

Rb–Sr systematics of Holocene pelitic sediments and their bearing on whole-rock dating

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Abstract – In many cases, when dealing with argillaceous fine-grained sedimentary rocks, the isotopic ages obtained from Rb–Sr whole-rock isochron calculations are of geological significance, despite the fact that the initial conditions of Sr isotopic homogenization are not fulfilled. To explain this, a mechanical mixing during deposition has been suggested, leading to an aggregate of mixed material with fairly uniform $^{87}\text{Sr}/^{86}\text{Sr}$ values, whatever Rb/Sr ratio is found in the analysed samples. This investigation of the behaviour of Rb and Sr during sedimentation and early diagenesis, involves study of more than 60 samples of fine-grained recent sediments from selected coastal localities of Brazil. The results indicate that pelitic samples from some recent to present-day transitional or shallow marine environments, such as the Jacarepaguá tidal flat and the Amazonas River mouth, where halmirolysis could have occurred, may produce nearly horizontal best-fit lines in a Rb–Sr isochron diagram. Moreover, the initial isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios appear to be well above 0.710. In open marine environments, such as the Campos Basin, where sampling was spread over more than 100 metres, exchanges between the argillaceous sediments and seawater potentially happen at low temperature, inducing a reduction of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of the sediments to nearly 0.710. An almost horizontal best-fit line is produced for the entire stratigraphic section, independent of the sedimentation age. We believe that in similar environments such ‘zero age isochrons’ are maintained for some time, testifying to exchanges between the sediment and the interstitial fluids, before the onset of burial diagenesis. The above described studies on fine-grained and recent argillaceous sediments seem to confirm the production of horizontal best-fit lines in isochron diagrams, justifying the application of the Rb–Sr whole-rock method to pelitic sedimentary rocks. The nature of the material is critical. The pelitic sediments to be analysed should contain only very limited amounts of coarse clastic material (especially feldspars and mica fragments) and consist mainly of fine clay minerals in which smectites, illite and mixed layers illite–smectite largely predominate.

Keywords: Rb–Sr, Holocene, clays, sedimentary rocks, absolute age, geochronology.

1. Introduction

Among geochronologists, scepticism is widespread regarding Rb–Sr whole rock isochron dating of shales, because the basic requirement of the method, the initial condition of Sr isotopic homogeneity of the material, cannot be met in such low-temperature environments where sediment deposition and diagenesis occur. Any set of samples representing a single sedimentation event, because of the presence of detrital material, is likely to show some kind of positive correlation between $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios since initial deposition. Thus, the possible best-fit regression lines in Rb/Sr isochron diagrams would already start with some positive slopes at ‘zero age’, and the age calculations would result in spurious values, of no geological significance, as the calculated age becomes higher than the true age of deposition. Odin (1982),

Faure (1986) and Clauer & Chaudhuri (1995), among others, present good discussions of this problem.

Nevertheless, and quite surprisingly, in many cases, when dealing with fine-grained argillaceous sedimentary rocks, the age values obtained from Rb–Sr whole rock isochron calculations seem to be of some geological significance, yielding ages in fair agreement with fossil content or with biostratigraphic criteria. Good examples can be found in Compston & Pidgeon (1962), Bofinger & Compston (1967), Chaudhuri & Brookins (1969), Faure & Kovacs (1969), Graham & Korsch (1985) and Mizusaki, Alves & Pedrão (1999).

How does this occur? In order to investigate the rationale for the apparent successes with Rb–Sr dating of sedimentary rocks, and at the same time try to assess the applicability of the method with objective criteria, the Geochronology Research Centre of the University of São Paulo began a few specific tests and projects, many of them in collaboration with PETROBRAS (Brazilian state-owned oil company).

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K. Kawashita (unpub. Ph.D. thesis, Univ. São Paulo, 1972), A. Thomaz-Filho (unpub. Ph.D. thesis, Univ. São Paulo, 1976), Thomaz-Filho, Cordani & Kawashita (1976), Thomaz-Filho & Lima (unpub. PETROBRAS report, 1979), Parenti-Couto *et al.* (1981), Cordani *et al.* (1985a) and A. M. Mizusaki (unpub. Ph.D. thesis, Univ. São Paulo, 1992), reported results of such research projects, and two main syntheses were presented by Cordani, Kawashita & Thomaz-Filho (1978) and Cordani *et al.* (1985b).

In the review by Cordani, Kawashita & Thomaz-Filho (1978), a mechanism was proposed to explain why fine-grained argillaceous sediments could fulfill the initial conditions of a uniform $^{87}\text{Sr}/^{86}\text{Sr}$ value. These authors suggested that the mineral grains from diverse sources would mix in a complete way, in a depositional environment favourable to sedimentation of pelitic material. In this case, despite the presence of small detrital particles containing Sr with different isotopic compositions, the sediment as a whole presents quite a uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The individual particles would not be isotopically identical, but the idea is that, for samples with a few centimetres in size, the extremely large number of well-mixed particles would statistically produce similar results in terms of the whole-rock Sr isotopic composition of each sample. Moreover, to be able to obtain good best-fit lines in Rb–Sr isochron diagrams, it is necessary that a reasonable spread in the Rb/Sr ratios occurs from sample to sample. Since Rb and Sr distribution within depositional environments depends on their chemical affinities, many complex exchanges may occur between sediments and fluids, normally seawater. Because of this, a relative spread in the Rb/Sr elemental ratios is likely to occur, independent of the uniformity of the Sr isotopic composition of the bulk material. Such premises, in the view of Cordani, Kawashita & Thomaz-Filho (1978) and Cordani *et al.* (1985b) are necessary and sufficient to validate whole-rock isochron dates of pelitic sediments.

Alternatively, Clauer & Chaudhuri (1995) were very sceptical in their review in relation to the basic assumptions indicated above, and maintained that the colinearities of whole-rock data points in Rb–Sr isochron diagrams represent mixing lines. They stated that the agreement between a whole-rock isotopic date of a sedimentary unit and its stratigraphic age would be fortuitous, and can only be expected in dating sediments derived directly from young underlying magmatic rocks. In their view, the available data suggest that very little merit can be found in determining the time of sedimentation by analysing whole-rock samples of shales.

In our view, the issue is still open, and the suggestion of mechanical mixing of fine-grained material in depositional environments deserves to be submitted to additional tests. There are many geological situations, for instance, those involving old unfossiliferous

sequences devoid of volcanic rocks, in which Rb–Sr dating of shales could be the only possible way of obtaining a reasonable indication of their stratigraphic age. In such cases, we strongly suggest the application of the proposed method, although we recognize that the necessary premises of the Rb–Sr dating are not fulfilled. Only a good approximation of the depositional or diagenetic age is required in most cases, and we believe that there are ample indications that the method may work adequately. For example, considering the Rb–Sr whole rock ages shown by Cordani *et al.* (1985b), we believe that they are reasonably close to their real ages of deposition, well beyond simple coincidence. On the other hand, we are also well aware that more work, employing more robust experiments, is necessary to demonstrate the effectiveness of the proposed mechanism.

