Statistical Evaluation of Analytical Methods for the Determination of Rare-Earth Elements in Geological Materials and Implications for Detection Limits

SURENDRA P. VERMA,[1] E. SANTOYO, AND FERNANDO VELASCO-TAPIA[2]

Centro de Investigación en Energía, Universidad Nacional Autónoma de México (UNAM), Priv. Xochicalco S/No., Col. Centro, Apartado Postal 34, Temixco, Mor. 62580, Mexico

Abstract

We briefly describe the analytical methods commonly employed for determining rare-earth elements (REE) in geological materials. A compilation of analytical data for 24 International Geochemical Reference Materials (IGRM) from the United States and Japan is used to evaluate statistically the inter-laboratory performance of various methods. The most frequently employed method groups for measuring REE include mass spectrometry (MS), nuclear methods (NM), and emission spectrometry (ES), although separation methods (SM) such as high-performance liquid chromatography (HPLC), ion chromatography (IC), or capillary electrophoresis (CE) have shown great potential as cheap, rapid, precise, and accurate methods. X-ray fluorescence (XRF), atomic absorption (AA), and classical colorimetric (CL) methods are not generally recommended for the determination of REE in geological materials, unless suitable pre-concentration procedures are used. The initial inter-laboratory REE data are generally positively skewed due to the presence of mostly high analyte concentration outliers. After an appropriate statistical rejection of outlying observations, the remaining data sets for individual groups of methods show that MS provides the most precise REE data.

Inter-laboratory detection limits obtained by weighted regression of a linear precision model are generally in the sub-ppm range (0.07–1.5 ppm for MS methods; 0.05–3.1 ppm for NM; 0.1–4.2 ppm for ES). No overall significant bias was found among the MS, NM, and ES groups of methods for the analysis of the REE, but the Student's *t*-test revealed significant differences (even at a strict significance level of 1%, equivalent to a confidence level of 99%) for some REE in a few IGRM (for MS-NM methods, La in granite JG-1, Ce in diabase W-1, Tb in basalt BHVO-1, Dy in andesite AGV-1, Tm in basalt BCR-1, and Lu in basalt BIR-1; for MS-ES methods, La in rhyolite JR-1). For these cases, the analytical data must be treated separately to define mean concentration values for methods and to assign one of the method means (probably from the most precise method MS, NM, or ES) as the mean value of that element in the IGRM. The average concentration data from well-established methods can be successfully used to evaluate the performance of other analytical methods such as SM and XRF, not in general use for determination of REE.

Finally, the method detection limits obtained for inter-laboratory data, as well as for individual laboratories are shown, for the first time, to depict a zigzag pattern, obeying the well-known "odd-even" effect of nuclear stability that governs element concentrations in the solar system and the abundance of individual isotopes We show that the REE detection limits for all analytical methods mimic completely the zigzag patterns for actual REE concentration data in all kinds of geological and cosmological materials, and we hypothesize, on this basis, that the analytical detection and quantification process is also governed by the same nuclear "odd-even" effect.

Introduction

THE LANTHANIDES, La to Lu, display a coherent geochemical behavior but are significantly fractionated in nature, and hence are of great importance in understanding various geological processes (Haskin et al., 1966; Hanson, 1980; Henderson, 1984; Verma, 1992, 1999; Rollinson, 1993; Jochum and Verma, 1996; Johannesson et al., 1997; Wood et al., 1997; Lewis et al., 1998; Terakado and Fujitani, 1998; Kikawada et al., 2001). Although Sc and Y have been grouped with the lanthanides to define the rare-earth elements (REE), here we will refer to

[1]Corresponding author; email: spv@cie.unam.mx
[2]Present address: Facultad de Ciencias de la Tierra, Universidad Autónoma Nuevo Leon (UANL), Ex-Hacienda de Guadalupe, Apartado Postal 104, Linares, N.L. 67700, Mexico.

the lanthanides as the REE, following the common practice in geochemical literature (e.g., Henderson, 1984).

Numerous important reasons exist for the use of REE and their accurate and precise determination in different types of geological and other materials. The presence of trace amounts of REE in high-purity materials (metals, semi- and superconductors, and glasses) has a significant influence on the electrical, magnetic, mechanical, and optical properties (Kantipuly andWestland, 1988; Rao and Biju, 2000; Buchmeiser, 2001). Environmental studies in nuclear industry also require the knowledge of the chemical mobilities of lanthanides and water-rock interaction processes for controlling the disposal of radioactive wastes (Wood et al., 1997). Because the lanthanides are generally present at trace levels in most geological materials and their chemical properties are very similar, their determination is a very complex analytical task due to either the preparation of representative samples or the presence of matrix interferences (Kantipuly and Westland, 1988; Na et al., 1995;Verma et al., 2000; Buchmeiser, 2001; Nash and Jensen, 2001). For a study of the controversial lanthanide tetrad effect in the variation of liquid-liquid distribution coefficients of the REE with their atomic number (Peppard et al., 1969; Masuda et al., 1987; Kagi et al., 1993; Minami and Masuda, 1997; Monecke et al., 2002; Takahashi et al., 2002), precise and accurate analytical methods for all the lanthanides are of the utmost importance.

Evaluation of the REE partition coefficients between various minerals and melts as well as the study of igneous rock petrogenesis also requires precise and accurate analytical methods for all the lanthanides (e.g., Schilling and Winchester, 1966; Peppard et al., 1969; Schilling, 1973; Kagi et al., 1993; Rollinson, 1993; Rao and Biju, 2000; Velasco-Tapia and Verma, 2001; Verma, 1999, 2001). For understanding mantle and crustal processes through modeling of trace elements such as REE, precise and accurate analytical data sets are of the utmost importance, because the nature of the mathematical equations is such that the errors of the predicted variables depend very strongly on the errors on the measured variables (trace-element concentrations and mineral/melt partition coefficients, see, e.g., Verma, 1996, 1998a, 2000).

Another requirement of high precision and accuracy in analytical data arises from those geological problems for which the data produced in many dif-

ferent laboratories have to be used for proposing a unified model of the origin and evolution of the Earth. To date, inter-laboratory data available on the IGRM have not been extensively employed to statistically evaluate the performance of the analytical methods used. The main objective of this review is to provide an up-to-date source of references on methods most useful in the determination of the REE in geological materials and to evaluate their inter-laboratory performance statistically (precision, accuracy, and detection limits) using a comprehensive database of 24 IGRM from the United States and Japan, with special emphasis on method detection limits.

Analytical Methods

A brief description of the analytical methods most useful in the determination of the REE in geological materials is presented here. References are generally limited to those papers that are oriented toward the analysis of such materials and give an account of the experimental procedures employed for the determination of REE. Numerous totally chemical papers have been omitted. About 14 years ago, Kantipuly and Westland (1988) compiled a comprehensive review on the methods for the determination of lanthanides in geological materials. After this compilation, isolated reviews related to some advances in the separation and quantification of the REE in a wide variety of materials have been published (e.g., Janos and Sulcek, 1990; Kumar, 1994; Rao and Biju, 2000; Buchmeiser, 2001; Lipschutz et al., 2001; Nash and Jensen, 2001).

Several papers and books provide detailed accounts of the experimental methods most used in the study of the REE in geological materials (Henderson and Pankhurst, 1984; Potts, 1987; Jarvis and Jarvis, 1992; Hall, 1992; Potts and Webb, 1992; Hoffman, 1992; Kallemeyn, 1993; Kumar, 1994; Smith, 1995; Heumann et al., 1995; Rao and Biju, 2000). A guide to field sampling for geological programs was provided by Richardson (1993), and sample preparation was reviewed by Saheurs et al. (1993) and Jackson et al. (1995). Comprehensive reviews on sample decomposition methods have also been published (e.g., Chao and Sanzolone, 1992; Totland et al., 1992; Yu et al., 2001). Comprehensive discussions of some methods for trace-element analysis have been presented by De Bruin (1992), Potts (1993, 2000), Balaram (1996), Sie (1997), Becker and Dietze (2000), and Hill et al. (2000).

Comparative costs of equipment were given by Henderson and Pankhurst (1984), Reed (1990), Hoffman (1992), and Voldet (1993).

Mass spectrometry (MS)

Mass spectrometry is based on the separation and detection of elements according to the mass/charge ratio of their ions. Various types of ion sources are now in general use with mass spectrometers (Becker and Dietze, 2000): thermal ionization (TIMS) and inductively coupled plasma (ICP-MS). Spark-source mass spectrometry (SSMS) has been used in isolated laboratories, e.g., Australian National University, Canberra, by Taylor and colleagues (Taylor, 1965, 1971; Taylor and Gorton, 1977); and Max-Planck-Institut für Chemie, Mainz, Germany by Jochum and colleagues (Jochum et al., 1981, 1990, 1994, 1997; Jochum and Jenner, 1994; Jochum and Verma 1996).

Isotope dilution can also be employed in conjunction with mass spectrometric methods. The combined method is called isotope dilution mass spectrometry using conventional thermal ionization source (ID-TIMS) (e.g., Schnetzler et al., 1967; Nakamura et al., 1989; Heumann et al., 1995; Raczek et al., 2001), or spark-source (ID-SSMS) (e.g., Knab and Hintenberger, 1980; Jochum et al., 1990; Rocholl et al., 1997). The lanthanides La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Lu can be analyzed with high precision using the ID-TIMS, whereas the other four elements Pr, Tb, Ho, and Tm are mono-isotopic and, therefore, cannot be determined by this method (Hanson, 1980), unless radioactive isotopes are used for the isotope dilution (ID). It should be noted, however, that ID-TIMS is a relatively time consuming method, requiring not only excellent pre-separation of the analytes, but also from three to five separate filament loadings and mass spectrometer runs per sample in order to overcome isobaric interferences (Hooker et al., 1975). A triple filament method allows sequential measurement of nine REE on a single loading, but earlier the analysis of each sample used to be five to seven hours of machine time (Thirlwall, 1982), although this time has been considerably reduced through the use of multiple-collector systems.

The SSMS was pioneered by Taylor (1965), and Graham and Nicholls (1969). A photographic detection system is commonly employed in the SSMS but, more recently, a multi-ion counting (MIC) system has been incorporated that reduces the measuring times considerably (to about 1 min to 1 h) for trace-element analysis at ppm to ppb levels (Jochum et al., 1994, 1997; Raczek et al., 2001).

Another class of instrument has evolved using an inductively coupled argon plasma source with a mass spectrometer: ICP-MS. This instrumental method has been increasingly used for REE determination, because of its lower detection limits for most elements (e.g., Riddle et al., 1988; Jenner et al., 1990; Longerich et al., 1990; Hall, 1992; Vandecasteele and Block, 1993; Su et al., 1998; Kin et al., 1999; Lee et al., 2000; Dulski, 2001; Yu et al., 2001). The ICP-MS generally requires introduction of the sample in solution form (Yoshida et al., 1992; Garve-Schönberg, 1993; Lipschutz et al., 2001), although a direct introduction of powdered samples is also possible (Hirata et al., 1990; Becker and Dietze, 2000). Slurry nebulization has been used for introducing solid samples in both ICP-MS and ICP-atomic emission spectrometry (ICP-AES), but with a reduced precision as compared to solution nebulization (Jarvis, 1992; Balaram, 1997; Jain et al., 2000). On-line sample introduction can considerably lower the detection limits of ICP-MS (Shabani and Masuda, 1991; Carignan et al., 2001). Very low detection limits (sub-ppm to ppb levels) have been achieved for ICP-MS in the analysis of REE in ultramafic rocks and their minerals (Jarvis, 1988; Ionov et al., 1992; Sen Gupta, 1994; Stroh et al., 1995), aqueous magmatic-derived fluids trapped in fluid inclusions (Banks et al., 1994; Su et al., 1998), hydrothermal fluids (Klinkhammer et al., 1994; Lewis et al., 1997), common silicate rocks (Jarvis, 1988; Sen Gupta, 1994; Lichte et al., 1987; Xie et al., 1994; Sen Gupta and Bertrand, 1995), single zircons (Grégoire et al., 1995; Lipschutz et al., 2001), meteorites (Albrecht et al., 1992; Liu et al., 1998), and seawater, groundwater, and surface waters (Hall et al., 1995; Halicz et al., 1999; Verplanck et al., 2001).

A modification using laser ablation (LA) in conjunction with ICP-MS has also proved a valuable application in the analysis of geological materials (Imai, 1990; Perkins et al., 1993; Jarvis and Williams, 1993; Cousin and Magyar, 1994; Watling et al., 1995; Becker and Dietze, 1999; Becker et al., 2000; Pickhardt et al., 2000; Prince et al., 2000; Song et al., 2001). Lasers are widely employed in mass spectrometry as a universal tool for evaporating and ionizing any solid material (Becker and Dietze, 2000). Similarly, a combination of ICP-MS with laser microprobe has been a useful method for in-situ determinations of REE in minerals (e.g., Jef-

fries et al., 1995a, 1995b). Operating a laser (Nd:YAG laser) in the Q-switched mode, LA-ICP-MS is based on using pressed powder pellets in a similar way as for XRF, and is capable of analyzing all lanthanides with a precision varying between about 5% for light REE to about 20% for heavy REE, and with sub-ppm detection limits (Jarvis and Williams, 1993). LPMA-ICP-MS (Jeffries et al., 1995b) uses a reduced laser beam divergence on a block of rock simply cut to fit the sample analysis chamber, and is capable of analyzing REE in both matrix and minerals, with detection limits in the sub-ppm range. This method is especially suited to determine solid-liquid partition coefficients without the tedious mineral separations.

Another class of mass spectrometric methods includes secondary ion mass spectrometry (SIMS), which has been used to analyze several REE in geological materials at sub-ppm level (Nesbitt et al., 1986; MacRae and Russell, 1987; Yurimoto et al., 1989; Bottazzi et al., 1991, 1992; Ottolini et al., 1992; Ottolini and Oberti, 2000; Rao and Biju, 2000). It employs polished thin sections for mineral analysis (e.g., MacRae and Russell, 1987) and fused glasses for whole rocks (e.g., Yurimoto et al., 1989). Quantitative analysis of REE in minerals by SIMS has been clearly demonstrated by Muir et al. (1987) and Vannucci et al. (1991).

The rapid growth of ICP-MS has also led to the commercial development of ICP time-of-flight mass spectrometry: ICP-TOF-MS (Willie and Sturgeon, 2001). Such an instrument was developed for improving the measurement of mass spectra, for lowering detection limits, and for reducing the influence of noise sources in analyses. TOF-MS has been applied recently in REE determination of geological materials (e.g., Becker and Dietze, 2000; Benkhedda et al., 2001; Willie and Sturgeon, 2001).

Despite success achieved by most ICP-MS methods for the determination of REE, some researchers have recently pointed out that the coupling of ICP-MS with some separation methods, such as HPLC or CE, constituted an excellent tool for measuring ultra-trace REE concentrations (e.g., Sutton et al., 1997; Itoh et al., 1999; Sutton and Caruso, 1999; Day et al., 2000; Rao and Biju, 2000; Buchmeiser, 2001; Nash and Jensen, 2001; Pedreira et al., 2001).

Nuclear methods (NM)

These include, in general, neutron activation analysis (NAA), both instrumental and radiochemi-

cal (Dams, 1990). NAA is capable of determining the REE from ppm to ppb levels, in many cases without the need to destroy the specimen. The sample is irradiated with a flux of neutrons in a nuclear reactor or other neutron source. After irradiation, gamma radiations emitted by the radioactive isotopes are separated, quantified, and compared with radiations from standards (Henderson and Pankhurst, 1984; Potts, 1987). The (lower) detection limits of NAA mainly depend on neutron capture cross-sections as well as half-lives of the radionuclides, although they also depend on neutron flux, irradiation time, and interference problems related to the type of matrix under study. As a byproduct of these nuclear methods, besides the REE one can determine several other geologically important trace elements such as Ba, Cr, Cs, Hf, Sb, Ta, and Zr, and a few major elements, *viz.* Fe, Mn, and Na (e.g., Pal and Terrell, 1978; Potts et al., 1981). Other methods of irradiation, such as α-particles, protons, or other types of charged particles, also can be used (e.g., Chowdhury et al., 2002). When protons are used, the method is commonly known as proton-induced X-ray emission (PIXE; e.g., Garten, 1984; Pineda and Peisach, 1991; Nekab et al., 1994).

