Characterization of a new set of eight geochemical reference materials for XRF major and trace element analysis

Rufino Lozano[*] **and Juan Pablo Bernal**

Departamento de Geoquímica, Instituto de Geología, Universidad Nacional Autónoma de México,
Ciudad Universitaria, 04510 México, D. F., Mexico.
* rufino@servidor.unam.mx

ABSTRACT

Eight new geochemical reference materials for the analysis of major and trace elements in typical geological matrices have been prepared, and their physical and chemical homogeneity has been thoroughly assessed. The materials (IGL sample series) consist of a lateritic soil, a dolomite, a limestone, an andesite, three different syenites and a gabbro, all of them sampled at different localities from Mexico. The results indicate that the IGL samples are physically homogeneous down to a sub-batch of 0.2 g with a 0.05 significance level. Major and trace element provisional composition of these materials was obtained by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF). Statistical evaluation to verify for "sufficient homogeneity" was applied and sufficient chemical homogeneity at the 0.05 significance level was demonstrated. Calibration curves were constructed using the IGL samples in order to assess their performance as reference materials. Analyses of international reference materials (RGM-1, AGV-1, SDO-1, and Es-3) demonstrate the reliability of the IGL samples for calibration and intercalibration purposes. Provisional concentrations for 24 major and trace elements, as well as FeO and loss on ignition (LOI) values, are provided for all IGL reference materials.

Key words: reference materials, WD-XRF, calibration, sufficient homogeneity, chemical analysis.

RESUMEN

Se ha preparado un conjunto de ocho nuevos materiales geoquímicos de referencia para el análisis de elementos mayoritarios y traza en matrices geológicas típicas. La serie de materiales IGL está compuesta de un suelo laterítico, una dolomía, una caliza, una andesita, tres diferentes tipos de sienita y un gabro, todos ellos colectados en diferentes localidades de México. La homogeneidad física y química de estos materiales ha sido valorada ampliamente. Los resultados que se presentan aquí indican que las muestras IGL son físicamente homogéneas cuando menos hasta 0.2 g, con un nivel de significancia de 0.05. La composición de los elementos mayoritarios y traza fue determinada por espectrometría de fluorescencia de rayos X en dispersión de longitudes de onda (WD-XRF). La evaluación estadística para verificar la "homogeneidad suficiente" ha sido aplicada, demostrando suficiente homogeneidad química con un nivel de significancia de 0.05. Con el fin de valorar el desempeño de las muestras de la serie IGL como material de referencia, se construyeron curvas de calibración para elementos mayores y traza utilizando WD-XRF, y se analizaron cuatro materiales internacionales de referencia geoquímica (RGM-1, AGV-1, SDO-1, Es-3) como muestras desconocidas. Los resultados demuestran la confiabilidad de la serie IGL para el propósito de calibración e íntercalibración. Se presentan los valores provisionales de las concentraciones de 24 elementos mayores y traza, FeO y pérdida por calcinación, para las muestras de referencia de la serie IGL.

Palabras clave: materiales de referencia, WD-XRF, calibración, homogeneidad suficiente, análisis químico.

INTRODUCTION

Standard reference materials (SRM) are constantly required in geoanalytical facilities to guarantee reliable analytical results. They play a pivotal role during the development of new analytical techniques, methodologies and new sample preparation procedures; for assessing short and long term stability of instrumentation; in detection of random and/or systematic errors during routine analysis; for cross-calibration of different analytical techniques and methodologies, and in laboratory intercalibrations (Ingamells and Pitard, 1986). Consequently, high-quality SRMs are one of the most valuable tools geoanalytical facilities may posses, after the analytical instrumentation itself, but they are difficult to obtain as they are usually highly-priced and available in limited amounts. New publication standards require that for any chemical or isotopic composition reported, the results obtained for "well-known" standard reference materials are analysed in the same laboratory as "unknowns", should also be included to ascertain the precision and accuracy (Deines *et al.*, 2003), and thus verify the robustness of the conclusions based upon such results. Hence, the rate of consumption of SRM is similar to many other consumables in the laboratory and, thus, quickly exhausted.

The importance of developing reference materials from Mexican samples has been long recognized. Pérez *et al.* (1979) reported the preliminary composition of four "in-house" reference samples which included two basalts (BCU-1 and BCU-2), a dacite (DCC-1), and a rhyolite (RSL-1). Despite the initial efforts, little work towards certification was further carried out. High-quality analytical data for these samples were reported for petrological purposes (Verma, 1984; Verma and Armienta-H., 1985; Verma, 2000), and suggest small heterogeneities in the %SiO$_2$ for some of them. While the exact reason for this is not known to us, it might stem from the relatively large particle size of the samples (~175 μm, 80 mesh), or uncertainties between gravimetric and spectrometric methods. Unfortunately, the limited amount of data available hinders any possibility for their composition to be further refined using a combination of several statistical methods (*e.g.,* Velasco-Tapia *et al.*, 2001). Since only 10–15 kg of each sample was originally collected (Pérez *et al.*, 1979), further work on these samples was considered impractical. This would require crushing and milling of the remaining materials to further reduce particle size to current standards (75 μm, 200 mesh), homogenization and physical characterization, as well as further sample collection from different localities where no guarantee of equivalence between the old and new batches exists.

More recently, with the establishment of isotope geochemistry procedures and methodologies at UNAM, a basalt from Sierra de Chichinautzin was prepared as "in-house" reference material BCU-3. Similar to previous attempts, it was analysed for major, trace, rare earth elements, and $^{87}Sr/^{88}Sr$ (Juárez-Sánchez *et al.*, 1995; Morton *et al.*, 1997),

and appears to be stable and homogeneous (Girón and Lozano-Santa Cruz, 2001). However, there is little information regarding the crushing and milling procedures, and no efforts have been made to certify this sample through the required inter-laboratory comparisons.

In the last few years, several new standard reference materials have been prepared by Mexico's Centro Nacional de Metrología (CENAM) (*e.g.,* Zapata *et al.*, 2000). From these, only three are of geological interest: a clay-limestone (DMR-59a, DMR64a, with composition certified for seven major elements), iron ore (DMR-88a, certified for one major element), and siliceous sand (DMR-73a, DMR-73-b, certified for five major elements). Although the geological materials produced by CENAM represent an important effort to generate high quality SRMs, they clearly fall short of the analytical requirements from the geochemical community, namely: certified composition of the ten major components (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_{3\,total}$, MnO, MgO, CaO, Na$_2$O, K$_2$O, and P$_2$O$_5$) and 14 trace elements (Rb, Sr, Ba, Y, Zr, Nb, V, Cr, Co, Ni, Cu, Zn, Th, and Pb), information or composition on trace elements, and wide variety of matrices (*i.e.*, samples from different geological contexts). Clearly more work has to be done if a set of useful reference materials from Mexican samples is desired, particularly since an increased number of geoanalytical facilities are being set up in the recent years.

Many metrological institutions (National Institute of Standards and Technology, Institute of Reference Methods and Materials) or geological surveys (*e.g.*, United States Geological Survey, USGS, Geological Survey of Japan, GSJ) have produced similar samples to those presented here, but as certified reference materials (see Govindaraju, 1994, and Potts *et al.*, 1992 for a comprehensive compilation). However, production of the latter must be an ongoing process; their development is slow, costly, and not always straightforward. Currently available reference materials are likely to be exhausted within few years after production, faster than produced, hence similar samples need to be readily available to substitute exhausted materials.

Under the light of these considerations, and following Verma (1999), we have developed eight new materials (lateritic soil, a limestone, a dolomite, an andesite, three syenites, and a gabbro) which have the potential to become high-quality (*i.e.*, homogeneous and well characterised) geological SRMs for major and trace element analysis. These have been collected from different localities in Mexico (Table 1), and are assessed as candidates for reference materials for major-element composition (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_{3\,total}$, FeO, MnO, MgO, CaO, Na$_2$O, K$_2$O, and P$_2$O$_5$), loss on ignition (LOI) and 14 trace elements (Rb, Sr, Ba, Y, Zr, Nb, V, Cr, Co, Ni, Cu, Zn, Th, and Pb). This included physical, chemical and mineralogical characterization of each material: particle-size analysis by laser scattering, X-ray powder diffraction (XRD) and standard petrographical analyses, wavelength-dispersive X-Ray fluorescence spectrometry (WD-XRF), gravimetric and wet methods. The

Table 1. Sample localities and description.

Sample type	Sample ID	Locality description	Number of 100 g sub-samples prepared
Lateritic soil	IGLs-1	Rancho Rosa de Castilla, Arandas, Jal. 20° 41.373' N, 102° 15.850' W	205
Dolomite	IGLd-1	Cerro El Mingú, Tepatepec, Actopan, Hgo. 20°17'17.9'' N, 99°07'00.8'' W	189
Limestone	IGLc-1	Cerro El Mingú, Tepatepec, Actopan, Hgo 20°17'32.5'' N, 99°07'04.7'' W	200
Andesite	IGLa-1	Ceboruco volcano, Nayarit 21° 09.6' N, 104° 23.47' W	195
Nepheline syenite	IGLsy-1	Rancho El Guayacán, San Carlos, Tamps. 24° 44.635' N, 99° 06.851'W	205
Aegirine-augite syenite	IGLsy-2	Rancho Carricitos, San Carlos, Tamps. 24°35.885' N, 99°01.237' W	203
Gabbro	IGLgb-3	Rancho Carricitos, San Carlos, Tamps. 24°35.885' N, 99°01.237' W	201
Aegirine syenite	IGLsy-4	Rancho Carricitos, San Carlos, Tamps. 24°35.885' N, 99°01.237' W	202

physical and chemical homogeneity of the materials was statistically assessed to insure that all samples comply with the highest possible quality standards. Finally, to assess the analytical performance of the IGL series, four Geological Reference Materials (RGM-1, AGV-1, SDO-1, and Es-3) were analysed by XRF using the former as calibration standards. The results indicate that the IGL series possess the quality required to be further assessed as reference materials by inter-laboratory comparison.

