The Pb/Pb age of the Minas Supergroup carbonate rocks, Quadrilátero Ferrífero, Brazil

Marly Babinski[a,b,*], Farid Chemale Jr.[c], William R. Van Schmus[b]

[a]*Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo, Caixa Postal 11049, CEP 05499, São Paulo, SP, Brazil*
[b]*Isotope Geochemistry Laboratory, Department of Geology, University of Kansas, Lawrence, KS 66045, USA*
[c]*Depto. de Geologia, Universidade do Vale do Rio dos Sinos, São Leopoldo, RS, Brazil*

Abstract

Pb/Pb isochron ages determined on carbonate rocks from the Minas Supergroup, Quadrilátero Ferrífero (QF), show that the deposition of the Gandarela Formation, the intermediate unit of the Minas Supergroup, took place at 2420 ± 19 Ma. The entire sedimentary sequence and underlying basement rocks have been deformed at a regional scale, and data from greenschist facies carbonate rocks from the Piracicaba Group indicate that the Pb isotopes were reset at about 2100 Ma. This age is in agreement with whole-rock Rb/Sr and U/Pb titanite ages determined by many authors for metamorphism of the surrounding Archean granite-gneiss terrane.

1. Introduction

The Minas Supergroup is well exposed in the Quadrilátero Ferrífero (QF), Minas Gerais State, Brazil, an important economic iron district. This supergroup is a large sedimentary sequence mostly comprising clastic rocks (conglomerates, quartzites, phyllites) and chemical rocks (iron formation and carbonates). Although the QF is one of the most intensively investigated geological areas in Brazil, only one isotopic age has been determined on rocks of the Minas Supergroup. Machado et al. (1989, 1992) determined a U/Pb age on detrital zircon from the uppermost part of the Minas Supergroup, and the age of 2125 ± 4 Ma was interpreted as the maximum age for the top of the sequence. Based on available Rb/Sr data from the basement of

the Minas Supergroup, Cordani et al. (1980, 1989) and Teixeira (1985) suggested that the sedimentation of the Minas Supergroup should have taken place before the main tectonic event (~ 2.1 Ga) which affected this sedimentary sequence. However, no direct ages of the Minas Supergroup deposition have been determined.

Recently the Pb/Pb isochron method has provided a useful technique for determining ages on carbonate rocks and to obtain ages of sedimentation (Moorbath et al., 1987; Jahn et al., 1990) or metamorphic activity (Jahn, 1988). This paper presents the results of Pb/Pb analyses of Minas Supergroup rocks and has the following purposes: (1) to show that the Pb–Pb isochron approach for dating Proterozoic carbonate rocks is useful; and (2) to determine the direct sedimentation age and a subsequent metamorphic age for the Minas Supergroup. To obtain the age of sedimentation and metamorphism of the Minas Supergroup (initially presented by Babinski, 1991a, b), we collected samples from two different stratigraphic horizons where car-

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* Corresponding author. Present address: Instituto de Geociências, Universidade de São Paulo, Caixa Postal 20899, CEP 01498-970, São Paulo, SP, Brazil.
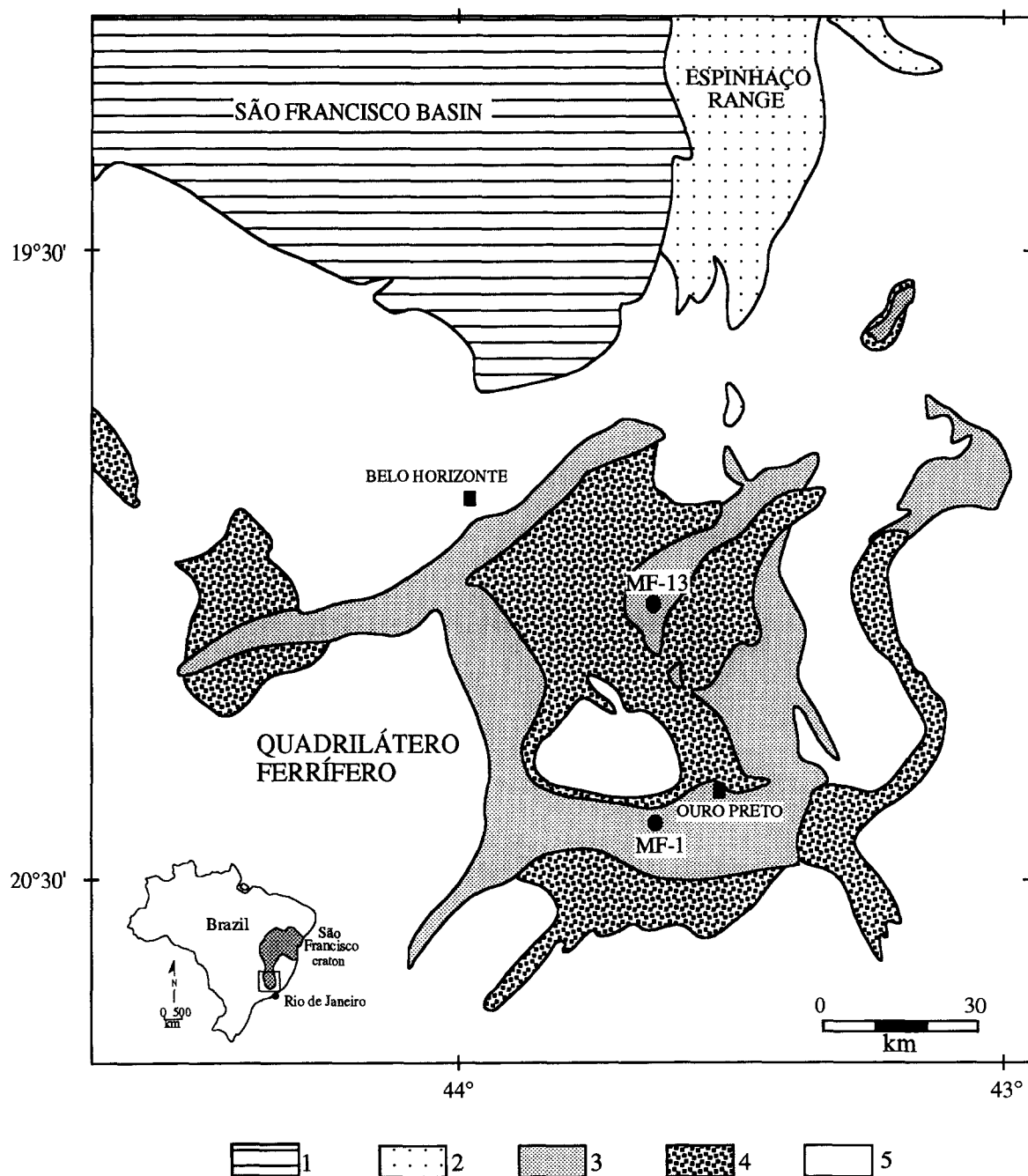
Fig. 1. Simplified geological map of the Quadrilátero Ferrífero (adapted from Inda et al., 1984) and location of the samples collected for this study. MF-1 = Fecho do Funil Fm.; MF-13 = Gandarela Fm.; 1 = São Francisco Supergroup; 2 = Espinhaço Supergroup; 3 = Minas Supergroup; 4 = Rio das Velhas Supergroup; 5 = granite-gneiss terranes.