Multi-element determinations are commonly performed using solid-state detectors (conventional lithium-drifted germanium (Ge-Li) or ultra-pure germanium (Ge) detectors), linked to a suitable counting device, such as a multi-channel analyzer, and without any chemical treatment (Kallemeyn, 1993). Such a method is usually referred to as instrumental neutron activation analysis: INAA (Brunfelt and Steinnes, 1966, 1969; Gordon et al., 1968; Henderson and Pankhurst, 1984). Several counting intervals from the time of irradiation to several days or months are usually involved in order to obtain the final results of the REE and several other trace elements (Voldet, 1993). Interference effects have to be overcome or minimized by a proper choice of γ-ray energies and use of high-resolution detectors. Shubina and Kolesov (1998) reported a software package for optimizing the INAA procedure, in particular for evaluating and minimizing interference problems.

INAA has been used in determination of the REE in a wide variety of geological materials: different types of IGRM (e.g., Pal and Terrell, 1978; Potts et al., 1981, 1985; Glascock and Anderson, 1993; Hallett and Kyle, 1993; Reddy and Pant, 1993; Aota et al., 1994; Rocholl et al., 1997; Kin et al., 1999); carbonatites (e.g., Ohde and Mataragio, 1999);

phosphorites (e.g., Al-Jobori and Kettaneh, 1989); sediments (e.g., Carmo-Freitas and Martinho, 1989; Hoffman, 1992; Al-Jundi et al., 1993; Crespi et al., 1993; Mannan et al., 1993; Bulnayev, 1995; Waheed et al., 2001); oceanic tholeiite (e.g., Minai et al., 1990); clays (e.g., Frost, 1991; Gungor et al., 1998); ultramafic rocks (e.g., Asubiojo and Ige, 1992); cement dust particulates (e.g., Weginwar and Garg, 1992); cosmochemical samples (e.g., Koeberl, 1993; Lipschutz et al., 2001); cosmic dust (e.g., Ni et al., 1997); soils (e.g., Fernandes et al., 1994); heavy metal deposition (e.g., Frontasyeva and Steinnes, 1995); minerals (e.g., Laul and Lepel, 1987; Hoffman, 1992; Balogun et al., 1997; Damarupurshad et al., 1997); environmental matrices (e.g., Orvini et al., 2000); and hydrothermal and surface waters (e.g., Honda et al., 1989; Oi et al., 1990; Yeh et al., 1994, 1995).

Pre-concentration of trace elements can help lower detection limits, making it feasible for INAA to determine some lanthanides at ultra-trace levels, such as those found in surface waters (Yeh et al., 1994, 1995), or brines and deposit samples (Yui et al., 1998). Similarly, Saiki (1989) employed a chemical procedure prior to irradiation to eliminate spectral interferences due to U, Th, Fe, Sc, Na, Ta, and Mo, both for reducing bias and for lowering the background.

On the other hand, when a chemical group separation is involved after the irradiation, the method is referred to as radiochemical neutron activation analysis: RNAA (Henderson and Pankhurst, 1984). This alternative (RNAA) typically takes advantage of a pre-concentration to reduce the interference from other elements and to minimize the background, thus facilitating REE determination in geological materials (Tomura et al., 1968; Morrison et al., 1969; Rey et al., 1970; Smet and Roelandts, 1978; Smet et al., 1978; Saiki, 1989; Parry, 1992; Reddy and Pant, 1993; Aota et al., 1994;Wang and Lipschutz, 1998, Wang et al., 1999a). A pre-irradiation group separation has also been employed to reduce matrix effects and to improve sensitivity and speed of INAA (Towell et al., 1965; Croudace, 1980; Duke and Smith, 1987; Terakado et al., 1989; Smith et al., 1990; Oi et al., 1991; Van Suc and Sinh, 1993; Ebihara et al., 1995; Van Suc, 1995). The coupling of HPLC in conjunction with INAA has recently demonstrated to be an effective analytical tool for measuring most REE with high sensitivity, accuracy, and precision (e.g., Lipschutz et al., 2001).

Emission spectrometry (ES)

Atomic emission spectrometry (AES) is based on the principle that an excited atom during its rapid (less than one nanosecond) decay to the ground state releases the absorbed energy that raised it from its ground to excited state, in the form of light at characteristic wavelengths, which can be measured and calibrated to give a concentration estimate of the element (Henderson and Pankhurst, 1984; Potts, 1987, 2000; Jarvis and Jarvis, 1992; Voldet, 1993; Evans et al., 1999). Compared to direct-current argon plasma (DCP), introduction of inductively coupled plasma (ICP) sources has greatly increased the usefulness of AES (giving rise to ICP-AES) and its application in the study of geological materials, because it is capable of detecting, besides the REE, a large number of other elements (Jarvis and Jarvis, 1988, 1992; Bauer-Wolf et al., 1993; Lihareva and Delaloye, 1997; Ramanaiah, 1998).

ICP-AES, with or without pre-concentration procedures, has been successfully employed for the determination of REE in a wide variety of geological samples, such as, rocks, ores, sediments, and soils (Rao and Biju, 2000). Application of DCP-AES to analyze REE in some geological materials has also been demonstrated (e.g., Cantillo et al., 1984; Feigenson and Carr, 1985; Kantipuly andWestland, 1988; Abdallah et al., 1994). Most or all REE can be routinely determined by ICP-AES, and show very low sub-ppm detection limits, particularly when combined with a prior group separation (Crock and Lichte, 1982; Govindaraju and Mevelle, 1987; Achilli et al., 1989; Roychowdhury et al., 1989; Webster and Gilstrap, 1990; Croudace and Marshall, 1991; Watkins and Nolan, 1992; Cantagrel and Pin, 1994; Germanique, 1994; Kawabe et al., 1994; Kawabe, 1995; Safronova et al., 1995; Hornig-Kjarsgaard, 1998; Ran and Liu, 1999; Wang et al., 1999b; Huang et al., 2000; D'Angelo et al., 2001; Premadas and Srivastava, 2002).

Fries et al. (1984) and Rucandio (1992) described ICP-AES procedures to determine REE in manganese nodules and in rare earth ores and concentrates, respectively. Rathi et al. (1991) used ICP-AES without a prior group-separation to determine 10 REE in IGRM. These authors concluded that group separation with ICP-AES is not essential, but their claim does not seem to be valid judging by discrepancies in their results for IGRM. Similarly, Wilson et al. (1994) used ICP-AES, without a prior group separation, to determine La, Ce, Nd, and Yb in three soil IGRM. ICP-AES has also been coupled

with HPLC to produce a powerful instrument for determination of REE (e.g., Yoshida and Haraguchi, 1984; Tielrooy et al., 1988; Wu et al., 2000; Nash and Jensen, 2001; Ruth et al., 2001). In this setup, separation of the REE with HPLC helped to avoid analytical bias resulting from spectral interferences.

Darbha and Gangadharan (1994) and Germanique (1994) described a multi-element method based on a variant of emission spectrometry, ICP-OES (inductively coupled plasma optical emission spectrometry), for the determination of REE at trace levels of concentration. ICP-OES is used in REE analysis of small samples, and is based on the principle that electrons excited (at high temperature) liberate light of a particular wavelength. The presence or absence of various elements is normally recognized by examining the appropriate spectral line(s) of their characteristic wavelengths. This method has been further developed for improving detection limits of REE analyses and also for minimizing complicated analytical tasks related to sample preparation (e.g., Jaron et al., 2000; Khorge et al., 2000; Lara et al., 2000).

X-ray fluorescence methods (FX)

This group of methods is based on the quantification of the characteristic X-rays emitted by the element of interest when excited by a suitable X-ray source. The emitted spectrum is dispersed, and the intensities of selected radiations are measured and ultimately converted to weight fractions using calibration curves. Two basic types of XRF instrumentation are in use: wavelength dispersive (WD-XRF) and energy dispersive (ED-XRF). More details can be found in Bower and Valentine (1986), Bower et al. (1990), Potts and Webb (1992), Potts (2000), and Potts et al. (2000, 2001). Some applications of ED-XRF to geological samples consist of REE quantification in rocks, lateritic materials, and xenotime, monazite, and britholite ores (Rao and Biju, 2000). Traces of REE have been determined by WD-XRF in geological materials, such as rocks, soils, coals, lateritic materials, minerals, and ores (Rao and Biju, 2000).

In general, however, in the analysis of silicate rocks, the XRF is probably applicable for the determination of only La and Ce, and less commonly for the other lanthanides (Leoni and Saitta, 1976; Nisbet et al., 1979; Robinson and Bennett, 1981; Stork et al., 1987; Muia and Van Grieken, 1991). A valid scheme was developed, however, which uses group separation of REE and removal of Ba as $BaSO_4$

before absorption of the REE on an ion exchange paper. Determination of REE by XRF was achieved with a precision of 10–20% at ppm level (Eby, 1972). Robinson et al. (1986) presented a modified ion exchange-XRF method, by which rapid determination of up to 12 REE in silicate rocks was possible with a precision and accuracy similar to that of INAA. Similarly, Bauer-Wolf et al. (1993) were able to determine all the lanthanides in one granite IGRM (with relatively high REE contents) from South Africa, using an ion-exchange and pre-concentration procedure with XRF. However, at lower concentration levels they were successful in determining only the more abundant REE.

XRF instrumentation has also been employed for determination of La, Ce, and Nd in small apatite samples (D'Angelo et al., 2001). Pre-concentration of La, Ce, and Pr using amberlite XAD-4 and XAD-7 and resins loaded with 8-Quinolinol 2-(2-(5 chloropyridylazo)-5-dimethylamino)-phenol, was employed to determine these three REE by XRF in synthetic materials (Masi and Olsina, 1993). The detection limits were about 0.4 ppm for La and Ce and 1 ppm for Pr. Pre-concentration or enrichment procedures for determination of Sm, Eu, and Gd by XRF have also been developed (De Vito et al., 1999, 2000, 2001).

Separation methods (SM)

SM have come into use as rapid, precise, accurate, and low-cost methods for the determination of the REE in geological materials (Weiss, 1986; Haddad and Jackson, 1990; Verma, 1991a, 1991b; Haddad, 1997; Sarzanini, 1999; and Verma et al., 2000). This group of methods (SM) includes chromatography, such as high-performance liquid chromatography (HPLC), ion chromatography (IC), and capillary electrophoresis (CE).

Classical HPLC relies on separation processes of a sample mixture, based on the distribution capacity of its species between a stationary phase (column packing) and a mobile phase (Lindsay, 1992; Meyer, 1994). On the other hand, the main principle of separation of IC is based on an ion-exchange process between the stationary phase (ion-exchange resin) and mobile phase (eluent). HPLC and IC methods normally use UV/Vis spectrophotometers as detectors for the quantification of REE. This photometry detection in some cases is carried out after a post-column derivatization reaction both for improving the response signal of REE and for lowering the detection limits (e.g., Cassidy, 1988; Verma, 1991b).

The first applications of HPLC and IC to determine only a few REE in geological samples were carried out by Cassidy and Elchuck (1981) and Mazzucotelli et al. (1985), although their procedure was capable of determining relatively high contents of only five elements, La to Sm (10-160 ppm). Cassidy (1988) demonstrated the applicability of the HPLC method to most of the REE at sub-ppm levels with a high precision (0.5–2.0%). All these chromatographic procedures were investigated for improving REE detection and separation, for reducing long analysis time, and for obtaining lower detection limits (e.g., Le Roex and Watkins, 1990; Verma, 1991a, 1991b; Watkins and Le Roex, 1992, 1993; Kuroda et al., 1993; Stijfhoorn et al., 1993; Na et al., 1995; Watkins et al., 1995; Bruzzoniti et al., 1996, 1997; Lu et al., 1997a; Nesterenko and Jones, 1997, 1998; Tsuyoshi and Akiba, 2000; Buchmeiser, 2001).

On the other hand, CE is a family of related separation methods that use narrow-bore capillaries (20–200 mm i.d.) for performing high-efficiency separations of both large and small molecules. These separations are facilitated by use of high voltages, which induce electro-osmotic and electrophoretic flow of buffer solutions (or electrolytes) and ionic species, respectively, within the capillary (Baker, 1995). In this context, CE is a variant of modern HPLC in which the flow of mobile phase through the column (i.e., the capillary tube) is maintained by an electric field rather than by applied pressure. Quantitative procedures based on the application of capillary electrophoresis (CE) for determining REE in geological materials have rarely been reported, because this is a relatively recent analytical method.

The first application of the CE method for measuring REE was carried out by Foret et al. (1990), who developed a procedure using an indirect UV absorbance detection system. The development of CE has rapidly gained practical importance in REE determination (Macka et al., 1998; Oztekin and Erim, 2000, 2001; Timerbaev and Shpigun, 2000; Verma et al., 2000).

Atomic absorption (AA)

Atomic absorption is the absorption of radiant energy at characteristic wavelengths by ground-state atoms in the gaseous state. Comprehensive reviews of atomic absorption spectrometry (AAS) are given by Viets and O'Leary (1992) and Fairman et al. (1998). Rao and Biju (2000) suggested the application of flame AAS for determining

REE in metallurgical samples and electronic materials.

Use of a graphite furnace for electrothermal atomization, micro-sampling, and tantalum-lining have considerably improved the sensitivity of AAS (Sen Gupta, 1981, 1982, 1984a, 1984b, 1985). Sen Gupta (1985) presented results for all REE in several IGRM. These results are comparable to other well-established methods. In spite of these findings, the AAS has not proved very successful in REE analysis at trace levels in geological materials, because aspiration of the sample solution into a nitrous oxide/acetylene flame produces a significant ionization of REE with a resultant loss of response (Henderson and Pankhurst, 1984). Nevertheless, a prior group separation of REE, when combined with AAS, has enabled these elements to be determined in some geological materials (Van Loon et al., 1971; Ooghe and Verbeek, 1974; Horsky and Fletcher, 1981; Juras et al., 1987; Balaram, 1996).

Colorimetry (CL)

Spectrophotometric analyses using visible and ultraviolet radiation are frequently called colorimetric methods. These procedures can be carried out directly on the aquo-complexes of some metals, without using a secondary color-forming reactive. Since the absorption bands of REE are sharp, their molar absorptivities are not as large as those metals of the colored complexes usually employed in colorimetric procedures (Kantipuly and Westland, 1988). Therefore, in REE analyses, the method requires complexing the analyte with a colored organic reactive or agent for measuring the resultant change in optical properties. Most of these methods involve reaction with a chromogenic reactive to form a compound with a high molar absorptivity. The reagent most commonly recommended for the REE is arsenazo III at low pH (1–4) under reacting conditions, although arsenazo I, antipyrine S, alizarin red S, carboxynitrazo, and 5-Br-PADAP could also be used at acid pH ranging from 1 to 5 (Kantipuly and Westland, 1988; Martinez et al., 1993). The absorptivity of the resulting compound depends on the amount of the element reacted, which makes it possible to quantify its concentration in the sample. However, generally this group of spectrophotometric methods is useful for determining only a few REE in geological materials (e.g., Ce: Aleksiev and Boyadjieva, 1966; Gd: Martinez et al., 1993; Ran and Liu, 1999).