ANALYTICAL METHODS

Crushing and milling

Figure 1 summarises the homogenisation procedure followed in this work. Between 40 and 70 kg of each specimen were collected. All samples were cleaned from evident allogenic material and/or weathered phases *in situ* and transported to our facilities where they were further reduced to pebble size (3–5 cm), with the exception of IGLs-1 (soil) which was sieved *in situ* (particle size <2 mm) and cleaned from plant-roots remains (according to Bowman *et al.*, 1979). Sample crushing and pulverizing was done at Instituto de Geología–Estación Regional del Noroeste (UNAM) using a "jaw-crusher" and a frontal disk-mill to reach a particle size <100 μm. Final pulverization was done using a Herzog H100 vibrating mill with a 200 cm^3 α-Al$_2$O$_3$ ceramic vial, with the exception of IGLs-1 which was milled within a hardened-steel vial, to avoid any potential damage to the α-Al$_2$O$_3$ ceramic vial, which could lead to sample cross-contamination. Finally, the samples were sieved through a #200 grid in order to achieve average particle sizes below 74 μm. Sample homogenization

was done in our facilities using a Riffle-type sub-divider adapted to a vibrating feeder to allow for 100 g sub-sampling delivered to 150 cm^3 jars. The number of sub-samples for each reference material candidate is presented in Table 1. Every possible precaution was followed to minimise any cross-contamination between samples (but not between batches of the same sample). These included thoroughly cleaning of all the grinding and homogenization equipment with compressed-air, distilled water and acetone to remove any remains from the previously crushed sample.

Although the sample preparation procedure described above is known to contribute slightly to the chemical composition of the final material, in particular to the Al$_2$O$_3$ content and some trace elements, it is expected to affect the composition of each sample in a similar degree to all samples and between batches, but not to affect the chemical homogeneity of the specimens. The results presented below strongly support this assertion.

Instrumental and wet methods

Particle-size analyses were done by laser diffractometry using a Beckman/Coulther LS-230 particle-size analyser by suspending 200 mg of each sample in deionized water and decanting through the analyser beam. The data presented below represent the average from at least three independent measurements from the same number of randomly selected sub-batches. Additionally, for IGLd-1, IGLs-1 and IGLgb-3, ten sub-batches were analysed in order to estimate the physical homogeneity of the samples and the repeatability of the methodology. When required, random selection was carried out with aid of a random number generator from a personal scientific calculator.

Procedure followed for the preparation of the
reference materials

```
┌─────────────────────────────┐
│     SELECTED BLOCKS         │
│       40 - 70 kg            │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   BLOCKS CLEANED AND        │
│  SPLIT INTO <5 cm PIECES    │
│         ~35 kg              │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│    MIXED AND CRUSHED        │
│    TO < 1 mm  ~30 kg        │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│  PASSED TWICE THROUGH CERAMIC │
│     SWING MILL   ~28 kg     │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│  SIEVED THROUGH 200 MESH IRON │
│     STEEL SIEVE ~25 kg      │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   PASSED TWICE THROUGH A    │
│  RIFFLER TYPE SUBDIVIDER  ~20 kg │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│   200 PACKETS OF ~100 g     │
└─────────────────────────────┘
```
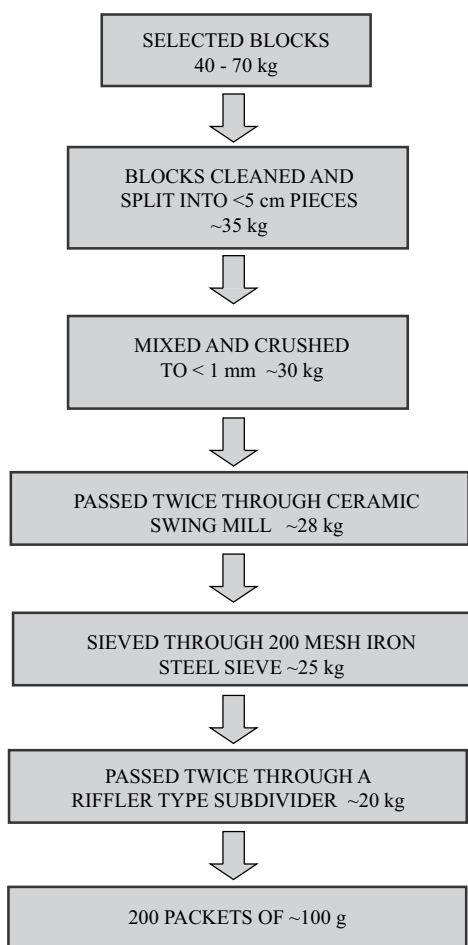
Figure 1. Schematic diagram of the stages used in the preparation of the IGL samples. The weights are approximate and do not account for sample losses.

The mineralogical characterization of the rock samples was done by X-ray diffraction (XRD) of randomly oriented samples, additionally petrographic inspection of thin sections was done for some samples (IGLa-1, IGLsy-1, IGLsy-2, IGLsy-4, and IGLgb-3). XRD analyses were carried out in a Philips 1400 X-ray diffractometer equipped with a Cu-anode tube as X-ray source and directing the collimated Cu $K_{\alpha 1,2}$ radiation ($\lambda = 0.15405$ nm) towards a randomly oriented sample. Standard scans were recorded from 4º–70º (2θ) with a step-scan of 0.02º and 2s/step. XRD analysis typically allows the detection of any crystalline fraction with a >3% abundance. X-ray diffractograms discussed below are available from the RMCG web site (electronic supplement 22-3-01).

Major element composition was obtained by X-ray fluorescence in fused $LiBO_2/Li_2B_4O_7$ disks using a Siemens SRS-3000 wavelength-dispersive X-ray fluorescence spectrometer with a Rh-anode X-ray tube as a radiation source.

Oven-dried samples from different batches were mixed with a 1:1 $LiBO_2/Li_2B_4O_7$ mixture in a 1:9 sample:flux ratio, and fused using a Claisse Fluxy-10 automatic fluxer (Lozano-Santa Cruz *et al.*, 1995). Our spectrometer was calibrated for major element analyses using fifteen geochemical reference materials: NIM-P, NIM-N, NIM-S, NIM-G, SARM 49, JG-1, JB-1a, JR-1, JLs-1, QLO-1, BHVO-1, Es-4, BE-N, GH, and GS-N. Trace element concentrations were also measured by XRF analyses of pressed pellets according to previously described methodologies (Verma *et al.*, 1996). The seventeen geochemical reference materials used for trace element calibration were: JA-1, SY-2, SY-3, BE-N, STM-1, JG-2, NIM-G, BCR-1, BHVO-1, JB-2, JB-1a, JGb-2, SARM 49, OU-4, CH-1, GS-N, and SIEM-04.

X-ray absorption/enhancement effects were corrected automatically using the Lachance and Traill (1966) method, included in the SRS-3000 software. The FeO content was determined by $Cr_2O_7^{2-}$ titration of dissolved samples using diphenyl amine as visual indicator. Loss on ignition (LOI) was measured by gravimetric methods; 1 g of oven-dried sample was heated to 1,000 ºC in porcelain crucibles for 1 hour. The analytical performance of these procedures has been thoroughly assessed over the recent years (Kiipli *et al.*, 2000; Potts *et al.*, 2001, 2003a, 2003b), resulting in highly reliable analytical methodologies for major and trace elements in geological samples. To estimate chemical homogeneity of the samples, ten replicate analyses were done for randomly selected samples.

SAMPLE DESCRIPTION

Samples were selected from localities where geological and geochemical data were readily available. A second selection criterion was based upon the composition of the samples so as they were reasonably spread along the concentration range, in order to yield a wide-range calibration curve.

Carbonate samples (IGLc-1 and IGLd-1) correspond to a limestone and a dolomite, respectively, collected at Cerro El Mingú, approximately 5 km N from Tepatepec, in the Hidalgo state. The samples correspond to marine carbonates from El Doctor Formation which appears to be early Cretaceous (del Arenal, 1978). Recent geochemical evidence suggests that some of the carbonates in the area were affected by karstification processes (Carrasco-Velázquez *et al.*, 2004). Approximately 65 kg of each sample were collected and yielded, after crushing and milling (see below), 189 and 200 sub-batches of 100 g of IGLd-1 and IGLc-1, respectively. XRD analysis of IGLd-1 showed that it is mostly composed of dolomite, although small amounts of calcite were also observed. Visual inspection of hand specimens shows small amounts of clays and sulphides, but on a proportion not detectable by XRD analysis. IGLc-1 (limestone) is mostly composed of calcite, similarly to IGLd-1, some allogenic material is sparingly scattered

throughout the specimen, being thus difficult to identify by XRD analyses due to its low abundance (<< 3%).

Sample IGLa-1 corresponds to an andesitic lava flow from the Ceboruco volcano, Nayarit, western Mexico, a Quaternary stratocone of andesite and dacite previously described (Thorpe and Francis, 1975; Nelson, 1980). The sample used in this work was collected approximately 10 km NE from the main edifice. Recent $^{40}Ar/^{39}Ar$ dating of the andesite flows indicates that these are less than 800 ka old, and most likely <100 ka (Frey *et al.*, 2004). Approximately 65 kg of the sample showing no evident signs of weathering were collected and, after crushing and milling, produced 195 sub-batches of 100 g. This sample is highly homogeneous with an aphanitic matrix, feldspars (sanidine and albite) being the major components.

Sample IGLgb-3 is a gabbro from the El Picacho complex, a tertiary intrusive from the Sierra de San Carlos, Tamaulipas, NE Mexico. Gabbro is the most abundant igneous rock in the complex and, according to cross-cutting relationships, also the oldest (Elías-Herrera *et al.*, 1991), although no radiometric age has been published for any geological unit from this complex. Approximately 65 kg of this sample were collected which yielded 201 sub-batches of 100g. This sample contains a large proportion of calcic plagioclase, kaersutite, biotite, ilmenite, and magnetite.

Samples IGLsy-1, IGLsy-2, and IGLsy-4 are leucocratic syenites also from El Picacho complex. These are located between the Cretaceous limestone and diorite derived from the gabbro. The syenites from El Picacho show a variation from syenite to alkali feldspar syenite and nepheline-bearing alkali feldspar syenite (Elías-Herrera *et al.*, 1991). Between 60 and 70 kg from each of the latter were collected, and produced 205, 203, and 202 sub-batches of 100g, respectively. IGLsy-1 is mostly composed of K-feldspar, with some nepheline, analcime, and pyroxene (aegirine-augite) and biotite. Some accessory minerals found are titanite, apatite, xenotime, and zircon. Some opaque crystals were also observed and are thought to be magnetite. IGLsy-2 is composed of pyroxene (aegirine-augite), amphibole (kaersutite), nepheline, biotite and felsdspars with some titanite, apatite, magnetite, and arfvedsonite. IGLsy4 contains significant amounts of albite, sanidine, kaersutite, biotite, pyroxene (aegerine-augite), and nepheline; some accessory minerals observed are titanite, xenotime, and zircon.

Sample IGLs-1 is a lateritic soil collected approximately 7 km E from Arandas, Jal., western Mexico. The soil was developed from weathering of basaltic flows, and was selected due to its apparent macroscopic homogeneity and accessibility, as well as the evident high Fe_2O_3 content. Approximately 45 kg of soil were collected, these were cleaned and sieved *in situ*, and yielded 205 sub-batches of 100g. This sample is composed of halloysite, hematite, maghemite, goethite, and quartz; traces of feldspars were also detected by XRD. The relatively high LOI values obtained for this sample (see results section) are mainly due to the presence of hydrated phases (clays and Fe oxy-hydroxides), considerable amount of organic matter and, possibly, pedogenic carbonates, although the latter in small amounts (<3%), otherwise they would have been detected in the XRD analyses.

