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CCRMP
Canadian Certified Reference Materials Project

PCMRC
Projet canadien de matériaux de référence certifiés

# Certificate of Analysis

First issued: January 2016 Version: January 2016

# REE-2

## Certified Reference Material for a Carbonatite with Rare Earth Elements

### Table 1 – REE-2 Certified Values

***note: For each element, please refer to its footnote which indicates the analytical methods used to determine its certified, provisional or indicative value. For more detailed information, please refer to the certification report.***

| Analyte | Units | Mean | Within-lab Standard Deviation | Between-labs Standard Deviation | 95% Confidence Interval of Mean |
|---|---|---|---|---|---|
| Al [a] | % | 0.761 | 0.015 | 0.049 | 0.020 |
| Ba [b] | % | 5.02 | 0.08 | 0.29 | 0.15 |
| Ca [a] | % | 13.68 | 0.16 | 0.37 | 0.16 |
| Ce [a] | µg/g | 9610 | 140 | 360 | 160 |
| Co [a] | µg/g | 7.71 | 0.31 | 0.51 | 0.27 |
| Dy [a] | µg/g | 69.2 | 1.4 | 1.6 | 0.8 |
| Er [a] | µg/g | 14.0 | 0.4 | 1.6 | 2.1 |
| Eu [a] | µg/g | 96.6 | 1.7 | 5.8 | 2.5 |
| Fe [a] | % | 12.14 | 0.17 | 0.42 | 0.17 |
| Ho [a] | µg/g | 7.87 | 0.20 | 0.56 | 0.25 |
| La (total) [b] | µg/g | 5130 | 80 | 110 | 50 |
| Li [a] | µg/g | 9.61 | 0.54 | 0.59 | 0.43 |
| Loss on ignition [c] | % | 31.38 | 0.07 | 0.19 | 0.11 |
| Mg (total) [b] | % | 6.26 | 0.06 | 0.21 | 0.10 |
| Mn (total) [b] | % | 1.316 | 0.015 | 0.051 | 0.024 |

*cont'd*

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## Table 1 – REE-2 Certified Values *cont'd*

| Analyte | Units | Mean | Within-lab Standard Deviation | Between-labs Standard Deviation | 95% Confidence Interval of Mean |
|---|---|---|---|---|---|
| Nd [a] | µg/g | 3660 | 60 | 170 | 70 |
| P [a] | % | 0.461 | 0.006 | 0.024 | 0.011 |
| Pr [a] | µg/g | 1075 | 22 | 52 | 26 |
| Rb [a] | µg/g | 1.22 | 0.17 | 0.24 | 0.13 |
| S(total) [d] | % | 1.745 | 0.041 | 0.092 | 0.057 |
| Sc [a] | µg/g | 57.5 | 1.1 | 3.6 | 2.0 |
| Si (total) [b] | % | 1.377 | 0.020 | 0.053 | 0.030 |
| Sm [a] | µg/g | 410 | 6 | 16 | 7 |
| Sn [a] | µg/g | 24.1 | 1.0 | 3.3 | 1.5 |
| Sr [a] | µg/g | 2300 | 40 | 210 | 80 |
| Ta [a] | µg/g | 1.17 | 0.11 | 0.25 | 0.15 |
| Tb [a] | µg/g | 20.3 | 0.4 | 1.4 | 0.7 |
| Th [a] | µg/g | 737 | 12 | 34 | 14 |
| Ti [b] | % | 0.1969 | 0.0048 | 0.0096 | 0.0049 |
| Tm [a] | µg/g | 1.383 | 0.042 | 0.044 | 0.022 |
| U [a] | µg/g | 3.73 | 0.13 | 0.27 | 0.12 |
| W [a] | µg/g | 9.9 | 0.6 | 1.3 | 0.9 |
| Y [a] | µg/g | 176 | 3 | 13 | 6 |

*a the data generally includes sets by digestion using four acids (hydrochloric, nitric, hydrofluoric and perchloric); various fusions; and for some elements, fused pellet, fusion or pressed powder pellet followed by x-ray fluorescence; and instrumental neutron activation analysis*

*b the data generally includes sets by various fusions, and fused pellet or fusion followed by x-ray fluorescence*

*c the data is based on samples of 0.8 to 2 grams ignited for 0.5 to 4 hours at 650 to 1050°C*

*d the data generally includes sets by combustion followed by infrared spectroscopy and various fusions*

