Whole-rock geochemistry and Sr-Nd isotopic composition of the pre-rift sequence of the Camamu Basin, northeastern Brazil
Whole-rock geochemistry and Sr–Nd isotopic composition of the pre-rift sequence of the Camamu Basin, northeastern Brazil

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Abstract

Whole-rock geochemistry, combined with Sr–Nd isotopic composition of pelitic sedimentary rocks, have been considered to be useful parameters to estimate not only their provenance but also to make inferences about their depositional environment as well as the weathering processes they have been through. The basal sedimentary units of the basins of the northeastern Brazilian continental margin, particularly those of the pre-rift sequence, have been subject of interest of studies based on chemical and isotopic data, since they lack fossil content to establish their age and, therefore, stratigraphic correlations are difficult. The major and trace element contents as well as Sr–Nd isotopic compositions of whole-rock shale samples from five outcrops attributed to the pre-rift supersequence of the Camamu Basin were analyzed with the purpose of characterizing and obtaining further information that would allow a better correlation between the sites studied. The geochemical data suggest that the rocks exposed in the studied outcrops are part of the same sedimentary unit and that they might be correlated to the Camamu Basin. The chemical index of alteration (CIA) suggests conditions associated with a humid tropical/subtropical climate at the time of deposition. Nd isotopic compositions indicate provenance from the Paleoproterozoic rocks of the Sao Francisco craton. The results presented here, therefore, show that the combined use of chemical and isotopic analyses may be of great interest to characterize and correlate lithologically homogeneous clastic sedimentary sequences.

1. Introduction

Whole-rock geochemistry, combined Sr–Nd isotopic compositions of detrital sedimentary rocks, have been considered to be a useful parameter to assess their provenance and also to obtain information on their depositional environment and weathering processes. The complexity of this natural system has been discussed by several authors (e.g. Roser, 2000; Taylor and McLennan, 1985), and the results are interesting especially to help understanding sections of complex stratigraphy.

In this sense, due to wide gaps in knowledge about depositional ages and to their complexity in terms of correlation and stratigraphic organization, the sedimentary units of the lower portion of the northeastern Brazilian passive continental margin have become subject of interest for the present study, based on chemical and isotopic data. The sequence investigated represents the most basal portion and corresponds to the Paleoproterozoic and pre-rift supersequences of the Brazilian marginal basins. They are usually homogeneous and lack diagnostic fossils, making difficult their identification and stratigraphic characterization.

Whole-rock major and trace element chemical compositions, as well as Sr–Nd isotopic compositions of rocks from five outcrops attributed to the pre-rift supersequence of the Camamu Basin were analyzed. In this basin, it is hard to identify the units associated with the pre-rift, since they are formed of red pelites with incipient lamination and locally with the presence of carbonate nodules. The main purpose of the present study was to characterize the outcrops...
and to obtain further data to allow a better correlation between them.

2. Geologic context

The Camamu Basin is located along the coastline of Bahia state, between parallels 13 and 14° S, and it forms the southern extension of the Recôncavo-Tucano-Jatobá rift system (Fig. 1) With an area of about 13,000 km² (of which emerged 2000 km²), the Camamu Basin contains some accumulations of oil and gas on land and offshore, all considered to originate from Eocretaceous lacustrine source rocks of the Morro do Barro Formation (Gonçalves et al., 2000).

To the north, the limits between the Camamu Basin and the Recôncavo and Jacuípe basins is marked by the Barra Fault, an important E–W structural regional feature. The Camamu and Jacuípe basins overlie Precambrian rocks of the São Francisco craton exposed to the west. To the south, the border with the Almada Basin is only geographic, since structural and stratigraphic continuities between these basins are observed.

The origin of the Camamu Basin, as well as of the other Mesozoic basins of the Brazilian continental margin, is correlated with crustal stretching, which climaxed during Gondwana breakup and the formation of the Atlantic Ocean (Ponte and Asmus, 1976; Asmus and Guazelli, 1981; Chang et al., 1992).