The amount collected for each sample in this work (40–70 kg) can be considered low according to Govindaraju (1993), who recommended collection of ~400 kg of the original specimen, or Kane *et al.* (2003) who suggested sampling of approximately 100 kg. Although collection of 40–70 kg of each sample will probably shorten the availability of the IGL samples in the long term, it is not a limitation for the production and certification of high-quality reference materials, as demonstrated by Luo *et al.* (1997), who collected less than 40 kg of each sample.

RESULTS AND DISCUSSION

Physical homogeneity

Particle-size analysis of the samples indicates that more than 97.5% of each batch has a particle size smaller than 74 µm. The remaining fraction corresponds to elongated particles with a short side smaller than 74 µm, allowing them to pass trough the grid #200. Less than 0.03% of the samples has a particle size larger than 150 µm. While it is desirable for 99% of the sample to be less than 99 µm (Kane *et al.*, 2003), further grinding was not carried out to avoid any possible overgrinding problems. These might result in an unstable sample easy to oxidise, hygroscopic, and probably size-segregated according to grain morphology and mineral hardness.

Figures 2a and 2b shows the average particle size distribution for all the IGL samples, each one displaying a particular size-distribution pattern. Carbonate samples IGLd-1 and IGLc-1 are highly homogeneous between 0.8 and 75 µm. Consequently, the average and modal particle size for these samples can be contrasting among batches, without showing large differences in the % volume for each size fraction. For example, sample IGLd-1-b150 (Table 2) has a modal particle size of 16.40 µm, a contrasting value when compared to other batches of the same sample showing modal particle size ~60 µm. However, we note that for sample IGLd-1-b150 the reported modal particle size corresponds to 1.99% volume of the sample, while the 66 µm size fractions corresponds to 1.85%, only slightly lower than the modal fraction, and well within uncertainty calculated for this sample. These results indicate that for the carbonate samples, no particle size strongly predominates above others. This is not the case for the rest of the samples, where bi-modal or multimodal distributions can be observed (Figure 2 and Table 3). Such distributions suggest incipient mineral segregation controlled by the material hardness, and produced during the milling process. Consequently, further particle size reduction would enhance such differentiation, in detriment of the physical qualities already achieved, and
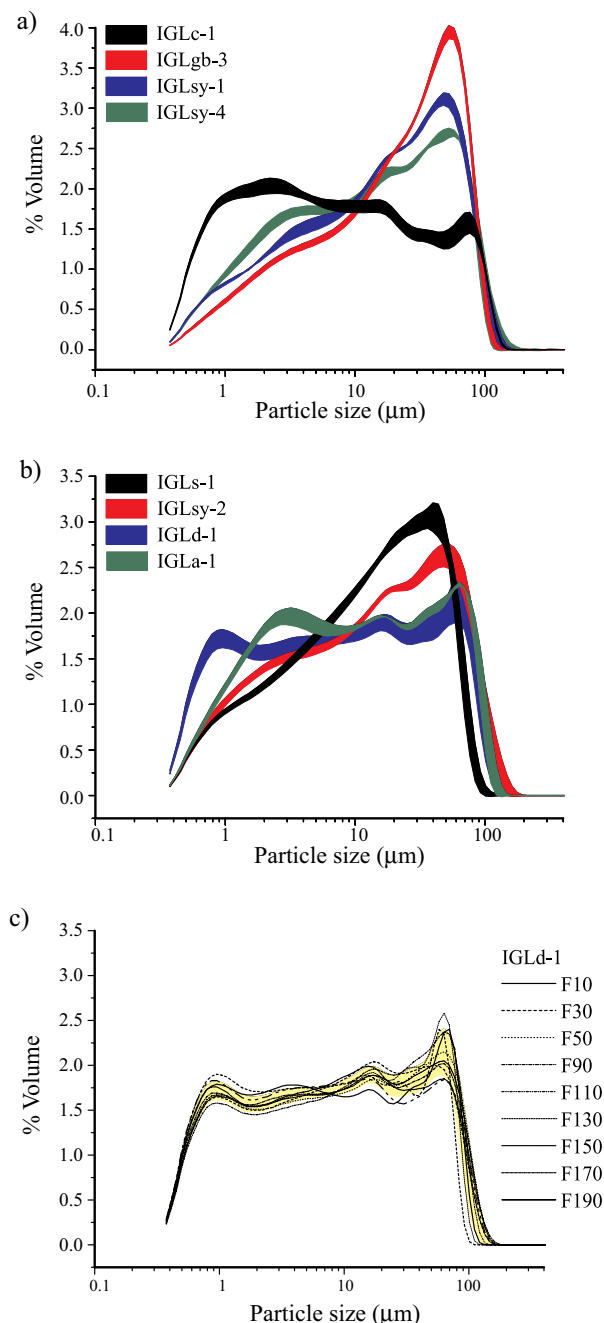
a)

b)

c)

Figure 2. a: Average particle size distribution for IGLc-1, IGLgb-3, IGLsy-1 and IGLsy-4. b: Average particle size distribution for IGLs-1, IGLsy-2, IGLd-1 and IGLa-1. Shaded areas correspond to particle size ± 1 standard deviation. Note the bi-modal particle size distribution of IGLsy-1, 2 and 4. c: Particle size distribution for different batches of IGLd-1. Shaded area corresponds to average ± confidence interval (99% significance, n=10).

probably affect the long-term stability of the materials.

The physical homogeneity of the samples was verified using a one-tail "F" test (Miller and Miller, 1988; Thompson and Wood, 1993). This test examines the null hypothesis *H:* $\sigma^2 = 0$ (*i.e.*, the difference between variances is negligible), and assesses whether the variation among different batches is significant at the 95% confidence level. In general it is

estimated by comparing the variance associated with the analytical method (s^2_{met}) after n_1 repeated observations or analyses of the same specimen, with that resulting from measuring a number, n_2, of different sub-samples of the same material (s^2_{batch}). F_{exp} (=s^2_{batch}/s^2_{met}) is then compared against a previously estimated critical value, F_{crit}, which is a function of the significance level, n_1 and n_2. Values of $F_{exp} < F_{crit}$ indicate that the uncertainty resulting from measuring the same sample several times is similar to the precision attainable by the analytical method and, thus, the samples are indistinguishable among themselves. In contrast, values of $F_{exp} > F_{crit}$ indicate that the uncertainty observed among samples is significantly larger than the analytical uncertainty, making the measured sample property significantly different among samples (*i.e.*, not homogeneous).

Figure 2c and Table 2 show the results of the F-test for sample IGLd-1. This material was selected for the test because it, apparently, shows the widest particle-size scattering pattern of all the IGL samples (see Figure 2b). The analysis of ten different IGLd-1 sub-samples (systematically selected every 20 jars to detect any potential bias induced during sample sorting and jar filling), indicates that the particle size distribution is similar among sub-batches (95% confidence level; Table 2). These results strongly suggest that the mixing and milling process used here produced sample batches with similar particle size distribution. Considering that the other materials studied here have particle-size distribution patterns with less scattering than IGLd-1 (Figures 2a, 2b), it seems reasonable to expect they will display similar particle-size homogeneity.

Chemical composition and assessment for "sufficient" chemical homogeneity

With the exception of liquid standard reference materials, all reference materials will display certain degree of heterogeneity. This is specially true for geological reference materials, where multi-mineralic powders are heterogenous at sufficiently small scale. Previous homogeneity tests (Thompson and Wood, 1993) have been demonstrated to yield "false" heterogeneities in samples which are truly homogeneous, as they fail to recognize for uncertainties which might be statistically significant, but negligible for intercomparison and calibration tests, where more significant sources of uncertainty, not necessary related to the sample itself, are to be considered. Under this light, a more adequate test (Fearn and Thompson, 2001) that examines the null hypothesis $H:s^2_{sam} \leq \sigma^2_D$, is used here, where σ^2_D corresponds to the highest allowable uncertainty to discriminate between homogeneous and heterogeneous specimens.

The assessment for "sufficient" chemical homogeneity (hereafter F-T test) is based upon the comparison between a "target standard deviation" (σ_D), and the experimental between-samples variance s^2_{samp}. Sufficient homogeneity is achieved when s^2_{samp} is smaller than a critical value *c:*

Table 2. Calculated "F" values to assess physical (particle size) homogeneity for the IGL series samples (one tail). F was estimated with a 95% significance and 9 × 2 degrees of freedom. Number between brackets indicate the %volume of the modal particle size.

Sub-Sample	Average (μm)	Mode μm (% vol.)	Standard deviation (μm)	Variance
IGLd-1 B10	6.911	63.41 (2.37)	4.26	18.20
IGLd-1 B30	8.975	57.77 (2.40)	4.89	23.98
IGLd-1 B50	8.616	66.44 (2.15)	4.88	23.90
IGLd-1 B70	8.15	66.44 (2.02)	4.81	23.18
IGLd-1 B90	8.97	66.44 (2.37)	4.75	22.58
IGLd-1 B110	11.25	66.44 (2.58)	4.85	23.56
IGLd-1 B130	8.461	66.44 (2.05)	4.80	23.13
IGLd-1 B150	7.675	16.40 (1.99)	4.71	22.24
IGLd-1 B170	7.354	16.40 (1.85)	4.78	22.91
IGLd-1 B190	8.285	16.40 (2.03)	4.65	21.65
		Sample batch average	*4.74*	*22.53*
IGLd-1 B10-1	5.335	10.97 (1.89)	4.141	17.15
IGLd-1 B10-2	7.559	72.94 (1.95)	4.778	22.83
IGLd-1 B10-3	7.563	14.94 (1.92)	4.701	22.10
		Method average	*4.5567*	*20.81*
		F_{CRIT} = 19.385 (95% confidence level)		F_{exp} = 1.08

$$c = A_1 \times \left(0.3 \times \sigma_D\right)^2 + A_2 \times s^2_{anal} \tag{1}$$

where s^2_{anal}, is the analytical variance, and A_1 and A_2 are two constants derived from χ^2, or obtained from Fearn and Thompson (2001). The first term of Eq. 1 represents the contribution from the target standard deviation to the overall uncertainty, while the second term represents the contribution from the measurement uncertainty. Thus, the F-T test accounts for effects introduced by instrumental instability (which may affect the data and produce false negatives), and sample heterogeneity (accounted and limited by σ_D). If the precision of the analytical technique used to assess homogeneity is low, the second term in Eq. 1 will be more important, and thus will obscure any contribution to the "heterogeneity" from the first term, resulting in "large" c values difficult to be exceeded by s^2_{samp}. In contrast, a large σ_D will result in c values dominated by the first term of the equation, and the analytical uncertainty during the measurement can be neglected, resulting in a homogeneous batch.

