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Article:

1   **Re-Os age constraints and new observations of Proterozoic glacial deposits in the Vazante Group,**

2   **Brazil**

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20

21   ABSTRACT

22   A new Re-Os radiometric age date for an organic-rich shale horizon from the Vazante Group in Brazil,

23   coupled with geological observations, provide evidence for late Mesoproterozoic glacial episodes,

24   conflicting with the general view of greenhouse conditions marked by a eustatic high stand at this time.

25   Field observations of a reverse fault juxtaposing older Mesoproterozoic sedimentary rocks above younger

26   Neoproterozoic strata provide a new stratigraphic framework and reconcile the apparent inversion of U-

27   Pb detrital zircon ages through the succession.   Combined, the geochronological, geochemical and

28   stratigraphic evidence suggest that the Vazante Group sediments accumulated along a passive margin of

29   the São Francisco craton and are correlative with the neighboring Paranoá Group. Biomarker, sulfur

30   isotope and iron speciation analyses support the interpretation of a strongly stratified water column during

31   post-glacial transgression and deposition of one of the bituminous shale horizons. The relationship of the

32   glaciogenic Vazante Group to other late Mesoproterozoic successions, such as the non-glacial Atar Group

33   in West Africa and Bylot Supergroup in arctic Canada, however, remains enigmatic.

34

35   Key words: Vazante Group; Mesoproterozoic glaciation; Re-Os geochronology; Fe-speciation

36

37   **1. Introduction**

38   The Precambrian geologic record contains evidence of widespread ice ages, including diamictite

39   left behind by melting glaciers, capped by texturally and isotopically anomalous carbonate and organic-

40   rich shale that accumulated in the wake of rising sea levels (Harland and Bidgood, 1959; Kaufman et al.,

41   1991; Kirschvink, 1992; Kennedy 1996; Hoffman et al., 1998; Schrag et al., 2002; Bekker et al., 2005).

42   Existing age constraints suggest that these Precambrian ice ages were episodic rather than continuous,

43   with a series of temporally discrete glaciation events occurring at the beginning and end of the

44   Proterozoic Eon (*cf*. Kaufman et al., 1997; Kennedy et al., 1998; Walter et al., 2000; Kendall et al., 2004;

45   2006) but with little evidence of glaciation in the intervening billion years.

46   Due to the general lack of radiometric determinations on sedimentary successions, however, the

47   absolute ages of many of the Proterozoic diamictites are poorly known. To advance understanding of the

48   tempo and mode of these ancient ice ages, researchers have applied a geochronometer based on the

49   radioactive decay of ^{187}Re to ^{187}Os, most commonly on samples of organic-rich shale preserved in drill

50   cores (Kendall et al., 2004; 2006; Azmy et al., 2008; Rooney et al., 2010) or syn-depositional sulfide

51   grains (Hannah et al., 2004). Published results for Neoproterozoic (1.0-0.542 Ga) successions support the

52   view that the Sturtian and Marinoan glacial epochs represented multiple discrete ice ages over a

53   protracted time frame (*cf*. Kaufman et al., 1997). Contrary to expectations, a Re-Os study of a dropstone-

54 laden shale horizon from the Vazante Group in south-central Brazil (Azmy et al., 2008) indicated a late

55 Mesoproterozoic age – a time previously believed to have been ice free.

56   In this paper, we re-evaluate the stratigraphic position of this shale, which was previously

57 interpreted to be syn-glacial in origin (Olcott et al., 2005) and support the Mesoproterozoic age with new

58 Re-Os work from a second shale horizon unrelated to glacial deposits, as well as identify a thrust fault

59 lower in the Vazante Group that juxtaposes older Mesoproterozoic strata above younger glaciogenic

60 sedimentary rocks of Neoproterozoic age. Detrital zircon U-Pb constraints for the Vazante Group

61 (Rodrigues et al., 2012), coupled with carbon and strontium isotope data and paleontological evidence,

62 are consistent with the stratigraphic inversion and our Re-Os age determinations.