Because of this, we sought independent evidence to support the feasibility of the whole-rock Rb–Sr isotopic method on pelitic samples, looking at Holocene sediments, and performing a series of preliminary tests dealing with samples of different sedimentary environments. In this study, we expected to check if such material, with uncontested ‘zero age’ of deposition, could yield horizontal lines in Rb–Sr isochron diagrams, in some situations. Only fine-grained, essentially pelitic sediments were studied in our work, since they are considered the only suitable ones to fulfill the envisaged conditions.

Moreover, in the case of obtaining some positive results in relation to the determination of stratigraphic age, we also wanted to verify a possible correlation with specific favourable material, and specific favourable depositional environments. The ultimate objective was to indicate possible conditions within depositional environments that could be important for the achievement of successful results.

In this study, the investigation of the behaviour of Rb and Sr during the depositional process was then carried out on whole rock samples of fine grained muds, collected in four distinct sedimentary environmental settings:

(1) two continental sites within river deltas, dominated by fresh water, with no direct contact with seawater: the deltaic regions of the Açu and Paraíba do Sul rivers.

(2) one coastal plain region, with tidal flats where halmirolysis (Russell, 1970) occurs when the sedimentary material comes into contact with seawater: the Jacarepaguá coastal plain near the city of Rio de Janeiro.

(3) one open sea environment, where surficial sediments and seawater interact intimately: the continental shelf at the mouth of the Amazon River.

(4) two open marine sites, where a section of unconsolidated sediments interacts with connate waters and formation fluids: the top of the stratigraphic sequences at well sites RJS-A and B, down to depths

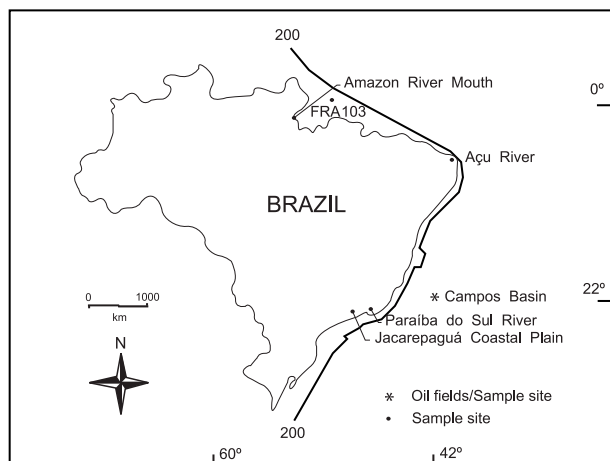


Figure 1. General location of the studied areas.

of several tens of metres, within the continental slope of Campos Basin, southeast Brazil.

The locations of the sampling sites are reported in Figure 1.

2. Methodology

More than 60 samples were studied by several techniques, including X-ray diffraction (XRD), scanning electron microscope (SEM) and thermal-ionization mass spectrometry (TIMS).

All of the analysed samples were fine-grained unconsolidated sediments. With the exception of the two well sites in the Campos Basin, where the bottom samples may be older, the samples were collected from sites considered to provide exclusively Quaternary sediments, preferably of Holocene age. The recent character of these geological units was confirmed in the case of the Paraíba do Sul River by radiocarbon dates between 2500 and 7500 years (Martin *et al.* 1984), and in the case of the Açu River, by radiocarbon dates between 5000 and 7000 years (Silva, pers. comm. 1990). The main experimental conditions of the methods employed in this work are given in the next sections.

2.a. Sample preparation

Samples of about 100 grams in a natural state were initially described according to colour, texture and water saturation, as well as the presence of salts, carbonates, micas, feldspars and organic matter. All were then dried in a temperature-controlled oven, never reaching more than 70 °C, to avoid possible damage to the structure of the clay minerals. Organic fragments were also separated out, first by hand picking and then by reaction with H₂O₂.

2.b. X-ray diffraction (XRD)

Clay minerals were identified in the fine fractions of all samples by XRD techniques using sections prepared with oriented material. The equipment was a diffractometer Jeol 8030 at the CENPES (PETROBRAS Research Centre, Rio de Janeiro), used under the following operational conditions: goniometer speed 2° 2Φ per minute, Cu target (35 kV, 20 mA) with Ni filter.

The clay fraction of grain size smaller than two microns (< 2 μm) was dispersed in water and separated by sedimentation techniques. Oriented preparations were investigated in the air-dried state and subsequently after glycolation and heat treatments (at 490 °C). The criteria used to identify each type of clay mineral and the procedure used to calculate their semi-quantitative contents in the samples are described in Alves (1987).

2.c. Scanning electron microscopy (SEM)

Selected samples were observed by scanning electron microscope (SEM) at CENPES to identify morphological evidence in the clay minerals, which might be indicative of recrystallization or neoformation processes. The instrument was a high resolution (70 Å), Hitachi model S-450, equipped with a detector of dispersive energy (EDAX), allowing a simultaneous semiquantitative chemical microanalysis of the mineral phases. Samples for the SEM observations were prepared according to the procedures described by Mizusaki (1986).

2.d. Rb–Sr analytical procedure

We chose to apply a systematic treatment to remove the carbonate fraction present in most samples. It is characterized by a well-defined Sr isotopic composition, corresponding to the seawater Sr of the time of deposition, for which the ⁸⁷Sr/⁸⁶Sr ratio is usually lower than that of the sedimentary material in which the terrigenous fraction predominates.

After some testing, the selected procedure was systematic acid leaching with HCl (1 N) for 10 minutes, a time period short enough to dissolve the carbonates without disturbing the structure of the clay minerals. However, we are aware that in a few cases, when the carbonate fraction was quite high, this procedure might have left behind some traces of carbonate. After the acid leaching, the samples were washed twice with standard acetone, centrifuged and dried. Semi-quantitative and quantitative determinations of Sr and Rb were performed by X-ray fluorescence, with errors estimated at 2 % or better in the case of the Rb/Sr ratios. In a few samples, such as those from Jacarepaguá, comprising only quartz plus kaolinite, Rb content was below the detection limit of the instrument; precise analyses by isotope dilution were not considered to be necessary and were not performed.

The samples were then dissolved using HF plus HClO_4 , and Sr was separated by passing the solutions through a cationic exchange resin stored in a column. Sr isotopic composition was determined using the single collector mass spectrometer VG-354 of the Geochronological Research Centre at the University of São Paulo. Absolute errors in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (2σ) were low, about 0.00003 on average; the isotopic determinations took place when the results obtained on the strontium carbonate NBS-987 were 0.71025 ± 0.00002 (2σ), after normalization of $^{86}\text{Sr}/^{88}\text{Sr}$ to 0.1194.