For this work, σ_D was established as ±1% relative to the mean central value (MCV) or average concentration. For example if the MCV for a given component is 50%, then $\sigma_D = 0.5\%$. (see electronic supplement 22-3-03 for detailed calculations, or Fearn and Thompson (2001) for an example). Therefore, a positive result from the F-T test means that the sample is homogeneous down to 1% of the MCV for the amount of sample tested, usually 1g. Table 4 shows the result from the F-T test for the ten major components analysed in geological material (data available from the RMCG web site; electronic supplement 22-3-03).

Table 5 presents the results from the more stringent F-test applied to the IGL materials, for major and trace elements. All the samples show sufficient homogeneity with a 95% confidence level and 1 g of sample, indicating that,

similar to the particle-size analyses, the mixing and milling process used here produced chemically homogeneous materials. We note, however, that it is not possible to assess the homogeneity of TiO_2, $Fe_2O_{3\,tot}$, Na_2O, K_2O, P_2O_5, and most trace elements in IGLd-1 and IGLc-1, because their concentrations are close to, or below their respective detection limits in our XRF spectrometer. This also applies to a few trace elements in the other IGL samples as marked in Tables 4 and 5 (see Table 6 for the relevant detection limits).

Analytical performance of the IGL samples as reference materials

The major and trace element provisional average compositions of the IGL samples are presented in Table

Table 3. Average and modal particle size for the IGL samples. % is % volume of the corresponding size fraction.

		Average	Mode
IGLc-1	μm	1.47	2.42
	%	1.97	2.03
IGLd-1	μm	1.56	63.41
	%	1.59	2.15
IGLs-1	μm	1.58	52.9
	%	0.91	3.95
IGLa-1	μm	1.51	63.41
	%	1.6	2.3
IGLsy-1	μm	1.58	52.6
	%	0.91	3.94
IGLsy-2	μm	1.35	52.2
	%	1.18	2.69
IGLsy-4	μm	1.55	52.62
	%	1.32	2.69
IGLgb-3	μm	1.56	47.9
	%	1.05	3.11

Table 4. Chemical composition for the eight samples analysed in this work and their analytical uncertainty ($\pm 1\sigma$, n = 10). S_{target} = target standard deviation, defined here as 1% relative to the average concentration (1% MCV), except for SiO_2 in IGLd-1 where a 1.5% value (*italics*) was used for sufficient homogeneity tests. S_{bws}= between samples variance, c as defined in Eqn. 1. *c* was estimated using F_1 = 2.01 and F_2 = 1.25 (from Fearn and Thompson 2003). NA = Test not applied since element concentration is close to or below detection limits. This table and the original data are available from the RMCG web site (electronic supplement 22-3-03).

	% SiO_2	% TiO_2	% Al_2O_3	%Fe_2O_3t	% MnO	% MgO	% CaO	% Na_2O	% K_2O	% P_2O_5
IGLc-1										
Average conc.	0.07	<0.004	0.152	<0.006	0.011	0.29	55.22	<0.03	<0.05	<0.004
$\pm 1\sigma$	0.01		0.003		0.001	0.01	0.01			
S_{target} (1% MCV)	0.0011	NA	0.0004	NA	0.0001	0.0029	0.5522	NA	NA	NA
S_{bws}	0	NA	0	NA	6.8×10^{-7}	0.	0	NA	NA	NA
c	0.0001	NA	0.0008	NA	7.0×10^{-7}	0.0001	0.1355	NA	NA	NA
Homogeneous?	yes	NA	yes	NA	yes	yes	yes	NA	NA	NA
IGLd-1										
Average conc.	1.74	<0.004	0.115	<0.006	0.005	18.590	33.770	<0.03	<0.05	<0.004
$\pm 1\sigma$	0.01		0.003		0.001	0.010	0.004			
S_{target} (1% MCV)	*0.0231*	NA	0.0004	NA	4.81E-05	0.1822	0.3405	NA	NA	NA
S_{bws}	0.0002	NA	0	NA	3.0×10^{-7}	0	0	NA	NA	NA
c	0.0003	NA	0.0019	NA	1.0×10^{-6}	0.0258	0.0637	NA	NA	NA
Homogeneous?	yes	NA	yes	NA	yes	yes	yes	NA	NA	NA
IGLs-1										
Average conc.	44.94	2.70	24.39	12.99	0.274	0.400	0.380	0.33	0.61	0.14
$\pm 1\sigma$	0.06	0.01	0.04	0.01	0.002	0.010	0.020	0.02	0.01	0.01
S_{target} (1% MCV)	0.4569	0.0278	0.2455	0.1409	0.0028	0.0042	0.0040	0.0041	0.0062	0.0014
S_{bws}	0.0588	0.0002	0.0035	0.0105	3.9×10^{-7}	0	1.2×10^{-5}	0	0	0
c	0.1831	0.0005	0.0578	0.0669	1.1×10^{-5}	0.0002	2.6×10^{-5}	0.0005	0.0001	1.2×10^{-5}
Homogeneous?	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
IGLa-1										
Average conc.	60.52	1.08	17.39	6.12	0.102	1.97	5.18	4.80	2.14	0.11
$\pm 1\sigma$	0.22	0.01	0.03	0.05	0.001	0.01	0.01	0.04	0.01	0.03
S_{target} (1% MCV)	0.6084	0.0109	0.1745	0.0618	0.0011	0.0195	0.0524	0.0483	0.0215	0.0041
S_{bws}	0.0061	0	0.0079	0.0005	4.4×10^{-8}	0	0	0.0013	0.0001	0
c	0.1565	0.0001	0.0117	0.0034	2.9×10^{-6}	0.0005	0.0013	0.0037	0.0003	3.2×10^{-5}
Homogeneous?	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
IGLsy-1										
Average conc.	52.15	0.05	21.68	4.19	0.182	0.32	2.47	9.55	5.90	0.422
$\pm 1\sigma$	0.12	0.01	0.06	0.13	0.001	0.01	0.02	0.06	0.02	0.003
S_{target} (1% MCV)	0.5215	0.0052	0.2164	0.0424	0.0018	0.0033	0.0249	0.0954	0.0589	0.0009
S_{bws}	0	0	0	0	0	2.5×10^{-5}	3.63×10^{-5}	0	0	0
c	0.0877	2.8×10^{-5}	0.0252	0.0139	9.74E-06	0.0001	0.0002	0.0117	0.0072	1.43E-05
Homogeneous?	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
IGLsy-2										
Average conc.	57.99	1.01	19.93	2.91	0.222	0.540	2.29	7.64	5.47	0.112
$\pm 1\sigma$	0.24	0.01	0.14	0.02	0.002	0.001	0.05	0.04	0.02	0.003
S_{target} (1% MCV)	0.5762	0.0102	0.1977	0.0393	0.0022	0.0055	0.0230	0.0764	0.0541	0.0011
S_{bws}	0.0188	0	0.0011	0	1.6×10^{-6}	0	0	0	0	0
c	0.0755	0.0001	0.0178	0.0011	3.1×10^{-6}	0.0001	0.0002	0.0084	0.0018	1.9×10^{-5}
Homogeneous?	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
IGLsy-4										
Average conc.	54.99	1.68	19.56	5.556	0.153	1.64	4.39	6.44	3.08	0.49
$\pm 1\sigma$	0.04	0.01	0.01	0.001	0.001	0.02	0.07	0.03	0.01	0.01
S_{target} (1% MCV)	0.5464	0.0168	0.1936	0.0557	0.0015	0.0163	0.0442	0.0643	0.0306	0.0047
S_{bws}	0	1.9×10^{-5}	0	0	0	0	0	5.2×10^{-5}	1.5×10^{-5}	0
c	0.1368	0.0001	0.0507	0.0029	5.7×10^{-6}	0.0005	0.0013	0.0159	0.0003	4.6×10^{-5}
Homogeneous?	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
IGLgb-3										
Average conc.	38.73	3.82	16.66	14.48	0.159	6.110	12.405	2.82	1.03	1.527
$\pm 1\sigma$	0.13	0.01	0.04	0.02	0.002	0.020	0.003	0.03	0.01	0.002
S_{target} (1% MCV)	0.3861	0.0380	0.1639	0.1504	0.0016	0.0649	0.1241	0.0279	0.0102	0.0144
S_{bws}	4.1×10^{-4}	4.9×10^{-5}	0	$1. \times 10^{-4}$	0	0	1.2×10^{-3}	1.3×10^{-3}	8×10^{-6}	0
c	0.0760	0.0003	0.0133	0.0063	1.87E-06	0.0065	0.0061	0.0016	4.5×10^{-5}	0.0002
Homogeneous?	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes

6 and Table 7, respectively. These were obtained from the analyses of, at least, ten independent replicates, and using the analytical methodologies described above. No normality tests (*e.g.*, Verma, 1997; Verma *et al.*, 1998) were carried out on the data. Reported uncertainties correspond to ±2×standard error. On the basis of these provisional compositions, our XRF spectrometer was calibrated using only the eight IGL samples as reference materials. Typical calibration plots (intensity *vs.* concentration) for some major and trace elements are presented in Figure 3, where a strong linear correlation between analyte concentration and raw fluorescence radiation intensity are observed for all elements. The data for major elements in Figure 3 have not been corrected for interelement effects, such as radiation absorption or enhancement (*e.g.*, Lachance and Traill, 1966). In contrast, trace element radiation intensity has been corrected for spectral overlaps (*e.g.*, Ti $K\beta_1$ over V $K\alpha_{1,2}$) and/or interelement effects as required. Correlation coefficients (R^2) > 0.99 for all elements (Figure 3) support a linear behaviour between radiation fluorescence and analyte concentration (minimum R^2 to support linearity: 0.834, 99% confidence level, CL, 6 degrees of freedom, DoF); it also demonstrates that the compositions in Tables 6 and 7 are reliable, and that IGL samples have the potential to be used as reference materials.