The crystalline basement of the Camamu Basin is part of the São Francisco craton (Almeida, 1977). It is characterized by the geotectonic units included in the so-called Jequié and Itabuna-Salvador-Curraçá blocks (Barbosa and Sabaté, 2002, 2003). These Archean and Paleoproterozoic terrains are, therefore, potential source areas of the detrital sedimentary rocks of the Camamu basin.

According to Caixeta et al. (2007), the sedimentary package of the Camamu Basin comprises five supersequences: Paleozoic, pre-rift, rift, post-rift, and drift (Fig. 2). The tectono-sedimentary evolution of the Camamu Basin might be described as a succession of stages: (1) syneclyse, which precedes the development of the continental margin and comprises continental and marine sediments of Permian age and which correspond, in lithostratigraphic terms, to the Afítigos Formation; (2) pre-rift sequence, comprising the fluvial-lacustrine sediments of Jurassic/Eocretaceous age of the Aliança, Sergi and Itaípe formations; (3) rift sequence, represented by Eocretaceous lacustrine deposits of the Morro do Barro and Rio de Contas formations; (4) post-rift sequence, which was deposited in an environment of asag-type basin, represented by Aptian transitional sediments of the Taipus-Mirim Formation; and (4) drift sequence, including the marine strata of Cretaceous to Tertiary age of the Algodões, Urucutuca, Rio Doce and Caravelas formations (Netto and Ragagnin, 1990; Gonçalves et al., 2000).

The pre-rift sequence – of Dom João – Rio da Serra (Neojurassic) age – was originally distributed over a large geographic area, comprising the Afro-Brazilian Depression (Estrella, 1972). Lithostratigraphically, the pre-rift section of the Camamu Basin corresponds to the Brotas Group and to the Santo Amaro Group. The Brotas Group includes the Aliança (Boipeba and Capianga members) and Sergi formations, whereas the Santo Amaro Group is composed of the Itaparica, Água Grande, and Candeias formations.

According to Caixeta et al. (2007), the sedimentation of this sequence is characterized by sandy clastic sediments and shales deposited by interlaced rivers, with aeolian reworking. Lacustrine transgressions of regional nature are expressed by a predominantly pelitic sedimentation, which characterizes the Capianga Member (Aliança Formation) and the Itaparica Formation.

The sedimentation of this stage is characteristically formed of oxidized, reddish sediments. In northeastern Brazil, the pre-rift sedimentation took place in the Afro-Brazilian Depression, named by Cesero and de Ponte (1972 apud Cesero and de Ponte, 1997) and

![Fig. 1. Location of the Camamu Basin, northeast Brazil.](image-url)
which comprised the area currently occupied by the Sergipe-Alagoas, Camamu and Almada basins, in the southern coast of the state of Bahia, including also the Recôncavo, Tucano and Jatobá basins and their African counterparts. Stratigraphically, the units of the pre-rift sequence of the basins of the Afro-Brazilian Depression are considered to be correlated with each other and of Neojurassic age.

3. Methodology

3.1. Samples analyzed and analytical procedures

The samples used in the present study were collected at five different outcrops in the Camamu Basin (Camamu 1, 2, 3, 4, and 5 sampling sites). The sedimentary rocks exposed in these outcrops have been considered to be part of the same sedimentary unit, an assumption that will be investigated here. The precise location of the sampling sites is shown in Fig. 3.

It must be highlighted that due to its stratigraphic location, rocks in the Camamu 4 outcrop (Fig. 4) were considered to belong to the Aliança Formation, Capianga Member (pre-rift supersequence). However, as shown in Fig. 4, there is a local contact with sediments identified as belonging to the Sergi Formation (Fig. 2).

In all outcrops, the rocks are described as reddish pelite with incipient plane-parallel lamination, locally with carbonate nodules and associated with a fluvial-lacustrine depositional environment.

Efforts were made to collect pelites that visually showed a smaller degree of weathering. However, the samples always showed evidence of intensive weathering processes and oxidation. Macroscopically, the samples collected at the five sampling sites are reddish argillites, locally with carbonate nodules always with the presence of white mica fragments.