The normal calculation procedures for the Rb–Sr method were not used, because determination of apparent ages, analytical errors and MSWD values were not within the objectives of the work. Also, the Rb–Sr diagrams were drawn only to give visual impressions for the groupings of the analytical points, and especially to indicate the degree of horizontality shown in some of the studied examples.

3. Interpretation of the results

3.a. Terrestrial environments: deltas of the Paraiba do Sul and Açu rivers

The deltaic complex of the Paraiba do Sul River (Silva, 1987), eastern Brazil, has a total area of 2500 square kilometres, and includes the terrestrial portion of the Campos Basin (M. B. Araújo *et al.* unpub. PETROBRAS report, 1975; see Fig. 2a).

Four samples (identified as PS2 to PS5) were obtained from the collection of the Laboratory of Marine Geology (Lagemar) of the Fluminense Federal University (UFF). These were collected from different outcrops several kilometres apart, within the mangrove swamp units of the area, with a vibracorer at very shallow depth. Another sample was collected at Atafona (PS1), within the flood plain of the Paraiba River. The samples are very heterogeneous; their mineralogical and geochemical characteristics are presented in Table 1. PS4 is made up of silt grains, essentially quartz with some K-feldspar. PS1, PS2 and PS3 are composed of between 25 and 40% clay fraction, in which kaolinite largely predominates over mixed layers illite–smectite. PS5 is made up by 70% clay, in which mixed layers illite–smectite predominates over kaolinite. The material is totally detrital, produced by weathering and alteration of the different terrains of southeastern Brazil.

Castro, Barrocas & Lima (1982) studied the delta of the Açu River, where the city of Macau is located (Fig. 2b). The depositional processes are related to the flooding of the Açu River, inducing a deposition of fine to very fine sands interbedded with silty and argillaceous layers, and with abundant organic remains.

Eight core samples were collected in two areas of the delta located about 30 km apart. In the first one, five samples were collected within the Holocene deltaic

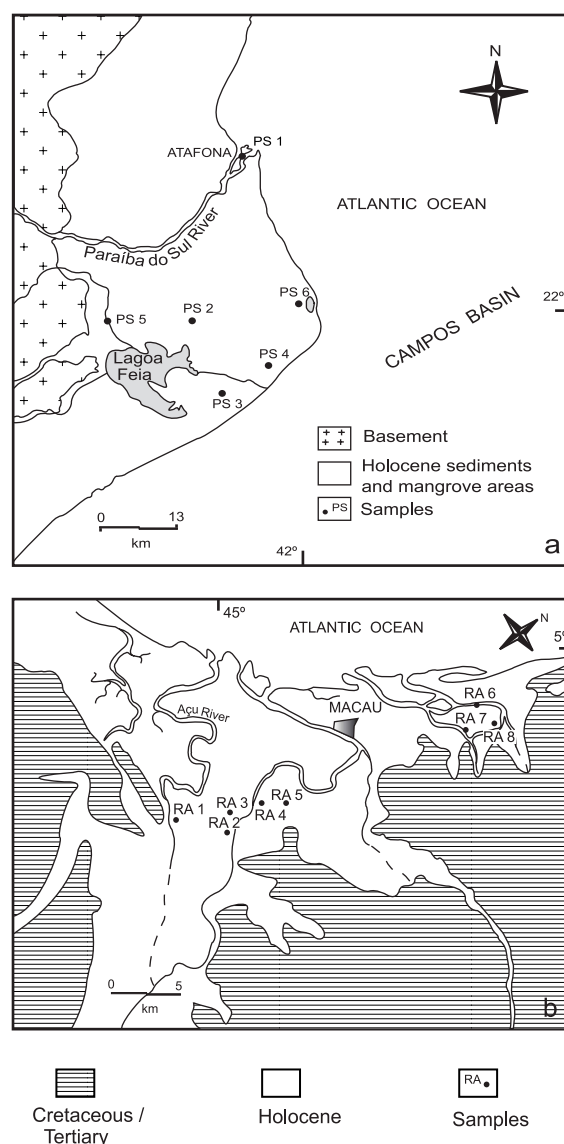


Figure 2. (a) Deltaic region of the Paraiba do Sul River (eastern Brazil). (b) Deltaic region of the Açu River (northeast Brazil).

sediments to the southwest of Macau (RA1 to RA5). The second set of three other samples (RA6 to RA8) was collected within the mud of tidal flats to the east of Macau. In both areas, the samples were collected a few hundred metres apart, at depths between two and four metres. Mineralogical and geochemical characteristics of the collected samples are included in Table 1. In all of them the clay fraction largely predominates, and here also all materials are detrital, originated by alteration of rocks from the Borborema province of northeastern Brazil. Kaolinite is the dominant clay mineral, but measurable proportions of mixed layers illite–smectite and illite are also present. Salt was detected in the samples from the tidal flat (RA6 to RA8), and some detrital minerals (quartz, K-feldspar and mica) were identified in all of them.

Figure 3 is a Rb–Sr isochron diagram showing the positions of the analytical points. The samples from the

Table 1. Semi-quantitative mineralogical compositions determined by XRD analyses on fine fractions and Sr isotopic ratios