To assess the analytical performance of the IGL samples as reference materials, four international geochemical reference materials (RGM-1, AGV-1, SDO-1, and Es-3) not used in our primary calibration (see *Analytical Methods* section) were analysed as unknowns. Five independent replicates from each reference material were analysed for major and trace elements. The results are presented in Table 8, where expected concentrations and uncertainties are also included (Smith, 1991; 1995a; 1995b; Govindaraju, 1994; Kiipli *et al.*, 2000; Velasco-Tapia *et al.*, 2001). The results in Table 8 are assessed for accuracy using the Sutarno-Steger Test (Sutarno and Steger, 1985). This test (SST hereafter) evaluates the accuracy of any measurement by comparing the difference between observed (x_{meas}) and expected (x_{rep}) concentrations, with the reported uncertainty (σ, s, for *certified* and *provisional* values, respectively). If the analysed sample concentration corresponds to a *certified* value, then SST is calculated as:

$$SST = \frac{\left|x_{meas} - x_{rep}\right|}{2\sigma} \qquad (2)$$

whereas for *provisional* concentrations, SST is calculated as:

$$SST = \frac{\left|x_{meas} - x_{rep}\right|}{4s} \qquad (3)$$

In general, a measurement can be considered as accurate if SST ≤ 1, which implies that the measured concentration falls within the uncertainty of the certified or

Table 5. Results from statistical analysis to assess chemical homogeneity of the IGL samples using the "F" test (one tail), All major elements were assessed with the same degrees of freedom (DoF) = 9x2 and significance level = 0.05. Trace element homogeneity was assessed with F_{crit} and DoF at the right end of the table. NA: the test was not carried out for the element since its concentration is at or below instrumental detection limit. Data available from the RMCG web site (electronic supplement 22-3-02).

	IGLc-1	IGLd-1	IGLs-1	IGLa-1	IGLsy-1	IGLsy-2	IGLgb-3	IGLsy-4
Major elements (F_{crit}= 19.38, DoF 9x2)								
SiO_2	0.8	15.1	1.1	16.3	6.3	16.7	15	14.2
TiO_2	NA	NA	2.3	1	2.5	7.3	3	1
Al_2O_3	14.9	10.4	3.1	1.4	0.8	18	1.4	1.2
Fe_2O_{3t}	NA	NA	5.7	1.1	8.1	17.2	13.9	2.1
MnO	1.6	8	1.4	0.4	5.2	0.3	2.6	1.4
MgO	2	1.8	2.2	0.4	3.6	0.5	0.4	0.6
CaO	4.3	1.2	2.1	0.9	5.9	10.1	17.2	2.6
Na_2O	NA	NA	6.2	6.3	0.6	14	9.3	1
K_2O	0.2	6.7	1.6	3.8	3	1.8	6.8	1.3
P_2O_5	1	1.9	1.2	0.6	0.6	1.9	1.1	5
Trace elements								
Rb	NA	NA	1	0.8	5	2.5	2.8	0.7
Sr	1.1	1.1	1.2	0.4	2.6	0.8	0.4	0.5
Ba	NA	0.7	0.4	1.3	0.3	1.9	1.5	17.6
Y	NA	NA	4.3	3.8	9.2	1.3	0.3	0.8
Zr	1.1	0.2	1.4	1.9	0.6	14.4	2.1	0.8
Nb	NA	NA	0.4	1.7	1.5	10.7	0.5	1.2
V	0.5	5.1	0.1	0.7	1	0.4	0.5	0.5
Cr	NA	NA	2.2	2.2	NA	NA	2.5	NA
Co	4.1	0.6	2.4	1.8	2.1	3.6	2.3	6.7
Ni	NA	NA	3.1	1.5	2.9	0.4	5.4	1.6
Cu	3	0.3	1.3	1.1	0.4	3.1	0.9	3.5
Zn	2.3	1.2	5.8	8.5	3.8	3.8	0.3	1.4
Th	3.8	NA	2.2	1.5	3.4	1	1.4	0.8
Pb	0.5	NA	0.8	0.7	6.9	0.8	1.4	0.7
F_{crit}	19.37	19.35	19.35	19.43	19.35	19.35	19.38	19.38
DoF	8x2	8x2	8x2	14x2	7x2	7x2	9x2	9x2

Table 6. Provisional average major element composition for the IGL samples (w/w %). All uncertainty values correspond to 2σ, n=10. DL are detection limits. Fe₂O₃c are calculated values. Data available from the RMCG web site (electronic supplement 22-3-02).

	IGLs-1	IGLd-1	IGLc-1	IGLa-1	IGLsy-1	IGLsy-2	IGLgb-3	IGLsy-4	DL
SiO_2	44.94 ± 0.06	1.74 ± 0.01	0.07 ± 0.01	60.52 ± 0.22	52.15 ± 0.12	57.99 ± 0.24	38.73 ± 0.13	54.99 ± 0.04	0.05
TiO_2	2.7 ± 0.01	<0.004	<0.004	1.08 ± 0.01	0.5 ± 0.01	1.01 ± 0.01	3.815 ± 0.014	1.68 ± 0.01	0.004
Al_2O_3	24.39 ± 0.04	0.115 ± 0.003	0.152 ± 0.01	17.39 ± 0.03	21.68 ± 0.06	19.93 ± 0.14	16.66 ± 0.04	19.56 ± 0.01	0.018
Fe_2O_3t	12.99 ± 0.01	<0.006	<0.006	6.12 ± 0.05	4.19 ± 0.13	3.91 ± 0.02	14.48 ± 0.02	5.556 ± 0.001	0.006
MnO	0.274 ± 0.002	0.005 ± 0.002	0.011 ± 0.001	0.102 ± 0.001	0.182 ± 0.001	0.222 ± 0.002	0.159 ± 0.002	0.153 ± 0.001	0.004
MgO	0.4 ± 0.01	18.59 ± 0.01	0.29 ± 0.01	1.97 ± 0.01	0.32 ± 0.01	0.54 ± 0.001	6.11 ± 0.02	1.64 ± 0.02	0.015
CaO	0.38 ± 0.02	33.77 ± 0.004	55.22 ± 0.01	5.18 ± 0.01	2.47 ± 0.02	2.29 ± 0.05	12.405 ± 0.003	4.39 ± 0.07	0.04
Na_2O	0.33 ± 0.02	<0.03	<0.03	4.8 ± 0.04	9.55 ± 0.06	7.64 ± 0.04	2.82 ± 0.03	6.44 ± 0.03	0.03
K_2O	0.61 ± 0.01	<0.05	<0.05	2.14 ± 0.01	5.9 ± 0.02	5.47 ± 0.02	1.03 ± 0.01	3.08 ± 0.01	0.05
P_2O_5	0.14 ± 0.01	<0.004	0.006 ± 0.001	0.43 ± 0.01	0.093 ± 0.003	0.112 ± 0.003	1.527 ± 0.002	0.49 ± 0.01	0.004
LOI	13.21 ± 0.08	45.17 ± 0.06	43.56 ± 0.02	0.06 ± 0.01	2.44 ± 0.02	0.98 ± 0.01	0.77 ± 0.04	0.72 ± 0.02	0.01
FeO	0.93 ± 0.02	< 0.01	< 0.01	3.74 ± 0.03	1.74 ± 0.02	1.75 ± 0.02	7.06 ± 0.03	3.09 ± 0.03	0.01
Fe_2O_3c	11.96			1.96	2.26	1.97	6.63	2.12	

provisional concentration.

The results for major elements in Table 8 indicate that the great majority of these are accurate, as most of them have SST values ≤ 1, with the exception of P_2O_5 in RGM-1. While the observed discrepancy between expected and measured concentrations is not large (0.01%), a SST value of 3.19 indicates poor accuracy. We note, however, that such SST value is the result of an unusually low uncertainty reported for RGM-1 (Velasco-Tapia *et al.*, 2001). Only in one case, the IGL calibration failed to yield the expected P_2O_5 concentration for Es-3, an Estonian limestone. For this sample, an SST value of 0.83 suggest good accuracy, however, a discrepancy of ~0.1% (absolute) indicates otherwise. Such bias is attributed to the lack of mathematical corrections for X-rays emission enhancement (*e.g.*, Lachance and Traill, 1966) and its high Ca content, which can enhance P $K\alpha_{1,2}$ radiation emission by ~30%.

The major and trace element concentrations in Table 8 are also presented in Figure 4 and Figure 5, where a comparison between expected and measured concentrations for major and trace elements, respectively, is presented. For most major elements (Figure 5), correlation coefficients (R^2) equal or higher than 0.99 (minimum $R^2 = 0.990$, CL = 99%, DoF= 2) and slope values close to unity (dashed line in Figure 5) are obtained, with intercepts not significantly different from zero, which implies that no significant systematic error is introduced to the calibration by using the IGL samples as reference materials, and, under the appropriate instrumental conditions, they can yield reliable major element concentrations for unknown geological samples.

The use of the IGL samples as reference materials for trace element analysis produce, in general, accurate results, as indicated by the SST values ≤1 for most elements in all samples (Table 8). Furthermore, graphical comparison between measured and expected concentrations (Figure 5) demonstrates that no significant systematic error has been introduced. While these results are very encouraging, they do show considerable more dispersion than for major elements. Such dispersion is produced by a combination of the following factors:

a) The number of reference materials (8) used to construct the calibration plots for the 14 different trace

Table 7. Provisional average trace element composition for the IGL samples (μg·g⁻¹). All uncertainty values correspond to 2σ, n=10, DL: detection limits. Data available from the RMCG web site (electronic supplement 22-3-02).

	IGLs-1	IGLd-1	IGLc-1	IGLa-1	IGLsy-1	IGLsy-2	IGLgb-3	IGLsy-4	DL
Rb	81 ± 1	< 2	< 2	32 ± 1	211 ± 3	142 ± 1	23 ± 1	59 ± 1	2
Sr	47 ± 1	164 ± 1	290 ± 2	592 ± 4	1,578 ± 15	992 ± 5	1,442 ± 7	1,391 ± 9	1
Ba	432 ± 11	< 11	< 11	930 ± 13	2,391 ± 15	2,422 ± 18	592 ± 9	13,731 ± 45	11
Y	46 ± 1	< 0.5	< 0.5	22 ±1	54 ± 2	41 ± 1	22 ± 1	15 ± 1	0.5
Zr	772 ± 14	1 ± 0	1.2 ± 0.5	224 ± 4	361 ± 5	464 ± 6	126 ± 2	153 ± 3	0.5
Nb	51.1 ± 0.4	< 0.7	< 0.7	20 ± 1	288 ± 3	217 ± 2	38 ± 1	65 ± 1	0.7
V	293 ± 4	8 ± 1	< 5	97 ± 6	17 ± 3	44 ± 3	439 ± 9	28 ± 3	5
Cr	267 ± 3	<2	<2	27 ± 2	< 2	< 2	12 ± 2	< 2	2
Co	58 ± 2	< 3	< 3	10 ± 1	< 3	4 ± 2	49 ± 2	6 ± 2	3
Ni	75 ± 3	< 0.5	< 0.5	7 ± 1	4 ± 1	5 ± 1	17 ± 1	6 ± 1	0.5
Cu	58 ± 1	4 ± 1	3 ± 1	17 ± 1	20 ± 2	10 ± 2	47 ± 2	14 ± 2	0.7
Zn	109 ± 1	1.3 ± 0.5	2 ± 1	74 ± 2	106 ± 3	89 ± 1	109 ± 2	65 ± 1	1.5
Th	14 ± 2	< 2	< 2	< 2	41 ± 2	29 ± 2	< 2	6 ± 1	2
Pb	29 ± 1	< 4	< 4	11 ± 2	20 ± 2	14 ± 1	5 ± 2	5 ± 2	4

elements, falls short from the recommended number for such analysis. In XRF spectrometry it is usually that, for the analysis of *n* elements, *n*-2 reference samples are required to plot an adequate set of calibration lines, in order to solve the interelement-effect correction matrix (Lachance and Traill, 1966; Lachance, 1996). Thus, using only the eight IGL samples for calibration purposes, we are unable to fully correct for inter-element effects.