A dual-line flow-injection system was described by Chartier et al. (1992) for spectrophotometric determination of Tb, Ho, and Eu by complexation with 4-(2-pyridylazo) resorcinol (PAR). They obtained detection limits comparable to ICP-AES systems. Determination of the sum of the REE in apatites by flow-injection analysis with arsenazo III was reported by Gladilovich et al. (1988). Lanthanum in monazite sands was determined after selective solvent extraction separation of the picrate with dibenzo-[24]-crown-8 (Saleh et al., 1995). Havel et al. (1994) developed a spectrophotometric method by flow-injection analysis based on their reaction with xylenol orange and cetylpyridinium bromide to determine REE. Despite the limited use of the CL methods for measuring REE, new colored organic chemicals are still being evaluated for improving their detection (e.g., Wang et al., 1995; Ni and Wu, 1999; Amin and Mohammed, 2001).

Prior Comparisons of Analytical Methods

Examples are given here of studies that compare two or more sets of methods for the REE. Tomura et al. (1968) evaluated NAA combined with a prior chemical group separation and INAA, and found the former to be advantageous in having a low background level. Qing-Lie et al. (1985) compared the performance of thin-film XRF and ICP-AES for the determination of REE in geological samples. For both methods, they used pre-concentration of the REE by ion exchange. Co-precipitation with $Fe(OH)_3$ for thin-film preparation and matrix modification was used with XRF. They obtained comparable results for 12 REE in the analysis of IGRM.

Roelandts (1988) compared the performance of NAA and ICP-AES for the determination of nine REE (La, Ce, Nd, Sm, Eu, Gd, Dy, Yb, and Lu) in IGRM. Both of these methods were recommended as suitable for the REE analysis in most common silicate rocks. NAA was recommended as the more adequate method for samples with very low REE abundances (e.g., ultramafic rocks), because besides being sensitive, this method is free from problems of reagent blank and contamination when chemical separations are done after sample irradiation. However, the expensive set up of irradiation facilities and special working conditions required for handling radioactive samples were reported as the major disadvantages. In contrast, ICP-AES shows the advantage of a greater speed of analysis, a lower capital cost, and no need for manipulating radioactive materials.

Hall et al. (1990) compared the performance of INAA and ICP-AES for the determination of La and Yb in a large number of rock samples and concluded that a significant bias existed between the two methods for both REE. INAA and ICP-AES were also compared by Al-Merey and Bowen (1991) for the determination of REE in phosphate rocks. Discrepancies were found for Ce, Nd, Sm, and Lu. Such discrepancies were similarly found by Kawabe et al. (1994) between their ICP-AES data and the reported INAA results for a high U/REE ratio carbonate reference rock from the Geological Survey of Japan. Jarvis (1990) critically evaluated two sample preparation methods (open acid digestion and lithium metaborate fusion) used for the determination of trace elements, including the REE, by ICP-MS and found no significant differences for the REE between these dissolution procedures in a variety of silicate and carbonate rocks.

A good performance of ICP-MS and INAA was demonstrated by Dulski (1992) for the determination of REE in iron formation standard materials. Hall and Plant (1992) also compared the performance of ICP-MS and INAA following an acid digestion method, and showed the inefficiency of mixed-acid attack in dissolving heavy REE (Gd to Lu) in samples containing resistant minerals such as sphene, zircon, garnet, and monazite. However, they found good agreement between ICP-MS and INAA following $LiBO_2$ fusion for all samples. Filby and Olsen (1994) also carried out a comparison between ICP-MS and INAA for the determination of La and Sm in crude oil samples but, because of relatively high detection limits, they were able to obtain quantitative data for only La in one oil sample. The two values differed significantly from each other. Kin et al. (1999) performed a comparative study between ICP-MS and INAA to measure REE in geological reference materials. The precision obtained by ICP-MS was generally better for the light REE, decreasing with increasing atomic number. Data with similar accuracy were obtained for the light REE determined by both methods, but with better accuracy for the middle and heavy REE by INAA. They also found larger uncertainties with ICP-MS mainly for elements at trace concentration levels, occurring at about 10 times the chondritic values.

A comparison of ICP-MS and ICP-AES and different dissolution methods was presented by Totland et al. (1992). For most samples, the three dissolution

methods (LiBO$_2$ fusion, open acid digestion, and microwave acid digestion) provided similar results for all REE, except for a marine mud, for which the two acid dissolution methods gave lower heavy-REE contents than the fusion method. This indicated incomplete digestion of heavy-REE bearing accessory minerals by acid attack. The two variants of methods involving plasma sources (ICP-MS and ICP-AES) were also compared by Sen Gupta (1994) for the analysis of mafic and ultramafic geochemical candidate reference materials, and by Balaram et al. (1995) for a polymetallic nodule reference sample. Both of them gave generally consistent results for all REE determined by these two methods.

Bauer-Wolf et al. (1993) compared the determination of REE in some IGRM by ICP-optical emission spectrometry (ICP-OES) and XRF methods. Both of them followed dissolution and group separation by ion exchange. For XRF, the REE were co-precipitated with rhodizonate and tannin and measured as a thin film on a membrane filter. Although the precision of the XRF method was poorer than the ICP-OES, the results were generally comparable for ppm levels.

A comparison of the SSMS and ICP-MS methods (Jochum and Jenner, 1994) using IGRM from Japan showed that both methods gave consistent results within the analytical errors down to sub-ppm concentration range. Different irradiation conditions and counting modes were compared by Wu and Landsberger (1994) for the determination of La in soil IGRM.

XRF and PIXE were evaluated favorably for the determination of REE in four minerals by Nekab et al. (1994). Recently, Figueiredo et al. (2000) carried out an analytical comparison between HPLC and INAA methods for the determination of REE in geological materials (AGV-1, GSP-1, and G-2; all from the USGS). The results obtained showed a good agreement with the certified values, giving relative errors less than 10%. La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu were determined by INAA. All the REE, except Dy and Y, were determined by HPLC.

Moraes and Iyer (1990) evaluated three methods (IDMS, INAA, and ICP-AES) for the determination of REE in IGRM and found that IDMS is the most precise and accurate method even at very low (sub-ppm) concentration levels. Ottolini et al. (1992) used SIMS to analyze the lanthanides at sub-ppm level in a gabbro and compared their results favorably with ICP-AES, INAA, and RNAA methods. Rocholl et al. (1997) compared variants of MS methods (ICP-MS, TIMS, and SSMS), and INAA and AAS methods, using a silicate glass certified reference material SRM610, with doped concentrations of many elements including the REE, at a very high concentration level of about 500 ppm. They found generally consistent results for the REE using different methods, with a standard deviation of about 3% at such high concentration levels. Recently, D'Angelo et al. (2001) evaluated three methods (ICP-AES, INAA, and XRF) for determining eight REE in apatite samples and found a good agreement among the analytical results obtained from these methods. Raczek et al. (2001) compared TIMS and SSMS methods using the old (BCR-1, BHVO-1, AGV-1, DTS-1, and GSP-1) as well as new series (BCR-2, BHVO-2, AGV-2, DTS-2, and GSP-2) of reference materials from the USGS. They used TIMS with isotope dilution and the SSMS with a multi-ion counting system, and obtained overall analytical uncertainties of about 1% for TIMS and about 3% for SSMS, with the exception of DTS-1 and DTS-2 with very low REE concentrations, for which considerably larger errors were observed.

It is surprising to note that almost none of the above-cited papers used proper statistical tests or procedures to evaluate bias, such as those presented in this paper (see below the section on "Results and Discussion on Comparison of Methods"). We suggest that such statistical methods (tests for normality, Student's t-test, ANOVA, tests of linearity, tests for intercept and slope, etc.; see Davies, 1973; Barnett and Lewis, 1994; Ebdon, 1988; Miller and Miller, 1988; Miller, 1991; Jensen et al., 1997; Otto, 1999) must be used for this purpose so that the conclusions drawn from method-comparisons are based on a solid scientific methodology, and therefore can be taken seriously.

New Database on IGRM

IGRM are frequently used in the evaluation of existing and new analytical methods. A wide variety of IGRM is currently available for this purpose (e.g., Govindaraju, 1989, 1993, 1994; Gladney and Roelandts, 1990a, 1990b; Gladney et al., 1991, 1992; Kane, 1991, 1992, 1993; Potts et al., 1992; Itoh et al., 1993; Govindaraju et al., 1994; Roelandts, 1994; Bowman, 1995; Richardson and Morrison, 1995; Imai et al., 1995, 1996a, 1996b; Terashima et al., 1995; Korotev, 1996; Lynch, 1996; Tredoux and McDonald, 1996; Velasco-Tapia et al., 2001). We have compiled a large number of analytical results

on 9 IGRM from the United States, as well as 15 from Japan.

The U.S. rocks compiled in our database are from the USGS as follows: granite G-1; diabase W-1; granite G-2 (a replacement of G-1); diabase W-2 (a replacement of W-1); andesite AGV-1; basalts BCR-1, BHVO-1, and BIR-1; and granodiorite GSP-1. Their descriptions and literature references were compiled by several earlier researchers (Fairbairn, 1951; Flanagan, 1967, 1969, 1976, 1984; Abbey, 1978; Gladney et al., 1983; Gladney and Roelandts, 1988a, 1988b; 1990a, 1990b; Govindaraju, 1989, 1994; Gladney et al., 1990; Potts et al., 1992).

IGRM from Japan compiled in our work are from the Geological Survey of Japan, as follows: granites JG-1, JG-1a, JG-2, and JG-3; gabbro JGB-1; basalts JB-1, JB-1a, JB-2, and JB-3; andesites Ja-1, JA-2, and JB-3; rhyolites JR-1 and JR-2; and peridotite JP-1. These IGRM were described and compiled earlier by Ando et al. (1987), Itoh et al. (1993), and Imai et al. (1995). In some of the discussion presented in this paper, the IGRM compiled in this work have been grouped into: extrusive rocks (AGV-1, BCR-1, BHVO-1, BIR-1, JB-1, JB-1a, JB-2, JB-3, Ja-1, JA-2, JB-3, JR-1, and JR-2); and intrusive rocks (G-1, W-1, G-2, W-2, GSP-1, JG-1, JG-1a, JG-2, JG-3, JGB-1, and JP-1).

The raw data for our database were collected from numerous papers, reports, and books. In order to limit the size of this paper (already too long), the complete list of source references and data sets is not included here. There may be very large analytical errors associated with some of these data—outliers present in the initial data sets (see, e.g., Verma, 1997, 1998b). We have therefore applied two powerful statistical tests (skewness and kurtosis coefficients—also known as third and fourth moments) on these individual raw data sets from each group of methods (MS, NM, ES, FX, SM, AA, and CL) in order to detect and eliminate outliers in these method-based subsets. Such a general division of all REE methods into seven groups was adopted in the present work for several reasons: (1) if the data were divided into more method categories, it would leave very few observations in each category, probably statistically significant only for a few cases; (2) the different dissolution methods were not always explicitly reported in such compilations (e.g., Gladney and Roelandts, 1988a, 1998b; Gladney et al., 1990, 1991; Itoh et al., 1993; Imai et al., 1995); these compilations served as the starting point for

our present compilations; (3) in the present work, our primary aim was to evaluate the inter-laboratory variations only between broad groups of methods and their overall effects for the determination of REE. These effects include inhomogeneity problems, if any, in the IGRM, different sample preparation errors (such as dissolution, group separation, etc.), instrumental calibration errors, and final geological sample measurement errors.

The importance of the two statistical tests (skewness and kurtosis) in the study of IGRM is well established (Dybczynski, 1980; Lister, 1982; Barnett and Lewis, 1987, 1994; Velasco and Verma, 1998; Verma, 1998b; Verma et al., 1998; Velasco et al., 2000). We have based most of our discussion on the censored statistical sample—i.e., the data remaining after the skewness and kurtosis tests. Furthermore, we have arbitrarily set a lower limit of 5 data as the minimum number of determinations initially required for them to be significant for some of the statistical comparison of the analytical methods. The minimum number ($n = 5$) is, in fact, also required for the skewness and kurtosis tests to be applicable for detection of outliers in univariate data (Barnett and Lewis, 1987, 1994). For other statistical tests, such as Student's t-test, the minimum number of data required is still greater, arbitrarily set at 10 data.

Results and Discussion
on the Comparison of Methods

A comparison of inter-laboratory performance of the analytical methods used in the determination of the REE in 24 IGRM from the United States and Japan is presented. The methodology and parameters compared are similar to those used in method validations and statistical tests (Draper and Smith, 1966; Davies, 1973; Thompson and Howarth, 1976, 1978; Thompson, 1982, 1988; Sutarno and Steger, 1985a, 1985b; Ripley and Thompson, 1987; Miller and Miller, 1988; Taylor, 1990; Miller, 1991; Ramsey et al., 1995; Kalantar et al., 1995).

The more important questions about the determination of the REE addressed in this paper are: (1) What is the overall frequency trend of different groups of analytical methods? (2) What is the proportion of outlying observations (as detected by sample skewness and kurtosis tests) in inter-laboratory analytical data obtained by these methods? (3) What kind of inter-laboratory precision can be obtained for REE determinations by different groups of meth-
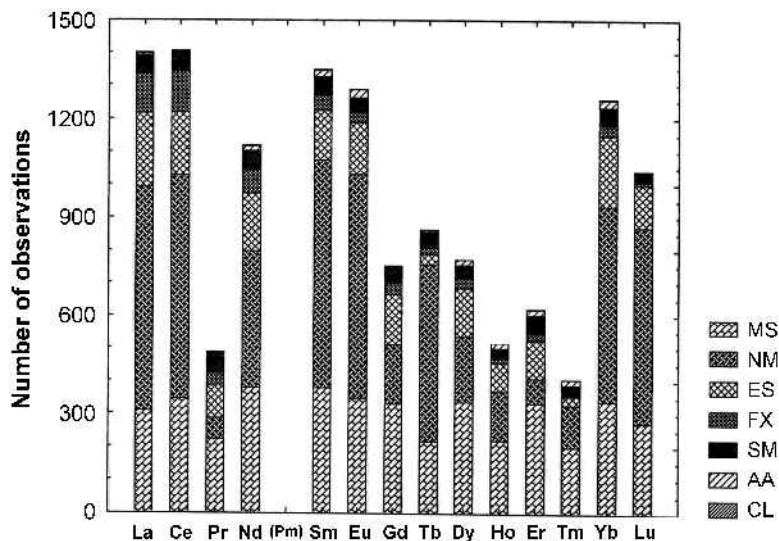
FIG. 1. Plot of total number of observations for the REE in 24 IGRM as a function of the seven groups of analytical methods. Abbreviations: MS = mass spectrometry; NM = nuclear methods; ES = emission spectrometry; FX = X-ray fluorescence spectrometry; LC = liquid chromatography; AA = atomic absorption spectrometry; CL = colorimetry.

ods? (4) What are the inter-laboratory detection limits for the determination of REE in rocks? Is there a systematic pattern for these detection limits? (5) Are there any significant differences among the analytical data obtained by different groups of methods? (6) Is there any analytical bias between different experimental methods used for the determination of the REE? (7) How can new or existing methods be evaluated statistically for their accuracy? (8) Can the results of question (4) be confirmed from detection limit data from individual laboratories?

Number of observations

Figure 1 compares schematically the cumulative number of observations for each lanthanide in 24 IGRM from the United States and Japan. The methods most frequently employed in the determination of the REE include MS, NM, and ES. The NM methods are more frequently used for the determination of La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu, whereas the MS methods are more often used for Pr, Gd, Dy, Ho, Er, and Tm. The ES methods are the next important group in the determination of REE. The other four groups (FX, SM, AA, and CL) have not yet found a common application in the study of REE. The FX methods are generally employed for La and Ce, although when combined with prior group separation, they are useful also for the other REE. More

recently, separation methods (SM) have come into use for most REE. It is expected that such methods will be more frequently used in the future due to both their low cost and high sensitivity. Finally, the AA and CL methods have had a very limited application in the study of REE in geological materials.

