

NEW Sm/Nd TECHNIQUE USING $^{149}\text{Sm}/^{145}\text{Nd}$ AS A COMBINED SPIKE

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INTRODUCTION

The fundamentals of Sm/Nd methodology of dating was entirely developed during early 1970 years (DePaolo, 1988; Kawashita and Torquato, 1998). In order to get precise $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, Sm and Nd are separated using two different exchange resin columns. In the first column the REE is separated from anions and mono and bivalent elements, among them rubidium and strontium. In the second column, Nd is separated from Sm, an hard task requiring usually more than 5 hours (Patchett and Ruiz, 1987). After has dried down, the spiked Sm and Nd are loaded onto two different filaments to get the corrected isotope ratios using a solid source mass spectrometer and then is calculated the above ratios using the well known equations of isotope dilution method.

In our technique, the Sm and Nd are not separated using the second column. Both spiked elements that appear incorporated with other REE are loaded onto one of tantalum side filaments and analyzed simultaneously. In order to avoid isobaric interferences in the mass 144 and 150, an enriched (ca. 90% purity) ^{145}Nd is used as spike for ^{144}Nd determinations, whereas ^{149}Sm (ca. 98% enrichment) combined with ^{145}Nd spike is used for ^{147}Sm content determinations. Because of the interferences on mass 144, including from tracer, is not possible to calculate a precise $^{143}\text{Nd}/^{144}\text{Nd}$ of the sample. In our case this ratio was obtained on unspiked solution, but derived from ratios $^{143}\text{Nd}/^{145}\text{Nd}$ and $^{145}\text{Nd}/^{146}\text{Nd}$. The last ratio was used for normalization purpose, likely in the conventional technique which assume $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The derived $^{143}\text{Nd}/^{144}\text{Nd}$ is obtained multiplying the normalized $^{143}\text{Nd}/^{145}\text{Nd}$ by a constant factor of 0.348403. This factor represents an average of 45 independent runs in two internal reference samples (SPEX and Johnson Matthey) for conventionally normalized $^{145}\text{Nd}/^{144}\text{Nd}$ ratios. We opted for this approach with the main purpose to keep the usual data and making ease the task of routine calculations and parameter (e.g. ϵNd) comparisons. The results obtained on three different samples, a tonalite (BR-126/8), a granite (PC-0025A) and including an international reference sample BHVO-2 basalt, illustrate the performance characteristics and validity of using this technique.

FUNDAMENTALS AND CHARACTERISTICS OF TECHNIQUE USING ^{145}Nd AS A TRACER

One advantage to use ^{145}Nd as a tracer is that is the less abundant (ca. 8.29%) among without isobaric interferences. For ^{147}Sm determinations ^{149}Sm as a spike should be recommended because is not interfered and is less abundant than other alternative represented by ^{147}Sm . Since the both spikes in combined form are free of isobaric interferences from other REE induced us to try this present experiment, i.e. carry out the isotopic measurements of 5 isotopes of Sm and Nd without classical separation of these elements using a second resin column. The whole REE is loaded in one of tantalum side filaments of triple arrangement (Ta,Re,Ta). The required currents to run simultaneously Nd and Sm were around 4.5 and 2.5 A, respectively for central and side filaments. The ionization efficiency was apparently better for Nd. The other elements seemed that did not inhibit the ionization of both elements of interest. The only care is control the barium emission, since one of oxide compounds correspond to mass 143. Barium is always present and can be monitored observing the 138 mass current. Generally, 100 to 150 ratios obtained in static mode with ^{146}Nd current equivalent to around 0.5 V and standard errors between 7 to 15 ppm were currently obtained on normalized ratios. The Sm signal intensities were slightly lower (0.1 to 0.3 V) and hence, the standard errors for Sm ratio was higher of ca. 20 to 30 ppm after normalization using the same normalizing factor applied for Nd. This procedure has revealed valid since the Sm and Nd appear almost simultaneously and fractionated at same level during the run. Only, when the standard error were higher than 30 ppm, this correction procedure has revealed inadequate and, the alternative was to use the two or three first blocks of 10 ratios. The Sm ratio can not be normalized by ratio observed on $^{147}\text{Sm}/^{152}\text{Sm}$ ratio because of three possible and variable interferences as is illustrated bellow. The interested ratios without or corrected for eventual isobaric interferences for the present work are: $^{147}\text{Sm}/^{149}\text{Sm}$, $^{143}\text{Nd}/^{145}\text{Nd}$, $^{145}\text{Nd}/^{146}\text{Nd}$ and $^{143}\text{Nd}/^{146}\text{Nd}$. An adequate ratio (e.g. 0.710) can be assumed for $^{143}\text{Nd}/^{146}\text{Nd}$ to normalize the other three ratios.

