# II-WORKSHOP OF INORGANIC MASS SPECTROMETRY – 2017

# Pb-Sr-NdISOTOPIC CHARACTERIZATION OF USGS REFERENCE MATERIALS BY TIMS AT CPGeo-USP

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Systematic analyses of Pb, Nd and Srisotopic compositions of USGS Reference Materials (BCR-1 and AGV-1) were carried out at the Geochronological ResearchCenter (CPGeo- USP). These measurements were performed either on a Thermo Triton or on Finnigan MAT 262 Thermal Ionization Mass Spectrometers (TIMS).

All chemical procedures were performed in class 10,000 clean room equipped with class 100laminar flow hoods.About 50 mg of rock powder was dissolved with HF, $HNO_3$ and HCl in Savillex® beakers on hot plate at 100 $^{o}$C.Pb, Sr, and Nd from the same sample solution were purified using the ion exchange chromatographic technique.The first stage was the separation of Pb from the others elements using an anion exchange resin AG1-X8 (Biorad®). The rinses discarded from this column were then dried down and reconstituted for exchange separation of Sr, using Sr Spec resin (Eichrom®), from the bulk solution. The rinses discarded from Sr Spec column were then processed through RE resin (Eichrom®) to separate rare earth elements. Nd was separated using Ln resin (Eichrom®).Each solution with the eluted element was dried down and loaded onto filaments for mass spectrometry measurements.

Pb isotopic compositions were measured on a multicollectorFinnigan MAT 262 Mass Spectrometer at 1200 – 1300 $^{o}$C. Samples were loaded on degassed Re filaments (99.995 % H. Cross®) with $H_3PO_4$ and silica gel. Single analysis consisted of 60 ratios. The mass fractionation factor of 0.11 %/amu was calculated based on the average measurements of NIST SRM 981 ratioscompared to the values proposed by Todt [1]. The reference material SRM 981 was run in every barrel and ion beam intensities for $^{208}$Pb were always higher than 2 V.

Sr isotopic analyses were carried out using degassed single Ta filament (99.959 % H. Cross®). Sr determinations were performed on a static mode multicollectorThermoTriton Mass Spectrometer at 1300 to 1500 $^{o}$C. The$^{87}$Sr/$^{86}$Sr ratios were normalized to the value of $^{86}$Sr/$^{88}$Sr = 0.1194 [2]using an exponential law. Also these measured ratios were corrected for Rb interference. Ion beam intensities of $^{88}$Sr for NIST SRM 987 standard were always higher than 1 V.

Nd isotopic analyses were performed on a Thermo Triton Mass Spectrometer using degassed double Re filaments (99.995 % H. Cross®) at ~ 1630 $^{o}$C. The $^{143}$Nd/$^{144}$Nd ratios were normalized to the value of $^{146}$Nd/$^{144}$Nd = 0.7219 [3], using an exponential law. Ion beam intensities of $^{145}$Nd for JNdi-1 standard were always higher than 1 V.

Pb, Sr and Nd Isotope Standards data from the last 12 months are presented. Analyses of NIST SRM 981 common Pb standard (n=46) yielded $^{206}$Pb/$^{204}$Pb = 16.897 ± 0.006, $^{207}$Pb/$^{204}$Pb = 15.438 ± 0.008, $^{208}$Pb/$^{204}$Pb = 36.532 ± 0.025 (average ± SD).

Individual runs of SRM 981 present daily variation due to instrument mass fractionation. The main reason for the difference in overall reproducibility is that among the four stable lead isotopes, only $^{204}Pb$ is non radiogenic so there is no naturally invariant ratio that can be used for internal normalization. Instrumental mass fractionation can only be estimated by analysis of standards and a general correction applied to all measurements with the implicit assumption that fractionation behavior is identical for all samples and standards [1].

Analyses of NIST SRM 987 Sr standard (n=38) yielded $^{87}Sr/^{86}Sr$ value of 0.710241 ± 0.000016 (average ± SD).

Replicate analyses of JNdi-1 Nd standard (n=28) showed$^{143}Nd/^{144}Nd$ ratios of 0.512103 ± 0.000003 (average ± SD).

Isotope standard data acquired for NIST SRM 987 and JNdi-1, over the analytical period, generate concordant ratios with certified values, i.e.: $^{87}Sr/^{86}Sr$ = 0.71034 ± 0.00026 (NIST certified value) and $^{143}Nd/^{144}Nd$= 0.512115 ± 0.000007 [4].

The isotopic compositions of USGS reference materials (BCR-1 and AGV-1)obtained during this study and the certified values are presented in Table 1.

Table 1. Data obtained for reference materials (AGV-1and BCR-1) during this study

| IsotopeRatios | ThisStudy | | Referencevalues |
|---|---|---|---|
| AGV-1 | | | |
| $^{87}Sr/^{86}Sr$ | 0.703981 ± 0.000047 | n=15 | 0.703996 ± 0.000020[5] |
| $^{143}Nd/^{144}Nd$ | 0.512782 ± 0.000010 | n=15 | 0.512784 ± 0.000018[5] |
| $^{206}Pb/^{204}Pb$ | 18.931 ± 0.013 | n=10 | 18.938 ± 0.003[6] |
| $^{207}Pb/^{204}Pb$ | 15.647 ± 0.019 | n=10 | 15.650 ± 0.004[6] |
| $^{208}Pb/^{204}Pb$ | 38.541 ± 0.062 | n=10 | 38.554 ± 0.019[6] |
| BCR-1 | | | |
| $^{87}Sr/^{86}Sr$ | 0.705026 ± 0.000037 | n=7 | 0.705025 ± 0.000019[5] |
| $^{143}Nd/^{144}Nd$ | 0.512628 ± 0.000005 | n=15 | 0.512629 ± 0.000014[5] |
| $^{206}Pb/^{204}Pb$ | 18.791 ± 0.021 | n=10 | 18.817 ± 0.005[6] |
| $^{207}Pb/^{204}Pb$ | 15.627 ± 0.007 | n=10 | 15.631 ± 0.004[6] |
| $^{208}Pb/^{204}Pb$ | 38.689 ± 0.023 | n=10 | 38.720 ± 0.014[6] |

Note: Errors are reported as 2 standard deviation on the mean.

The Pb, Nd, and Sr isotopic ratios obtained at CPGeo agree with the certified values of the AGV-1 and BCR-1USGS reference materials.However, Pb average isotopic composition for AGV-1 and BCR-1 show precision (2SD) between 318 and 1617 ppm. These data confirm heterogeneous lead isotope compositions in the first generation of the Reference Materials [5,7,8].

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