Sc_2O_3			0.01?
B_2O_3	0.03?	0.04?	
P_2O_5	0.44	0.55	0.08
V_2O_5	0.01	0.01	0.09
Nb_2O_5		0.02?	0.01?
F	0.47?	0.66	0.03?
S	0.01	0.05	0.06
Cr_2O_3			0.07
NiO			0.02
CoO			0.01
CuO			0.02
MnO	0.32	0.33	0.17
BaO	0.05	0.05	0.01
SrO	0.03	0.04	0.03
PbO	0.01	0.01	
ZnO	0.03	0.03	0.02
Li_2O	0.02	0.02	
Rb_2O	0.02	0.02	
U_3O_8	0.03	0.08	
Σ	100.41?	100.59?	100.20?
O/F,S	0.20?	0.30	0.04?
(corrected)	100.21?	100.29?	100.16?
Fe_2O_3TR ††	6.34	6.45	17.84
Fe_2O_3TC	6.32	6.47	17.93

* After Abbey *et al.* (1975)

† RE_2O_3(T): Total rare-earth oxides.

††Fe_2O_3TR: Total iron, expressed as ferric oxide, reported as such.

Fe_2O_3TC: Total iron, expressed as ferric oxide, calculated from FeO and Fe_2O_3.

TABLE 5. RECOMMENDED VALUES FOR "TRACE ELEMENTS" IN SYENITES AND GABBRO*

	SY-2		SY-3		MRG-1		
	ppm	Oxide %	ppm	Oxide %	ppm	Oxide %	Oxide
As	18?		21?		2?		
B	84?	0.03?	110?	0.04?			B_2O_3
Ba	460	0.05	460	0.05	71	0.01	BaO
Be	25		21?				
Ce	260?	0.03?	2400?	0.29?			CeO_2
Co	11		24		87	0.01	CoO
Cr	12		14		450	0.07	Cr_2O_3
Cs	2?		2?		0.5?		
Cu	7		18		135	0.02	CuO
Eu	2?		15?				
Ga	29?		26?		18?		
La	88?	0.01	1400	0.17	10?		La_2O_3
Li	86	0.02	85	0.02	4?		Li_2O
Nb	27?		145?	0.02			Nb_2O_5
Nd			840?	0.10			Nd_2O_3
Ni	11		11		190	0.02	NiO
Pb	83	0.01	135	0.01	12		PbO
Rb	220	0.02	210	0.02	8?		Rb_2O
Sc	7?		11?		50?	0.01?	Sc_2O_3
Sn	3?		5?		3?		
Sr	270	0.03	310	0.04	270	0.03	SrO
Th	370?	0.04?	980?	0.11?	1?		ThO_2
U	290	0.03	640	0.08	0.4?		U_3O_8
V	46	0.01	50	0.01	520	0.09	V_2O_5
Y	135	0.02	750	0.10	21?		Y_2O_3
Yb	16?		62?	0.01	3?		Yb_2O_3
Zn	250	0.03	240	0.03	185	0.02	ZnO
Zr	270	0.04	320	0.04	110?	0.01?	ZrO_2

* After Abbey *et al.* (1975)

PREPARATION AND CERTIFICATION OF REFERENCE ORES

Although there has been some variation in the programs for assigning recommended values to the reference materials described above, the majority of the ores has been treated by a scheme that permits the assignment of recommended values, the usefulness of which, for particular applications, can be expressed quantitatively in terms of their confidence intervals and their certification factors (Sutarno & Faye 1975), as will be discussed below. The user of the reference ores is provided with detailed documentary information that shows how the precision of the recommended values for the selected elements is influenced by the degree of homogeneity of the ore, the reproducibility of the analytical methods used in its certification, and the extent of agreement among the methods, the number of laboratories providing results, and the number of replicate determinations from each laboratory. With such information the user can readily assess whether the particular reference material is useful for his own needs.

Although information is also given for three recently-issued reference rocks (Table 4), the nature of the interlaboratory program for their certification was somewhat different from that outlined below for ores. For an understanding of the scheme used for the rocks, the reader is directed to reports by Abbey (1975) and Abbey *et al.* (1975).

Interlaboratory scheme for certification

To put these matters into perspective, the following description of the interlaboratory certification scheme of the CCRMP is presented.

The round-robin (interlaboratory) approach is used by the CCRMP for the practical reason of obtaining a large number of analytical results, by a number of methods, from a relatively large number of collaborators, rather than attempting to tie up permanently a few highly-skilled analysts in one or two laboratories. The interlaboratory scheme also reflects the fact that the reference materials are intended for a wide variety of uses. It is noteworthy, too, that more potential methodological information is obtainable from the multi-method round-robin approach than by other schemes.