b) Although we have extensively analysed the IGL samples against a series of international reference materials for major and trace elements by XRF spectrometry, the results in Tables 6 and 7 are only provisional values.
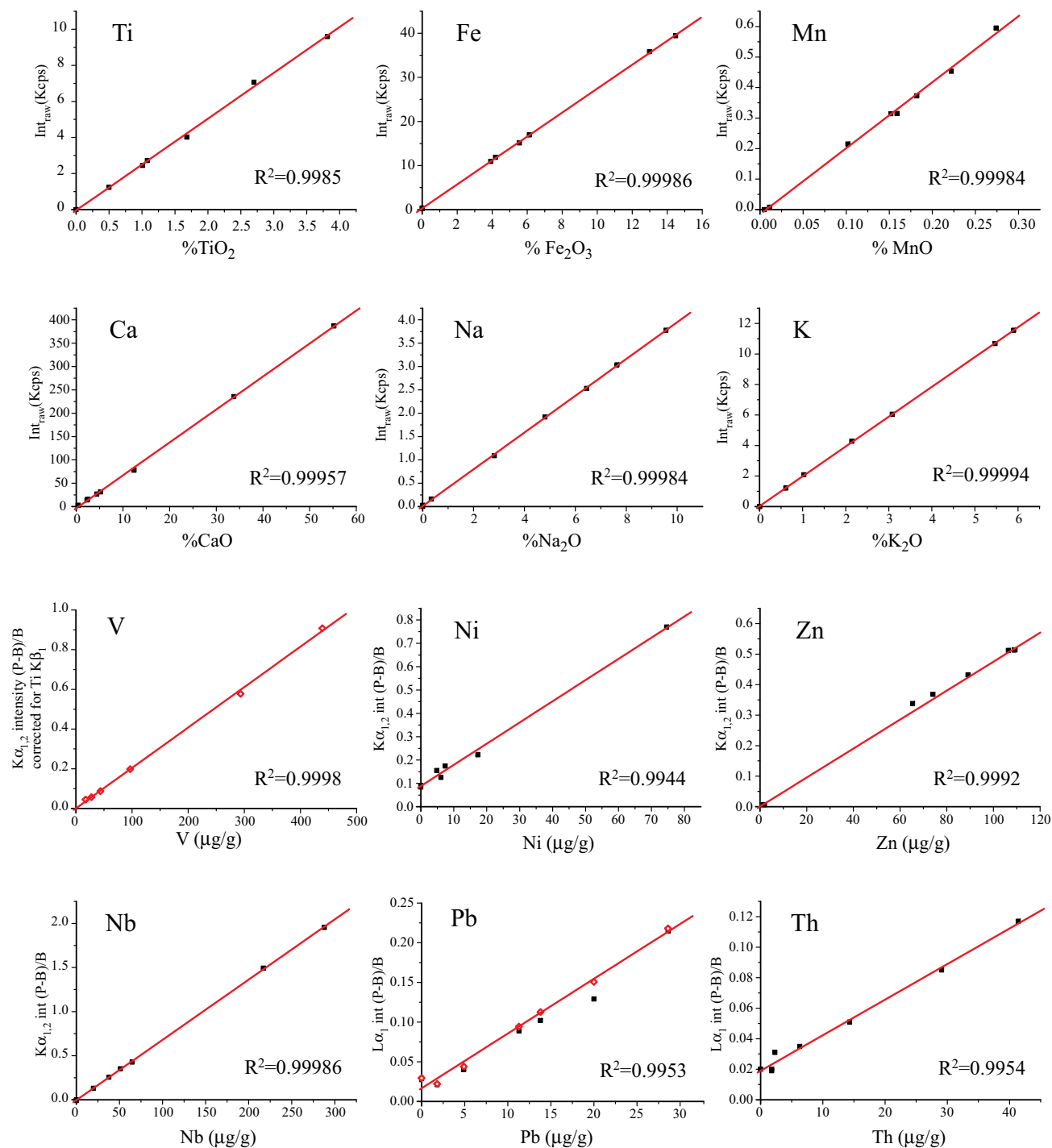
Figure 3. Typical X-ray fluorescence intensity *vs.* element concentration for the IGL samples. Intensity data for major elements has not been corrected for radiation absorption or enhancement effects, while corrections have been applied to some trace elements. Correlation coefficients for each calibration is presented in the corresponding plot. Filled symbols are raw intensities; open symbols are intensities corrected for absorption/enhancement effects.

Lozano y Bernal

Table 8. Comparison of expected and measured major and trace element compositions for four international reference materials obtained using the IGL samples as reference materials. Expected compositions from Potts *et al.* (1992), Govindaraju (1994), Kiipli *et al.* (2000), and Velasco-Tapia *et al.* (2001). Numbers in italics are provisional values. SST = Sutarno-Steger Test (Sutarno and Steger, 1985), calculated with Eq. 2 for certified or statistically refined concentrations (*e.g.*, Velasco-Tapia *et al.*, 2001), or Eq. 3 for provisional values. Measured uncertainties correspond only to the replicate uncertainty and do not consider the uncertainty from the calibration.