Approximately 500–700 g of rock were collected from each sampling site. Care was taken not to contaminate the samples with fragments from other units; carbonate nodules were rejected. A minimum of four samples was collected at each outcrop, always maintaining a minimum distance of 1 m horizontally between each sample, according to the methodology described by Thomaz Filho and Lima (1979).

The samples were crushed in an agate mortar and dried at <70 °C, to obtain the whole rock (WR) sample powder. The WR samples were quartered in order to obtain fractions for X-ray diffractometry (XRD), X-ray fluorescence (XRF), and mass spectrometry analyses.

3.2. Chemical analysis

Major elements and all trace elements, except for Sr and Nd, were determined in 67 samples by X-ray fluorescence (XRF) technique using a Rigaku Model RDX 2000 device set at 50 kV and 50 mA, in the Laboratory of X-ray Fluorescence of the Geosciences Institute of the Federal University of Rio Grande do Sul (UFRGS). The samples were prepared as pressed-powder tablets obtained from 10 g of rock powder. The chemical composition (major and trace elements) of the samples and their corresponding averages are shown in Tables 1 and 3.

3.3. Isotopic analysis

Sm–Nd isotopic analyses were performed in the Center of Geochronological Research of the University of Sao Paulo (CPGeo/USP). Rb–Sr analyses were performed in the Laboratory of Isotopic Geology of the Federal University of Rio Grande do Sul (UFRGS). Initially, the samples were dried under controlled temperature (up to 70 °C) in order to avoid damage to the structure of the clay minerals. The semi-quantitative and quantitative determination of Rb, Sr, Sm and Nd contents was achieved by X-ray fluorescence. About 0.1–0.2 g of powdered rock from each sample were dissolved in HNO3 and HF in Savillex vials, with the addition of isotopic tracers. Rb, Sr and REEs were separated in cation exchange AG-50W-X8 resin columns (200–400 mesh), and Sm was separated from Nd with anionic exchange LN-B50-A resin columns (100–200 μm). Isotopic ratios were obtained using a VG Sector 54 mass spectrometer, with multi-collection system, and Rb–Sr and Sm–Nd results were calibrated respectively against NBS-987 (strontium carbonate, mean 0.71026 ± 0.000014) and La Jolla (mean 0.51830 ± 0.00001) standards. Blank values were lower than 150 pg for Sr and Sm and 750 pg for Rb and Nd. The isotopic ratios obtained are shown in Tables 2 and 4.

3.4. Analysis by X-ray diffractometry

In the present work, X-ray diffractometry was used in order to support the chemical and isotopic interpretations, with the purpose of identifying clay minerals present in the samples.

Analyses were performed in the X-ray Diffractometry Laboratory of the Institute of Geosciences of the Federal University of Rio Grande do Sul (UFRGS). The equipment used was a Siemens Bruker AXS D500 diffractometer equipped with copper anode, nickel filter, 1° slits, 40 mA current, and 30 kV beam current.
Sample preparation followed the procedures described by Alves (1987), with slides undergoing three preparations, from which three spectra were obtained (standard, glycolated, and calcined); their combined interpretation was used to identify the clay minerals present in the samples, since their physical and chemical characteristics show different responses to the treatments.

After these procedures, we performed the analyses, compared the diffractograms, and identified the clay minerals by standard procedure according to Brown and Brindley (1980) from the measure of the height of the major peaks.

4. Results

4.1. Classification and composition of the rocks analyzed

Macroscopically and as described previously, the samples investigated were reddish pelites, locally with carbonate nodules, always with white mica fragments.

Clay fractions of the Camamu 2, 3, 4, and 5 samples are constituted mainly of illite (I), smectite (S), interstratified illite-smectite (IS) as traces, and possibly quartz and K-feldspar. Kaolinite (K), illite (I), and quartz traces prevailed in the Camamu 1 samples.

The rocks analyzed were classified according to the method proposed by Herron (1988), which, according to Roddaz et al. (2006), is appropriate for clastic clay rocks (Fig. 5).

In the present proposition, most samples analyzed can be classified as Fe-shales. These samples are characterized by high levels of Fe₂O₃ (8–12%, Table 1). Following Kasanzu et al. (2008), this is a good descriptive classification to these rocks.