bonate rocks are exposed. One set of samples is from the Gandarela Formation, which is low in the section and has carbonate rocks with well preserved stromat-

olite structures. The other set is from the stratigraphically younger Fecho do Funil Formation, which contains a lens of deformed and recrystallized dolo-

mitic carbonate with poorly preserved columnar stromatolites.

2. Geological setting

The Minas basin, represented by sediments of the Minas Supergroup, is interpreted either as an intracratonic basin (Chemale et al., 1994), or as a platform supracrustal sequence with a sialic substrate (Cordani et al., 1980; Marshak and Alkmim, 1989; Teixeira and Figueiredo, 1991). The distribution of the Minas Supergroup in the southeastern part of the São Francisco Craton (Almeida, 1977) defines the quadrangular shape of the Quadrilátero Ferrífero (Fig. 1). Basement to the Minas Supergroup in the Quadrilátero Ferrífero consists of granite-gneiss terranes and Rio das Velhas greenstone belts which formed during the Archean, with the main magmatic activity at 2.8 to 2.7 Ga (Machado et al., 1992; Machado and Carneiro, 1992).

The overlying Minas Supergroup (Fig. 2), generally assumed to be Paleoproterozoic, is made up of a basal unit of clastic rocks (Caraça Group), a middle unit of chemical rocks (carbonates and iron formations; Itabira Group), and an upper unit of interlayered clastic and chemical rocks (Piracicaba Group). The basal Caraça Group does not contain carbonate units and was not sampled for dating. The Itabira Group conformably overlies the Caraça Group, but the contact is tectonized and detailed relationships are obscure. The Itabira Group has extensive banded iron formations and is divided into the Cauê and Gandarela Formations (Dorr, 1969). The lower Cauê Formation is represented by normal, dolomitic and amphibolitic banded iron formation, compact hematite bodies, and phyllites. The overlying Gandarela Formation consists dominantly of carbonate rocks deposited in shallow water. In the Gandarela Syncline, which is one of the most important tectonic features of the Quadrilátero Ferrífero, stromatolitic structures occur in the intermediate member of the Gandarela Formation (Souza and Müller, 1984). Samples of those used in the present study were collected near Gandarela Farm (MF-13, Fig. 1). The samples are limestone with light and dark alternating bands that are about 20 cm thick and which display laminated stromatolitic structures (LLH and SH stromatolite types and oncolites; Logan et al., 1964). The sample

locality is in the central part of the Gandarela Syncline, which is a very low-strain area that has escaped the main tectonic events that affected Minas Supergroup units elsewhere.

The lower part of the Piracicaba Group is conformable and transitional with the Itabira Group. Lenses of dolomitic marble occur in the Fecho do Funil Formation (MF-1, Fig. 1), in the lower part of the Piracicaba Group (Fig. 2). The samples were collected from the Cumbi Quarry, near the town of Cachoeira do Campo (Fig. 1). In this region the Fecho do Funil Formation is represented by an association of terrigenous and chemical sedimentary platform facies, and the rocks have been deformed and recrystallized (Garcia et al., 1988). A 60 m thick dolomitic lens with poorly preserved columnar stromatolite structures is exposed at the top of this sequence. Samples are from light-gray, greenish and pinkish in color, deformed carbonate which contains columnar stromatolites as well as oncolites. A precise classification of the columnar stromatolites is not possible because the internal structures have been affected by the deformation and greenschist facies metamorphism (Dardenne and Campos Neto, 1975).