Sample	C	P	KF	Q	CL	Ch	K	I	IS	Rb (ppm)	Sr (ppm)	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Rb/ ⁸⁶ Sr
Deltaic region of the Paraíba do Sul River, Brazil													
PS1	–	–	10	65	25	–	80	–	20	75.5	92.7	0.72893	2.36
PS2	tr	–	5	55	40	–	80	–	20	65.0	201.7	0.71674	0.93
PS3	–	–	5	65	30	–	85	–	15	68.8	150.1	0.71602	1.33
PS4	5	–	5	85	5	–	75	–	25	30.9	212.7	0.71188	0.42
PS5	tr	–	5	25	70	–	20	–	80	56.8	42.6	0.72668	3.86
Deltaic region of the Açu River, Brazil													
RA1	10	–	5	5	80	–	45	25	30	115	408	0.71378	0.82
RA2	–	–	5	5	90	–	30	40	30	140	166	0.72069	2.44
RA3	10	–	5	5	80	–	40	20	40	113	409	0.71324	0.80
RA4	–	–	10	10	80	–	30	35	35	151	122	0.72169	3.58
RA5	–	–	5	5	90	–	40	30	30	140	205	0.71756	1.98
RA6	10	–	5	5	85	–	50	15	35	101	460	0.71208	0.64
RA7	10	–	5	5	80	–	50	20	30	111	427	0.71215	0.75
RA8	10	–	5	5	80	–	50	15	35	108	478	0.71175	0.65
Jacarepaguá coastal plain, near Rio de Janeiro city, Brazil													
JA1	–	–	10	30	60	–	80	10	10	74.5	54	0.72800	3.99
JA2	–	–	15	30	55	–	80	5	15	79	54.5	0.72779	4.19
JA3	–	–	–	–	100	–	100	–	–	41	40.5	0.73867	2.93
JA4	–	5	15	60	20	–	75	–	25	103	115	0.73920	2.59
JA5	–	5	5	25	65	–	80	10	10	95	72	0.72835	3.82
JA6	–	–	–	60	40	–	100	–	–	<2	23	0.71948	<0.25
JA7	–	–	–	65	35	–	100	–	–	6	11	0.72038	1.58
JA8	–	–	–	50	50	–	100	–	–	<2	9	0.71741	<0.64
JA9	–	–	–	55	45	–	100	–	–	<2	10	0.71791	<0.58
JA10	–	–	–	40	60	–	100	–	–	<2	15	0.71861	<0.39
JA11	–	10	10	50	30	–	40	30	30	43	73.5	0.71889	1.69
JA12	–	10	10	50	30	–	40	30	30	53	80	0.71872	1.92
JA13	–	10	10	50	30	–	40	30	30	63	73.5	0.71928	2.48
JA14	–	10	10	50	30	–	30	25	45	93	121	0.71995	2.22
JA15	–	10	10	65	15	–	30	20	50	96	103	0.71956	2.70
JA16	tr	10	15	60	15	–	35	20	45	79	107	0.71952	2.14
JA17	tr	10	20	45	25	–	30	25	45	78	117	0.71719	1.93
JA18	tr	25	20	40	15	–	10	20	50	95	113	0.71915	2.43
JA19	tr	15	20	35	35	–	50	–	50	193	262	0.71670	2.13
JA20	tr	15	20	35	35	–	45	–	55	220	303	0.71711	2.10
JA21	tr	10	30	20	20	–	50	–	50	207	307	0.71774	1.95
JA22	tr	15	25	25	25	–	45	–	55	170	361	0.71390	1.36
Continental shelf near the Amazon River mouth, Brazil (*samples FRA103)													
1*	–	10	5	40	45	30	–	30	40	121	119	0.71617	1.77
2*	10	10	5	45	30	45	–	20	35	105.5	222	0.71467	1.38
3*	5	15	10	40	45	50	–	25	25	78.5	146	0.71687	1.56
4*	5	10	5	40	30	45	–	20	35	119	209	0.71609	1.65
5*	–	20	10	40	30	20	–	45	35	114	218	0.71524	1.51
6*	5	10	10	35	40	45	–	20	35	147	186	0.71697	2.29
Continental slope, Campos Basin, Brazil (*samples RJS)													
*A1 (4 m)	5	–	20	45	30	15	10	15	60	85.1	212.3	0.71220	1.16
*A2 (18 m)	5	–	20	45	30	20	10	10	60	80	254.4	0.71216	0.91
*A3 (37 m)	15	–	25	35	25	20	10	25	45	99.4	272.9	0.71182	1.05
*A4 (46 m)	5	–	30	35	30	15	5	15	65	110.2	192.4	0.71331	1.66
*A5 (65 m)	25	5	15	35	20	20	10	20	50	61.5	365.5	0.71040	0.49
*A6 (75 m)	30	30	25	25	25	20	15	20	45	63.8	556.8	0.71036	0.33
*A7 (84 m)	45	10	–	30	15	10	50	5	35	56.3	931.8	0.70945	0.17
*A8 (93 m)	25	5	10	35	25	15	10	10	65	80.9	361.1	0.71021	0.65
*A9 (112 m)	15	–	10	45	30	20	10	15	55	84	392.1	0.71032	0.62
*A10 (132 m)	15	–	10	30	40	20	10	20	50	80.5	361.1	0.71074	0.65
*A11 (145 m)	10	–	25	30	35	25	10	20	45	93.5	252.1	0.71041	1.07
*B1 (0.15 m)	20	5	5	35	35	–	45	15	40	71	733	0.71019	0.28
*B2 (10 m)	15	15	–	30	40	20	10	35	35	96	450	0.71116	0.62
*B3 (19 m)	10	15	–	35	40	15	10	25	50	119	284	0.71204	1.21
*B4 (29 m)	15	10	–	30	45	20	10	30	40	103	279	0.71193	1.07
*B5 (34 m)	10	10	–	40	40	20	5	30	45	124	235	0.71290	1.53
*B6 (39 m)	10	10	–	40	40	20	10	30	40	109	244	0.71253	1.29
*B7 (48 m)	15	10	–	25	50	15	15	30	40	108	362	0.71285	0.86
*B8 (59 m)	10	10	–	35	45	20	5	30	45	91	250	0.71201	1.05
*B9 (72 m)	15	10	–	30	45	15	30	30	45	82	464	0.71052	0.51
*B10 (79 m)	20	10	–	30	40	20	30	30	45	121	422	0.71077	0.83
*B11 (110 m)	10	10	–	30	50	20	35	35	40	106	235	0.71168	1.31

C–carbonates; KF–potassium feldspar; Q–quartz; P–plagioclase; CL–clay fraction; Ch–chlorite; K–kaolinite; I–illite; IS–mixed layers illite-smectite.

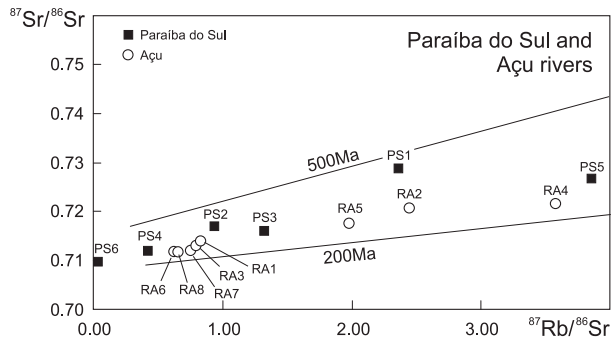


Figure 3. Rb–Sr isochron diagram for samples from the deltaic regions of the Paraíba do Sul and Açu rivers.

Paraíba do Sul delta are quite heterogeneous, the silt fraction being the predominant one. Their analytical points are dispersed in the isochron diagram, due to variable Rb/Sr ratios. The samples collected within the Açu River delta also show a similar dispersion in the isochron diagram. No precise or clear trend is established in Figure 3, although a certain correlation is present between the Rb/Sr ratios and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. All the analytical points are positioned within an envelope bounded by the 500 and 200 Ma reference isochrons, drawn for visual purposes only, and the detrital nature of the studied material is readily apparent.

In the present example, the conditions for the mechanism proposed by Cordani, Kawashita & Thomaz-Filho (1978) were not satisfied. On the one hand, sample collection was made in different outcrops, separated by several kilometres, not respecting the criteria proposed by Thomaz-Filho & Lima (unpub. PETROBRAS report, 1979). On the other hand, we think that the sediments were not adequately dispersed and mixed in the restricted depositional conditions of a continental delta.