Isotopic results were measured with a multi-collector VG Sector 54 Mass Spectrometer. The cup configuration adopted in the present work and named Sm & Nd 146 Axial is illustrated in Table 1. Some isobaric interferences could be serious to our technique. They are ^{152}Gd and oxide compounds of barium and cesium. Fortunately, barium and cesium are bivalent and univalent elements, hence mostly are eluted before the REE which are trivalent. Even, if present as is common,

both elements can be burn out previously at lower temperature required for Sm and Nd emissions. Indeed, taking in account these facts, only 5 collectors (L3, L1, AXIAL, H1 and H2) are required for static or dynamic measurements. The configuration illustrated in Table 1 and adapted for the present work is very practical, since the classical method using for example ^{150}Nd or ^{148}Nd as spike can be used without any change, with exception for normalizing factor.

Table 1 – Cup configuration adopted in the present work.

Coletores	L4	L3	L2	L1	Axial	H1	H2	H3	H4
Isótopos	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{149}Sm	^{150}Nd	^{152}Sm
Interferentes	^{142}Ce		^{144}Sm		BaO		(Ba, Cs)O	^{150}Sm	^{152}Gd , (Ba, Ce)O

Table 2 – Sm-Nd data for the samples using the combined tracer of the LGI-UFRGS.

Average of 3 independent determinations following the convencional method. a.The combined tracer used was RS-1A; b.The combined tracer used was RS-1B. c. Relative standard error (ppm): $\text{SE} = [\sum \delta_i^2 / n(n-1)]^{1/2} \times 10^6$.

Sample	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	Error (ppm) ^c	$\epsilon_{\text{Nd}(0)}$	T_{DM} (Ma)
Tonalite ^a	2,58	15,15	0,1034	0,512428	18	-4,1	847
Granite ^a	8,52	51,41	0,1009	0,511527	13	-21,5	2020
Basalt ^b	5,79	23,26	0,1504	0,513063	9	8,29	-

Table 3 – Sm-Nd isotopic results for the three selected samples using the combined tracer RS-6. Average of 3 independent determinations following the suggested method

Sample	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	Error (ppm)	$\epsilon_{\text{Nd}(0)}$	T_{DM} (Ma)
Tonalite	2,83	16,56	0,1040	13	-2,07	726
Tonalite	2,78	16,34	0,1035	12	-2,07	722
Tonalite	2,78	16,33	0,1036	16	-2,07	723
Mean	2,80	16,41	0,1037	14	-2,07	724
Granite	9,03	54,41	0,1015	10	-22,66	2144
Granite	9,28	55,32	0,1021	13	-22,66	2156
Granite	9,22	55,13	0,1017	11	-22,66	2149
Mean	9,18	54,95	0,1018	11	-22,66	2149
Basalt	5,35	21,44	0,1518	13	6,59	-
Basalt	4,99	20,10	0,1510	8	6,59	-
Basalt	4,98	20,16	0,1503	9	6,59	-
Mean	5,11	20,57	0,1510	10	6,59	-

Table 4 – Results for the $(^{143}\text{Nd}/^{145}\text{Nd})_n$ and $(^{143}\text{Nd}/^{144}\text{Nd})_{d,n}$ on unspiked sample.

Sample	$(^{143}\text{Nd}/^{145}\text{Nd})_n$	$(^{143}\text{Nd}/^{144}\text{Nd})_{d,n}$
Tonalite	1,471089	0,512532
Granite	1,468059	0,511476
Basalt	1,472364	0,512976

RESULTS AND CONCLUSIONS

Three previous analyzed samples using the conventional technique which is described in Table 2 were selected. The RS-1A and RS-1B are a combined $^{149}\text{Sm}/^{150}\text{Nd}$ spike solution of similar concentrations which has been used in the conventional technique. The combined $^{149}\text{Sm}/^{145}\text{Nd}$ spike solution was designated as RS-6 and the concentrations calibrated against normal solutions were 2.5466 ($\pm 0.020\%$) ppm and 0.7258 ($\pm 0.13\%$) ppm, for Nd and Sm spikes, respectively. The results obtained using also this combined spike for comparison purposes are illustrated in Table 3.