The Minas Supergroup units were affected at least by two main tectonic events in the Proterozoic, the first event being Transamazonian in age (~ 2.1 Ga), and the second one Brasiliano in age (~ 0.6 Ga). A Mesoproterozoic (~ 1.3 Ga) deformational event has also been postulated for this region (Cordani et al., 1980; Marshak and Alkmim, 1989; Teixeira and Figueiredo, 1991), but it is not well defined.

3. Analytical procedures

Preliminary dissolution experiments (Babinski, 1993) were carried out on the carbonate rocks using HCl (cf. Moorbath et al., 1987; Jahn, 1988), but subsequent tests showed that lower blanks (~ 0.1 to 0.2 ng; Tables 1 and 2) were obtained for samples dissolved with 0.6N HBr rather than 0.5N HCl, and we used HBr in subsequent studies, including this one. HBr was tested because the leachate can be prepared for the ion exchange column with less handling (see below). During our early experiments, samples were dissolved in five successive leaches using 2 ml of acid for each leach (e.g. 0.6N HBr). In most cases we observed that
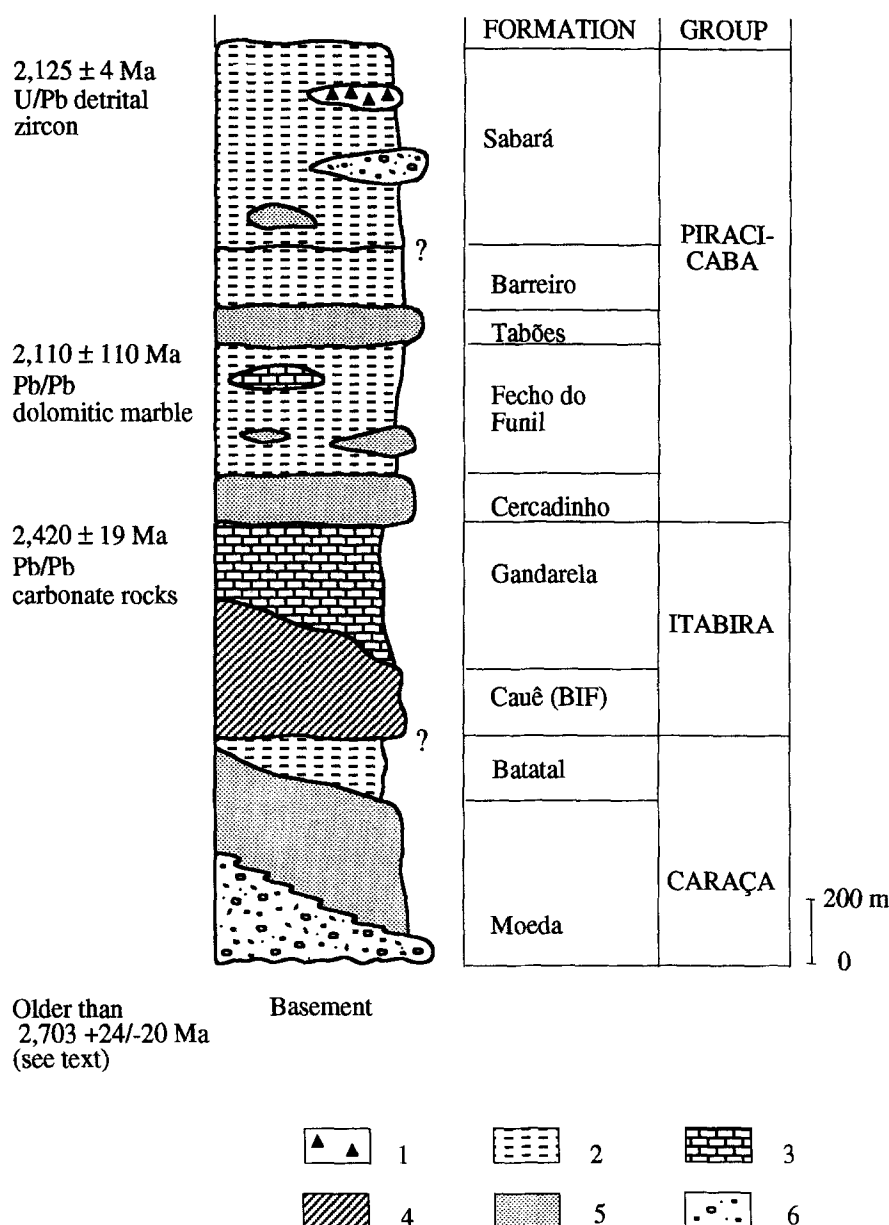
2,125 ± 4 Ma
U/Pb detrital
zircon

2,110 ± 110 Ma
Pb/Pb
dolomitic marble

2,420 ± 19 Ma
Pb/Pb
carbonate rocks

Older than
2,703 +24/-20 Ma
(see text)