63

64 **2. Geologic and Geochronologic Background**

65   The Vazante Group is a sedimentary succession that occurs in wide swaths atop the eastern part

66 of the Brasília Fold Belt (BFB) on the western margin of the São Francisco craton throughout Minas

67 Gerais, Brazil (Fig. 1). Surface outcrops are strongly weathered and the succession has been exposed to

68 sub-greenschist facies metamorphism (Babinski et al., 2005; Azmy et al., 2008), but well preserved

69 carbonate and organic-rich shale are available in drill core. Figure 2 shows a generalized stratigraphy of

70 the Vazante Group, including three potential glacial horizons, as well as the reverse fault located near the

71 town of Lagamar (Pinho and Dardenne, 1994), which resulted in older strata of the Vazante Group –

72 including the shale horizons studied here – to overly younger sedimentary rocks (see Section 5.1 for

73 further details and implications). The basal Vazante diamictite (St. Antônio do Bonito Formation) has

74 long been interpreted as glacial in origin based on the presence of faceted and striated cobbles of mixed

75 lithology, including basement clasts, floating in a mudstone matrix (Dardenne, 2000). The two upper

76 Vazante Group diamictites at the base of the Morro do Calcário and Lapa formations are characterized by

77 carbonate breccia or laminated shale disrupted by carbonate dropstones. Further evidence for a glacial

78 origin for the two upper Vazante diamictites includes: 1) their widespread distribution across the basin; 2)

79 the observation that cobbles and boulders in the Morro do Calcário (previously attributed to the Serra do

80   Poço Verde Formation) are both rounded and angular, with the rounded stones often faceted (Fig. 3A, B);

81   3) the thick black Morro do Calcário shale contains glendonite, a pseudomorph of ikaite, a carbonate

82   mineral that forms in organic-rich sediment at temperatures between -1.9 to 7°C (*cf.* Olcott et al., 2005);

83   4) the uppermost strata of the Lapa diamictite are Fe-oxide cemented with local accumulations of iron-

84   formation (*cf.* Derry et al., 1992; Kaufman et al., 1997; Hoffman et al., 1998); and 5) the carbonates and

85   marl overlying both diamictites preserve negative $\delta^{13}C$ excursions typical of post-glacial cap carbonates

86   (Azmy et al., 2001; 2006; Brody et al., 2004).

87   The three shale horizons sampled for Re-Os analysis in this study were from, in ascending order,

88   the pre-glacial Serra do Garrote Formation and the post-glacial Morro do Calcário and Lapa formations.

89   The Serra do Garrote Formation consists of dark grey shale hundreds of meters thick that has been

90   metamorphosed to a greenish slate in some areas; the shale can be carbonaceous and/or pyrite bearing

91   (Dardenne, 2000). The Morro do Calcário and Lapa formations are both composed of laminated shale

92   and dolostone, which contain intermittent ice-rafted debris and based on core observations are each

93   several hundred meters thick (Dardenne, 2000). The true thickness of these units, however, is difficult to

94   ascertain insofar as outcrops are discontinuous and coupled with the likelihood of tectonic repetition of

95   strata due to thrust faulting. The Morro do Calcário and Lapa formations accumulated during post-glacial

96   transgression over sub-glacial valleys largely filled with carbonate breccia. Sub-glacial unconformities cut

97   through underlying carbonate platform deposits of the Serra do Poço Verde and Morro do Calcário

98   formations (indicated by the heavier formation-boundary lines in Fig. 2); in some cores it appears that the

99   two upper Vazante Group diamictites are in direct contact while in others they are separated by a variety

100   of bedded lithologies.

101   The age of the Vazante Group is controversial. Cloud and Dardenne (1973) argued that the

102   presence of the stromatolite *Conophyton metula Kirichenko* (Fig. 3C) near the base of the Lagamar

103   Formation suggests an age ranging between 1350 and 950 Ma. Stromatolite biostratigraphy, however, is

104   poorly constrained and competing tectonic models suggest a Neoproterozoic initiation of Vazante Group

105   sedimentation either in a rapidly subsiding foreland basin associated with the Brasíliano collision (*ca.* 790

106 Ma; Dardenne, 2000) or along a passive continental margin during supercontinent breakup (*ca*. 900 Ma;

107 Pimentel et al., 2001). Whole rock Rb-Sr data for a Vazante Group shale yielded an isochron age of ~600

108 Ma, but this age likely represents a date related to Brasíliano metamorphism (Amaral and Kawashita,

109 1967). A Neoproterozoic age for the upper Vazante Group was suggested based on a comparison of time-

110 series isotope trends (Azmy et al., 2001), although an alternative interpretation of these variations

111 suggested an older potential age for the succession (Misi et al., 2007). Most recently, Re-Os dates of 993

112 ± 46 and 1100 ± 77 Ma (excluding Re- and Os-poor samples) were determined from a dropstone-laden

113 shale in the Vazante Group previously believed to be part of the Lapa Formation (Azmy et al., 2008) but

114 here is assigned to the Morro do Calcário Formation (see below).