3.b. Coastal plain at Jacarepaguá, Rio de Janeiro

The Jacarepaguá coastal plain is the general term for the southern part of the Rio de Janeiro municipality (Fig. 4). Roncaratti & Neves (unpub. PETROBRAS report, 1976) described a variety of depositional environments related to different sedimentation processes. The region includes 120 square kilometres of Holocene sediments mainly of continental origin, as well as 150 square kilometres covered by marine sedimentation. The source area of the continental sediments corresponds to the mountains and hills located in the vicinity of the coastal plain. Sampling was carried out in different localities, following the criteria proposed by Thomaz-Filho & Lima (unpub. PETROBRAS report, 1979), consisting of a close-spacing network between samples from the same site, collected systematically not more than a few metres apart and between 20 and 40 cm depth. Two of the sites

correspond to the flood plain of the Guandu River. The first one is a large outcrop along the BR-101 highway (samples JA1 to JA5), and the second is at the São Francisco channel, about 3 km from its mouth into the Marambaia Lagoon (samples JA6 to JA10). A tidal flat environment was sampled at Grota Funda (samples JA11 to JA18), and samples JA19 to JA22 were collected at the Vargem Pequena River channel.

Mineralogical and geochemical characteristics of the samples are included in Table 1 and correspond to detrital material, derived from weathering processes and rock alteration. Samples JA1 to JA5 contain different proportions of silt and clay, and most of them comprise detrital components. Kaolinite makes the bulk of sample JA3 and predominates in all clay fractions, although some illite and mixed-layers illite–smectite may also be present. Samples JA6 to JA10 exhibit a much simpler mineralogical content, being made up only of quartz and kaolinite, with some traces of gibbsite. In samples JA11 to JA18 the silt fraction predominates, made up by quartz, K-feldspar and plagioclase. Salt is present in all samples, and a small amount of carbonate was detected in samples JA16, JA17 and JA18. Within the clay fraction, kaolinite, mixed-layers illite–smectite and illite are present in relevant proportions. The silt fraction also predominates in samples JA19 to JA22, and includes a great deal of detrital material such as quartz, K-feldspar and plagioclase grains. The clay fraction of these samples comprises more or less equal proportions of kaolinite and mixed-layers illite–smectite.

Figure 5 displays the entire set of samples from the Jacarepaguá coastal plain, plotted in the same Rb–Sr isochron diagram so that results can be compared immediately.

Samples JA1 to JA5, collected within the flood plain (Fig. 4a), have the largest content of detrital material, including large mica fragments, and present the most dispersed results, shown at the upper right in Figure 5. Samples JA6 to JA10 were collected within the same flood plain (Fig. 4a) and present a much simpler mineralogy with quartz, kaolinite and gibbsite, considered neutral minerals in relation to Rb–Sr systematics. This material is a product of rock alteration, but continental weathering after deposition may also be considered. Rb and Sr in these samples are probably present adsorbed on kaolinite. The chemical analyses yielded very low element contents (Table 1), Rb being in some cases even below the detection limits of the XRF instrument. The Sr isotopic composition ranges from 0.7174 to 0.7204, with an average value close to 0.719.

The samples collected at the Vargem Pequena River channel (JA19 to 22) contained detrital material, but also carbonates and a great deal of mixed-layers illite–smectite. These samples yielded the highest Rb and Sr values (Table 1), but had very similar Sr isotopic compositions, close to 0.717. One exception was

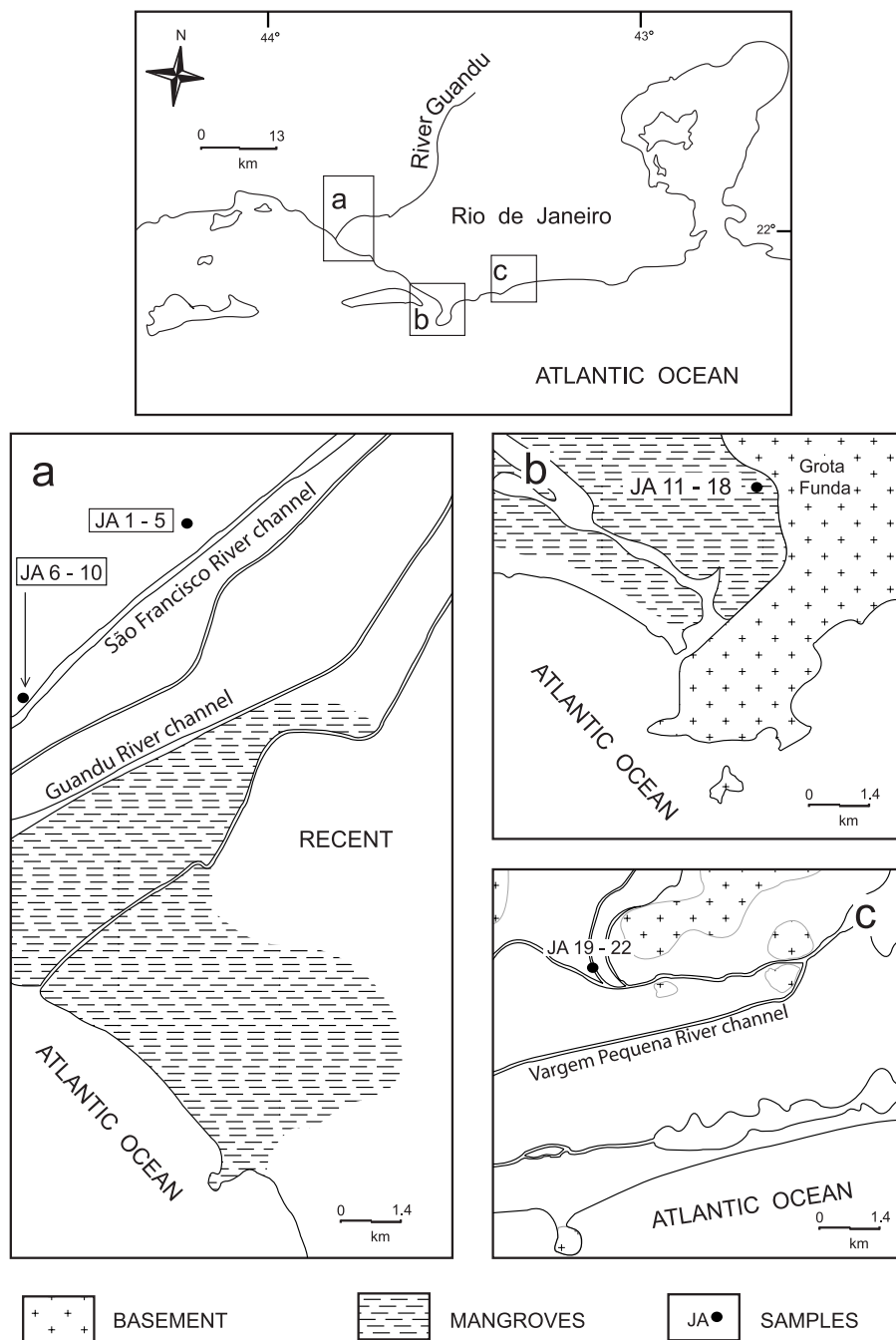


Figure 4. Jacarepaguá coastal plain, Rio de Janeiro (Brazil) and sampling sites.