FORMATION	GROUP
Sabará	PIRACI-CABA
Barreiro	
Tabões	
Fecho do Funil	
Cercadinho	
Gandarela	ITABIRA
Cauê (BIF)	
Batatal	CARAÇA
Moeda	

Basement

200 m

0

Fig. 2. Litostratigraphy of the Minas Supergroup (modified from Marshak and Alkmim, 1989): 1 = graywackes; 2 = phyllites and schists; 3 = carbonate rocks; 4 = banded iron formations; 5 = quartzites; 6 = conglomerates.

the Pb isotopic ratios became more radiogenic from the first to the last leach; however, the U and Pb concentrations were variable and did not follow a simple trend. In most cases, the Pb isotopic ratios obtained from the five-leach procedure showed moderate scatter on a $^{207}Pb/^{204}Pb$ vs $Pb^{206}Pb/^{204}Pb$ diagram. In order to min-

imize this scatter, a simpler dual-leach procedure was tested. The first leach, to remove any potential loosely bound or surface Pb, dissolved about 1/7 of the sample chips, and the second leach dissolved about 5/7 of the sample chips, extracting Pb primarily from interiors of chips (leaving about 1/7 of the chips undissolved). In

Table 1
Analytical data for the Gandarela Formation

Sample name	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Pb (ppm)	U (ppm)
MF-13-A1-L1-LP[a]	96.486	27.960	39.241	0.69	–
MF-13-A1-L2-LP[a]	109.680	29.916	39.790	0.80	0.58
MF-13-B1-L1-LP[b]	28.584	17.435	38.568	0.01	–
MF-13-B1-L2-LP[b]	39.959	19.792	38.948	0.15	–
MF-13-C1-L1-LP[a]	35.241	18.555	39.011	0.15	0.04
MF-13-C1-L2-LP[a]	46.226	20.548	39.491	0.15	0.06
MF-13-D1-L1-LP[b]	27.250	17.001	37.708	0.02	–
MF-13-D1-L2-LP[b]	38.543	19.441	39.043	0.14	0.08
MF-13-D2-L1-LP[a]	37.130	19.118	39.148	0.15	–
MF-13-D2-L2-LP[a]	37.964	19.366	38.967	0.17	–
MF-13-E1-L1-LP[b]	100.461	28.272	37.065	0.01	–
MF-13-E1-L2-LP[b]	136.764	34.766	37.861	0.49	0.48
MF-13-E2-L1-LP[a]	134.751	34.499	37.933	0.48	–
MF-13-E2-L2-LP[a]	144.318	35.979	37.926	0.57	–
MF-13-E3-L1-LP[a]	100.566	28.892	37.417	0.42	0.11
MF-13-E3-L2-LP[a]	117.698	31.898	37.922	0.48	0.37
MF-13-F1-L1-LP[a]	30.883	17.763	37.798	0.05	–
MF-13-F1-L2-LP[a]	36.623	19.054	38.092	0.12	0.02
MF-13-G1-L1-LP[a]	104.768	29.863	37.883	0.45	0.13
MF-13-G1-L2-LP[a]	118.035	32.058	37.908	0.51	0.31
MF-13-A1-L1-DP[a]	37.371	18.975	39.608	0.24	0.07
MF-13-A1-L2-DP[a]	41.924	19.916	40.325	0.29	–
MF-13-B1-L2-DP[b]	38.498	19.530	40.308	0.11	0.04
MF-13-C1-L2-DP[b]	49.685	21.021	40.351	0.27	0.13
MF-13-C2-L1-DP[a]	47.890	20.707	40.184	0.31	0.04
MF-13-C2-L2-DP[a]	50.008	21.065	40.435	0.50	0.17
MF-13-D1-L2-DP[b]	41.285	19.771	40.827	0.20	0.06
MF-13-D2-L1-DP[a]	40.675	19.705	40.516	0.26	0.02
MF-13-D2-L2-DP[a]	41.773	19.837	40.882	0.42	0.07
MF-13-E1-L2-DP[b]	40.235	19.576	40.302	0.11	0.11
MF-13-E2-L1-DP[a]	42.511	20.001	39.410	0.33	0.04
MF-13-E2-L2-DP[a]	44.332	20.224	39.651	0.53	0.18
MF-13-F1-L2-DP[b]	43.301	20.002	39.433	0.16	0.06
MF-13-G1-L1-DP[a]	38.791	19.279	38.260	0.36	0.03

LP = light band and DP = dark band. Isotopic ratios in Tables 1 and 2 have been corrected for fractionation using 0.13%/amu, as determined through multiple analyses of NBS-981 common Pb standard. Concentrations were determined using a mixed U–Pb spike with 5.3686 ppm ^{235}U and 0.6374 ppm ^{208}Pb. Total blanks for data from leach 1 (L1) is less than 0.1 ng, and for leach 2 (L2) less than 0.2 ng. The Pb concentrations presented in this paper are slightly different from those published in Babinski et al. (1991a, b) due to corrections made on the equations.
[a] = Dissolution with 1.2N HBr. [b]Dissolution with 0.6N HBr.

general, Pb isotopic compositions from the second leaches plotted more coherently and with less scatter. For most samples the Pb isotopic compositions obtained in the first leaches did not fit on the lines defined by the respective second leaches, implying another component of Pb such as contamination from sample handling (crushing, hand picking, etc.) which can interfere with the Pb isotopic ratios.