Skewness and kurtosis

The initial statistical samples of REE data for the IGRM were generally highly skewed due to the presence of outliers (these distributions are not shown in order to limit the size of this paper). Positive skewness coefficients (many distributions with skewness above +3) were more common than the negative values (very few distributions with skewness less than −3), implying that high-concentration data were more frequent outliers than the low values. Similarly, positive kurtosis coefficients were much more common in the initial statistical samples. These skewed distributions are consistent with Thompson and Howarth (1980), who demonstrated that the frequency distribution of analytical errors approached a normal distribution, but small deviations, especially a positive skew, were common in analytical data.

After the application of the skewness and kurtosis tests for detection and rejection of outliers in analytical data generated from individual group of
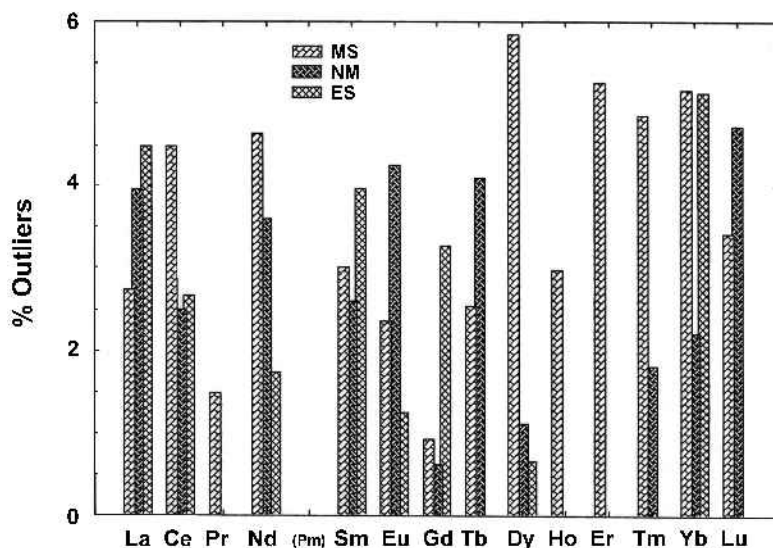
FIG. 2. Plot of the percentage of outlying observations for the REE in 24 IGRM for three main groups of analytical methods (MS, NM, and ES).

methods, the corresponding "censured" statistical samples became "normal," i.e., they now pertain to a univariate normal distribution. As noticed earlier by Verma et al. (1998), the actual reasons for the outlying observations are not always clear in such inter-laboratory compilations (i.e., inappropriate sample or standard preparation methods; dissolution procedures, incorrect calibration of the instrument used, incorrect regression methods used, sources of systematic errors, serious matrix interference effects, etc., are not generally reported by the authors of outlier data), and cannot, therefore, be used as justification criteria for rejection of these outliers. As a consequence, one has to rely largely on statistical criteria. After the elimination of outliers, the analytical data (censured statistical samples) can be evaluated by the Student's *t*-test provided, in addition, some other conditions are met. This is explained in detail in the section on "Student *t*-test on inter-laboratory data."

Outliers

Figure 2 presents a comparison of outliers detected for three groups of analytical methods most employed in the determination of REE. The percentage outliers (as a function of the number of observations in the original data set) for these methods are, in general, low (from about 0.5% to 6%).

This implies that the initial data sets were generally coherent for these three groups (MS, NM, and ES). La, Tb, and Lu showed the lowest percentage outliers for MS methods; Ce, Sm, Gd, Tm, and Yb presented the lowest percentage of outliers for NM, and Nd, Eu, and Dy for ES methods.

Inter-laboratory precision

A summary of the inter-laboratory precision for the REE is presented in Figure 3. The overall average percentages of relative standard deviation (%Rsd), their standard deviation values, as well as 95% confidence limits are plotted and compared for four groups of analytical methods. The precision for the MS is generally better than the other three groups.

MS methods. The %Rsd for most elements determined by these methods were fairly uniform, except for Tm by MS (Fig. 3A). The average %Rsd values were between about 8% and 10% for La, Ce, Nd, Sm, and Dy; 10%–15% for Pr, Eu, Gd, Tb, Ho, Er, and Yb; and 15%–18% for Tm and Lu.

NM methods. The %Rsd values were more variable for this group of methods, particularly for Eu, Dy, and Tm (Fig. 3B). The average %Rsd varied from 7% to 10% for La, Ce, and Sm; 10%–15% for Nd, Eu, Gd, Yb, and Lu; 15%–20% for Tb and Ho; and 20%–25% for Dy and Tm. Pr and Er values were difficult to analyze by these methods.

ES methods. The %Rsd values were low and fairly uniform by these methods, except for Eu and Er (Fig. 3C). The average %Rsd ranged from 7% to 10% for La, Ce, Nd, Sm, Gd, Dy, Ho, and Yb; 10%–15% for Pr, Eu, and Lu; and ~16% for Er. Tb and Tm were difficult to determine by ES methods.

FX methods. Only two lanthanides, La and Ce, had enough data to be included in Figure 3D. Their % Rsd values were the highest and most variable among the four groups of analytical methods. The average %Rsd values were between 18% and 20%.

Regression coefficients of the precision model: Simple regression

The Thompson and Howarth method (1976) was used to derive regression coefficients of a linear precision model. The resulting detection limits for REE are based on the inter-laboratory data sets for 24 IGRM. However, instead of taking averages, as done for duplicate analyses by Thompson and Howarth (1976) and Ramsey et al. (1995), individual averages and standard deviations were used to carry out a linear regression analysis for the precision model ($s_c = s_o + kc$), because each of the individual averages represents at least 5 or more observations. In the precision model, s_c is the standard deviation of the mean concentration c of an analyte, s_o is the intercept of the linear regression, and k is the slope.

Tables 1–4 present the results of these regressions for all IGRM analyzed by the MS, NM, ES, and FX methods, respectively. The data on slopes and intercepts of the regressions on all REE in the IGRM are included in these tables, except when the intercept had a negative value or in situations where fewer than five IGRM were analyzed for a given element. Also included in these tables are the regression data on two subsets: extrusive and intrusive rocks, but only for those elements for which the linear regression slopes were significant ($p_k < 0.05$). An example of regression lines for La is presented in Figure 4, where the slope increases from the MS to the FX methods.

MS methods. The linear correlation coefficients (*r*) were significant (at the 95% confidence level) (Thompson and Howarth, 1980) for some REE only (La to Gd, and Ho) determined by MS methods. Statistically significant positive slopes (at the 95% confidence level) were obtained for La to Gd, but not for Tb to Lu (Table 1). This probably reflects large dispersion of precision for all REE heavier than Gd or a relatively smaller concentration range covered in comparison to the detection limit. A meaningful
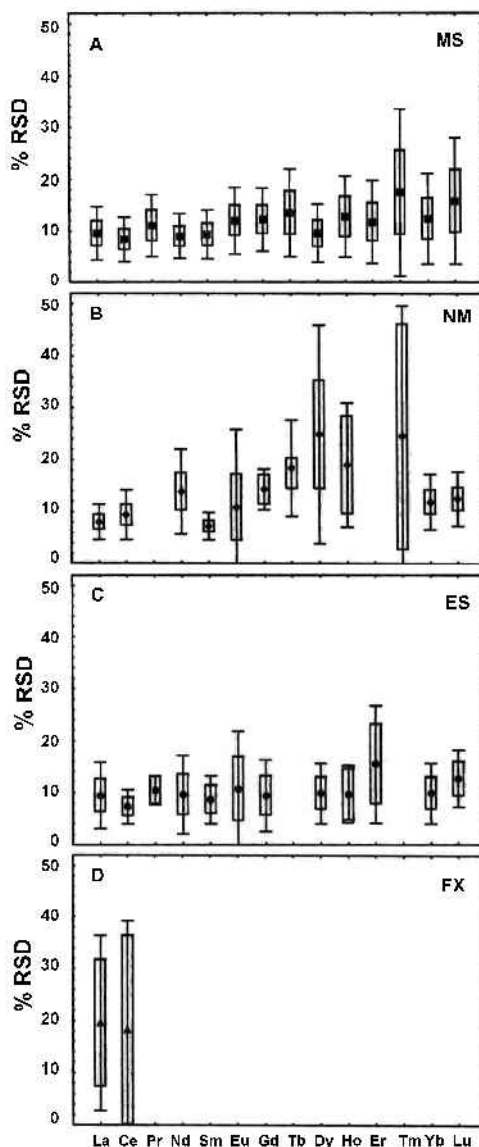
FIG. 3. Plots of average values (small solid circles), 95% confidence limits (small boxes), and one standard deviation (error bars) for %Rsd (relative standard deviation) for 24 IGRM, according to the analytical method grouping: A. MS. B. NM. C. ES. D. FX.

intercept was obtained only for Pr. When the REE data were separated into extrusive and intrusive rocks, statistically significant positive correlations were obtained for eight and seven lanthanides respectively (Table 1). The slopes of regressions for all lanthanides, except Pr, in extrusive rocks were
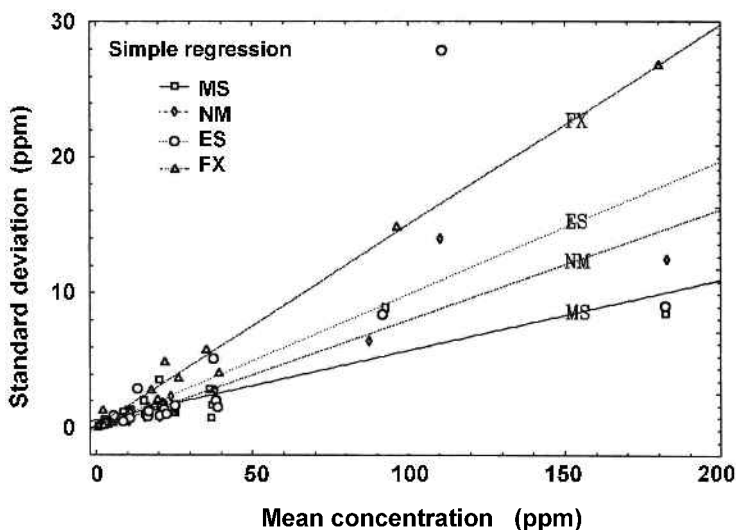
FIG. 4. A graphical representation of the estimation of precision by a simple regression model of analytical data for La for 24 IGRM.

smaller than those for the corresponding elements in intrusive rocks. This means that standard deviations increase less rapidly with the concentration of REE for extrusive than for intrusive rocks. In other words, the final errors for intrusive rocks seem to have a larger pre-instrumental error, such as sampling error (heterogeneity problems) or chemical preparation error (dissolution problems).We suggest that this is an important conclusion drawn from the statistical treatment of inter-laboratory analytical data generated from the precise group of methods (MS). This conclusion was also confirmed from a more appropriate weighted regression model (see below).

NM methods. The linear correlation coefficient (*r*) and positive slopes were significant for all REE determined by nuclear methods, except for Dy, Ho, and Tm (Table 2), but a meaningful intercept was obtained only for Lu. Statistically significant correlations and slopes were obtained for seven elements in extrusive as well as intrusive rocks. The slopes for extrusive rocks were smaller than for the corresponding elements in intrusive rocks, with the exception of Lu.

ES methods. The linear correlation coefficient (*r*) and positive slopes were significant for all REE from La to Gd, and for Lu (Table 3). Although for Yb, the slope was not significant, a meaningful intercept was obtained. Statistically significant correlations and slopes were obtained for six and five lan-

thanides in extrusive and intrusive rocks, respectively. Further, for the only two cases available (Ce and Gd) in both rock types, the slopes for extrusive rocks were smaller than for intrusive rocks.

FX methods. La and Ce are the only two REE with sufficient data available to be included in Table 4. The linear correlation coefficient (*r*) and positive slopes were significant for them in these IGRM. The slopes are, however, the largest of all four groups of methods (Tables 1–4).

Regression coefficients of the precision model: Weighted regression

Although simple regression of the precision model (Thompson and Howarth, 1976) has been used even more recently by Ramsey et al. (1995), it was found to be inadequate by Thompson (1988) to describe the varying, generally increasing, precision of the *y* values (standard deviation of the mean) as a function of the *x* (mean concentration values). This was overcome by carrying out weighted regressions of the data (Thompson, 1988). A similar weighted regression of the IGRM data was carried out in the present work by assigning a weight to the *y* values according to the reciprocal of the variances ($1/s_c^2$) and, thus, obtaining a weighted regression slope and intercept of the linear precision model ($s_c = s_o + kc$).

Tables 5–8 present the results of these weighted regressions for all IGRM analyzed by the MS, NM,

TABLE 1. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for MS Methods[1]

REE	n	r	Slope, k			Intercept, s_o		
			k	s.e._k	p_k	s_o	s.e._so	p_{so}
			All rocks					
La	20	0.882	0.052*	0.007	<0.001	0.560	0.321	0.098
Ce	21	0.848	0.079*	0.011	<0.001	0.526	0.294	0.526
Pr	18	0.827	0.033*	0.006	<0.001	0.340*	0.081	0.001
Nd	21	0.918	0.083*	0.008	<0.001	0.253	0.427	0.561
Sm	21	0.966	0.158*	0.010	<0.001			
Eu	21	0.454	0.072*	0.032	0.039	0.040	0.042	0.344
Gd	21	0.609	0.100*	0.030	0.003	0.097	0.155	0.539
Tb	18	0.315	0.078	0.058	0.203	0.038	0.045	0.406
Dy	21	0.245	0.047	0.042	0.284	0.183	0.182	0.325
Ho	18	0.449	0.105	0.052	0.062	0.019	0.045	0.678
Er	21	0.278	0.049	0.039	0.223	0.135	0.097	0.179
Tm	18	0.444	0.253	0.128	0.065			
Yb	21	0.318	0.049	0.038	0.159	0.132	0.083	0.130
Lu	18	0.259	0.048	0.045	0.300	0.029	0.018	0.114
			Extrusive rocks					
La	13	0.624	0.036*	0.014	0.023	0.519	0.293	0.104
Ce	13	0.570	0.042*	0.018	0.042	0.774	0.776	0.340
Pr	12	0.715	0.080*	0.025	0.009	0.071	0.127	0.587
Nd	13	0.675	0.076*	0.026	0.013			
Ho	12	0.610	0.118*	0.048	0.035			
Er	13	0.592	0.100*	0.041	0.033			
Tm	12	0.744	0.104*	0.029	0.006	0.008	0.013	0.579
Lu	12	0.739	0.086*	0.025	0.006			
			Intrusive rocks					
La	7	0.887	0.048*	0.011	0.008	1.314	0.875	0.194
Ce	8	0.827	0.074*	0.020	0.011	0.886	3.609	0.454
Pr	6	0.862	0.029*	0.008	0.027	0.512	0.202	0.064
Nd	8	0.926	0.077*	0.013	0.001	1.340	1.026	0.240
Sm	8	0.991	0.156*	0.008	<0.001			
Gd	8	0.815	0.103*	0.030	0.014	0.178	0.184	0.372
Tm	6	0.853	0.860*	0.263	0.031			

[1]Simple linear regression. Abbreviations: n = number of IGRM included in regression analysis; r = linear regression correlation coefficient; SE = standard error; p = probability; * = statistically significant at 95% confidence ($p < 0.05$). No entries of data when the intercept has a negative value.