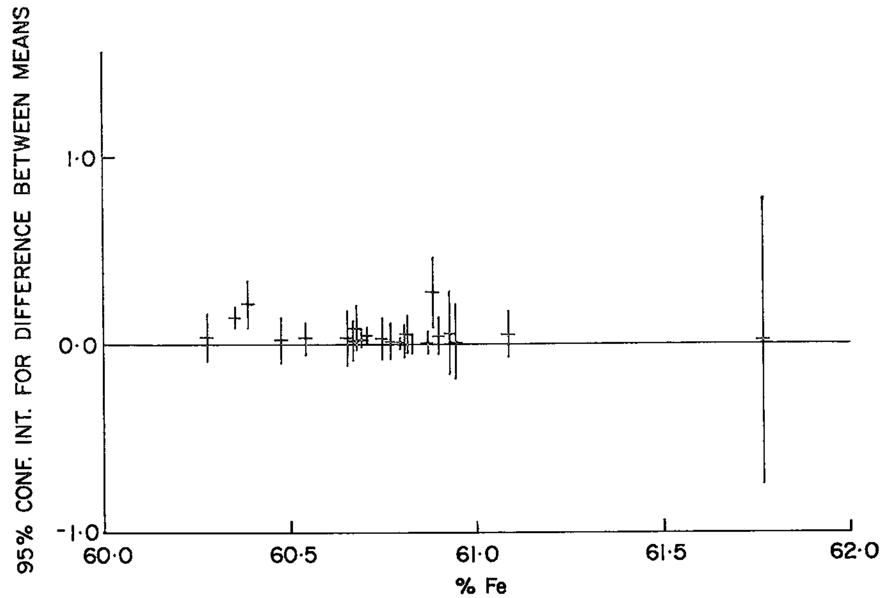

FIG. 1. Means of two bottles of iron ore SCH-1. Ordinate is 95% confidence interval for difference between means.

Preparation and testing for homogeneity before distribution

In most cases the dried ore samples (up to 315 kg) are dryground to minus 200 mesh by ball-milling and are then 'homogenized' in a conical shell blender for approximately 8 hours. The degree of homogeneity of the powdered material is assessed by taking six samples from various locations within the blender. These are then analyzed, in quintuplicate, for one or more constituents of importance by X-ray fluorescence and/or chemical methods. If the result of a one-way analysis of variance (ANOVA) shows that the difference among samples is not detectable at the 5% level of significance, the bulk ore is bottled, in 100- to 400-g units, for storage and distribution.

Distribution to laboratories and assessment of homogeneity

Because the degree of homogeneity of a reference material is so important, it is essential that this property be assessed thoroughly, both between and within bottles, to ensure that the inhomogeneity variance is low compared with other sources of variance. Thus, each participating laboratory is requested to analyze two randomly-selected bottles for selected constituents by methods of its choice. For each bottle, five replicate determinations are required for each selected constituent. The means of the results reported by each laboratory for each bottle are compared by a *t*-test at the 5% level of significance. This test usually confirms the previous 'in-house' homogeneity testing done at CANMET.

The results of a typical *t*-test are shown in Figure 1 in which, for each laboratory, the difference between the means for iron in the two bottles of iron ore SCH-1 (Steger *et al.* 1975) are plotted against the overall mean of the same two bottles. The length of the vertical bars represents the magnitude of the 95% confidence intervals of the above difference for each set of results. In the three cases where the bottom of the bar does not intersect the horizontal axis, rejection of the homogeneity hypothesis is indicated. However, this rejection rate (3 out of 24 sets) does not invalidate the conclusion that SCH-1 is sufficiently homogeneous to be a valuable reference material in laboratories using methods similar to those that were used to generate the data for the certification of the selected constituents.

In most cases it is considered that, for each constituent, 10 results from each of approximately 20 participants (laboratories) yield enough chemically and statistically acceptable data to assign to the chosen constituents recommended values with usefully narrow confidence limits. Moreover, valuable inter-method comparisons are often possible with such a pool of data.

TABLE 6. ESTIMATES OF STATISTICAL PARAMETERS FOR REFERENCE ORE KC-1

	Zinc			Lead			Tin			Copper			Silver		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Mean, %	20.36	20.36	20.37	6.98	6.98	6.98	0.67	0.67	0.67	0.114	0.114	0.114	0.114	0.114	0.114
95% conf. int. of mean, % Low	20.34	20.30	20.31	6.97	6.94	6.94	0.66	0.65	0.65	0.113	0.112	0.112	0.113	0.113	0.112
High	20.38	20.43	20.43	6.99	7.02	7.02	0.67	0.68	0.68	0.114	0.115	0.116	0.114	0.115	0.115
Certification factor			1.6			1.8			2.5			3.3			2.2

Assignment of recommended values and their confidence intervals

In the technical reports that accompany orders for reference materials, it is shown how the statistical parameters for the selected elements are computed from the 'raw' analytical data. Thus, the user can judge whether the material and the precision of the assigned values are suitable for particular applications. Indeed, if desired, the user can interpret the raw data in his own way.