For this study the dual-leach procedure was applied using either 0.6N or 1.2N HBr. The initial aim of using 1.2N HBr was that using smaller amounts of acid could result in lower procedure blanks. However, there was no significant difference in blanks using either acid, and any potential advantage was apparently offset by less selectivity of phases dissolved in the first leach using 1.2N HBr (see Sect. 4), so that 0.6N HBr was preferred toward the end of the study. Hand samples were first crushed into small (0.2 to 0.5 cm) pieces, washed three times with 2-bottle (Mattinson, 1972) distilled H_2O (2B H_2O), and dried on a hot plate. About

Table 2
Analytical data for the Piracicaba Group

Sample name	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Pb (ppm)
MF-1-A1-L1[b]	23.599	16.672	40.692	0.06
MF-1-A1-L2[b]	23.650	16.842	40.523	1.90
MF-1-B1-L1[b]	22.921	16.487	40.238	0.01
MF-1-B1-L2[b]	24.173	16.886	40.389	1.51
MF-1-C1-L1[b]	21.311	16.138	39.832	0.01
MF-1-C1-L2[b]	23.337	16.778	40.261	1.37
MF-1-D1-L1[b]	24.512	16.725	40.573	0.13
MF-1-D1-L2[b]	24.413	16.908	40.421	1.89
MF-1-D2-L1[b]	23.153	16.478	40.187	0.01
MF-1-D2-L2[b]	24.387	16.912	40.409	1.94
MF-1-E1-L1[b]	25.363	16.971	41.556	0.10
MF-1-E1-L2[b]	25.129	17.003	41.212	1.50
MF-1-F1-L1[b]	25.934	17.015	41.657	0.04
MF-1-F1-L2[b]	25.467	17.062	41.108	1.41
MF-1-G1-L1[b]	24.150	16.942	40.989	0.10
MF-1-G1-L2[b]	24.399	17.001	40.885	1.33
MF-1-H1-L1[b]	23.579	16.730	40.446	0.02
MF-1-H1-L2[b]	23.888	16.903	40.598	1.30
MF-1-I1-L1[b]	24.697	16.996	41.629	0.13
MF-1-I1-L2[b]	24.291	16.972	40.838	1.52

For explanation see Table 1.

430 mg of clean sample chips was weighed in a Teflon Savillex beaker. The first leach (L1) was performed with 2 ml of 0.6N HBr or 1 ml of 1.2N HBr, with about 60 mg of sample being dissolved after reaction had ceased (about 3 h). The solution and residue were transferred to a test tube and centrifuged for about 4 min. The clear solution was split into a 75% aliquot for Pb isotopic composition and a 25% aliquot for Pb and U concentration analysis using a mixed $^{208}Pb-^{235}U$ spike. The residual chips were transferred to a Savillex beaker, washed three times with 2B H_2O, dried and weighed. For the second leach (L2), 10 ml of 0.6N HBr (5 ml of 1.2N HBr for some samples) was added to the residue of L1 and allowed to react overnight to achieve complete reaction. For L2 the samples were also aliquoted for Pb isotopic composition and Pb and U concentration analyses after the solutions were centrifuged.

After the aliquots of solution were prepared, they were dried and 2–3 ml of 0.6N HBr was added to the residue (if the normality of HBr exceeds 1.0N, Ca is also retained on the resin). The Pb and U were extracted using ion exchange techniques, with AG-1X8, 200–400 mesh, anion resin. Polyethylene columns with 0.03 ml of resin were pre-washed with 3.0 ml of 6N HCl

and 0.3 ml of 2B H_2O and then conditioned with 0.3 ml of 0.6N HBr. The sample solution was added and the resin was rinsed three times with 0.3 ml of 0.6N HBr to remove Ca and other elements from Pb (for spiked samples the rinses were saved for further U purification); Pb was collected with 1.0 ml of 6N HCl. This solution was dried and subjected to a second purification of Pb following the same procedure. The final solutions were dried with one drop each of 7N HNO_3 and 0.25N H_3PO_4. Pb blanks were ⩽0.1 ng for L1 and ⩽0.2 ng for L2. For L2 fractions of carbonate having Pb concentrations of 1 to 2 ppm (e.g., MF-1; ~300–600 ng Pb per analysis), the blank has negligible effect on the Pb isotopic compositions measured. However, for L1 fractions with low Pb concentrations, the blank could have a significant effect on the measured Pb isotopic compositions.

The solution containing U from a spiked aliquot was dried and 2.0 ml of 7N HNO_3 was added. This solution was passed through an ion exchange column filled with 2.0 ml of AG-1X8, 200–400 mesh, anion resin previously rinsed twice alternatively with 2.0 ml of 6N HCl and 2.0 ml of 2B H_2O and preconditioned with 2.0 ml of 7N HNO_3. The sample and resin were eluted three times with 2.0 ml of 7N HNO_3, and the U was collected

by eluting with 2.0 ml of 2B H_2O followed by 2.0 ml of 6N HCl. The U-bearing solution was dried with one drop of 0.25N H_3PO_4. U blanks were generally below detection limits (<0.01 ng).