ES, and FX methods, respectively. As for simple regression, the data on slopes and intercepts of the weighted regressions on all REE in the IGRM are included in these tables, except in cases where the intercept had a negative value, or when fewer than five IGRM were analyzed for a given element. Similarly, statistically significant weighted regression data for extrusive and intrusive rock groups are also included in these tables. An example of the weighted regression lines for La is presented in Fig-

TABLE 2. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for NM Methods[1]

REE	n	r	Slope, k			Intercept, s_o		
			k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
All rocks								
La	23	0.937	0.081*	0.007	<0.001			
Ce	23	0.960	0.080*	0.005	<0.001	0.239	0.532	0.658
Nd	22	0.944	0.096*	0.008	<0.001	0.660	0.365	0.086
Sm	23	0.908	0.074*	0.007	<0.001	0.003	0.055	0.955
Eu	23	0.642	0.055*	0.014	0.001	0.023	0.018	0.197
Gd	10	0.817	0.086*	0.022	0.005	0.295	0.139	0.067
Tb	23	0.517	0.153*	0.055	0.012	0.018	0.045	0.694
Dy	18	−0.059	−0.038	0.161	0.818	1.089	0.686	0.132
Ho	9	0.203	0.062	0.113	0.601	0.087	0.093	0.381
Tm	8	0.694	0.762	0.323	0.056			
Yb	22	0.648	0.076*	0.020	0.001	0.078	0.051	0.143
Lu	23	0.759	0.065*	0.012	<0.001	0.018*	0.006	0.004
Extrusive rocks								
La	13	0.918	0.054*	0.007	<0.001	0.175	0.157	0.291
Ce	13	0.831	0.066*	0.013	<0.001	0.390	0.576	0.512
Sm	13	0.764	0.073*	0.019	0.002			
Eu	13	0.854	0.038*	0.007	<0.001	0.023*	0.009	0.025
Gd	6	0.953	0.159*	0.025	0.003			
Yb	13	0.821	0.094*	0.020	0.001	0.007	0.057	0.904
Lu	13	0.684	0.073*	0.024	0.010	0.015	0.011	0.190
Intrusive rocks								
La	10	0.929	0.080*	0.011	<0.001	0.209	0.839	0.810
Ce	10	0.961	0.078*	0.008	<0.001	0.830	1.218	0.515
Nd	10	0.957	0.096*	0.010	<0.001	0.787	0.698	0.292
Sm	10	0.918	0.071*	0.011	<0.001	0.060	0.107	0.591
Eu	10	0.791	0.086*	0.024	0.006	0.016	0.028	0.578
Tb	10	0.757	0.232*	0.071	0.011			
Lu	10	0.834	0.060*	0.014	0.003	0.019*	0.007	0.022

[1]Simple linear regression. For explanation of codes, see note in Table 1.

ure 5, where although all slopes are lower than in the respective simple regression model (Fig. 4), the slope for the FX method still has the highest value and the lowest for MS. Lower slopes were, in fact, obtained, in general, for all cases in the weighted regression (Tables 5–8) than the simple regression (Tables 1–4).

MS methods. Statistically significant positive slopes (at 95% confidence level) were obtained for La, Ce, Pr, Nd, Eu, Gd, Tb, and Tm (Table 5). All slopes were smaller than the respective values for the simple regression (Table 1). Significant mean-ingful intercepts were obtained only for Eu and Dy. For separate groups of extrusive and intrusive rocks,

TABLE 3. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for ES Methods[1]

REE	n	r	Slope, k			Intercept, s_o		
			k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
All rocks								
La	18	0.687	0.098*	0.026	0.002	0.078	1.512	0.960
Ce	16	0.985	0.085*	0.004	<0.001			
Pr	7	0.994	0.118*	0.006	<0.001			
Nd	17	0.843	0.132*	0.022	<0.001			
Sm	14	0.872	0.086*	0.014	<0.001	0.002	0.121	0.987
Eu	15	0.710	0.110*	0.030	0.003			
Gd	15	0.908	0.335*	0.043	<0.001			
Dy	16	0.123	0.018	0.039	0.649	0.339	0.189	0.095
Ho	6	−0.287	−0.040	0.067	0.582	0.127	0.066	0.128
Er	11	−0.023	−0.008	0.113	0.947	0.380	0.298	0.235
Yb	19	0.028	0.005	0.045	0.909	0.373*	0.121	0.007
Lu	13	0.564	0.066*	0.029	0.045	0.019	0.013	0.157
Extrusive rocks								
La	11	0.703	0.071*	0.024	0.016	0.034	0.572	0.953
Ce	10	0.619	0.038*	0.017	0.056	0.189	0.745	0.321
Pr	5	0.929	0.063*	0.014	0.023	0.201	0.089	0.110
Gd	9	0.738	0.157*	0.054	0.023			
Dy	10	0.654	0.058*	0.024	0.040	0.069	0.121	0.585
Lu	9	0.791	0.078*	0.023	0.011	0.007	0.011	0.554
Intrusive rocks								
Ce	6	0.993	0.085*	0.005	<0.001			
Nd	7	0.819	0.118*	0.037	0.024	2.005	2.965	0.529
Sm	5	0.891	0.081*	0.024	0.042	0.169	0.305	0.618
Eu	6	0.959	0.186*	0.027	0.002			
Gd	6	0.987	0.365*	0.030	<0.001			

[1]Simple linear regression. For explanation of codes, see note in Table 1.

statistically significant positive correlations were obtained for eight and three lanthanides, respectively (Table 5). The slopes of regressions for lanthanides in extrusive rocks are smaller than those for the corresponding elements in intrusive rocks.

NM methods. Significant positive slopes were obtained for La, Ce, Nd, Sm, Eu, Gd, and Lu by weighted regression of the data determined by nuclear methods (Table 6). Meaningful intercepts were obtained for many lanthanides (La, Ce, Eu, Tb, Dy, Ho, Yb, and Lu). Similarly, statistically signifi-

cant slopes were obtained for six elements in extrusive and three in intrusive rocks. Further, as for MS, the weighted regression slopes for extrusive rocks were consistently smaller than for the corresponding elements in intrusive rocks.

ES methods. The weighted linear regression model predicted significant positive slopes for only La, Ce, Pr, Nd, and Lu, and a meaningful intercept for only Eu (Table 7). Statistically significant slopes were obtained for five and three lanthanides in extrusive and intrusive rocks, respectively. Further,
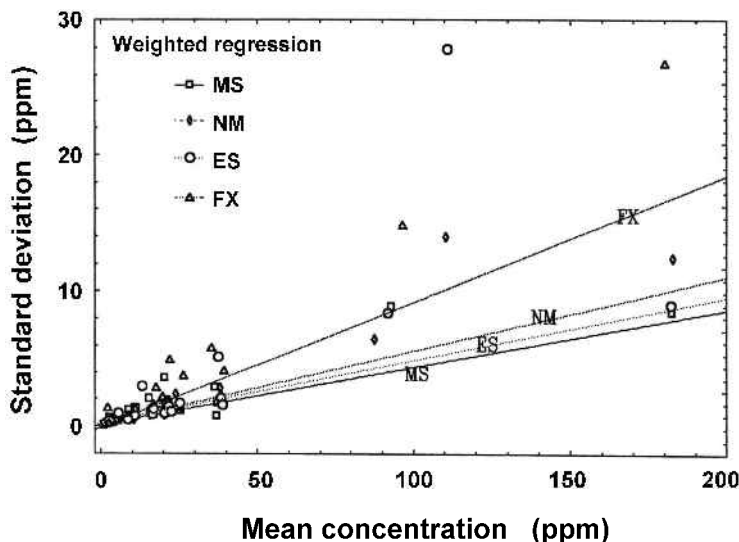
FIG. 5. A graphic representation of the estimation of precision by a weighted regression model of analytical data for La for 24 IGRM.

TABLE 4. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for FX Methods[1]

REE	n	r	Slope, k			Intercept, s_o		
			k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
			All rocks					
La	10	0.993	0.148*	0.006	<0.001	0.162	0.413	0.706
Ce	8	0.974	0.129*	0.012	<0.001			
			Extrusive rocks:					
La	7	0.867	0.117*	0.030	0.012	0.856	0.743	0.302

[1]Simple linear regression. For explanation of codes, see note in Table 1.

for the only two cases available (La and Nd) for ES in both rock types, the slopes for extrusive rocks were smaller than for intrusive rocks.

FX methods. Sufficient data were available for La and Ce by FX methods and significant positive slope was obtained only for La in extrusive rocks (Table 8).

Inter-laboratory detection limits

Significant (confidence level of 95%; probability ≤ 0.05) meaningful ($s_o > 0$) intercepts are required to estimate method detection limit (MDL) as $3s_o$ (Long and Winefordner, 1983; Analytical Methods Committee, 1987; Thompson, 1988; Ramsey et al.,

1995). In cases where this is not possible, only the maximum method detection limit (MMDL) can be estimated (Ramsey et al., 1995) by:

$$MMDL = 3 \cdot (s_o + t_{(n-2)} \, se_{so}),$$

where se_{so} is the standard error of the value s_o, $t_{(n-2)}$ is from the t-distribution with $(n-2)$ degrees of freedom (n is the number of data points used in the simple or weighted linear regression), at a 95% confidence level (probability $p = 0.05$). The data table for t-distribution can be found in Davies (1973) or Ebdon (1988); $t_{(n-2)}$ values for a significance level of 2.5% (or $p = 0.05$) were used in this

TABLE 5. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for MS Methods[1]

		Slope, k			Intercept, s_o		
REE	*n*	k	s.e.$_k$	p$_k$	s$_o$	s.e.$_{so}$	p$_{so}$
				All rocks			
La	20	0.043*	0.008	<0.001	0.078	0.043	0.086
Ce	21	0.034*	0.007	<0.001	0.132	0.099	0.200
Pr	18	0.063*	0.010	<0.001	0.001	0.011	0.910
Nd	21	0.034*	0.010	0.004	0.204	0.139	0.158
Sm	21	0.016	0.016	0.340	0.101	0.066	0.145
Eu	21	0.029*	0.012	0.032	0.036*	0.012	0.008
Gd	21	0.048*	0.019	0.021	0.123	0.074	0.115
Tb	18	0.082*	0.026	0.007	0.004	0.016	0.823
Dy	21	0.005	0.019	0.794	0.196*	0.079	0.022
Ho	18	0.048	0.027	0.098	0.013	0.019	0.486
Er	21	0.040	0.030	0.204	0.030	0.064	0.644
Tm	18	0.109*	0.044	0.025			
Yb	21	0.011	0.027	0.681	0.081	0.057	0.167
Lu	18	0.018	0.038	0.645	0.014	0.013	0.282
				Extrusive rocks			
La	13	0.037*	0.009	0.001	0.078	0.045	0.115
Ce	13	0.032*	0.008	0.002	0.146	0.095	0.154
Pr	12	0.069*	0.012	<0.001			
Nd	13	0.026*	0.010	0.026	0.217	0.135	0.136
Tb	12	0.093*	0.029	0.010			
Ho	12	0.129*	0.032	0.002			
Er	13	0.069*	0.030	0.040			
Tm	12	0.099*	0.024	0.002	0.005	0.009	0.612
				Intrusive rocks			
La	7	0.069*	0.017	0.010	0.072	0.143	0.638
Nd	8	0.076*	0.021	0.011	0.288	0.328	0.414
Gd	8	0.105*	0.035	0.023	0.022	0.120	0.858

[1]Weighted linear regression. For explanation of codes see footnote in Table 1.

work for MMDL estimations (Davies, 1973; Ramsey et al., 1995).

The results of MDL and MMDL are given in Table 9 for all rocks and in Table 10 for separate groups of extrusive and intrusive rocks. Simple regression detection limits (Table 9) are, in general, smaller for MS than for NM and ES methods, except for Eu, Yb, and Lu (smaller for NM). All MDL and MMDL data obtained for simple regression are found to be much greater than the weighted regression. However, following Thompson's (1988) argu-

ments, the weighted results are considered to be more representative of the inter-laboratory detection limits. Thus, for all rocks, the detection limits corresponding to these methods are in the sub-ppm range (< 1 ppm), except for Ce and Nd (all methods), Dy by NM, and Sm, Ho, and Er by ES (Table 9). These detection limits, based on the weighted regressions, are lowest for seven lanthanides (Ce, Pr, Nd, Tb, Dy, Ho, and Er) by MS and for five lanthanides (La, Sm, Eu, Yb, and Lu) by NM. The results for extrusive and intrusive rocks are also quite similar. The

TABLE 6. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for NM Methods[1]

REE	n	Slope, k			Intercept, s_o		
		k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
				All rocks			
La	23	0.055*	0.005	<0.001	0.097*	0.037	0.016
Ce	23	0.054*	0.007	<0.001	0.383*	0.161	0.027
Nd	22	0.066*	0.021	0.006	0.254	0.375	0.505
Sm	21	0.046*	0.010	<0.001	0.018	0.032	0.583
Eu	23	0.041*	0.008	<0.001	0.019*	0.006	0.007
Gd	10	0.145*	0.019	<0.001			
Tb	23	–0.034	0.028	0.249	0.088*	0.024	0.002
Dy	18	–0.020	0.046	0.671	0.440*	0.206	0.048
Ho	9	–0.124	0.080	0.164	0.170*	0.071	0.048
Tm	8	0.068	0.052	0.235	0.022	0.018	0.269
Yb	22	0.034	0.019	0.097	0.104*	0.041	0.018
Lu	23	0.048*	0.017	0.009	0.015*	0.006	0.013
				Extrusive rocks			
La	13	0.053*	0.005	<0.001	0.107*	0.028	0.003
Ce	13	0.047*	0.010	<0.001	0.429*	0.192	0.047
Nd	12	0.062*	0.029	0.050	0.516	0.503	0.329
Sm	13	0.043*	0.012	0.004	0.030	0.039	0.465
Eu	13	0.037*	0.005	<0.001	0.018*	0.004	0.002
Gd	6	0.172*	0.012	<0.001			
				Intrusive rocks			
La	10	0.061*	0.013	0.002	0.021	0.149	0.890
Ce	10	0.065*	0.012	<0.001	0.312	0.333	0.376
Sm	10	0.051*	0.018	0.022	0.002	0.061	0.974

[1]Weighted linear regression. For explanation of codes see footnote in Table 1.

weighted regressions are considered to provide a more realistic estimate of the detection limits (Table 10). Extrusive rocks show lower detection limit values than the intrusive group. The MMDL for La by FX is also of a comparable magnitude in the simple regression model, but no detection limit data were obtained for FX by the more realistic weighted regression model (Tables 9 and 10).