115

116 **3. Methods**

117　　　　All samples were taken from two pristine drill cores provided by Votorantim Metais. For Re-Os

118 analysis, samples were selected from the Serra do Garrote Formation in drill hole 134-86, from roughly

119 coeval horizons of the Morro do Calcário Formation in drill holes 42-88 and 134-86 and from the Lapa

120 Formation in drill hole 134-86. The upper two shale horizons in core 134-86 are separated by a thick

121 interval of carbonate breccia, quartzite and iron-cemented diamictite (Brody et al., 2004). In 2009, we re-

122 examined this core and concluded that the shale horizon Azmy et al. (2008) studied from drill hole

123 MASW-01 belonged to the Morro do Calcário Formation, rather than the Lapa Formation as previously

124 discussed.

125

126 *3.1 Re/Os*

127　　　　The Re-Os system can provide precise depositional ages for organic-rich shale because these

128 facies are often deposited in anoxic environments where Re and, to a lesser extent, Os may be sequestered

129 from seawater in their reduced states and incorporated into organic matter (Ravizza and Turekian, 1989;

130 Cohen et al., 1999; Selby and Creaser, 2003; Kendall et al., 2004). Once incorporated in the sediment,

131 ^{187}Re undergoes beta decay to ^{187}Os with a half-life of approximately ~42 Ga. With the assumption that

132   all of the shale samples in a suite have the same initial osmium isotopic composition (from coeval

133   seawater) and a wide range in parent:daughter ratios, it is possible to generate an isochron, which yields

134   the age of incorporation of Re and Os into the system and, hence, of deposition. Since shale facies

135   contain both hydrogenous and terrigenous components, it is necessary to digest the samples with a less-

136   aggressive medium, such as Cr^{VI}-H_2SO_4, which preferentially attacks the organic component while

137   leaving the detrital quartz and feldspar largely intact (Selby and Creaser, 2003).

138   Approximately 50 mg of powdered whole rock was accurately weighed along with a known

139   quantity of a ^{190}Os-^{185}Re spike and Cr^{VI}-H_2SO_4 digestion solution (Selby and Creaser, 2003) and

140   transferred to frozen Carius tubes that were chilled using a mixture of dry ice and ethanol before being

141   sealed with an oxy-propane torch (Shirey and Walker, 1995). Once thawed, the Carius tubes were placed

142   in an oven heated to 240°C for 48 hours to fully oxidize the Re and Os to their highest valence states.

143   Following digestion, the tubes were frozen in liquid nitrogen and opened. The Os was separated from the

144   mixture via solvent extraction using carbon tetrachloride, back extracted into HBr and purified by micro-

145   distillation prior to being loaded onto a Pt filament and analyzed using negative thermal ionization mass

146   spectrometry (N-TIMS; Birck et al., 1997; Cohen and Waters, 1996). Following Os separation, the

147   remaining solution was treated with sulfurous acid to reduce the Cr^{6+} to Cr^{3+}, and Re was separated using

148   anion exchange chromatography before being taken up in 2% nitric acid and analyzed using inductively

149   coupled plasma mass spectrometry (ICP-MS). All of the preparation chemistry and spectrometry were

150   conducted at the University of Maryland's Geochemical Laboratories. Samples were blank corrected,

151   with total analytical blanks averaging 19 pg and < 1 pg for Re and Os, respectively. These blanks were

152   sufficiently low as to have no effect on analytical uncertainties. Reproducibility was determined using a

153   ^{185}Re spiked in-house standard of the Agpalilik iron meteorite, where $^{185}Re/^{187}Re = 1.331 \pm 0.002$ (n = 10;

154   2SDM) over a two-month measuring period and a UMD Os standard where $^{187}Os/^{188}Os = 0.1140 \pm 0.0003$

155   (n = 9; 2SDM) and $^{190}Os/^{192}Os = 1.981 \pm 0.002$ (n = 9; 2SDM) over a nine-month measuring period.