The normalized $^{143}\text{Nd}/^{144}\text{Nd}$ required for model age calculations is obtained through unspiked sample analysis using the equation 1, the results are illustrated in Table 4.

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_n = \left(\frac{^{143}\text{Nd}}{^{145}\text{Nd}} \right)_n \left(\frac{^{145}\text{Nd}}{^{144}\text{Nd}} \right)_N \quad (1)$$

Where $(^{143}\text{Nd}/^{145}\text{Nd})_n$ is the normalized ratio assuming $^{145}\text{Nd}/^{146}\text{Nd} = 0,48262$ and $(^{145}\text{Nd}/^{144}\text{Nd})_N = 0,348403$ (average of 45 independent determinations on internal Nd reference samples from Spex and Jhonson Matthey).

Regarding the Sm-Nd method, the most important data is the ratio $^{143}\text{Nd}/^{144}\text{Nd}$ and, secondary the $^{147}\text{Sm}/^{144}\text{Nd}$. Usually the Nd ratio is obtained with standard error close to 10ppm, while the Sm/Nd error is much more higher because involve spike content calibrations besides the adequate spiking and ratio error

determinations. Most of laboratories exhibit standard deviations close to 0.1% for this ratio as in the present study which are in the range 0.029 to 0.155%. However the Sm/Nd ratios are not generally agreeing at 2σ level when compared with results obtained on conventional method. The most significant discrepancies occur with Sm and Nd content determinations, in special with BHVO-2 basalt. We believe that possible reasons are lack of homogeneity in master solutions and/or samples and partial digestion. Despite of these facts is worthy to observe the calculated T_{DM} model ages and also the ϵ_{Nd} parameter. They are within the expected values. This new technique, could be perfectly used when the main purpose is to get model ages. If you are intending to get precise results for internal isochron the present protocol has to be evaluated better. Optimistically, we have no major objection to adopt the present methodology, in special for laboratories where the Rb-Sr method is in routine use.

REFERENCES

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RESUMO

Este trabalho discorre sobre o desenvolvimento de uma nova técnica para análise isotópica de Sm-Nd com uso de um traçador combinado de $^{145}\text{Nd}/^{149}\text{Sm}$ e de somente da coluna primária para separação dos ETR. A razão $^{143}\text{Nd}/^{144}\text{Nd}$ necessária para idades, é obtida em amostras sem traçador, enquanto que a razão $^{147}\text{Sm}/^{144}\text{Nd}$ é calculada a partir da razão $^{147}\text{Sm}/^{149}\text{Sm}$ e das razões de Nd ($^{143}\text{Nd}/^{145}\text{Nd}$, $^{143}\text{Nd}/^{146}\text{Nd}$ e $^{145}\text{Nd}/^{146}\text{Nd}$) medidas simultaneamente sem nenhuma interferência isobárica. A razão $^{143}\text{Nd}/^{144}\text{Nd}$ é derivada da multiplicação da razão $^{143}\text{Nd}/^{145}\text{Nd}$ obtida na amostra natural normalizada para $^{145}\text{Nd}/^{146}\text{Nd}=0,482620$ (média de 45 análises independentes em duas amostras de referência laboratorial). por um fator constante de 0,348403. A razão $^{147}\text{Sm}/^{149}\text{Sm}$ e as razões de Nd são obtidas simultaneamente utilizando um arranjo triplo de filamentos. A configuração dos coletores requerida para as medidas das razões é a mesma da utilizada para as análises independentes de Sm e Nd no convencional. A presença de outros ETR não interferiu na eficiência de ionização, sendo as emissões do Sm e do Nd praticamente simultâneas. Esse fato implica que para corrigir o fracionamento observado na razão $^{147}\text{Sm}/^{149}\text{Sm}$ pode-se usar a razão do Nd de normalização e depois desnormalizada para o data reduction. Esse método analítico foi aplicado em três amostras pré-selecionadas. A razão $^{143}\text{Nd}/^{144}\text{Nd}$ calculada e a idade T_{DM} são concordantes quando comparadas aos valores obtidos pelo método convencional. Pequenas discrepâncias, provavelmente atribuíveis à não homogeneização da solução final, podem ser irrelevantes, uma vez que as razões $^{147}\text{Sm}/^{144}\text{Nd}$ e $^{143}\text{Nd}/^{144}\text{Nd}$ derivada estão dentro dos erros experimentais (2σ).