Mass spectrometry analyses for Pb isotopic composition and Pb and U concentrations were carried out with a multicollector VG Sector Mass Spectrometer. Samples were loaded on single Re filaments with silica gel and H_3PO_4 and measured as Pb^+ and UO_2^+. The Pb isotopic ratios were corrected to a fractionation factor of 0.13% per atomic mass unit, based on successive determinations of NBS 981 Common Pb standard.

The Pb concentrations determined on L1 fractions of MF-13 are significantly lower than those determined for L2 fractions when the sample is dissolved with 0.6N HBr (versus the case for using 1.2N HBr). Also, the L1 Pb isotopic compositions are less radiogenic compared to L2 compositions (Table 1). The less radiogenic nature of L1 fractions is probably due to greater influence of blank (non-radiogenic) Pb, primarily because of the lower total amounts of sample Pb in L1 fractions. However, the differences in Pb concentrations determined for L1 and L2 fractions when using the lower normality HBr are still not well understood. One possible explanation is that the first 0.6N HBr leach preferentially dissolved a low-Pb carbonate phase, while the second leach dissolved a remaining, higher-Pb carbonate phase; this effect would be much less pronounced for 1.2N leaches because the higher normality could be less selective for dissolving the hypothetical low-Pb phase. However, microscopic inspection of chips after the first leach with 0.6N acid did not reveal evidence for such selective dissolution, since most chips had relatively smooth outer surfaces rather than deep etch pits that one would expect if one mineral phase (or intergranular or vein material) were preferentially dissolved. Furthermore, X-ray diffraction analyses of MF-13 samples did not suggest preferential dissolution of calcite relative to dolomite (dolomite is only a minor constituent for MF-13). Another possibility is that Pb released during the 0.6N leach was adsorbed onto the surface of the remaining chip, but that use of 1.2N acid prevented this adsorption. However, the reaction goes to completion, so that the acid is effectively neutralized and the end solutions in both cases should be chemically similar. A third possibility is that stronger acid (1.2N HBr) not only leaches the carbonate phase but also attacks some other

phase (clays or dolomite) that could be present and which has higher Pb concentration. However, if this were the case, we would expect to see a significant shift in Pb compositions for 1.2N L1 leaches relative to 0.6N L1 leaches, and none is apparent from the data in Table 1. Thus, we have no explanation for this phenomenon at present; it is under further investigation, and in this paper we will only base our conclusions on data from the L2 fractions, which are most representative of the bulk samples.

4. Results

Seven samples from dark bands and seven samples from light bands of very weakly deformed stomatolitic limestones from the Gandarela Formation (MF-13) were analyzed for Pb isotopic composition; Pb concentrations were determined for selected samples (Table 1). Because of the less precise results from L1 fractions (see above), all conclusions are based on L2 fractions.

The Pb isotopic compositions from MF-13 (Gandarela Formation) show a large range in values which, when plotted on a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 3), fall into three groups: (a) highly radiogenic Pb from some of the light bands; (b) less radiogenic Pb from the other light bands; and (c) less radiogenic Pb from the dark bands. Data from groups (a) and (b) (except sample A1) define a Pb–Pb isochron age of 2420 ± 19 Ma ($P < 0.01$, MSWD = 187); the low uncertainty for the age results mainly from the large range in data, which overrides uncertainties due to scatter about the regression line. Group (c) data from the dark samples appear to be parallel to, but slightly below, this isochron, suggesting that its initial ratio had a slightly lower initial $^{207}Pb/^{204}Pb$ ratio. However, inclusion of all L2 data (except A1 light and B1 dark, which clearly plot separately from the rest of their respective groups) yields an indistinguishable isochron age of 2430 ± 15 Ma ($P < 0.01$, MSWD = 1150). Rock textures, including excellent preservation of stromatolite structures and lack of deformation, suggest that this age may represent the depositional age for the limestones of MF-13 in particular and the Gandarela Formation in general (in any case it is a minimum age; see further discussion below).

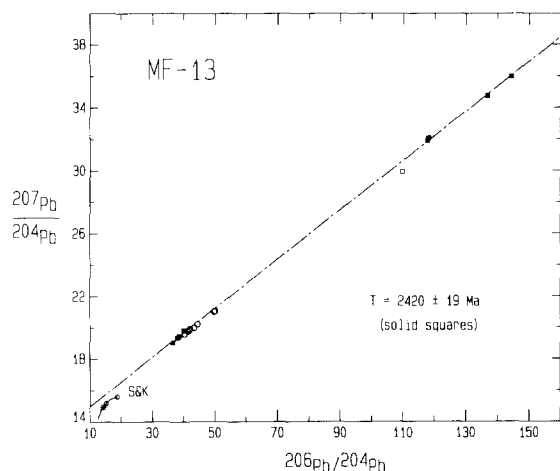Dolomitic carbonates from the Fecho do Funil Formation, Piracicaba Group, were collected from two dif-