## Table 2 – REE-2 Provisional Values

| Analyte | Units | Mean | Within-lab Standard Deviation | Between-labs Standard Deviation | 95% Confidence Interval of Mean |
|---|---|---|---|---|---|
| Be [a, b] | µg/g | 3.31 | 0.14 | 0.14 | 0.13 |
| Bi [c] | µg/g | 2.00 | 0.10 | 0.39 | 0.22 |
| C [d] | % | 9.06 | 0.06 | 0.26 | 0.17 |
| Cd | µg/g | 1.11 | 0.10 | 0.24 | 0.19 |
| Cr (total) [e] | µg/g | 32.7 | 1.3 | 8.7 | 7.3 |
| Cu (AD) [a, f, g] | µg/g | 5.55 | 0.44 | 0.44 | 0.27 |
| Gd [b] | µg/g | 219 | 4 | 21 | 10 |
| Hf [b, c] | µg/g | 0.95 | 0.39 | 0.39 | 0.17 |
| In [b] | µg/g | 1.403 | 0.055 | 0.063 | 0.056 |
| K [b] | % | 0.0172 | 0.0021 | 0.0050 | 0.0040 |
| Lu [b] | µg/g | 0.92 | 0.03 | 0.16 | 0.07 |
| Mo | µg/g | 154 | 3 | 13 | 6 |
| Na [b, c] | % | 0.120 | 0.008 | 0.025 | 0.013 |
| Nb [b] | µg/g | 1060 | 30 | 130 | 60 |
| Ni (AD) [a, f] | µg/g | 8.99 | 0.28 | 0.70 | 0.75 |
| Ni (total) [a, e] | µg/g | 13.1 | 1.6 | 2.7 | 2.4 |
| Pb [c] | µg/g | 40.8 | 3.2 | 9.6 | 4.3 |
| Sb [b, c] | µg/g | 0.89 | 0.06 | 0.14 | 0.09 |
| Tl [b] | µg/g | 0.240 | 0.009 | 0.036 | 0.028 |
| V (total) [e] | µg/g | 79 | 2 | 16 | 8 |
| Yb [b] | µg/g | 7.2 | 0.2 | 1.0 | 0.5 |
| Zn (AD) [f] | µg/g | 369 | 13 | 47 | 34 |
| Zn (total) [e] | µg/g | 420 | 11 | 62 | 38 |
| Zr (total) [e] | µg/g | 32.2 | 3.2 | 7.9 | 4.3 |

***a** statistical analysis of the data warrants classification as provisional despite only 6 or 7 sets of data*

***b** the data generally includes sets by digestion using four acids (hydrochloric, nitric, hydrofluoric and perchloric), various fusions and; for some elements, fused pellet, fusion or pressed powder pellet followed by x-ray fluorescence*

***c** data fulfills the conditions for certified but the element was reclassified as provisional since the between-laboratories standard deviation is 15% or more of the mean; and/or a considerable amount of data consists of one significant figure*

***d** the data was generally obtained from a combustion infrared apparatus*

***e** the data generally includes sets by various fusions; and for some elements, fused pellet, fusion or pressed powder pellet followed by x-ray fluorescence*

***f** the data includes digestion using two acids (nitric and hydrochloric) and four acids*

***g** the data for copper using acid digestions appears to yield a lower value than that by fusion. However, due to lack of agreement, it was not possible to assign a total value*

## Table 3 – REE-2 Indicative Values (semi-quantitative only)

| Analyte | Units | Mean | No. accepted laboratories / values |
|---|---|---|---|
| Ag | µg/g | 1 | 5 / 25 |
| Cr (AD4) [a] | µg/g | 14 | 5 / 25 |
| Cs [b] | µg/g | 0.09 | 7 / 35 |
| Ga [a] | µg/g | 60 | 3 / 15 |
| Ge [b] | µg/g | 7 | 5 / 35 |
| La (AD4) [a] | µg/g | 4600 | 4 / 20 |
| Mg (AD4) [a] | % | 5.7 | 5 / 25 |
| Mn (AD4) [a] | % | 1.1 | 5 / 25 |
| Moisture [c] | % | 0.4 | 13 / 65 |
| S (AD4) [a] | % | 0.7 | 3 / 15 |
| V (AD4) [a] | µg/g | 60 | 4 / 20 |
| Zr (AD4) [a] | µg/g | 20 | 4 / 20 |

***a the data includes sets by digestion using four acids (hydrochloric, nitric, hydrofluoric and perchloric) only***
***b the data includes sets by digestion using four acids and various fusions***
***c the data was obtained from samples of 0.8 to 2 grams dried for 0.5 to 4 hours at 105°C***

**SOURCE**
REE-2 is a carbonatite with rare earth elements obtained from a Canadian mining company.

**DESCRIPTION**
The mineral species include: dolomite (35.4%); ankerite (22.6%); siderite (13.0%); barite (8.6%); chlorite (5.0%); apatite-REE and calcite (each at 3.1%); hornblende (1.7%); pyrite (1.3%); fergusonite (1.1%); allanite (0.9%); galgenbergite and monazite (each at 0.6%); apatite and magnetite (each at 0.4%); rutile-Nb (0.3%); hastingsite, parisite, quartz and Y-Ti-niobate (each at 0.2%); bastnaesite , biotite, Ca-Fe-REE, Ca-Ti-Ce-Nd-silicate, chevkinite, hematite, sphalerite, titanite-REE and Y-Ca-silicate (each at 0.1%); annite and Ca-betafite (each at 0.03%); molybdenite and titanite (each at 0.02%); ilmenite, orthoclase and thorite (each at 0.01%).