|	RGM-1			AGV-1			SDO-1			Es-3		
	Expected	Measured	SST	Expected	Measured	SST	Expected	Measured	SST	Expected	Measured	SST
%												
SiO_2	73.45 ± 0.5	73.47 ± 0.43	0.02	59.2 ± 0.7	58.3 ± 0.3	0.64	49.3 ± 0.63	50.01 ± 0.07	0.58	4.84 ± 0.96	4.91 ± 0.1	0.04
TiO_2	0.267 ± 0.028	0.279 ± 0.003	0.21	1.06 ± 0.06	1.06 ± 0.01	0.00	0.71 ± 0.03	0.74 ± 0.01	0.48	0.08 ± 0.013	0.08 ± 0.001	0.01
Al_2O_3	13.72 ± 0.15	13.46 ± 0.04	0.88	17.1 ± 0.37	16.98 ± 0.08	0.16	12.3 ± 0.23	12.39 ± 0.04	0.26	1.1 ± 0.16	1.33 ± 0.06	0.72
Fe_2O_3	1.87 ± 0.09	1.87 ± 0.01	0.00	6.76 ± 0.21	6.83 ± 0.03	0.17	9.34 ± 0.21	9.26 ± 0.03	0.19	0.61 ± 0.07	0.7 ± 0.09	0.67
MnO	0.037 ± 0.004	0.041 ± 0.003	0.58	0.1 ± 0.009	0.093 ± 0.003	0.17	0.04 ± 0.005	0.047 ± 0.002	0.50	0.06 ± 0.004	0.06 ± 0.003	0.50
MgO	0.275 ± 0.026	0.32 ± 0.01	0.92	1.52 ± 0.1	1.51 ± 0.01	0.05	1.54 ± 0.038	1.61 ± 0.008	0.92	0.85 ± 0.18	0.91 ± 0.009	0.16
CaO	1.14 ± 0.06	1.186 ± 0.005	0.38	4.94 ± 0.15	4.884 ± 0.016	0.19	1.05 ± 0.047	1.047 ± 0.004	0.03	50.5 ± 0.81	50.8 ± 0.03	0.19
Na_2O	4.05 ± 0.16	4.11 ± 0.04	0.20	4.26 ± 0.11	4.21 ± 0.02	0.23	0.38 ± 0.036	0.39 ± 0.01	0.14	0.08 ± 0.05	0.04 ± 0.005	0.45
K_2O	4.29 ± 0.1	4.32 ± 0.02	0.15	2.91 ± 0.1	2.91 ± 0.01	0.00	3.35 ± 0.061	3.41 ± 0.01	0.49	0.51 ± 0.09	0.67 ± 0.01	0.89
P_2O_5	0.049 ± 0.0018	0.060 ± 0.002	3.19	0.49 ± 0.05	0.52 ± 0.006	0.30	0.11 ± 0.007	0.112 ± 0.002	0.14	*0.42 ± 0.03*	0.52 ± 0.05	0.83
($\mu g \cdot g^{-1}$)												
Rb	148 ± 8	161.1 ± 2.4	0.82	67.6 ± 4.2	67.6 ± 0.4	0.00	126.0 ± 3.9	126.2 ± 0.9	0.03	*10 ± 2*	8.3 ± 0.4	0.22
Sr	107 ± 13	132 ± 0.8	0.96	660 ± 20	671.8 ± 1.4	0.29	75.1 ± 11.0	81.4 ± 1.4	0.29	*178 ± 27*	177.8 ± 0.4	0.00
Ba	800 ± 70	805 ± 9.3	0.04	1200 ± 100	1212.2 ± 30.5	0.06	397 ± 38	398 ± 11.4	0.01	*29 ± 10*	22.6 ± 1.4	0.16
Y	25.0 ± 4.1	39 ± 1.4	1.71	20 ± 6	20.6 ± 1.4	0.05	40.6 ± 6.5	43.3 ± 0.8	0.21	*13 ± 2*	8.0 ± 0.3	0.63
Zr	216 ± 16	217.8 ± 0.4	0.06	227 ± 20	216 ± 1	0.28	165 ± 24	133.6 ± 0.7	0.65	*18 ± 5*	8.5 ± 0.1	0.48
Nb	9.4 ± 0.07	9.1 ± 0.1	2.14	15.5 ± 3.4	13.7 ± 0.9	0.26	11.4 ± 1.2	12.5 ± 0.4	0.46	*1.5 ± 0.7*	0.5 ± 0.1	0.35
V	13.4 ± 3	15.9 ± 1.3	0.42	123 ± 14	115.3 ± 5.7	0.28	160 ± 21	153.3 ± 1.6	0.16	*9 ± 3*	13.2 ± 1.7	0.35
Cr	3.7 ± 1.2	19.3 ± 1.5	6.50	11.3 ± 3.4	18 ± 3.7	0.99	66.4 ± 7.6	53.5 ± 7.4	0.65	*9 ± 5*	19.9 ± 1.1	0.55
Co	1.9 ± 0.11	<3	--	16.7 ± 2.6	20.1 ± 1.7	0.65	46.8 ± 6.3	51.3 ± 2	0.36	*1.8 ± 0.5*	2.8 ± 0.5	0.99
Ni	*3.8 ± 1.7*	7.5 ± 0.6	0.54	16.5 ± 3.2	19.5 ± 1.5	0.47	99.5 ± 9.9	97.1 ± 1.9	0.12	*4 ± 3*	5.1 ± 1.5	0.09
Cu	11.9 ± 2.2	12.3 ± 0.2	0.09	60 ± 7	67 ± 0.7	0.50	60.2 ± 9.6	60.3 ± 3.2	0.01	*3 ± 2*	4.0 ± 0.5	0.12
Zn	*31 ± 9*	34.1 ± 0.7	0.17	88 ± 10	87.9 ± 0.8	0.00	64.1 ± 6.9	63.8 ± 2.7	0.02	*4 ± 2.1*	4.7 ± 0.5	0.08
Th	15.0 ± 1.6	15.8 ± 3.5	0.25	6.5 ± 0.6	6 ± 0.1	0.42	10.5 --	10 ± 3.2	--	*2.3 ± 1.1*	2.1 ± 0.9	0.05
Pb	24 ± 3	32.2 ± 2.5	1.37	37 ± 7	34.8 ± 2.4	0.16	27.9 ± 5.2	31.8 ± 0.5	0.38	*5 ± 3*	3.8 ± 0.6	0.10
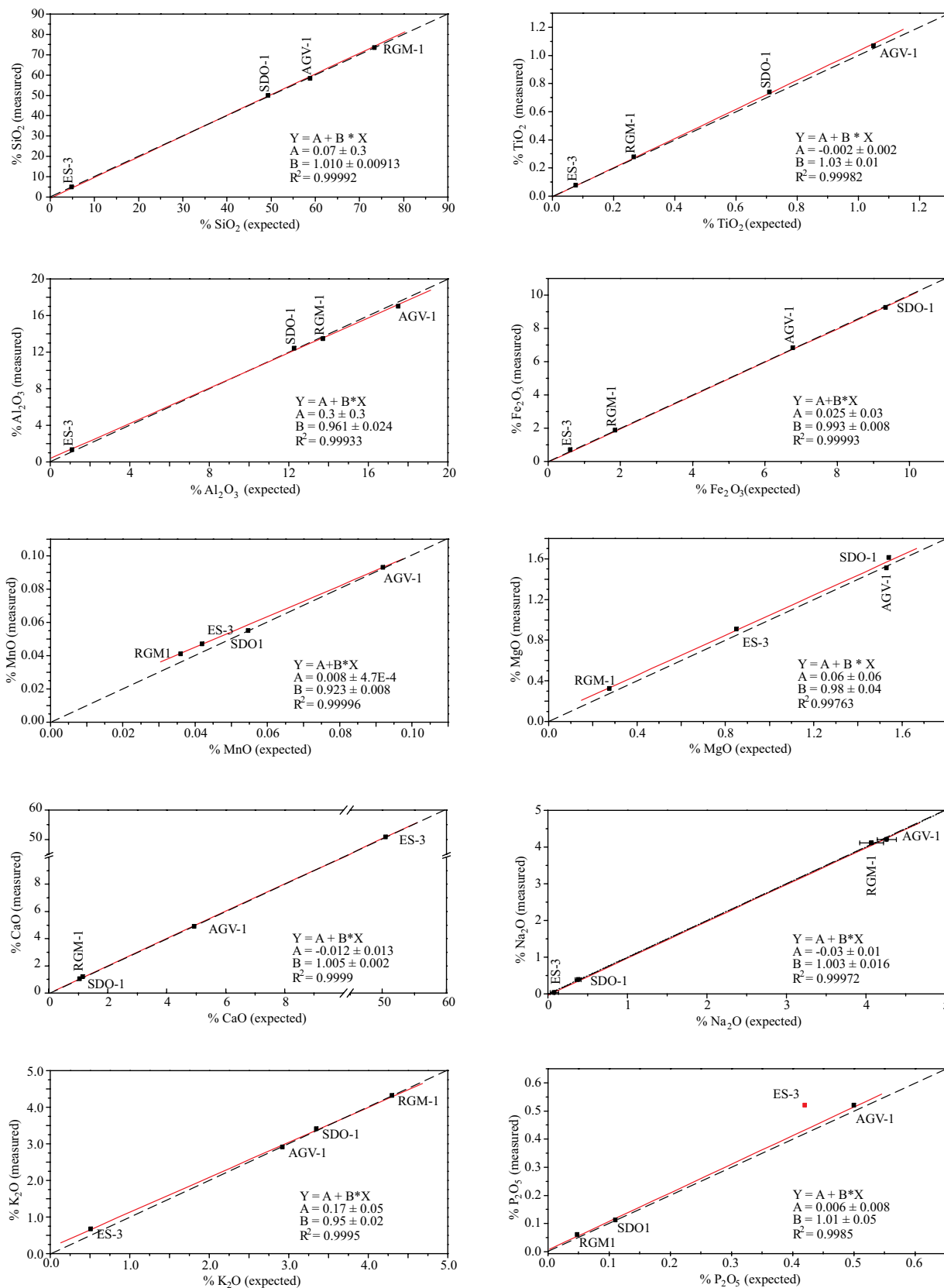
Figure 4. Graphical comparison between expected (X-axis) and measured (Y-axis) major element composition for the four international reference materials using the IGL samples as reference materials. Dashed: 1:1 line, continuos line: linear regression. Some error bars might be smaller than the symbol size. Symbols in red were not accounted for the regression (see text for details). A and B are linear regression constants on the form Y = A + BX.
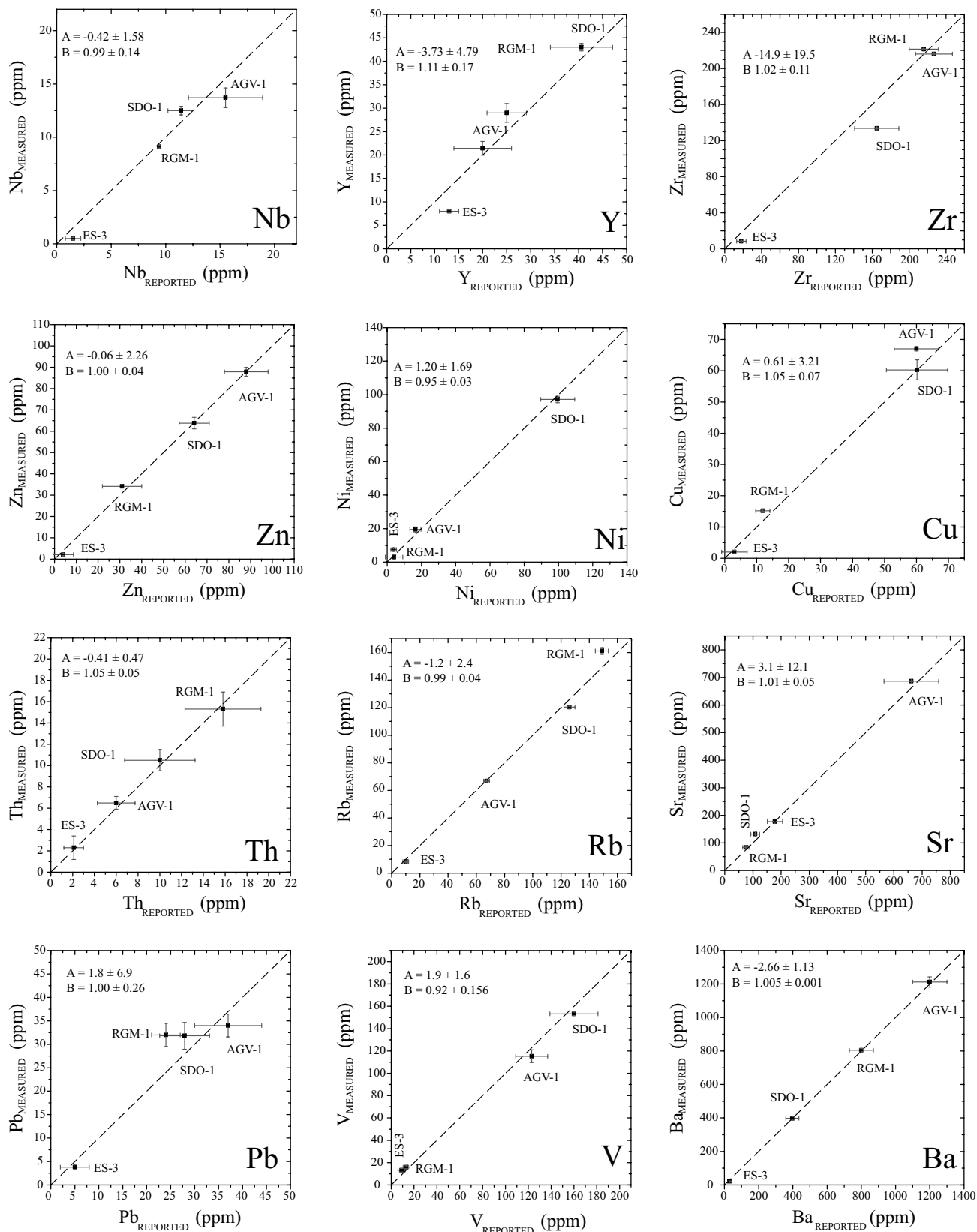
Figure 5. Graphical comparison between expected (X-axis) and measured (Y-axis) trace element composition for the four international reference materials using the IGL samples as reference materials. Dashed: 1:1 line. Some error bars might be smaller than the symbol size. A and B are linear regression constants on the form Y = A + BX.

Consequently, small biases introduced by the use of the IGL reference samples for calibration purposes cannot be ruled out, and its effect on the analysis of unknowns is still to be fully assessed.

THE FUTURE OF THE IGL SAMPLES

The results presented here demonstrate that the IGL samples posses adequate physical and chemical properties for an interlaboratory round robin. Samples have been sent to several laboratories worldwide for such purposes, and involves analyses by several analytical techniques, including XRF, ICP-MS (solution and laser ablation), ICP-AES and Instrumental Neutron Activation Analysis. It is expected that, for most elements, working values will not differ greatly from the results presented here, particularly for major element composition. Once we finalize collecting the data for such exercise, final working values will probably be estimated using robust statistical methods (*e.g.*, Verma *et al.*, 1998; Velasco-Tapia *et al.*, 2001).