4.2. ⁸⁷Sr/⁸⁶Sr ratios and the “pseudo-isochrons”

Initially, the ⁸⁷Sr/⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr results were plotted in an isochron diagram (according to the model of Ludwig, 2003). The purpose was to verify the possibility of establishing the depositional age, since this method has been successfully applied to
Table 1: Chemical composition of the Camamu Basin samples (oxides in % of weight, trace elements in ppm, and CIA in %).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major element</th>
<th>Trace element</th>
<th>CIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camamu 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VA 01</td>
<td>56.1</td>
<td>19.6</td>
<td>11.3</td>
</tr>
<tr>
<td>VA 02</td>
<td>54.8</td>
<td>21.4</td>
<td>10.4</td>
</tr>
<tr>
<td>VA 03</td>
<td>62</td>
<td>13.8</td>
<td>1.35</td>
</tr>
<tr>
<td>VA 04</td>
<td>57.7</td>
<td>20.4</td>
<td>1.06</td>
</tr>
<tr>
<td>VA 05</td>
<td>55.5</td>
<td>21.7</td>
<td>0.92</td>
</tr>
<tr>
<td>VA 06</td>
<td>58.3</td>
<td>20.3</td>
<td>1.39</td>
</tr>
<tr>
<td>VA 07</td>
<td>58.4</td>
<td>21.3</td>
<td>0.83</td>
</tr>
<tr>
<td>VA 08</td>
<td>55.4</td>
<td>20.3</td>
<td>1.16</td>
</tr>
<tr>
<td>VA 09</td>
<td>55.3</td>
<td>20.4</td>
<td>1.06</td>
</tr>
<tr>
<td>VA 10</td>
<td>55.4</td>
<td>20.4</td>
<td>1.06</td>
</tr>
<tr>
<td>VA 11</td>
<td>57.2</td>
<td>19.9</td>
<td>0.81</td>
</tr>
<tr>
<td>VA 12</td>
<td>57.9</td>
<td>20.9</td>
<td>0.93</td>
</tr>
<tr>
<td>VA 13</td>
<td>57.2</td>
<td>20.9</td>
<td>0.93</td>
</tr>
<tr>
<td>VA 14</td>
<td>56.6</td>
<td>21.5</td>
<td>0.99</td>
</tr>
<tr>
<td>VA 15</td>
<td>58.5</td>
<td>19.7</td>
<td>0.94</td>
</tr>
<tr>
<td>VA 16</td>
<td>57</td>
<td>21.6</td>
<td>0.91</td>
</tr>
</tbody>
</table>


(continued on next page)
basal sections of basins of the Brazilian continental margin, with results that can be correlated with depositional age (Silva et al., 2012, 2006).

The Rb–Sr radiometric method is traditionally used to assess the absolute ages in igneous rocks. In a sedimentary environment, characterized by lower temperatures, the behavior of Rb and Sr ions...
interstratified primarily of expansive clay minerals such as smectite and careful selection of samples with a high clay fraction content pointed out by Mizusaki (1992) and Mizusaki et al. (1998) during their deposition is valid, successful radiometric dating of sedimentary rocks. If the assumption of Sr isotope homogenization in sediments during their deposition is valid, successful radiometric dating of sedimentary rocks.

As shown in Fig. 6, no meaningful isochronic regression line could be calculated using all results from the isotopic ratios obtained for the five outcrops, due to their great dispersion. Therefore, a selection of points was performed as proposed by Thomaz Filho and Lima (1979). The points selected were plotted once more in a selection of points was performed as proposed by Thomaz Filho and Lima (1979). The points selected were plotted once more and the remaining points were discarded. This may indicate contribution from a different source. However, some samples of the Camamu 1 and 5 outcrops did not fit in and align along a different regression line. This may indicate contribution from a different source.

The age of 470 ± 17 Ma (Fig. 7) is considered here to be too old to represent the depositional age, in the light of the tectonic models proposed for the Camamu Basin (Caixeta et al., 2007).