**INTENDED USE**
REE-2 is suitable for the analysis of rare earth elements and other elements in ores at concentrations ranging from major, minor to trace levels. Examples of intended use include quality control and method development.

**INSTRUCTIONS FOR USE**
REE-2 should be used “as is”, without drying. The contents of the bottle should be thoroughly mixed before taking samples. The values herein pertain to the material when produced. CanmetMINING is not responsible for changes occurring after shipment.

**HANDLING INSTRUCTIONS**
Normal safety precautions for handling fine particulate matter are suggested, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

## METHOD OF PREPARATION

After crushing, milling and sieving, the recovery of the minus 75 µm fraction was 70%. The product was blended, and then bottled in 100-gram units. This is the only size that is available.

## HOMOGENEITY

The homogeneity of the stock was investigated using fifteen bottles chosen according to a stratified random sampling scheme. Three subsamples were analyzed from each bottle. Subsamples of 0.05 grams were digested using hydrochloric, nitric and hydrofluoric acids in a microwave oven, and analyzed by inductively coupled plasma – atomic emission spectroscopy for calcium and cerium; and by inductively coupled plasma – mass spectrometry for erbium, samarium and thorium.

Use of a smaller subsample than specified above will invalidate the use of the certified values and associated parameters. A one–way analysis of variance technique (ANOVA)[1] and statistical analyses were used to assess the homogeneity of these elements. No significant between-bottle variation was observed for all elements.

## CERTIFIED VALUES

Twenty-one industrial, commercial and government laboratories participated in an interlaboratory measurement program using methods of their own choice.

Methods for the determination of the elements included digestion with various combinations of acids on a hot plate; and various types of fusions followed by the determination using inductively coupled plasma – atomic emission spectroscopy and inductively coupled plasma – mass spectrometry. Instrumental neutron activation analysis and X-ray fluorescence on a pressed powder pellet, fused pellet or after a fusion were used for many elements.

The concentration of carbon was determined using combustion followed by infrared spectrometry.

The concentration of sulphur was determined using combustion followed by infrared spectrometry; acid digestion using four acids or fusions followed by inductively coupled plasma – atomic emission spectroscopy, inductively coupled plasma – mass spectrometry or X-ray fluorescence.

ANOVA was used to calculate the consensus values and other statistical parameters from the data from interlaboratory measurement program. Values are deemed to be certified if derived from 10 or more sets of data that meet CCRMP's statistical criterion regarding the agreement of the results. Thirty-three analytes were certified (see Table 1).

Full details of all work, including the statistical analyses, the methods and the names of the participating laboratories are contained in the Certification Report. For more details on how to use reference material data to assess laboratory results, users are directed to ISO Guide 33:2015, pages 14-17, and the publication, "Assessment of laboratory proficiency using CCRMP reference materials", at www.cccrmp.ca.

## UNCERTIFIED VALUES

Twenty-four provisional values (Table 2) were derived from 8 or 9 sets of data that fulfill the CCRMP statistical criterion regarding agreement; or 10 or more sets of data, that do not fulfill the CCRMP statistical criteria required for certification; or 6 or 7 sets of data for which the statistical analysis of the data warranted provisional status. This latter group includes beryllium; and both copper and nickel, specifically by acid digestion. Indicative values for 12 analytes, shown in Table 3, were derived from the means of a minimum of 3 sets of data.

## TRACEABILITY

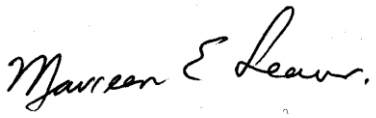
The values quoted herein are based on the consensus values derived from the statistical analysis of the data from the interlaboratory measurement program, and the standards used by the individual laboratories. The report gives the available details.

**CERTIFICATION HISTORY**
REE-2 was released as a new material in January 2016.

**PERIOD OF VALIDITY**
The certified values are valid until January 30, 2036.

**LEGAL NOTICE**
CanmetMINING has prepared this reference material and statistically evaluated the analytical data of the interlaboratory measurement program to the best of its ability. The purchaser, by receipt hereof, releases and indemnifies CanmetMINING from and against all liability and costs arising out of the use of this material and information.

**CERTIFYING OFFICERS**



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**FOR FURTHER INFORMATION**
The Certification Report is available free of charge upon request to:

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**REFERENCES**
1. Brownlee, K.A., Statistical Theory and Methodology in Science and Engineering; John-Wiley and Sons, Inc.; New York; 1960.