An interesting observation about the detection limit values (weighted regression) is their behavior similar to the well-known "odd-even" effect on the nuclear stability (see, e.g., Kaplan, 1963, p. 538), implications of which will be further explored in the section on "Method detection-limit data from individual laboratories." Figure 6 shows this effect graphically where the detection limits for all rocks are plotted on a linear scale against REE atomic number. Actual concentration data on IGRM BIR-1 (having relatively low concentrations of REE) are also plotted here for comparison purposes. The similarities of all patterns are noteworthy (Fig. 6). Detection limits for the MS and NM methods are generally very similar and smaller than those for the ES method group. A further point is that the inter-laboratory detection limits are not much smaller than the REE concentrations in BIR-1, which therefore makes it a difficult IGRM to be analyzed for REE in inter-laboratory trials. These results can also explain the large dispersions observed for REE in such compilations for IGRM

TABLE 7. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for ES Methods[1]

REE	n	Slope, k			Intercept, s_o		
		k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
All rocks							
La	18	0.047*	0.008	<0.001	0.213	0.120	0.095
Ce	16	0.029*	0.011	0.016	0.609	0.365	0.118
Pr	7	0.078*	0.011	<0.001	0.125	0.061	0.096
Nd	17	0.043*	0.017	0.022	0.016	0.273	0.955
Sm	14	0.041	0.028	0.163	0.062	0.135	0.653
Eu	15	−0.003	0.017	0.883	0.045*	0.020	0.042
Gd	15	0.073	0.039	0.081			
Dy	16	0.062	0.040	0.144			
Ho	6	−0.053	0.068	0.478	0.126	0.069	0.144
Er	1	0.007	0.045	0.874	0.215	0.119	0.104
Yb	19	0.072	0.037	0.067	0.006	0.079	0.937
Lu	13	0.053*	0.023	0.048	0.014	0.008	0.102
Extrusive rocks							
La	11	0.042*	0.009	0.001	0.247	0.111	0.053
Ce	10	0.025*	0.011	0.048	0.684	0.333	0.074
Pr	5	0.066*	0.009	0.006	0.174*	0.045	0.030
Nd	10	0.031*	0.015	0.071	0.130	0.238	0.600
Yb	11	0.100*	0.032	0.013			
Intrusive rocks							
La	7	0.057*	0.022	0.050	0.110	0.465	0.822
Nd	7	0.152*	0.036	0.009			
Gd	6	0.378*	0.105	0.020			

[1]Weighted linear regression. For explanation of codes see footnote in Table 1.

having low REE concentrations (e.g., basalts BIR-1 and JB-1, peridotites JP-1 and PCC-1, dunite DTS-1, and feldspars JF-1 and JF-2; Jochum and Jenner, 1994; Jochum et al., 1994; Verma 1998b; Guevara et al., 2001; Velasco-Tapia et al., 2001), and, consequently, probably erroneous concentration values assigned for some of these elements in existing compilations (Gladney et al., 1991; Govindaraju, 1989, 1994; Potts et al., 1992; Itoh et al., 1993; Imai et al., 1995). In fact, there are also other reasons for this problem of concentration value assignment; these have been discussed earlier by Verma (1997, 1998b) and Verma et al. (1998).

Student's t-test on inter-laboratory data

In order to test whether any significant differences exist between the inter-laboratory analytical data obtained by different groups of methods (MS, NM, and ES), the Student's *t*-test (e.g., Davies, 1973; Ebdon, 1988) was carried out on respective sample pairs of analytical data in individual IGRM. The basic assumptions necessary to perform the *t*-test were first taken into account. These include the randomness of the statistical samples, that they are normally distributed, and possess equality of variances (Davies, 1973). Because the statistical samples (analytical data) originated from a large number of laboratories located in many different countries, their randomness is likely. Furthermore, because the initial data pertaining to the statistical samples were tested using skewness and kurtosis tests, the final data were close to normal at least from these two powerful criteria for normality. Although other tests for a normal distribution are

TABLE 8. Computation of Linear Regression Coefficients of Precision Model ($s_c = s_o + kc$) for FX Methods
(Weighted Linear Regression)

REE	n	Slope, k			Intercept, s_o		
		k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
				All rocks			
La	10	0.140	0.093	0.251			
Ce	8	0.095	0.046	0.086			
				Extrusive rocks			
La	7	0.144*	0.033	0.008			

[1]Weighted linear regression. For explanation of codes see footnote in Table 1.

available (Barnett and Lewis, 1987, 1994; Verma, 1997, 1998b), we did not include them in the present work, because the skewness and kurtosis tests are very powerful against normality (Barnett and Lewis, 1987, 1994; Velasco and Verma, 1998; Velasco et al., 2000) and are applicable for a very wide range in number of observations (from 5 to 1000 for skewness and 5 to 2000 for kurtosis). The equality of variances was tested by the f statistical test (Davies, 1973). A further condition was that both sets of data should contain at least 10 observations. It was only when all these conditions were met that the t-test was performed.

The results of the t-test for MS-NM and MS-ES are presented in Figures 7 and 8, respectively. Most of the analytical data lie above the t-test probability value of 0.05, but several cases of paired data do fall below this value. This means that although, for most of these IGRM, no significant differences exist between the data generated by these groups of methods (i.e., the analytical data are drawn from the same or identical populations), for some of them (Figs. 7 and 8) these differences are significant at 5% level of significance (95% confidence level; i.e., some cases fall below the t-test probability of 0.05), for some even at a much more strict significance level of 1% (99% confidence level; i.e., some cases fall even below the t-test probability of 0.01), and for a few even at the strictest level of 0.1% (99.9% confidence level; i.e., some cases fall even below the t-test probability of 0.001). The cases with strictest (99.9%) confidence level include: for MS-NM methods, Ce in diabase W-1, Tb in basalt BHVO-1, and Tm in basalt BCR-1, whereas those with a somewhat less strict level (99% confidence level) include (besides the above cases): for MS-NM methods, La in granite

JG-1, Dy in andesite AGV-1, and Lu in basalt BIR-1; for MS-ES methods, La in rhyolite JR-1.

The results of the Student's t-test can be visualized graphically using box-and-whisker plots. Examples are given in Figures 9 and 10 for Er and Tm, respectively. It is clear that the MS and NM gave similar results for Er (t-test probability = 0.933), but different for Tm (t-test probability = 0.0007).

These results are surprising, and invalidate the common practice of pooling together analytical data from all methods to draw conclusions concerning the best estimate of the mean concentration in the IGRM, without carrying out the t-test of these statistical samples. Although some authors (e.g., Jochum and Jenner, 1994; Jochum et al., 1994) have questioned, without any statistical tests, the mean values proposed for some IGRM, and have pointed out that the data from a specific method or group of methods better represent the mean concentration values, we have shown here from the Student's t-test that extreme care is required in processing the geochemical database for the IGRM in order to derive proper mean concentration values.

In a series of papers, Verma and colleagues (Verma, 1997, 1998b; Verma et al., 1998; Velasco-Tapia et al., 2001; Guevara et al., 2001) have shown that the application of a set of statistical tests for normal univariate data (Barnett and Lewis, 1987, 1994), along with a prior application of the Student's t-test, should provide more reliable mean values, with a smaller standard deviation, for most constituents in the IGRM, than the methods employed by many compilers to derive concentration values (e.g., Gladney and Roelandts, 1988a, 1988b, 1990a, 1990b; Gladney et al., 1990, 1991,

TABLE 9. Detection Limit Data (in ppm or µg/g) for REE in all Rocks, Computed as Method Detection Limit (MDL) or Maximum Method Detection Limit (MMDL)[1]

REE	MS		NM		ES		FX	
	MDL	MMDL	MDL	MMDL	MDL	MMDL	MDL	MMDL
All rocks (simple linear regression)								
La		3.7				9.8		3.3
Ce		3.4		4.0				
Pr	1.0							
Nd		3.4		4.3				
Sm				0.4		0.8		
Eu		0.4		0.2				
Gd		1.3		1.8				
Tb		0.4		0.3				
Dy		1.7		7.6		2.2		
Ho		0.3		0.9		0.9		
Er		1.0				3.2		
Yb		0.9		0.5	1.1			
Lu		0.2	0.05			0.14		
All rocks (weighted linear regression)								
La		0.5	0.3			1.4		
Ce		1.0	1.1			4.2		
Pr		0.07				0.8		
Nd		1.5		3.1		1.8		
Sm		0.7		0.3		1.1		
Eu	0.11		0.06			0.14		
Gd		0.8						
Tb		0.11		0.3				
Dy	0.6			1.3				
Ho		0.16	0.5			1.0		
Er		0.5				1.4		
Tm				0.2				
Yb		0.6	0.3			0.5		
Lu		0.12	0.05			0.10		

[1]MDL and MMDL are defined, after Ramsey et al. (1995), as follows: $MDL = 3s_0$ and $MMDL = 3(s_0 + t_{(n-2)} s.e._{s0})$, where $t_{(n-2)}$ = critical value of t for $(n-2)$ degrees of freedom at a confidence level of 95%, after Davies (1973).

1992; Itoh et al., 1993; Govindaraju et al., 1994; Imai et al., 1995, 1996a, 1996b). In fact, Verma (1998b) has shown that the two-standard deviation method used by U.S. and Japanese compilers (e.g., see papers by Ando et al., 1987, 1989; Gladney and Roelandts, 1988a, 1988b, 1990a, 1990b; Gladney et al., 1991; Itoh et al., 1993; Imai et al., 1995) is statistically wrong, and, therefore, should be abandoned for IGRM database processing and handling. Instead of this presumably wrong procedure, more appropriate outlier detection and rejection methods or, alternatively, so-called robust methods must be used for this purpose (see Barnett and Lewis, 1994, for more details).

On the basis of this discussion, it is proposed that inter-laboratory data from different methods or

TABLE 10. Detection Limit Data (in ppm) for REE in Separate Groups of Extrusive and Intrusive Rocks, Computed as Method Detection Limit (MDL) or Maximum Method Detection Limit (MMDL)[1]

REE	MS		NM		ES		FX	
	MDL	MMDL	MDL	MMDL	MDL	MMDL	MDL	MMDL
Extrusive rocks (simple linear regression)								
La		3.5		1.6		4.0		8.3
Ce		7.4		5.0		5.7		
Pr		1.1				1.4		
Eu			0.07					
Dy						1.0		
Tm		0.11						
Yb				0.4				
Lu				0.12		0.10		
Intrusive rocks (simple linear regression)								
La		10.7		6.4				
Ce		29.2		10.9				
Pr		3.2						
Nd		11.6		7.2		28.9		
Sm				0.9		3.4		
Eu				0.2				
Gd		0.9						
Lu			0.06					
Extrusive rocks (weighted linear regression)								
La		0.5	0.3			1.5		
Ce		1.1	1.3			4.4		
Pr					0.5			
Nd		1.5		4.9		2.0		
Sm				0.3				
Eu			0.05					
Tm		0.08						
Intrusive rocks (weighted linear regression)								
La		1.3		1.1		3.9		
Ce				3.2				
Nd		3.3						
Sm		0.9		0.4				

[1]For explanation of codes and equations se footnote in Table 9.

groups of methods (i.e., the corresponding statistical samples), even when they are well-established, should first be tested by the Student's *t*-test or ANOVA (analysis of variance), and if they differ from each other at a probability of less than 0.01 (confidence level of better than 99%), they must not be combined, and the mean concentration values for that particular element in that IGRM be reported only individually for different methods. The most precise data (generally by MS or NM) could then be used as a sample mean concentration estimate, and its quality probably judged from the criteria pro-
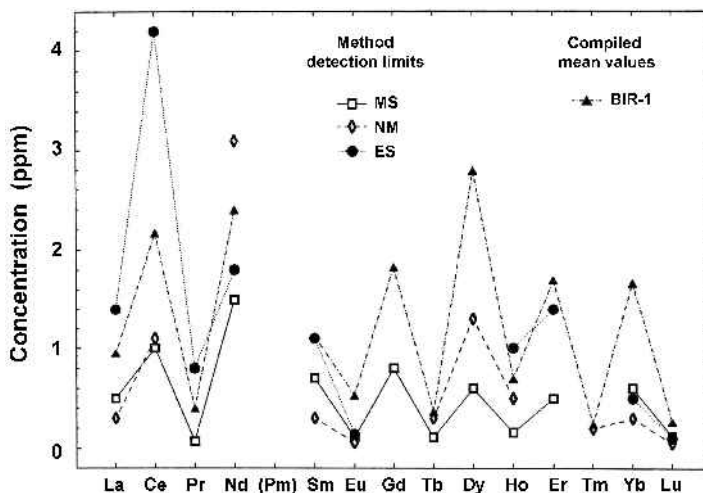
FIG. 6. Concentration plot of detection limits as a function of the REE atomic number. For comparison an IGRM BIR-1 (having rather low concentrations of all REE) is also included. Note the similar zigzag pattern of the detection limits and the IGRM.

posed by Potts and Kane (1992), with modifications by Verma (1997). Alternatively or complementary to ANOVA, other statistical methods for testing bias between two methods can be used (e.g., Ebdon, 1988; Miller, 1991; Jensen et al., 1997; Otto, 1999), such as those discussed below.

Analytical bias among methods

The analytical bias among methods was tested by both simple and weighted regressions of all REE data in the IGRM. The results are reported in Table 11 for MS-NM and Table 12 for MS-ES methods. Weighted regressions are considered to give a more realistic estimate of analytical bias than simple regressions (Thompson, 1982; Ripley and Thompson, 1987; Miller, 1991; Kalantar et al., 1995). No significant bias for weighted regression slopes or intercepts was obtained between MS and NM methods (Table 11). Similarly, the MS and ES methods are also generally free from analytical bias (Table 12) as judged by the weighted regression method, except for the slope for La and intercept for Lu. For these two cases, the average slope (La 1.034) and intercept (Lu 0.027) values fall very slightly outside the corresponding confidence limits.

Evaluation of inter-laboratory FX and LC methods

The REE data obtained by FX and LC can be statistically evaluated using the analytical data from well-established MS, NM, and ES groups of methods (Sutarno and Steger, 1985a, 1995b; Kane, 1991). Typical results of this evaluation for two IGRM (BCR-1 and JA-1) are presented in Table 13. Mean concentrations from well-established methods are first computed. These are based on a combination of the MS, NM, and ES methods, except when the t-tests indicated significant differences at a confidence level of 99%. Thus, although only the MS mean value and related standard deviation are used for Tm in BCR-1 (Figs. 7 and 10), NM data for Tm could equally be used for this test.

The inter-laboratory precision for BCR-1 shown by FX values was generally poorer (about 2.5% to 33%; Table 13) than LC methods (about 0.8% to 5%). Nevertheless, the Sutarno-Steger test indicated that both FX and LC methods provided generally "accurate" REE data (SST values generally < 1), except for a small bias in Yb and Lu by FX (SST > 1).

The literature data by MS, NM, and ES are less numerous for JA-1 than BCR-1, but of an overall good quality (rv = recommended value and cve = certified value equivalent) for their use in the evaluation of FX and LC. These data are also less numerous for JA-1 than for BCR-1. Their agreement among different laboratories is also poorer for JA-1 than for BCR-1 (Table 13). The Sutarno-Steger test indicated significant differences for some REE in this IGRM (Ce and Sm by FX; Lu by LC). These two examples serve the purpose of illustrating how the accuracy of new methods can be established.
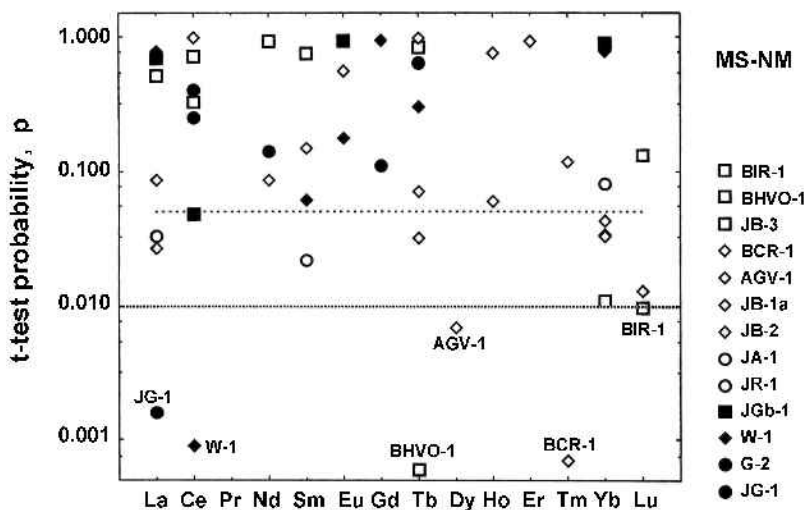
FIG. 7. Plot of *t*-test probability of all the REE data by MS and NM groups of analytical methods for individual IGRM. The upper dotted horizontal line represents the significance level of 0.05 and the lower heavily-dotted horizontal line shows that of 0.01. Note the high level <0.01 of significance (>99% confidence) that differences exist between mean values by MS and NM for samples of analytical data for some REE (La, Ce, Tb, Dy, Tm, and Lu) for six IGRM (four extrusive and two intrusive types, for which $p < 0.01$).
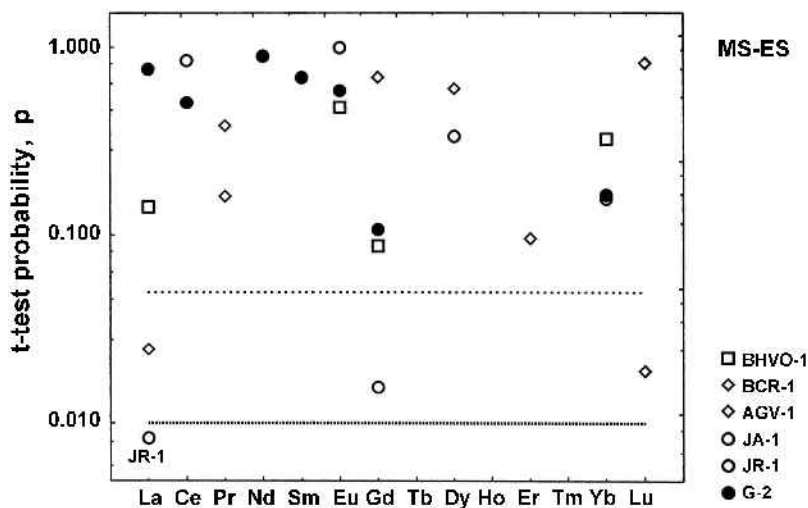
FIG. 8. Plot of *t*-test probability of all the REE data by MS and ES groups of analytical methods for individual IGRM. As in Figure 7, note the high level of significance (0.01) by which La in JR-1 by ES differs significantly from MS.