CONCLUSIONS

The IGL samples are an interesting set, since it comprises a wide variety of samples and matrices, which gives them wide applicability throughout several geological and environmental research topics. Statistical analysis of the particle-size distribution and chemical composition of the samples have enabled us to verify that mixing, milling, and sorting of the samples did produce, in fact, a chemically and physically homogeneous material, a pivotal characteristic for high quality reference materials.

The analytical performance of the IGL samples as reference materials is remarkable, providing geochemically reliable results for most major and trace elements. It is worth noting, however, that the use of the IGL samples as reference materials for trace element analysis by XRF should be done in conjunction with additional reference materials, and bearing in mind that the compositions reported here are only provisional values.

The results in this work indicate that the IGL samples have the physical and chemical characteristics to become high quality reference materials following the recommended protocol (Kane *et al.*, 2003). Intercalibration studies have already started, and while major element composition are not expected to vary significantly, their uncertainty values will be reduced considerably, and the concentration for some trace elements are expected to change slightly due to possible systematic biases in our XRF analyses. Results from such exercise will be published in the near future. Further work on the IGL samples should be focused on their rare-earth element concentrations, as well as the assessment of their long-term stability. Finally, the IGL sample set is available for anyone interested in contributing to the analysis of major and trace elements in these set of geological samples.

REFERENCES

Bowman, W.S., Faye, G.H., Sutarno, R., McKeague, J.A., Kodama, H., 1979, Soil Samples SO-1, SO-3, and SO-4 certified reference materials: CANMET, 79-3, 32 p.

Carrasco-Velázquez, B.E., Morales-Puente, P., Cienfuegos, E., Lozano Santa Cruz, R., 2004, Geoquímica de las rocas asociadas al paleokarst cretácico en la plataforma de Actopan: evolución paleohidrológica: Revista Mexicana de Ciencias Geológicas, 21(3), 383-396.

Deines, P., Goldstein, P., Oelkers, S.L., Rudnick, E.H., Walter, R.L., 2003, Standards for publication of isotope ratio and chemical data in Chemical Geology: Chemical Geology, 202(1-2), 1-4.

del Arenal, R., 1978, Carta hidrogeográfica del área de Actopan-Ixmiquilpan, Estado de Hidalgo: Universidad Nacional Autónoma de México, Revista del Instituto de Geología, 2(1), 98-103.

Elías-Herrera, M., Rubinovich-Kogan, R., Lozano Santa Cruz, R., Sánchez-Zavala, J.L., 1991, Nepheline-rich foidolites and rare-earth mineralization in the El Picacho Tertiatry intrusive complex, sierra de Tamaulipas, northeastern Mexico: The Canadian Mineralogist, 29, 219-336.

Fearn, T., Thompson, M., 2001, A new test for 'sufficient homogeneity': The Analyst, 126(8), 1414-1417.

Frey, H.M., Lange, R.A., Hall, C.M., Delgado-Granados, H., 2004, Magma eruption rates constrained by $^{40}Ar/^{39}Ar$ chronology and GIS for the Ceboruco-San Pedro volcanic field, western Mexico: Geological Society of America Bulletin, 116(3-4), 259-276.

Girón, P., Lozano Santa Cruz, R., 2001, El uso de tarjetas de control como herramienta de la calidad en el laboratorio de FRX, reportes a largo plazo del BCU-3: Actas INAGEQ, 7, 26.

Govindaraju, K., 1993, Geostandards; preparation, sources and evaluation, *in* Riddle, C. (ed.), Analysis of Geological Materials: New York, Marcel Dekker, 303-342.

Govindaraju, K., 1994, 1994, Compilation of Working Values and Sample Description for 383 geostandards: Geostandards Newsletter, 18(2), 331.

Ingamells, C.O., Pitard, F.F., 1986, Applied Geochemical Analysis: New York, John Wiley & Sons, 733 p.

Juárez-Sánchez, F., Morales-Contreras, J.J., Hernández, T., Schaaf, P., Martínez-Serrano, R.G., Morán, D., 1995, Análisis isotópico del basalto de C.U. (BCU-1, 2, 3) como estándar del laboratorio

universitario de geoquímica isotópica (LUGIS): Actas INAGEQ, 1, 209-214.

Kane, J.S., Path, P.J., Wiedenbeck, M., Carignan, J., Wilson, S.A., 2003, International Association of Geoanalysts' protocol for the certification of geological and environmental reference materials: Geostandards Newsletter, 27(3), 227-244.

Kiipli, T., Batchelor, R.A., Bernal, J.P., Cowing, C., Hagel-Brunnstrom, M., Ingham, M.N., Johnson, D., Kivisilla, J., Knaack, C., Kump, P., Lozano, R., Michiels, D., Orlova K., Pirrus, E., Rousseau, R.M., Ruzicka, J., Sandstrom, H., Willis, J.P., 2000, Seven sedimentary rock reference samples from Estonia: Oil Shale, 17(3), 215-223.

Lachance, G.R., 1996, Introduction to alpha coefficients: Corporation Scientifique Claisse, 189 p.

Lachance, G.R., Traill, R.J., 1966, A practical solution to the matrix problem in X-ray analysis, I. Method: Canadian Spectroscopy, 11(2), 43-48.

Lozano-Santa Cruz, R., Verma, S.P., Girón, P., Velasco, F., Morán, D., Viera, F., Chávez, G., 1995, Calibración preliminar de fluorescencia de rayos X para análisis cuantitativo de elementos mayores en rocas ígneas: Actas INAGEQ, 1, 203-208.

Luo, D.H., Chen, J.W., Bao, Q.E., Wang, J.Z., Shen, H.J., 1997, Four Chinese Sulfide Reference Materials: Preparation and Certification: Geostandards Newsletter, 21(1), 145-156.

Miller, J.C., Miller, J.N., 1988, Statistics for Analytical Chemistry: Chichester, Ellis Horwood, 2nd ed., 211 p.

Morton, O., Hernández, E., Lounojeva, E., Armienta-H., M.A., 1997, Desarrollo y aplicación de un método analítico para la determinación de lantánidos en materiales geológicos por DE ICP-MS: Actas INAGEQ, 3, 259-264.

Nelson, S.A., 1980, Geology and petrology of Volcan Ceboruco, Nayarit, Mexico: Geological Society of America Bulletin, 91(11), 639-643.

Pérez, J., Pal, S., Terrel, D.J., Urrutia, J., López, M., 1979, Preliminary report on the analysis of some "In-house" geochemical reference samples from Mexico: Geofísica Internacional, 18(2), 197-209.

Potts, P.J., Tindle, A.G., Webb, P.C., 1992, Geochemical Reference Material Compositions: Rocks, Minerals, Sediments, Soils, Carbonates, Refractories & Ores Used In Research & Industry: Boca Raton, FL, CRC Press, 313 p.

Potts, P.J., Thompson, H.A., Kane, J.S., Webb, P.C., Watson, J.S., 2001, GeoPT9; An international proficiency test for analytical geochemistry laboratories, report on round 9/July 2001 (OU-6 Penrhyn slate): International Association of Geoanalysts, 22 p.

Potts, P.J., Thompson, H.A., Chenery, S., Webb, P.C., Batjargal, B., 2003a, GeoPT12; An international proficiency test for analytical geochemistry laboratories, report on round 12/January 2003 (GAS serpentinite): International Association of Geoanalysts, 12 p.

Potts, P.J., Thompson, M., Chenery, S.R.N., Webb, P.C., Kasper, H.U., 2003b, GeoPT13; An international proficiency test for analytical geochemistry laboratories, report on round 13/July 2003 (Köln Loess): International Association of Geoanalysts, 22 p.

Smith, D.B., 1991, Report of Analysis, Reference Shale Sample SDO-1: Reston, VA., United Stated Geological Survey, 2 p.

Smith, D.B., 1995a, USGS Certificate of Analysis, Rhyolite, Glass Mountain, RGM-1: Denver, CO., United States Geological Survey, 2 p.

Smith, D.B., 1995b, USGS Certificate of Analysis, Andesite, AGV-1: Denver, CO., United States Geological Survey, 2 p.

Sutarno, R., Steger, H.F., 1985, The use of certified reference materials in the verification of analytical data and methods: Talanta, 32(6), 439-445.

Thompson, M., Wood, R., 1993, International harmonized protocol for proficiency testing of (chemical) analytical laboratories: Pure & Applied Chemistry, 65(9), 2123-2144.

Thorpe, R.S., Francis, P.W., 1975, Volcan Ceboruco: A major composite volcano in the Mexican volcanic belt: Bulletin of Volcanologique, 39, 201-213.

Velasco-Tapia, F., Guevara, M., Verma, S.P., 2001, Evaluation of concentration data in geochemical reference materials: Chemie der Erde/Geochemistry, 61(2), 69-91.

Verma, S.P., 1984, Sr and Nd isotopic evidence for petrogenesis of mid-Tertiary felsic volcanism in the mineral district of Zacatecas, Zac. (Sierra Madre Occidental), Mexico: Isotope Geoscience, 2, 37-53.

Verma, S.P., 1997, Sixteen Statistical Tests for Outlier Detection and Rejection in Evaluation of International Geochemical Reference Materials; Example of Microgabbro PM-S: Geostandards Newsletter, 21(1), 59-75.

Verma, S.P., 1999, Propuesta para materiales mexicanos de referencia geoquímica: Actas INAGEQ, 5(1), 25-26.

Verma, S.P., 2000, Geochemistry of the subducting Cocos plate and the origin of subduction-unrelated mafic volcanism at the volcanic front of the central Mexican Volcanic Belt, *in* Delgado-Granados, H., Aguirre-Díaz, G.J., Stock, J.M., Cenozoic Tectonics and Volcanism of Mexico: Geological Society of America, Special Paper 334, 195-222.

Verma, S.P., Armienta-H., M.A., 1985, $^{87}Sr/^{86}Sr$ alkali and alkaline earth element geochemistry of Chichinautzin sierra, México: Geofísica Internacional, 24(4), 665-678.

Verma, S.P., Lozano Santa Cruz, R., Girón, P., Velasco, F., 1996, Calibración preliminar de Fluorescencia de Rayos X para análisis cuantitativo de elementos traza en rocas ígneas: Actas INAGEQ 2, 231-242.

Verma, S.P., Orduña-Galván, L.J., Guevara, M., 1998, SIPVADE: A new computer programme with seventeen statistical tests for outlier detection in evaluation of international geochemical reference materials and its application to Whin Sill Dolerite WS-E from England and Soil-5 from Peru: Geostandards Newsletter, 22(2), 209-234.

Zapata, E., Ramírez, E., Martínez, F., 2000, Informe de la intercomparación en análisis cuantitativo de Fe total, Mg, Ca y K en un mineral de hierro por espectrometría de fluorescencia de rayos X: Querétaro, Centro Nacional de Metrología, 32 p.