Therefore, one may suggest that it represents a "pseudo-isochron", i.e., with no geochronological significance. Even using samples collected from the different outcrops and positioned in individual isochrons, no meaningful value was obtained for the sedimentation age. The values obtained were always older than expected, considering the current knowledge on this sedimentary section.

In order to obtain preliminary information about the provenance of the units, we use a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio to obtain the isochron age. The isotopic values used for obtaining the isochron are represented mainly by samples from the Camamu 2, 3, and 4 outcrops.

Possible reasons for the scatter of the analytical points of the Camamu 1 and 5 samples are:

- sediment provenance
- high level of chemical alteration (Table 1) when compared to the remaining points
- slightly different mineralogical composition, especially of the Camamu 1 samples; XRD analyses of these samples did not show expansive clay minerals, which favor isotopic homogenization of Sr.

### Table 2 (continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>Error</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA-09</td>
<td>4.39125</td>
<td>0.03402</td>
<td>0.73161</td>
<td>0.0002</td>
</tr>
<tr>
<td>CA-10</td>
<td>4.78777</td>
<td>0.03892</td>
<td>0.73422</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-12</td>
<td>2.67524</td>
<td>0.02124</td>
<td>0.72494</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-13</td>
<td>4.37411</td>
<td>0.03590</td>
<td>0.73156</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-14</td>
<td>4.30932</td>
<td>0.03609</td>
<td>0.73125</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-06</td>
<td>3.99433</td>
<td>0.03054</td>
<td>0.73279</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-07</td>
<td>6.67668</td>
<td>0.05331</td>
<td>0.74140</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-08</td>
<td>6.02965</td>
<td>0.06585</td>
<td>0.78556</td>
<td>0.00002</td>
</tr>
<tr>
<td>CA-09</td>
<td>4.39125</td>
<td>0.03402</td>
<td>0.73161</td>
<td>0.00002</td>
</tr>
<tr>
<td>CA-10</td>
<td>4.78777</td>
<td>0.03892</td>
<td>0.73422</td>
<td>0.00001</td>
</tr>
<tr>
<td>CA-12</td>
<td>2.67524</td>
<td>0.02124</td>
<td>0.72494</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

### Table 3

Average chemical composition of samples of the Camamu Basin and of pre-rift sedimentary units of the Recôncavo Basin (source: Silva et al., 2012). Oxides in % of weight, and trace elements in ppm.

<table>
<thead>
<tr>
<th>Result</th>
<th>Outcrop</th>
<th>Camamu Basin</th>
<th>Reconcavo Basin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Camamu 1</td>
<td>Camamu 2</td>
</tr>
<tr>
<td>Major element</td>
<td>SiO$_2$</td>
<td>57.0</td>
<td>57.5</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>20.4</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Fe$_2$O$_3$ (T)</td>
<td>9.3</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>MnO</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>1.4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>Na$_2$O</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>K$_2$O</td>
<td>2.2</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>P$_2$O$_5$</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>P.F.</td>
<td>7.6</td>
<td>6.9</td>
</tr>
<tr>
<td>Total</td>
<td>99.2</td>
<td>99.5</td>
<td>99.8</td>
</tr>
<tr>
<td>Trace element</td>
<td>Y</td>
<td>78.6</td>
<td>231.7</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>54.5</td>
<td>36.5</td>
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<tr>
<td></td>
<td>Ni</td>
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<td>97.2</td>
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<tr>
<td></td>
<td>Cu</td>
<td>50.3</td>
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<tr>
<td></td>
<td>Ga</td>
<td>57.7</td>
<td>52.1</td>
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<tr>
<td></td>
<td>Sr</td>
<td>75.8</td>
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<td></td>
<td>Zr</td>
<td>488.9</td>
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<td></td>
<td>Zn</td>
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<td>217.7</td>
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<td></td>
<td>Nb</td>
<td>111.5</td>
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<tr>
<td></td>
<td>Rb</td>
<td>386.4</td>
<td>533.4</td>
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<tr>
<td></td>
<td>As</td>
<td>22.1</td>
<td>16.1</td>
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<td></td>
<td>Cr</td>
<td>199.9</td>
<td>243.5</td>
</tr>
<tr>
<td></td>
<td>Ba</td>
<td>978.5</td>
<td>2602.9</td>
</tr>
<tr>
<td></td>
<td>CIA</td>
<td>89.9</td>
<td>82.4</td>
</tr>
</tbody>
</table>
The results obtained can be explained by the abundant presence of detritic muscovite in the samples, even in the fine fraction. Mica contributed with radiogenic Sr from the source rock, and, moreover, its structure does not allow Sr isotopic homogenization (Mizusaki, 1992), thus, contributing to the anomalously old results. The results might be, alternatively, attributed to a possible contribution of K-feldspar, according to results of the X-ray diffraction analyses.