Method detection-limit data
from individual laboratories

   Method detection-limit data for the REE from individual laboratories and average concentration data for some IGRM (Table 14), along with several useful characteristics of the REE and their cosmic abundances (Table 15), were also compiled in this work, in order to check or confirm the conclusions
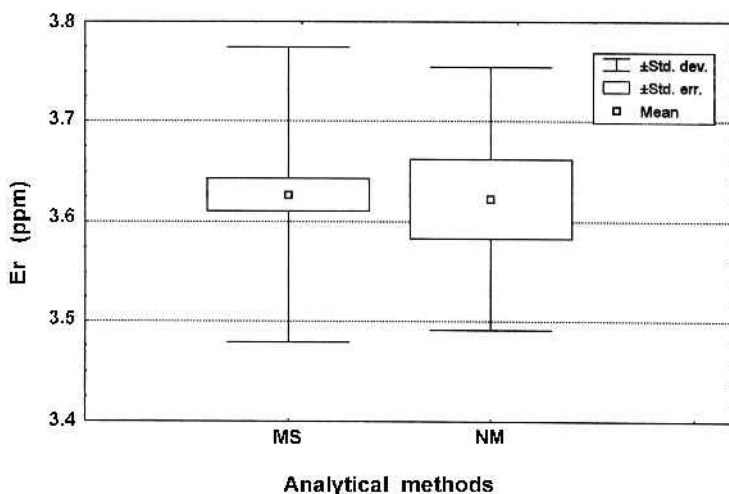
FIG. 9. Box-and-whisker plot for Er data in BCR-1 by MS and NM, illustrating that the two mean values do not differ significantly.
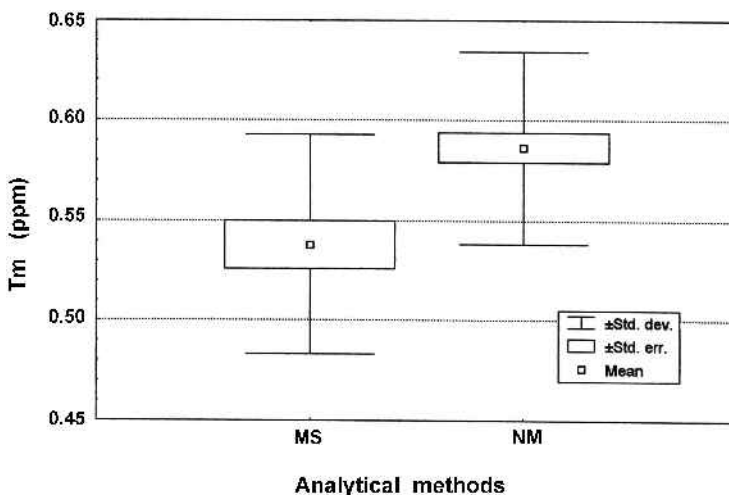
FIG. 10. Box-and-whisker plot for Tm data in BCR-1 by MS and NM, illustrating that the two mean values differ significantly.

drawn from the compilation and statistical analysis of REE data on 24 IGRM from a large number of laboratories. In this regard, it is interesting to recall that the method detection limits computed from inter-laboratory data (Fig. 6) show a zigzag pattern very similar to that depicted by REE concentrations in the solar system (see, e.g., carbonaceous chondrite data in Fig. 11A) and for most, if not all, geological materials (see, e.g., IGRM andesite AGV-1 in Fig. 11B) and detection-limit data from all individual laboratories (see, e.g., ICP-MS detection limit data in Fig. 11C). Here we use the term "zig-

TABLE 11. Evaluation Parameters of Analytical Bias between MS and NM Methods[1]

REE	n	Slope, k			Intercept, s_o		
		k	$s.e._k$	p_k	s_o	$s.e._{so}$	p_{so}
				Simple linear regression			
La	20	0.991	0.009	<0.001	0.659	0.452	0.162
Ce	21	0.935	0.019	<0.001	4.541	2.150	0.048
Nd	20	0.910*	0.011	<0.001	2.482*	0.570	<0.001
Sm	21	0.921*	0.014	<0.001	0.422*	0.112	0.001
Eu	21	0.971	0.037	<0.001	0.025	0.048	0.605
Gd	10	0.921	0.061	<0.001	0.471	0.381	0.252
Tb	18	1.006	0.058	<0.001	0.034	0.045	0.455
Dy	18	0.834	0.137	<0.001	0.682	0.584	0.260
Ho	8	0.878	0.161	0.001	0.125	0.136	0.393
Tm	7	0.372	0.497	0.487	0.311*	0.193	0.168
Yb	21	1.000	0.059	<0.001	0.101	0.146	0.498
Lu	18	1.080	0.052	<0.001	0.006	0.020	0.786
				Weighted linear regression			
La	20	1.019	0.011	<0.001	0.059	0.066	0.382
Ce	21	1.018	0.128	<0.001	−0.057	0.229	0.806
Nd	20	1.000	0.024	<0.001	0.311	0.394	0.439
Sm	21	1.040	0.024	<0.001	−0.055	0.079	0.493
Eu	21	0.995	0.010	<0.001	0.013	0.086	0.145
Gd	10	0.958	0.050	<0.001	0.304	0.173	0.116
Tb	18	0.040	0.050	<0.001	0.024	0.034	0.482
Dy	18	0.930	0.071	<0.001	0.420	0.319	0.206
Ho	8	0.895	0.120	<0.001	0.113	0.101	0.307
Tm	7	1.047	0.142	0.001	0.019	0.049	0.716
Yb	21	0.975	0.049	<0.001	0.093	0.107	0.392
Lu	18	1.022	0.044	<0.001	0.009	0.015	0.549

[1]Symbols: * = statistically significant at 95% confidence level.

zag" in the sense that the concentrations of alternate elements show systematically lower and higher values throughout the REE group.

Such a "regular" zigzag distribution of the REE concentrations in nature has been known for decades (see, for example, Mason, 1966; Wedepohl, 1971). It actually gave rise to the well-known Masuda-Coryell normalized plots proposed in the early sixties (Coryell et al., 1963; Masuda and Matsui, 1963) to understand REE behavior; these plots were, in fact, precursors to the diversity of multi-element normalized diagrams so frequently used in geochemistry (e.g., Rollinson, 1993).

This zigzag behavior in concentrations of chemical elements was explained by the "odd-even" effect on nuclear stability and its influence in synthesis of these elements during the creation of the solar system (see, e.g., Kaplan, 1963, p. 538). Thus, the "odd-even" effect concerns certain criteria for nuclear stability; this simply means that nuclei with odd numbers of both protons and neutrons are the least stable, nuclei for which either the proton or the neutron number is even are intermediate in stability, and nuclei with even numbers of protons and neutrons are the most abundant and presumably the most stable. Thus, La with an atomic number (num-

TABLE 12. Evaluation Parameters of Analytical Bias between MS and ES Methods[1]

REE	n	Slope, k			Intercept, s_o		
		k	s.e.$_k$	p_k	s_o	s.e.$_{so}$	p_{so}
				Simple linear regression			
La	17	0.993	0.005	<0.001	0.953	0.287	0.005
Ce	16	0.908*	0.011	<0.001	5.296*	1.336	0.001
Pr	7	0.905*	0.010	<0.001	0.557*	0.221	0.053
Nd	17	0.902*	0.021	<0.001	3.495*	1.205	0.011
Sm	14	0.918*	0.011	<0.001	0.554*	0.101	<0.001
Eu	15	1.065	0.034	<0.001	−0.051	0.046	0.287
Gd	15	0.895*	0.053	<0.001	0.702	0.300	0.036
Dy	16	1.001	0.065	<0.001	0.174	0.296	0.566
Ho	6	0.933	0.089	0.001	0.070	0.088	0.473
Er	11	0.876	0.101	<0.001	0.404	0.258	0.152
Yb	19	0.982	0.049	<0.001	0.220	0.124	0.095
Lu	12	0.961	0.022	<0.001	0.029*	0.010	0.012
				Weighted linear regression			
La	17	1.034*	0.014	<0.001	−0.015	0.209	0.945
Ce	16	0.992	0.017	<0.001	0.815	0.538	0.152
Pr	7	0.969	0.040	<0.001	0.034	0.239	0.894
Nd	17	1.008	0.030	<0.001	0.166	0.452	0.719
Sm	14	1.020	0.032	<0.001	−0.007	0.151	0.965
Eu	15	0.999	0.016	<0.001	0.010	0.017	0.570
Gd	15	0.991	0.064	<0.001	0.237	0.297	0.440
Dy	16	0.966	0.052	<0.001	0.307	0.234	0.210
Ho	6	0.914	0.091	0.001	0.084	0.088	0.391
Er	11	0.927	0.070	<0.001	0.193	0.177	0.304
Yb	19	0.966	0.042	<0.001	0.159	0.096	0.116
Lu	12	0.965	0.025	<0.001	0.027*	0.009	0.012

[1]Symbols: * = statistically significant at 95% confidence level.

ber of protons) of 57 (an odd number) has a lower cosmic abundance than the nearest neighbor Ce, with an even atomic number of 58 (Table 15). Similarly, the isotope of La, ^{139}La, with an odd number of protons (57) and an even number of neutrons (82) has a much greater abundance (99.111%) than the other stable isotope of La, ^{138}La (abundance of 0.089%), with an odd number of protons (57) and also with an odd number of neutrons (81). For promethium (Pm), with an odd atomic number of 61, only radioactive isotopes exist (^{145}Pm being the isotope with the highest half-life of 17.7 y; Walker et al., 1977); no stable isotope has been observed. Effects such as those mentioned for the La-Ce pair

are observed throughout the REE group—e.g., Ce-Pr, Pr-Nd, …, Yb-Lu, etc.

A close examination of the data compiled in Tables 14 and 15 shows a nearly one-to-one correspondence between the detection limits for different methods in a wide range of individual laboratories and the REE concentrations for a wide variety of materials (solar system, meteorites, rocks, minerals, ores, water samples, etc.). Although detection limits from individual laboratories using ICP-MS, ICP-AES, and INAA, etc., show wide variations, the zigzag trend is almost universally valid, particularly for the middle and heavy REE (from Pm to Lu). Furthermore, for the methods listed in Table 14, the

TABLE 13. Evaluation of Accuracy of FX and LC data in Two IGRM

REE	(MS + NM + ES)					FX					LC				
	n	x	SD	%Rsd	$Q_v{}^1$	n	x	SD	%Rsd	SST[2]	n	x	SD	%Rsd	SST[2]
							BCR-1								
La	211	25.2	1.3	5.2	rv	15	26.3	3.7	14.1	0.42	5	24.1	0.71	3.0	0.42
Ce	223	53.3	2.5	4.7	cve	17	55.8	8.1	14.5	0.50	5	51.5	1.4	2.7	0.35
Pr	45	6.78	0.51	7.5	rv	5	6.87	0.17	2.5	0.09	5	6.53	0.19	2.9	0.24
Nd	218	29.1	1.8	6.3	rv	10	28.8	3.07	10.7	0.08	5	27.5	0.80	2.9	0.43
Sm	260	6.62	0.37	5.6	cve	6	6.56	1.28	19.5	0.08	5	6.29	0.20	3.2	0.44
Eu	227	1.96	0.07	3.6	cve	5	2.00	0.14	7.0	0.29	5	1.93	0.02	1.0	0.24
Gd	142	6.65	0.56	8.3	rv	5	7.16	0.49	6.8	0.46	5	6.62	0.12	1.8	0.02
Tb	143	1.05	0.10	9.5	rv	3	1.24	0.41	33.1	0.95	5	1.03	0.04	3.9	0.09
Dy	135	6.36	0.25	3.9	cve	5	6.42	0.26	4.0	0.10	3	6.35	0.14	2.2	0.03
Ho	71	1.25	0.15	12.0	rv	3	1.25	0.23	18.4	0.00	2	1.32	0.01	0.8	0.23
Er	104	3.62	0.16	4.4	cve	5	3.61	0.24	6.6	0.03	5	3.63	0.18	5.0	0.04
Tm [3]	21	0.54	0.06	10.2	rv						2	0.56	0.04	7.1	0.18
Yb	221	3.40	0.14	4.1	cve	5	3.05	0.28	9.2	1.25	5	3.40	0.10	2.9	0.01
Lu	181	0.52	0.03	5.6	cve	1	0.45			1.21	2	0.50	0.02	4.0	0.43
							JA-1								
La	39	5.29	0.60	11.3	rv	3	7.2	4.3	59.7	1.59	2	5.22	0.88	16.8	0.05
Ce	40	13.5	1.2	8.1	rv	2	23.5	0.7	3.0	4.55	2	12.0	3.4	28.3	0.68
Pr	16	1.86	0.50	26.9	rv	1	3.80			1.94	2	1.41	1.0	70.9	0.45
Nd	26	10.4	1.8	17.3	rv	1	12.6			0.61	2	11.0	0.64	5.8	0.17
Sm	43	3.45	0.25	7.2	cve	1	7.80			8.70	2	3.57	0.04	1.1	0.24
Eu	38	1.16	0.06	5.2	cve						1	1.17			0.08
Gd	27	4.31	0.37	8.6	rv						1	4.59			0.38
Tb	21	0.74	0.14	18.9	rv						1	0.74			0.00
Dy	28	4.56	0.56	12.3	rv	1	3.50			0.96	1	3.40			1.04
Ho	18	0.94	0.09	9.6	rv						2	0.92	0.17	18.5	0.11
Er	23	2.99	0.29	9.7	rv						2	2.94	0.19	6.5	0.09
Tm [3]	12	0.48	0.06	12.2	rv						2	0.46	0.06	13.0	0.25
Yb	35	2.89	0.19	6.6	cve	1	3.00			0.29	2	2.20	1.1	50.0	1.82
Lu	35	0.45	0.05	11.1	rv						2	0.84	0.52	61.9	3.90

[1]Quality value after Potts and Kane (1992); Abbreviations: rv = recommended value; cve = certified value equivalent.
[2]$SST = |x_{(MS+NM+ES)} - x_{(FX\ or\ LC)}|/(2 \times sd_{(MS+NM+ES)})$; Sutarno-Steger test (Sutarno and Steger, 1985a, 1985b).
[3]Only MS data used for Tm as reference values.