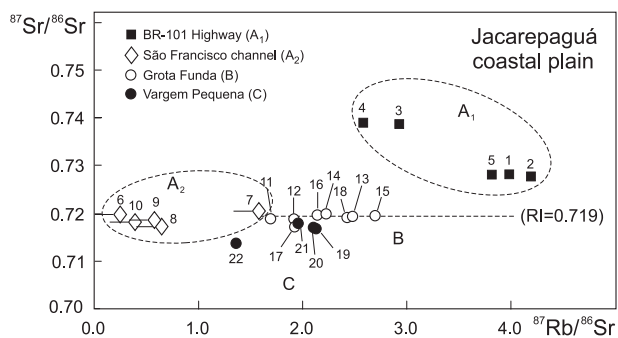


Figure 5. Rb–Sr isochron diagram for samples from the Jacarepaguá coastal plain.

sample JA22, that yielded a much lower value of about 0.714. In this case we speculate that our lixiviation process may not have been completely effective in removing the existing carbonates.

The samples from Grotta Funda (JA11 to JA18) produced the most interesting results. In these samples, detrital material was present, especially quartz within the silt fraction, which was predominant. Kaolinite was always present, but illite with mixed layers illite–smectite was more abundant (Table 1). For these samples, there was a variation of up to *c.* 50 % in the Rb/Sr ratio, despite the fact that collection of all of these was made within a few metres. Moreover, with

the exception of sample JA17, all the others yielded remarkably similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Table 1), with an average value of about 0.7193 ± 0.0008 . The overall plot of these samples is a near-horizontal Rb–Sr best-fit line. In other words, a ‘zero age’ has been approached for the Holocene fine-grained sediments of Grota Funda. We consider these results in such tidal flats as the most significant in this study, and our preferred explanation is as follows: a fine-grained sediment, including a great deal of detrital material, attains a Sr uniform isotopic composition by mechanical mixing and dispersion within the sedimentary environment. In addition, the sediment acquires a variation in the Rb/Sr ratio from sample to sample, when it comes into contact with seawater. In such an environment, the process of halmirolysis might produce chemical changes because of the reduction in particle transport velocity of the water channel, and also because of flocculation processes (Eisenhauer *et al.* 1999). As a speculation that requires testing, we believe that physical-chemical exchanges may occur between seawater Sr and the Sr contained in the structure of the clay minerals, especially smectites. The major effect of such exchanges will be a net loss of Sr to the seawater, consequently producing an increase in the overall Rb/Sr ratio of the sediment, but also diverse Rb/Sr values in the sub-systems represented by the individual samples. At the same time, such exchanges between clays and seawater within the tidal flats are limited, preventing a complete replacement of the Sr within the clays by seawater Sr. As a consequence, the overall Sr isotopic composition resulting from the process of mechanical mixing is kept unchanged, or it is only slightly affected by halmirolysis.

3.c. Continental shelf at the Amazon River mouth, equatorial Atlantic Ocean

The shelf at the mouth of the Amazon River is considered one of the largest depositional sites in the world, due to the immense amount of material carried by this river and discharged into the equatorial Atlantic Ocean. The recent sediments spread out in a region at least 700 km long and more than 250 km wide (Appi *et al.* 1988).

Six samples (FRA103-1 to FRA103-6) of Holocene muds, belonging to the collection of the Laboratory of Marine Geology (Lagemar) of the Fluminense Federal University (UFF), were used in this work. They were obtained by ‘kasten coring’, a technique which permitted collection of samples at regular intervals of 10 cm (the deepest one at 60 cm), always weighing around 100 grams. All samples are from a site located more than 100 km from the coast (see Fig. 1), and were recovered from the topmost sedimentary layer, at about 30 metres depth (Nittrouer, Sharara & DeMaster, 1983). All samples are similar, greyish in colour and rich in organic remains. In all of them the silt

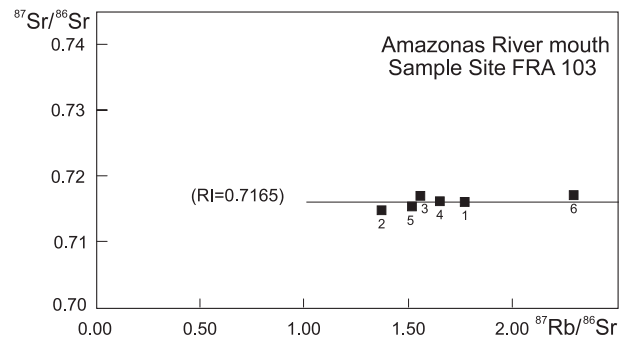


Figure 6. Rb–Sr isochron diagram for samples from the continental shelf at the Amazon River mouth, Brazil.

fraction predominates over the clay fraction, and quartz, feldspars and some carbonates were detected by XRD (Table 1), indicating the importance of the detrital component. Chlorite is the most important of the clay minerals, but illite and mixed layers illite–smectite are also present in relevant proportions. Kaolinite was not observed.

The analytical points of the samples FRA103-1 to FRA103-6 are plotted in Figure 6. Very likely the material has been in contact with seawater for some time, perhaps up to several decades, but very probably less than 100 years, giving the high sedimentation rate related to the huge discharge of the Amazon catch basin. With the exception of one sample, the Sr isotopic composition of the others is relatively uniform, as indicated in Figure 6. The lowest value, plotting significantly below the horizontal reference line drawn in Figure 6, corresponds to sample FRA103-2. In this sample, a relevant portion of calcite was observed (Table 1), and some might have remained even after the HCl lixiviation process. If this sample is not taken into account, the calculated average for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the remaining samples is 0.7165. Also, although the samples exhibit similar mineralogical composition and quite similar Sr isotopic ratios, they show differences in their Rb/Sr ratios by a factor of 2. Once more, an almost horizontal best-fit line is found. In our interpretation, following the suggestion of Cordani, Kawashita & Thomaz-Filho (1978), this almost ‘zero age’ isochron line may have been obtained during an episode of mechanical mixing associated with halmirolysis, a process that, in this case, had enough time to act. Diagenetic processes apparently have not yet started to influence the sedimentary material.