Table 2 shows that $^{87}\text{Sr}/^{86}\text{Sr}$ values are high, evidencing contributions from fragments of old continental rocks, whose source will be verified next.

### 4.3. Characteristics of the whole-rock geochemistry

The geochemical composition of sedimentary rocks is a complex result of various variables such as source material, weathering, transportation, physical sorting, and diagenesis (Middleton, 1960; Piper, 1974; Bhatia, 1983; McLennan, 1989; Cox and Lowe, 1995). Examples of studies using geochemical data from sediments to understand sedimentary processes such as weathering, provenance, diagenesis, sorting, and recycling are increasing in the literature because of the sensitiveness of some key trace elements in identifying minor components that are not readily recognized petrographically (e.g. Hiscott, 1984; Garver et al., 1996).

The chemical composition of samples represents their primary mineralogy, which frequently underwent intense pre- and post-

![Fig. 5. Chemical classification of the analyzed rocks (modified from Herron, 1988).](image)

![Fig. 6. $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram.](image)

![Fig. 7. Isochron for the samples of the Camamu Basin, according to Ludwig's model (2003).](image)

![Fig. 8. $^{87}\text{Sr}/^{86}\text{Sr}$ (ratio) versus $1/\text{Sr}$ (concentration) diagram.](image)
depositional chemical weathering processes (Nesbitt and Young, 1982). According to Button and Tyler (1979), cations such as Al, K, Mg, and Rb are always retained in weathering profiles, while cations of smaller ionic range, such as Na, Ca, and Sr, are rapidly leached and removed from the system. In addition, the amount of elements that is lost is proportional to the extent of the weathering processes. Table 1 shows the results of XRF analyses of samples from selected outcrops of the Camamu Basin.

Fig. 9. Variations of major elements (%) versus Al₂O₃ (%).
Fig. 10. Variations of trace elements (ppm) versus \( \text{Al}_2\text{O}_3 \) (%).
The diagrams were initially drawn based on the abundance of $\text{Al}_2\text{O}_3$ and taking into account that the samples come from predominantly clay-rich rocks. According to Weaver (1989), clays preserve source rock chemical signatures due to the fact their mineralogy is rarely affected by post-depositional processes as diagenesis or metamorphism. The variance diagrams for the samples are shown in Figs. 9 and 10.

This suggests that the abundance of elements is controlled by the content of clay minerals. Pelites have higher K$_2$O and are depleted in Na$_2$O, revealing a higher proportion of clay minerals, especially illite and interstratified illite-smectite, according to XRD analyses.

Although potassium is thought to be highly soluble in water, it tends to be conserved in some pelites because of the chemical stability of illite (Norrish and Pickering, 1983). Illite is relatively resistant to weathering and is potentially stable in soils except under extreme weathering conditions.

Co$_2$O values are very low (Table 1), suggesting very fast alteration of plagioclase, according to the criteria of Roser (2000). No traces of plagioclase were found in the fine fraction of the samples. TiO$_2$ and $\text{Al}_2\text{O}_3$ are refractory oxides that are highly resistant to weathering in all but the most extreme environments, for example in long-lived weathering profiles in hot and humid conditions (Hill et al., 2000). This geochemical information contrasts with CaO, Na$_2$O and Sr, which are relatively mobile and can be easily lost from pelites. On the other hand, Rb tends to be incorporated into clay minerals by adsorption and cation exchange during chemical weathering of fresh continental rock (Nesbitt et al., 1980). There is a strong negative correlation between Na$_2$O and Rb which indicates that clay minerals in the clay mineral-rich fraction host the Rb. Elevated Rb and depleted CaO and Sr might suggest intense weathering conditions but could alternatively be explained by a more felsic, Rb-rich source rock. Incompatible elements such as Rb, Y, Th and U are preferentially fractionated into melts during crystallization (e.g. Hall, 1996 and references therein) and as a result these elements are enriched in felsic rather than mafic rocks.