detection limits actually depend on the isotope to be used for the analysis of a given element, yet these differences in isotopic abundances cannot explain the zigzag pattern observed. Differences in detection limits between light and heavy REE have been documented for separation methods such as IC, which are insensitive to isotopic abundances (e.g., Lu et al., 1997b). In this respect, it is noteworthy that unpublished data on HPLC (also an "isotope-insensitive" method) show such a well-defined zigzag trend in detection limits and analytical sensitivities of this separation method (Santoyo and Verma, in prep.); i.e., the elements with lower concentrations in nature have lower detection limits, and vice versa. We suggest that any deviations in method detection limits from these zigzag trends must be

TABLE 14. Some Detection-Limit Data from Individual Laboratories
and their Comparison with Some IGRM Compositions

REE	ICP-MS (ng/L) [R1]	ICP-MS (ng/L) [R2]	ICP-MS (ng/L) [R3]	ICP-MS (ng/L) [R4]	ICP-MS (ng/L) [R5]	ICP-MS (ng/L) [R6]	ICP-MS (ng/L) [R6]	ICP-MS (ng/L) [R7]	ICP-MS (ng/L) [R8]	ICP-MS (ng/L) [R9]
La	0.32	75	0.10	10	7	25	7.0	0.30	0.0014	0.022
Ce	0.63	100	0.12	10		6	2.0	0.50	0.0020	0.051
Pr	0.15	90	0.06	10	19	2	0.7	0.30	0.0010	0.007
Nd	0.61	200	0.27	20	3	4	1.0	0.60	0.0058	0.024
(Pm)										
Sm	0.50	200	0.22	40	13	8	3.0	0.70	0.0050	0.018
Eu	0.15	60	0.05	20	10	3	1.0	0.20	0.0030	0.020
Gd	0.33	100	0.21	40	20	6	2.0	0.40	0.0050	0.012
Tb	0.06	30	0.11	10	13	2	0.7	0.06	0.0008	0.003
Dy	0.32	100	0.19	40	24	12	4.0	0.20	0.0020	0.008
Ho	0.06	40	0.15	10	7	1	0.3	0.09	0.0005	0.004
Er	0.22	60	0.25	20	26	10	3.0	0.20	0.0020	0.015
Tm	0.09	10	0.18	10	10	2	0.7	0.05	0.0008	0.005
Yb	0.21	60	0.17	30	25	4	1.0	0.20	0.0020	0.012
Lu	0.12	50	0.13	10	10	3	1.0	0.02	0.0009	0.004

REE	ICP-MS (ng/L) [R10]	ICP-MS (ng/L) [R11]	ICP-AES (µg/L) [R12]	ICP-AES (µg/kg) [R13]	INAA (µg/g) [R14]	NM (µg/g) [R15]	AGV-1 (µg/g) [C1]	W-1 (µg/g) [C1]	JG-1 (µg/g) [C2]	PM-S (µg/g) [C3]
La	0.670	0.05	3.80	13	0.83		37.8	10.9	22.6	2.9
Ce	0.032	0.04	9.40	67	2.50		67.0	22.6	46.6	6.8
Pr	0.008	0.04	9.90	89		0.20	7.30	3.16	5.1	1.08
Nd	0.037	0.29	7.30	18	7.70		32.8	13.9	20.3	5.6
(Pm)										
Sm	0.025	0.07	5.00	27	0.17	0.10	5.90	3.49	4.62	1.8
Eu	0.010	0.03	0.39	8	0.08	0.02	1.67	1.10	0.72	1.07
Gd	0.012	0.05	5.50	47	6.50	0.30	5.03	3.94	4.04	2.0
Tb	0.003	0.02	3.50	35	0.15		0.71	0.64	0.73	0.35
Dy	0.020	0.09	6.00	12			3.61	3.94	3.70	2.1
Ho	0.005	0.02	2.10	32	2.83	0.01	0.67	0.76	0.74	0.42
Er	0.013	0.05	2.50	36		0.06	1.71	2.29	2.00	1.12
Tm	0.005	0.02	2.00	25	0.57	0.02	0.30	0.32	0.36	0.17
Yb	0.018	0.14	0.32	2.8	0.23		1.70	2.10	2.40	1.00
Lu	0.004	0.02	0.14	2.6	0.17		0.27	0.33	0.40	0.16

[1]Ref. (references) are: [R1] = Halicz et al. (1996), detection limit determined using seawater reference material (data plotted in Fig. 11C), method used for determining new REE values in this material; [R2] = Jarvis (1988), detection limit determined using a synthetic REE standard solution, method used for determining REE in IGRM of rocks and minerals; [R3] = Yan et al. (1999), detection limit determined using a synthetic REE standard solution, method used for determining REE in IGRM of rocks and water samples; [R4] = Murty and Chakrapani (1996), detection limit determined using a synthetic REE standard solution, method used for determining REE in groundwater and seawater samples; [R5] = Li et al. (1997), detection limit determined using repeated injections of a blank solution, method used for determining REE impurities in high purity cerium oxide; [R6] = Augagneur et al. (1996), detection limit determined using a synthetic REE standard solution, method used for determining REE in wine samples; [R7] = Augagneur et al. (1996, Table 3, ELAN 5000 column); [R8] = compiled by Balaram (1996); [R9] = Ødegård et al. (1998) using high resolution double-focusing type LA-ICP-MS, detection limit determined using Specpure SiO$_2$ fused sample with 7 parts of Li$_2$B$_4$O$_7$, method used for determining REE in IGRM of rock and minerals; [R10] = Benkhedda et al. (2001) using time-of-flight (TOF) ICP-MS, detection limit determined using repeated injections of a blank solution, average detection limit values for different isotopes reported here, method used for determining REE in saline water reference materials; [R11] = Willie and Sturgeon (2001) using time-of-flight (TOF) ICP-MS, detection limit determined using repeated injections of a blank solution, average detection limit values for different isotopes reported here, method used for determining REE in IGRM of seawater samples; [R12] = Satynarayana (1996), detection limit determined using a synthetic REE standard solution, average detection limit values for La and Dy reported here, method used for determining REE in IGRM of niobate-tantalates and carbonatite samples; [R13] = Rucandio (1997), detection limit determined using a synthetic REE standard solution, most appropriate or recommended isotope used for each element for reporting detection limit values, method used for determining REE in IGRM of rock samples; [R14] = compiled by Balaram (1996); [R15] = Chowdhury et al. (2002) using charged particle activation analysis (CPAA), detection limit were determined but the method not explicitly stated, method used for determining REE in IGRM of rock samples; [C1] = Velasco-Tapia et al. (2001), concentration data for IGRM andesite AGV-1 and diabase W-1; [C2] = Guevara et al. (2001), concentration data for IGRM granodiorite JG-1; [C3] =Verma (1997), concentration data for IGRM microgabbro PM-S.

TABLE 15. Isotopic Characteristics of the REE with Cosmic and Chondrite Abundances

REE	Isotope[1]	Abundance (%)[1]	No. of protons[1]	No. of neutrons[1]	Cosmic [SU56][2]	Cosmic [C59][2]	Cosmic [C82][2]	Cosmic [AE82][2]	Chondrite [MS95][3]
La	139	99.111	57	82	2.00	0.36	0.37	0.448	0.237
	138	0.089	57	81					
Ce	140	88.48	58	82	2.26	1.17	1.2	1.16	0.613
	142	11.08	58	84					
	138	0.25	58	80					
	136	0.19	58	78					
Pr	141	100	59	82	0.40	0.17	0.18	0.174	0.093
Nd	142	27.2	60	82	1.44	0.77	0.79	0.836	0.457
	144	23.8	60	84					
	146	17.2	60	86					
	143	12.2	60	83					
	145	8.3	60	85					
	148	5.7	60	88					
	150	5.6	60	90					
Pm	–	–	61	–	–	–	–	–	–
Sm	152	26.7	62	90	0.664	0.23	0.24	0.261	0.148
	154	22.6	62	92					
	147	15.1	62	85					
	149	13.9	62	87					
	148	11.3	62	86					
	150	7.4	62	88					
	144	3.1	62	82					
Eu	153	52.1	63	90	0.187	0.091	0.094	0.0972	0.056
	151	47.9	63	88					
Gd	158	24.8	64	94	0.684	0.34	0.42	0.331	0.199
	160	21.8	64	96					
	156	20.6	64	92					
	157	15.7	64	93					
	155	14.8	64	91					
	154	2.1	64	90					
	152	0.20	64	88					
Tb	159	100	65	94	0.0956	0.052	0.076	0.0589	0.036
Dy	164	28.1	66	98	0.556	0.36	0.37	0.398	0.246
	162	25.5	66	96					
	163	24.9	66	97					
	161	19.0	66	95					
	160	2.34	66	94					
	158	0.100	66	92					
	156	0.057	66	90					
Ho	165	100	67	98	0.118	0.090	0.092	0.0875	0.055
Er	166	33.4	68	98	0.316	0.22	0.23	0.253	0.160
	168	27.1	68	100					
	167	22.9	68	99					
	170	14.9	68	102					
	164	1.56	68	96					
	162	0.14	68	94					
Tm	169	100	69	100	0.0318	0.035	0.035	0.0386	0.025
Yb	174	31.6	70	104	0.220	0.21	0.20	0.243	0.161
	172	21.9	70	102					
	173	16.2	70	103					
	171	14.4	70	111					
	176	12.6	70	106					
	170	3.16	70	100					
	168	0.14	70	98					
Lu	175	97.4	71	104	0.050	0.035	0.035	0.0369	0.025
	176	2.6	71	105					

[1]Isotopic abundance and other information from Walker et al. (1977).
[2]Cosmic abundances (in the solar system) are in number of atoms per 10^6 atoms of Si; the sources are: SU56 = Suess and Urey (1956); C59 = Cameron (1959) cited in Wedepohl (1971); C82 = Cameron (1982) cited in Anders and Ebihara (1982); AE82 = Anders and Ebihara (1982).
[3][MS95] = After McDonough and Sun (1995), concentration data for CI carbonaceous chondrites in $\mu g/g$.
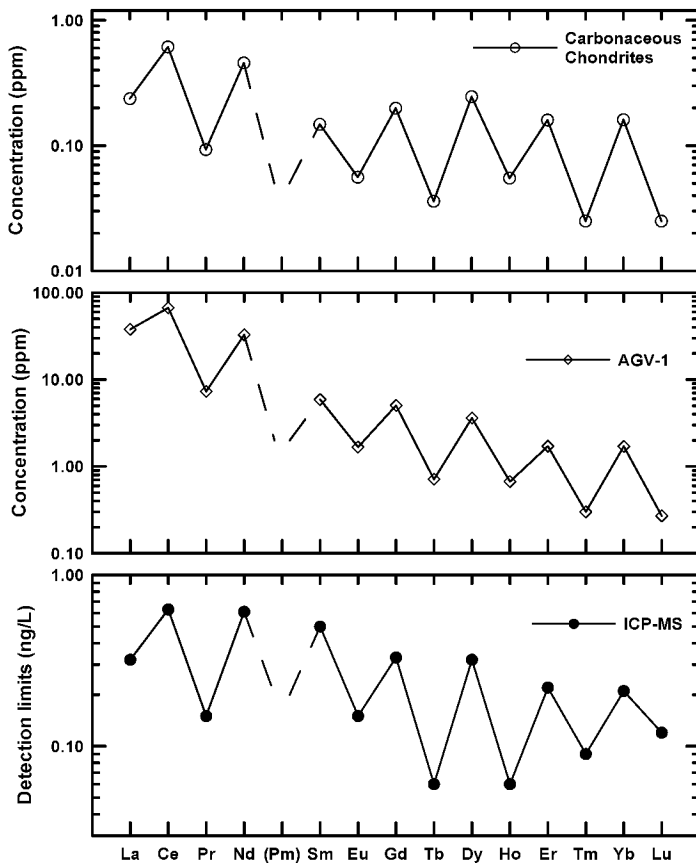
FIG. 11. Concentration multi-element plots for the REE (for data and their sources see Table 15). A. Carbonaceous chondrite data (Table 15). B. IGRM AGV-1 (Table 14). C. Detection limit data for ICP-MS (Table 14; Halicz et al., 1996).

examined with caution, and probably be interpreted as analytical problems in the estimation of these detection limits and the concentrations of the corresponding elements. Caution also is required when computer programs coupled with analytical instruments are used to infer detection limits and other chemometric parameters *without* knowing the details of the methods programmed (e.g., Brereton, 1987).

The zigzag patterns of both concentration and lower limit data presented and emphasized in this paper, mean that, for some unknown reason, nature itself is helping us to decipher its secrets. If this were *not* the case—i.e., if the detection limits kept constant values from La to Lu, and did not follow the zigzag trend—it would have been difficult, if

not impossible, to quantify the heavy REE (Ho to Lu), with considerably lower abundances than the light (La to Nd) or middle REE (Sm to Dy). Although, at present, we do not have a clear explanation for the results related to the detection limits, we consider that these findings, reported or emphasized for the first time in the geological literature, are important by themselves. In the absence of a better explanation, we hypothesize that probably it is the "odd-even" effect (which once governed the creation process of the chemical elements and is probably still governing them in stars) that also governs the analytical process of their quantification, irrespective of the actual physical or chemical mechanism operating in a given instrumentation.

Conclusions

The following points emerge from this review of REE methods and statistical treatment of compiled data.

1. The methods most frequently employed in the determination of the REE include MS, NM, and ES, although the SM group has shown great potential as a cheap, rapid, precise, and accurate group of methods.

2. FX, AA, and classical CL methods are not generally recommended for the determination of the REE, unless they are accompanied by quantitative group-separation procedures and tests for accuracy.

3. The proportion of outliers in the IGRM studied in the present work is generally low (< 6%). Their detection and elimination by the skewness and kurtosis tests are successful in obtaining final statistical samples with a normal distribution.

4. Comparable inter-laboratory high-average precision (better than 10%) is obtained for La, Ce, and Sm by MS, NM, and ES; Nd and Dy by MS and ES; and Gd, Ho, and Yb by ES.

5. Medium values of inter-laboratory average precision (between 10% and 15%) are obtained for Pr by MS and ES; Nd by NM; Eu by all methods; Gd and Yb by MS and NM; Tb, Ho, and Er by MS; and Lu by NM and ES.

6. Low inter-laboratory average precision (more than 15%) is shown by results for Tb, Dy, and Ho for NM; Er by ES; Tm by MS and NM; and Lu by MS.

7. Pr and Er are not generally analyzed by NM; and Eu and Er not by ES.

8. Detection limits for the three main groups of methods (MS, NM, and ES) are generally in the sub-ppm range. Lowest values are found for seven lanthanides (Ce, Pr, Nd, Tb, Dy, Ho, and Er) by MS and for five lanthanides (La, Sm, Eu, Yb, and Lu) by NM.

9. Although, with two exceptions (La slope in MS-ES and Lu intercept in MS-ES), no overall significant bias was found between the MS, NM, and ES groups in the analysis of the REE, the Student's t-test revealed very significant differences (at 99% confidence level, and even at 99.9%) for some REE in a few IGRM. For them, it is recommended that the analytical data be treated separately to draw mean concentration method values, and probably assign the most precise method mean value as the concentration in the IGRM.

10. Statistical procedures are also successfully applied to evaluate analytical methods such as FX and LC using the data from well-established methods (MS, NM, and ES).

11. Method detection limits from inter-laboratory data as well as those obtained from individual laboratories world-wide, show the same zigzag pattern as depicted by REE concentrations in a wide variety of geological and cosmological materials, and probably means that the "odd-even" effect that governed the abundances of the chemical elements and their isotopes during the creation of the solar system, also governs the analytical detection and quantification process.

Acknowledgments

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