There are several ways in which the recommended values can be computed. One way (A in Table 6) is to treat all results as though they were independent and reject all results that deviate from the overall mean by more than two standard deviations. Because the results are not independent but depend on the laboratory from which they come, this is technically an unacceptable procedure. Although a good estimate of the mean is obtained by this method, the confidence intervals are unrealistically narrow (Table 6). Because there is a relatively wide range in the degree of precision obtained by the contributing laboratories, a second method of computation (B in Table 6) can be used that involves weighting the analytical results by a factor which is a function of within-laboratory variance. This gives statistical parameters that are very similar to those that are ultimately assigned; however, when an occasional set of results shows no variance, undue weight is placed on it by this method. Finally, the third and the most suitable method (C in Table 6) for assigning the recommended values and confidence intervals, is an analysis of variance that takes into account the existence of interlaboratory variations. Table 6 shows clearly that it is the precision of the recommended values rather than their magnitude that is influenced by the method of computation, and it is the precision that may dictate whether the reference material is suitable for a particular application.

Criterion for deciding certifiability

Recently, it was shown (Sutarno & Faye 1975) how objective decisions can be made about the certifiability of consensus values obtained in the CCRMP interlaboratory programs by calculating a 'certification factor' for each constituent being considered for certification. This factor is the ratio of the confidence interval of the consensus value, expressed as a percentage, to the mean of the within-laboratory coefficient of variation. It is thus a measure of quality of the reference material (with respect to a particular constituent) because it takes into account the degree of precision required for the consensus value in normal applications.

Long-term experience in the CCRMP (48 cases) has shown that when the precision of the consensus value is as good as, or better than, the precision of the methods that were used in the interlaboratory program (and presumably in general use for that particular kind of material), the certification factor has a value of 4 or less. That the critical value is 4 is a consequence of statistical considerations that need not be explained here (Sutarno & Faye 1975). As an example, Table 6 shows that factors for the five selected elements in reference ore KC-1 are less than 4 and as a consequence, the consensus values have been assigned as 'certified' or 'recommended' values.

FUTURE PLANS OF CCRMP

The CCRMP has on hand ores of antimony, niobium and tantalum, and commercial-grade sulfide concentrates of copper, lead and zinc. These materials will be processed as time permits and it is planned to certify for the principal metals of economic interest, as well as for a number of minor and trace elements in the case of sulfide concentrates.

STUDIES ON THE STABILITY OF SULFIDE MINERALS AND ORES

It is known well that some sulfide minerals (*e.g.* pyrrhotite, marcasite) oxidize rapidly under certain conditions; consequently there is some concern about the shelf-life, or stability, of reference materials containing substantial concentrations of sulfide minerals. To obtain quantitative information on this problem, Dr. H. F. Steger of CANMET has undertaken experiments in which samples of various reference ores are subjected to conditions of 30 to 62°C and 40 to 80% relative humidity. On the basis of changes in weight, the water-extractable metals, and elemental sulfur content of the altered samples (Steger 1975a) it has been concluded that ores MP-1, KC-1 and SU-1 can be stored safely for long periods in capped bottles under laboratory conditions, *i.e.* without changing significantly (Steger 1975b). The stability of other ores and minerals is currently under study.

Studies on the alteration of samples of pure sulfide minerals at 54°C and 72% relative humidity demonstrate the relative instability of sphalerite and especially of pyrrhotite. At the much less severe laboratory conditions, sphalerite-containing materials are, fortunately, sufficiently stable for use as a reference material.

References

Abbey, S. (1975): Studies in "standard samples" of silicate rocks and minerals. Part 4: 1974 edition of "usable" values. *Geol. Surv. Can. Pap.* **74-41.**

———, Gillieson, A. H. & Perrault, G. (1975): SY-2, SY-3 and MRG-1. A report on the collaborative analysis of three Canadian rock samples for use as certified reference materials. *Can. Centre Mineral Energy Tech., Tech. Rep. MSL* **75-132**(TR).

Canadian Association for Applied Spectroscopy (1961): Report of non-metallic standards committee. *Appl. Spectros.* **15**, 159-161.