3.d. Continental slope in the Campos Basin, South Atlantic Ocean

The Campos Basin is the most important of the Brazilian marginal basins for oil production. It comprises an area of about 100 000 square kilometres, with a depth of more than 5000 metres. Only a small part of this basin is emerged, near Campos in eastern Brazil (Dias *et al.* 1990). Sedimentation along the

continental slope, at more than 150 km from the coast, is strictly fine grained, extremely well sorted, and made up by silt and clay fractions. The samples for this work were obtained from two drillings made by PETROBRAS for geotechnical purposes, related to the fixation of oil production platforms. Eleven samples were obtained from drill site RJS-A, from the surface to about 144 metres, and 11 from the drill site RJS-B, from the surface to about 90 metres. The two sites (location in Fig. 1) are about 100 km apart. All samples consist of unconsolidated pelitic sediments, quite homogeneous, and comprising large amounts of microorganisms (especially Foraminifera). The clay fraction corresponds to 25–40 % in the RJS-A well site and to 35–50 % in the RJS-B site. Within the silt fraction, quartz and feldspar are the main components; detrital mica fragments were not observed. K-feldspar is common in site RJS-A, and plagioclase predominates in site RJS-B. Carbonate, especially calcite, is present throughout the sediments, and the clay fraction includes variable portions of chlorite, kaolinite, illite and mixed layers illite–smectite. The mineralogical and geochemical characteristics of these samples are included in Table 1.

In well site RJS-A, the samples were obtained at irregular intervals, down to 145 metres. The $^{87}\text{Rb}/^{86}\text{Sr}$ of the samples is close to 1.0 down to about 50 metres, and below that it drops by a factor of two. The sample at 84 metres depth (RJS-A7) has a Sr content of more than 900 ppm, much greater than in all the other samples. In well site RJS-B, the samples were also taken at irregular intervals, down to 90 metres. With the exception of the sample collected at the surface, which presents a Sr content of more than 700 ppm, the Rb/Sr ratios in this well are more uniform.

Given the relatively thick stratigraphic interval sampled in each well site, a few different depositional systems may have been recorded, and the sampling criteria envisaged by Thomaz-Filho & Lima (unpub. PETROBRAS report, 1979) are not fulfilled. In this case, we cannot expect the uniform dispersion associated with mechanical mixing, as recognized by Cordani, Kawashita & Thomaz-Filho (1978), producing a ‘zero age’ isochron for the entire set of samples. Moreover, the deposition of several tens of metres of sediments at the continental slope may have taken a great deal of time. Given the estimates of rates of sedimentation, it is feasible to consider the sediments at both well sites as being deposited over the whole of Holocene and Pleistocene times, and possibly the later part of the Pliocene. Since they are still unconsolidated, and diagenesis is only incipient, they must have been continuously in contact first with seawater, and later with the formation fluids.

The analytical points of the samples have been included in Figure 7. For site RJS-A, the four topmost samples (RJS-A1 to RJS-A4) yield reasonably similar Sr isotopic compositions, between 0.7118 and 0.7133.

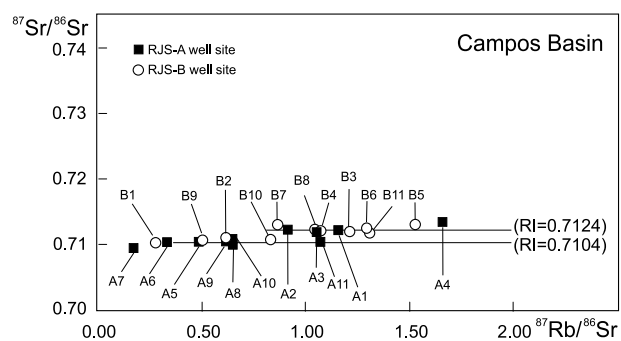


Figure 7. Rb–Sr isochron diagram for samples from the continental slope within the Campos Basin, Brazil.

For the seven other samples, down to the bottom of the profile, if sample RJS-A7 is not taken into account because of its different Sr content, the others yield quite homogeneous Sr isotopic compositions with an average of 0.7104 ± 0.0002 .

For site RJS-B, the distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with depth is more complex. The values are low for the two topmost samples (RJS-B1 and RJS-B2) and for samples RJS-B9 and RJS-B10 near the bottom of the profile. Higher values were found for the deepest sample and for the six samples collected within the 19 to 59 metres interval. These yield very similar results, with average value of 0.7124 ± 0.0004 (Fig. 7)

In addition to mechanical mixing, we suggest that the RJS-A and RJS-B well sites were subjected to varied chemical processes. Exchanges among clay particles and seawater and/or formation fluids within the sediments may have occurred in a prolonged time frame. The samples, collected at increasing depths, must have quite different stratigraphic ages and none of them yields a Sr isotopic composition with a distinctive detrital signature. Their isotopic ratios all range around 0.710–0.712, which is not very much above the seawater value. We believe that Sr mobility was pervasive and rapid, even at temperatures of surface environments, to produce the atomic replacements needed to achieve a near equilibration of the Sr isotopic composition. In such environments, some clays, especially smectites, are capable of reacting with formation fluids, which in a general way (especially in regard to Sr isotopic ratios) seem to be not very different from seawater. Therefore, we envisage that, given enough time, the Sr atomic exchanges between clays and fluids will induce an isotopic homogenization with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the clay-type material trending towards those of seawater Sr.

In the present example, the samples of the Campos Basin are from the topmost stratigraphic interval of an open marine environment, at depths of less than 150 metres. Although a slight correlation between Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may still be noted, horizontal best-fit lines are approached. We consider that this is the prevailing geochemical process in such surroundings

where early diagenesis occurs, and where the sedimentary environment controls the chemical composition of interstitial waters (see, e.g. Velde, 1995, and Clauer & Chaudhuri, 1995).

Looking toward future lines of research, we suggest that this process of Sr replacement in clays continues until the sediment undergoes effective burial and is compacted. The formation fluids are progressively losing contact with the clay material, and the systems become closed for Rb and Sr exchanges. Since each depositional basin exhibits a unique evolution, with specific rates of sedimentation and thermal subsidence, the depth at which lithogenesis imposes the closing of the Sr isotopic system within the resulting shale may vary greatly. In our view, the unconsolidated sediments that lie above this critical depth interval will be subjected to the described isotopic equilibration, and 'zero age' isochrons will be approached. Such a sedimentary pile, with recent sediments on top, may include layers at the bottom that could be as old as several tens of millions of years.

4. Discussion

A direct comparison of the results obtained for the different case studies chosen in this work is not possible, because of the great differences in the pelitic materials available, as described in the previous section. The selected samples exhibit differences in the content of siltose relative to argillaceous material, in the type and amount of detrital components, in the presence and amount of carbonates, as well as in the type and relative proportion of clay minerals. However, from the evidence produced in this study, some general ideas can be put forward, with a bearing on the interpretations of Rb–Sr dating of pelitic sediments.