According to the proposition by Taylor and McLennan (1985), Zr occurs predominantly in heavy minerals. The Camamu 1 samples show significantly increased Zr contents. Due to the mineralogy (prevalence of kaolinite) and their chemical contents, these samples form the potentially most weathered set, which would explain the higher concentration of resistate minerals, such as zircon.

With regard to minor elements, we found that barium (Ba) concentrations are, in average, always higher than those of strontium (Sr). These elements usually tend to accompany calcium (Ca) in detritic minerals, such as feldspar and mica, but they are also found in clay minerals.

As shown in Table 3, the chemical average compositions (major and trace elements) of the sampling sites were compared among them, as well as with the preliminary results obtained from correlated sedimentary units of Paleozoic and pre-rift sections of the Recôncavo Basin (Silva et al., 2012). The chemical signatures of the studied Camamu outcrops are very similar not only amongst them, but also to those of the Aliança Formation (Capianga Member), Recôncavo Basin pre-rift (Fig. 2, Table 3). This similarity suggests that the rocks exposed in the sampling localities are part of the same sedimentary unit, which is correlated with the Aliança Formation (Capianga Member), thus corroborating the assumption for the Camamu 4 outcrop. The samples of the Aliança Formation (Silva et al., 2012) of the Recôncavo Basin are pelites and have kaolinite, illite, smectite, as well as traces of interstratified illite-smectite in their fine fraction. Based on the average chemical composition of the samples of the Capianga Member, they were classified as Fe-shales (Fig. 5), and the average CIA value is 80.9 (Table 3). These data represent further evidence of similarity between the sampling sites of the Camamu Basin.

### 4.4. Chemical index of alteration (CIA)

The degree of weathering in source rocks can be obtained by various chemical indices, based on their major element compositions.

In the present study, in order to measure the degree of weathering, the CIA index was used (Nesbitt and Young, 1982), which is based on the proposition that during chemical weathering the prevailing processes are feldspar degradation and clay minerals formation. The CIA (calculated as $\text{CIA} = 100 \times \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}$) of pelites of the Camamu Basin is given in Table 1 and shows that a progressive weathering leads to loss of Na, Ca and K and increases in Al contents, as highlighted by Andersson et al. (2004).

The CIA, therefore, is potentially a very useful index to characterize pelites in terms of the degree of weathering of the sediment source and in terms of variable source terrains of the Camamu samples. Worldwide average shale CIA values range between about 70 and 75; fresh granites give values of around 50 (Visser and Young, 1990) while extreme weathering may produce values approaching 100. The Camamu samples have CIA between 71.63 and 91.03 indicative of high degradation. The average CIA of Camamu 1 samples is higher, suggesting stronger weathering processes, which is evidenced by the mineralogical composition, in which kaolinite and illite prevail.

High CIA values are associated with humid tropical or temperate climates with heavy rainfall, favoring the development of extensive vegetation (Goldberg and Humayun, 2010). Therefore, this might have been the climatic conditions during the pre-rift deposition, since CIA values are elevated and the mineralogical composition indicates high chemical weathering.

The Al/Na ratio $\times$ CIA (Fig. 11) plot indicates that the samples are positioned in fields corresponding to intermediate to extreme weathering, although under almost anomalous conditions, since they showed near-zero values for Na$_2$O.

Kaolinite-enriched sediments (Camamu 1) coupled with high Sr isotopic ratios and low $\varepsilon^{47}$Sr suggest intense chemical weathering in the hinterland following Kessarkar et al. (2003).