Cabri, L. J. & Laflamme, J. H. G. (1975): The mineralogy of the platinum-group elements from some copper-nickel deposits of the Sudbury area, Ontario. Submitted to Econ. Geol.

———, Owens, D. R. & Laflamme, J. H. G. (1973): Tulameenite, a new platinum-iron-copper mineral from placers in the Tulameen river area, British Columbia. *Can. Mineral.* **12**, 21-25.

Cameron, E. M. (1972): Three geochemical standards of sulphide-bearing ultramafic rock: UM-1, UM-2, UM-4. *Geol. Surv. Can. Pap.* **71-35.**

Faye, G. H. (1975): Description of ultramafic rock (ore) samples UM-1, UM-2, UM-4: a correction. *Chem. Geol.* **15**, 235-237.

———, Bowman, W. S. & Sutarno, R. (compilers) (1971): Molybdenum ore PR-1, its characterization and preparation for use as a standard reference material. *Mines Branch Tech. Bull.* **TB139**, Can. Dep. Energy Mines Res.

———, ——— & ——— (compilers) (1972): Zinc-tin-copper-lead ore, MP-1: its characterization and preparation for use as a standard reference material. *Mines Branch Tech. Bull.* **TB 155**, Can. Dep. Energy Mines Res.

———, ——— & ——— (compilers) (1973a): Copper-molybdenum ore, HV-1: its characterization and preparation for use as a standard reference material. *Mines Branch Tech. Bull.* **TB 167**, Can. Dep. Energy Mines Res.

———, ——— & ——— (compilers) 1973b): Nickel-copper-cobalt ores, SU-1 and UM-1: their characterization and preparation for use as standard reference materials. *Mines Branch Tech. Bull.* **TB 177**, Can. Dep. Energy Mines Res.

———, ——— & ——— (compilers) (1974): Zinc-lead-tin-silver ore, KC-1: its characterization and preparation for use as a certified reference material. *Mines Branch Tech. Bull.* **TB 193**, Can. Dep. Energy Mines Res.

———, ——— & ——— (compilers) (1975a): Tungsten ores, CT-1, BH-1 and TLG-1: their characterization and preparation for use as certified reference materials. *Can. Centre Mineral Energy Tech., Tech. Rep.* MSL **76-5.**

———, ——— & ——— (compilers) (1975b): Gold ore, MA-1: its characterization and preparation for use as a certfiied reference material. *Can. Centre Mineral Energy Tech., Tech. Bull.* MSL 75-29(TR).

Gillieson, A. H. (1969): Announcement, Spectroscopy Society of Canada. *Anal. Chim. Acta* **46**, 325-326.

McAdam, R. C., Sutarno, R. & Moloughney, P. E. (1971): Characterization and preparation of standard reference materials that contain noble metals: (A) PTA (ores) and (B) PTM (nickel-copper matte). *Mines Branch Tech. Bull.* **TB138**, Can. Dep. Energy Mines Res.

———, ——— & ——— (1973a): Noble-metals-bearing nickel-copper matte. PTM: its characterization and preparation for use as a standard reference material. *Mines Branch Tech. Bull.* **TB 176**, Can. Dep. Energy Mines Res.

———, ——— & ——— (1973b): Noble-metals-beoring nickel-copper matte, PTM: its characterization and preparation for use as a standard reference material. *Mines Branch Tech. Bull.* **TB 182**, Can. Dep. Energy Mines Res.

Perrault, G., Hebert, P. & Kubat, V. (1974): MRG-1: un nouveau matériau de référence de gabbro à pyroxène et olivine du Mont-Royal, P.Q. Canada. *Can. J. Spectros.* **19**, 63-67.

Sine, N. M., Taylor, W. O., Webber, G. R. & Lewis, C. L. (1969): Third report of analystical data for CAAS sulphide ore and syenite rock standards. *Geochim. Cosmochim. Acta* **33**, 121-131.

Steger, H. F. (1975a): Determination of the elemental sulphur content of minerals and ores. *Talanta* (in press).

——— (1975b): The stability of the certified reference ores, MP-1, KC-1 and SU-1 to air oxidation. Submitted to Talanta.

——— Bowman, W. S., Sutarno, R. & Faye, G. H. (1975): Iron ore, SCH-1: its characterization and preparation for use as a certified reference material. *Can. Centre Mineral Energy Tech., Tech. Rep.* MSL 75-168 (TR).

Sutarno, R. & Faye, G. H. (1975): A measure for assessing certified reference ores and related materials. *Talanta* **22**, 675-681.

Webber, G. R. (1965): Second report of analytical data for CAAS syenite and sulphide standards. *Geochim. Cosmochim. Acta* **29**, 229-248.

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