Fig. 3. $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram from the Gandarela Formation: solid squares = light bands (except sample MF-13-A1); open square = samples MF-13-A1; circles = dark bands. *S&K = Pb isotopic compositions at 2.4 Ga according to the Stacey and Kramers (1975) model. Isochron ages assuming two-stage evolution and calculated using the reduction program of Ludwig (1983), with input errors of 0.1% (2σ) for all isotopic ratios. Errors in calculated ages are at 95% confidence level. Decay constants used: $\lambda^{238}U = 0.155125$ Ga^{-1}, $\lambda^{235}U = 0.98485\ Ga^{-1}$.
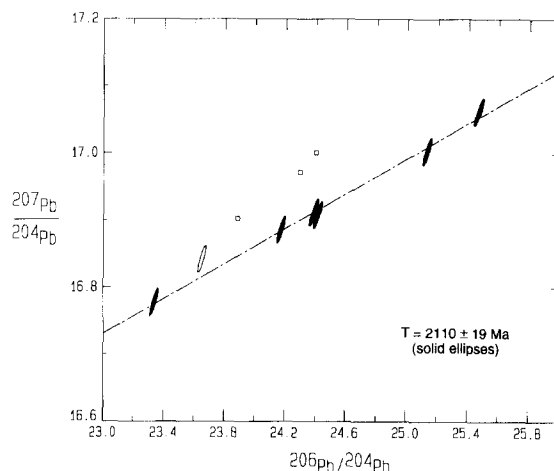

Fig. 4. $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram from the Fecho do Funil Fm.: solid ellipses = samples MF-1-B to F; open ellipse = sample MF-1-A; open squares = samples MF-1-G to I. The parameters are the same as those of Fig. 3.

ferent vertical sections about 30 m apart in the same quarry (samples MF-1). Six samples (MF-1A to F) were collected from one section, and three samples (MF-1G to I) from the other. Both localities appear to have experienced similar degrees of deformation. All the samples from the Fecho do Funil Formation were dissolved with 0.6N HBr; the data are shown in Table 2. For these samples the Pb concentrations determined on L1 were also significantly lower (see discussion above for MF-13). As for MF-13, the following conclusions are based on L2 fractions only. Pb from MF-1 samples is distinctly less radiogenic than that from MF-13, but Pb concentrations in MF-1 samples are distinctly higher. This could be due either to incorporation of more common Pb in MF-1 samples during deposition or to additions of non-radiogenic Pb from circulating aqueous solutions during subsequent deformation and metamorphism; we have no basis for choosing between these alternatives at present, and the question does not bear on the conclusions presented below. When L2 Pb data from the first section (samples A–F) are plotted on a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram, they yield a coherent isochron that has a short

range ($^{206}Pb/^{204}Pb$ from 23.3 to 25.5) and some scatter (Fig. 4), yielding an apparent age of 2050 ± 230 Ma ($P = 0.02$) with a relatively large uncertainty due primarily to the small spread in the Pb isotopic compositions. Data for samples G, H, and I plot above this isochron, suggesting that the rocks sampled at the second section may have retained a significant amount of their original radiogenic Pb during 2.1 Ga alteration (see below). However, the apparent age derived from them is $\sim 2710 \pm 150$ Ma, too old to represent a depositional age, indicating that they do not represent simple closed systems. Since sample A1 plots above the main array defined by samples B–F, it may also have retained a small amount of older radiogenic Pb. Exclusion of sample A1 yields a more precise regression age of 2110 ± 110 Ma ($P = 0.45$), which we prefer as the best estimate of the "age" represented by these samples. In any case, the Pb isotopes from this locality suggest an event at ~ 2100 Ma. Because of the deformed and metamorphosed character of the rock in this quarry, we interpret this age as representing a metamorphic event which caused loss or re-equilibration of radiogenic Pb in most samples; it is a minimum age of deposition.

5. Discussion

A sedimentation age for the Minas Supergroup has been suggested by many authors using indirect meth-

ods. Dardenne and Campos Neto (1975) suggested an age of about 1350 Ma for the Piracicaba Group based on types of stromatolite structures from the Fecho do Funil Formation. Paleoproterozoic sedimentation ages have been suggested by other authors (Cordani et al., 1980, 1989; Teixeira, 1985) based on Transamazonian metamorphism of the Minas Supergroup rocks and on the age of regional deformation determined from the basement rocks using Rb/Sr whole-rock data (2.2–2.0 Ga). Machado et al. (1989) published a U/Pb age of 2125 ± 4 Ma from detrital zircon in the uppermost formation (Sabará Fm.) of the Minas Supergroup, which they interpreted as the maximum depositional age of this formation. Also, a metamorphic age of 2060 to 2030 Ma determined on sphene from granitic gneisses in the Quadrilátero Ferrífero area is considered as a minimum age of deposition for Minas Supergroup units (Machado et al., 1992).

According to the data cited above, there is general agreement for an age of about 2.0 to 2.1 Ga for the regional metamorphic event that took place in the Quadrilátero Ferrífero area and affected the Minas Supergroup units. Our Pb/Pb isochron age of ∼2100 Ma determined from deformed dolomitic carbonates from the Fecho do Funil Formation is also interpreted as a Transamazonian metamorphic age affecting the Minas Supergroup (Cordani et al., 1980, 1989; Teixeira, 1985; Marshak and Alkmim, 1989; Chemale et al., 1994). We do not interpret 2100 Ma as the depositional age: (a) because of the deformed and metamorphic nature of the rocks, and (b) because it is from rocks stratigraphically significantly older than the Sabará Formation.