### 4.5. Correlations between Nd isotopes, provenance and geochemistry

The relatively immobile character of rare earth elements (REE) in most sedimentary processes (DePaolo, 1988; McLennan et al., 1990) allows the application of the Sm–Nd isotopic
system to provenance research, even considering a possible slight modification of parameters during the sedimentary cycle (Awwiller and Mack, 1991; Zhao et al., 1992). Allied with the immobile nature of the REE elements in the weathering and sedimentary environments, is the geochemical similarities between the LREE, suggesting that the Sm/Nd ratios are hardly affected by these processes (e.g. McLennan et al. 1990). Therefore, the measured ratios and calculated parameters in sedimentary rocks will reflect the characteristics of the source rocks. Therefore, $^{143}$Nd/$^{144}$Nd isotopic ratios, model age (TDM) and parameters such as $\varepsilon_{Nd}$ have been used as provenance tracers in recent sediments (McLennan et al., 1990), Paleozoic turbidites (Gleason et al., 1995), and Neoproterozoic siltstones and sandstones (Farmer et al., 2001).

Relatively lower $^{143}$Nd/$^{144}$Nd ratios indicate crustal sources, while higher $^{143}$Nd/$^{144}$Nd ratios suggest the input of mantle-derived juvenile material (DePaolo, 1988). This may be evaluated using the $\varepsilon_{Nd}$ parameter and by mantle extraction TDM ages. Positive or near-zero $\varepsilon_{Nd}$ Values, and TDM values near the crystallization age of an igneous suite, correspond to juvenile, mantle-derived components. On the other hand, negative results and significant difference between ages of extraction (TDM) and crystallization point to contamination by inherited, crustal material.

Weathering does not influence Nd isotopes and $\varepsilon_{Nd}$ correlates well with the clay mineral associations, indicating source rock composition or mixing of source sediments.

The calculation and correct interpretation of TDM model ages is based on the idea that the $^{147}$Sm/$^{144}$Nd ratio of the Earth’s crust is more or less homogeneous (including granitic rocks and detrital sediments) of approximately 0.12 ± 0.02.

Therefore, in the case of the studied samples, whose $^{147}$Sm/$^{144}$Nd ratios did not fit this assumption, there might have been a fractionation between Sm and Nd. This means that the TDM model age, calculated based on this ratio, cannot be interpreted as crust formation ages.

As shown in the diagram $\varepsilon_{Nd}$ versus time (Fig. 12), the results show that the samples originate from the erosion of Paleoproterozoic rocks of the São Francisco craton. This interpretation is based on $\varepsilon_{Nd}$ values at the time of deposition (approximately 150 Ma), since their values are around –25 and –15, a characteristic signature of Paleoproterozoic rocks of the Itabuna-Salvador-Curaçá orogen, in the São Francisco craton (Barbosa and Sabaté, 2002, 2003).

![Diagram of Nd versus Time](image)

**Fig. 12.** Diagram $\varepsilon_{Nd}$ versus Time (according to DePaolo, 1981) for the studied samples.

5. Conclusions

The samples collected from outcrops of the Camamu Basin can be described as homogeneous, reddish, micaceous pelites showing disperse carbonate nodules. They show reasonable whole-rock chemical and isotopic similarities and, therefore, it is assumed that they comprise the same sedimentary unit. Based on whole-rock geochemistry, this sedimentary unit might also be correlated with the Aliança Formation (Capianga Member), Recôncavo Basin pre-rift.

When plotted in classification diagrams, most of these samples show to be Fe-shales, since Fe$_2$O$_3$ values are high.

The mineralogical composition based on XRD analyses shows the presence of illite, interstratified illite-smectite, smectite, kaolinite, and traces of K-feldspar and quartz. Samples of the Camamu 1 outcrop are kaolinite-enriched, showing a strong weathering process. The CIA is increased and the results indicate humid tropical or temperate climatic conditions during deposition, with heavy rains that favored the development of extensive vegetation and strong chemical weathering.

The evidence of provenance obtained with Nd isotopes shows contribution from Paleoproterozoic rocks of the Itabuna-Salvador-Curaçá Block of the São Francisco craton (Barbosa and Sabaté, 2002, 2003).

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References