The basic principle remains the use of the detrital silicate components of pelites for stratigraphic Rb–Sr dating. All the samples examined in this work contained detrital clays in different proportions, resulting ultimately from basement rock alteration. In the case of Holocene sediments, the nature of the material, either deposited in continental or marine environments, would not necessarily be very important for the main working hypothesis of mechanical dispersion and mixing leading to a uniform Sr isotopic composition. However, precise horizontal best-fit lines are not to be expected, because irregular distributions of the analytical points in the isochron diagrams will be a normal consequence of the different character of the detrital components in each sample.

In the case of the terrestrial environments of the Paraíba do Sul and Açu river deltas, no horizontal lines were obtained in the Rb–Sr diagrams. Such continental sites yield Rb–Sr systematics typical of detrital material, where the position of the analytical points in the diagrams is more or less constrained by the Sr isotopic composition of the source material

(Fig. 3). This also occurs to some extent with the samples of the Jacarepaguá coastal plain, but in this case an almost horizontal best-fit line was obtained in the tidal flat environment. This environment appears to be most appropriate for chemical exchanges among clay minerals and seawater. We have related this apparently successful result to the action of the process of halmirolysis, basically producing a partial removal of Sr into seawater (Fig. 5). This process might have enhanced the Rb/Sr ratio in a variable way in different samples, without interfering with the uniform value of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio obtained as a result of mechanical mixing.

When dealing with open marine sites, more time in contact with each other would permit ample chemical exchanges between the clay minerals and the seawater. This could improve the flattening of the best-fit lines in the Rb–Sr isochron diagrams, as can be seen in the case of the Amazon River mouth (Fig. 6). In this example, it should be noted that although a 'zero age' is almost obtained, the Sr isotopic composition is quite different from seawater value.

A much different interpretation has to be envisaged for the study of the two sites at the Campos Basin, where samples were taken in vertical profiles, down to certain depths. In both cases, nearly flat best-fit lines were obtained, with average Sr isotopic ratios not far from seawater value. It would have been convenient for direct comparison if the two sites were similar in terms of clay mineralogy. Unfortunately that was not possible, because the studied samples were the only ones available at the start of this work.

It seems that more energetic processes, such as those associated with the last phases of diagenesis, are connected with thermal subsidence and the evolutionary pattern of the clay material. Normally this results in a Sr loss and Rb gain, which means a general increase of the mixed-layers illite–smectite within the clay fraction, and in many cases the formation of relevant amounts of illite. At the same time, given the chemical exchanges among clays, a true Sr isotopic homogenization occurs, and these are the premises for the establishment of good internal Rb–Sr isochrons, with ages that could be much younger than sedimentation. Examples are given, for instance, by K. Kawashita (unpub. Ph.D thesis, Univ. São Paulo, 1972), Thomaz-Filho, Cordani & Kawashita (1976), Parenti-Couto *et al.* (1981), J. P. Morton (unpub. Ph.D. thesis, Univ. Texas, 1983) and Morton (1985), among many others.

5. Conclusions

Figures 3, 5, 6 and 7 indicate what may happen with the Sr isotopic systematics in pelitic sediments, in continental to open marine environments. Terrestrial environments seem to be inadequate to yield horizontal best-fit lines in Rb–Sr diagrams. However, when samples from environments such as tidal flats are

analysed, the best-fit lines may become more horizontal in the isochron diagrams. This can be attributed to halmirolysis, which would produce almost immediate preferential loss of Sr relative to Rb to seawater, enhancing the Rb/Sr ratios of the material. In such cases, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the resulting mud would be still very dependent on the source material, well above 0.710. This is also confirmed in open marine environments, provided that the time was not enough to induce thorough exchanges of the sedimentary clays with seawater. Given enough time, however, exchanges with formation fluids seem to induce the Sr isotopic composition of the sediments to approach the seawater value.

From the above, we believe that the dynamics of the general process of sedimentation of argillaceous material, as well as the chemical exchanges related to early and late diagenesis could provide relatively reliable Rb–Sr isochrons. These may be achieved either within such transitional environments where halmirolysis occurs, or within environments where the diagenetic processes induce the formation of ‘zero age’ isochrons in shallow sedimentary piles. We maintain that, when a sedimentary rock where clays are predominant (especially smectite and illite) is dated by the Rb–Sr whole rock isochron method, there are good possibilities of obtaining a meaningful age. Thomaz-Filho & Lima (unpub. PETROBRAS report, 1979) reported the sampling criteria, already mentioned. Their suggestion is to work at the decimetre scale. We think that for pelites, even if we downsize the samples further, to the centimetre scale, the possibility of achieving significant results is high. The resulting age values may well be younger than depositional age, but will be in any case a good indication marker for the geological history of the dated stratigraphic unit. As reported by Cordani *et al.* (1985b), this could be the only dating method available in many cases, and would be particularly useful when Precambrian unfossiliferous rocks are the targets of an age dating program (see, e.g. Parenti-Couto *et al.* 1981).

In conclusion, for isotopic dating of pelitic rocks, we recommend that some conditions regarding the depositional environments must be fulfilled. In our view, the following sequence of sedimentary processes and physical–chemical conditions of surface environments can be envisaged:

(1) In many large-scale depositional sites, mechanical mixing at the surface might be observed, following the proposal by Cordani, Kawashita & Thomaz-Filho (1978). In some favourable environments, such as in transitional or shallow marine ones, because of the influence of halmirolysis, the Rb–Sr best-fit lines may become more horizontal in isochron diagrams, with $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios well above 0.710.

(2) In open marine basins, exchanges with seawater occur at low temperature, inducing a reduction of the

$^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio to nearly 0.710. A ‘zero age’ isochron is maintained for some time while exchanges characteristic of early diagenesis are kept between the sediment and the formation fluids, before complete burial and expulsion of such fluids, when a first closing of the isotopic system occurs.

(3) When thermal subsidence and anchi- to epi-metamorphism are imposed upon the sediments, a true Sr isotopic homogenization is produced, even at the whole-rock level. The final closing of the system occurs in relation to regional cooling, and the age determination might yield an isochron age much younger than deposition, and with a $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio well above seawater value.

Up to now, in our studies (Cordani, Kawashita & Thomaz-Filho, 1978; Cordani *et al.* 1985b, and this work) we have only produced some preliminary evidence for the conditions described above. We would be glad to see much more evidence from different environments and different types of fine-grained material.

An essential part of our ideas is not yet tested. For the second of the conditions stated above we only have a hint, the Campos Basin example. To test the reality of the supposed ‘zero age’ isochrons in open marine environments, it will certainly be necessary to study other sedimentary situations, involving argillaceous material still in a pre-diagenetic stage. We hope that good evidence will be produced in future studies.

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