A 2420 ± 19 Ma Pb/Pb isochron age was determined on weakly deformed stromatolitic carbonate rocks from the Gandarela Formation, which belongs to the intermediate Itabira Group of the Minas Supergroup, and overlies the BIFs of the Cauê Formation. Because the carbonate rocks are exposed in the central area of the Gandarela Syncline, the least deformed part of the structure where well-preserved primary structures as stromatolites (Souza and Müller, 1984), bedding, and flaser-structures can be found, the age of 2420 ± 19 Ma is interpreted as the depositional age of the upper part of the Itabira Group. However, in view of the ∼2100 Ma age inferred for deposition of the Sabará Formation, as discussed above, it is important to be certain that the age for the Gandarela Formation is correct and com-

patible with the age of the Sabará Formation. The age is defined by the isochron in Fig. 3, which is controlled by data from the light bands in this rock. The very radiogenic nature of the Pb and the high U concentrations for samples E1, E2, E3, and G1 preclude an exotic source for this Pb, which must have formed by the in-situ decay of uranium. The only perturbation that would be reasonable would be for partial radiogenic Pb loss, as inferred for sample A1, which would result in an age that was too young, rather than too old. Alternatively, the less radiogenic Pb from samples B1, C1, D1, D2, and F1 could be argued to be secondary enrichment, causing the lower end of the isochron to be rotated to yield an older apparent age. However, the lower end of the isochron already passes above an average crustal Pb growth curve (Fig. 3), as represented by the two-stage model of Stacey and Kramers (1975), implying that initial Pb for the suite was significantly more radiogenic (higher-μ environment) than one would normally infer for 2.4 Ga crustal Pb. For secondary Pb to have brought the lower end of the isochron down, creating a falsely old age, the initial Pb in samples E and G must have been even more radiogenic than implied for the preferred case. Thus, we interpret the data for the light layers to represent Pb that is a mixture of 2420 Ma old radiogenic Pb with ∼2420 Ma initial Pb from a high-μ environment. The lower end of the growth curve intersects a Stacey and Kramers (1975) second-stage 2420 Ma geochron at a μ-value of 14.5 (initial $^{206}Pb/^{204}Pb \approx 15.83$, $^{207}Pb/^{204}Pb \approx 15.92$). Calculation of the $^{206}Pb/^{238}U$ age for sample E1 yields $t \approx 3300$ Ma, showing that some uranium has probably been leached from the sample during near-surface exposure.

The time of the initial deposition of the Minas Supergroup is still poorly known. The initial sedimentation of the Minas Supergroup, which corresponds to Caraça Group deposition, should have started at some point before 2420 Ma and after uplift and erosion of the Archean basement. According to Machado et al. (1992) the main volcanic and granitoid emplacement in the Rio das Velhas Supergroup occurred at 2776 Ma, and the late- to post-orogenic granitic dykes that mark the end of the orogeny were intruded at 2703 $^{+24}_{-20}$ Ma (Machado and Carneiro, 1992). Thus deposition of the Caraça Group must have begun significantly after 2700 Ma, allowing time for uplift and erosion. This group consists primarily of coarse clastic rocks which could have accumulated relatively rapidly, so that deposition

of the Itabira Group could have begun soon after deposition of the Caraça Group started. Therefore the maximum lower limit for the age of the Itabira Group is 2700 Ma, although one could argue that ~2600 Ma is more reasonable.

Deposition of the Itabira (intermediate) and Piracicaba (upper) Groups is assumed to be nearly continuous, since the contacts between formations of these units are gradational, except between the Barreiro and Sabará Formations, for which the contact is abrupt. The Sabará Formation displays a maximum depositional age of 2125 ± 4 Ma (Machado et al., 1989, 1992). The Gandarela and Sabará Formations are thus separated by an interval of about 300 Ma, which may correspond to a normal but slow sedimentation rate for the Itabira and Piracicaba Groups. However, a time interval of non-deposition in the sequence cannot be ruled out. If an unconformity is present, we suggest it is between the Barreiro and Sabará Formations, where the contact is abrupt and there are compositional differences between the lithologies of the two formations.

6. Conclusions

The Pb/Pb isochron age of 2420 ± 19 Ma determined on weakly deformed stromatolitic carbonate rocks from the Gandarela Formation, which we interpreted as the depositional age for this intermediate unit of the Minas Supergroup, is the first age directly determined on the Minas Supergroup rocks. In addition, we suggest that the initial sedimentation of the Minas Supergroup (Caraça Group) started soon after the stabilization and erosion of the underlying 2.7 Ga Rio das Velhas Supergroup rocks, e.g., 2600 to 2700 Ma. A Pb/Pb isochron age of 2110 ± 110 Ma defined on deformed dolomitic carbonates from the Fecho do Funil Formation, Piracicaba Group, is interpreted as representing the Transamazonian metamorphic event in the Quadrilátero Ferrífero area; it is in agreement with the previous ages of metamorphism determined on the basement rocks and inferred to have affected the Minas Supergroup units.

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