156   Regressions were performed with *Isoplot V.4.15* (Ludwig, 2011) using a value of 1.666×10^{-11} yr^{-1} for the

157   ^{187}Re decay constant and 2σ uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os as determined by numerical

158   error propagation.

159

160   *3.2 Total Organic Carbon and Stable Isotopes*

161   Shale horizons were sampled from drill cores 134-86 and 42-88 for time-series analyses.

162   Samples were ground with a ceramic mortar and pestle and aliquots were used for measuring total organic

163   carbon (TOC) abundance, stable S and C isotope analyses, as well as Fe-speciation. TOC was determined

164   using Dumas combustion techniques on pre-acidified powders and quantified on a vacuum distillation

165   line. The δ^{13}C of the TOC was determined by combustion in a Eurovector elemental analyzer in-line with

166   an Isoprime gas source isotope ratio mass spectrometer (EA-IRMS). Sulfide sulfur in the shales was

167   isolated using a chrome-reduction solution (*cf*. Canfield et al., 1986) to release H_2S, which was carried in

168   a stream of nitrogen gas through a Milli-Q ultrapure water trap to remove chloride. Sulfur was then

169   trapped as Ag_2S with a 0.02 M solution of $AgNO_3$ and 1.55 M HNO_3. Silver sulfide solutions were set in

170   the dark for approximately seven days, then filtered and rinsed with ~250 ml Milli-Q water and ~5 ml 1N

171   ammonia solution (NH_4OH). Samples were aged to allow for the dissolution of oxygen-bearing

172   contaminants that precipitate with the silver sulfide. The black Ag_2S precipitate was then filtered and

173   dried for ~48 hours and combined with excess V_2O_5 in tin cups for EA-IRMS measurement of sulfur

174   isotope compositions. Uncertainties of carbon and sulfur isotope analyses based on multiple analyses of

175   urea and NBS-127 standards were better than 0.1 and 0.3‰, respectively.

176

177   *3.3 Fe-Speciation*

178   Iron-speciation analyses, based on measured abundances of Fe in carbonate, oxide and sulfide

179   mineral phases, as well as total Fe in samples, were conducted following procedures outlined by Poulton

180   and Canfield (2005). Sulfide iron abundance (Fe-S) is calculated from Ag_2S yields in CRS extractions

181   (see Section 3.2), performed sequentially after checking for Fe present as acid volatile sulfides. For the

182   carbonate and oxide fractions, fresh bulk powders are sequentially leached with: 1) 1 M sodium acetate

183   ($C_2H_3NaO_2$) adjusted to pH 4.5 with acetic acid (CH_3COOH) for 48 hours at 50°C to release carbonate

184   iron (Fe_{carb}); 2) dithionite solution (mixture of 50 g L^{-1} sodium dithionite ($Na_2S_2O_4$), 0.2 M sodium

185   citrate ($Na_3C_6H_5O_7 \cdot H_2O$) and 0.35 M acetic acid) for two hours to release iron from ferric oxides such as

186   hematite and goethite (Fe_{ox}); and 3) ammonium oxalate solution (mixture of 0.2 M ammonium oxalate

187   ($C_2H_8N_2O_4$) and 0.17 M oxalic acid ($H_2C_2O_4 \cdot H_2O$) for six hours to extract iron from magnetite (Fe_{mag}).

188   The iron extracted from carbonates, oxides and sulfides are combined to yield the highly reactive pool

189   (Fe_{HR}). This Fe_{HR} pool represents Fe minerals that are reactive towards dissolved sulfide on diagenetic

190   timescales (Canfield et al., 1992; Poulton et al., 2004a). Total iron concentrations (Fe_T) were determined

191   by total digestion with concentrated HF, HNO_3 and $HClO_4$. All Fe extracts were analysed by Flame

192   Atomic Adsorption Spectroscopy, with repeat analyses yielding RSD's of <5% for all stages.

193

194   **4. Results**

195

196   *4.1 Re-Os*

197   Results of Re and Os analyses for the Serra do Garrote, Morro do Calcário and Lapa formation

198   shales are reported in Table 1. In the Serra do Garrote samples, Re and Os concentrations ranged from ~1

199   to 16 ppb, and ~60 to 600 ppt, respectively. The isotopic data show a generally isochronous relationship

200   (Fig. 4A) indicating an age of 1354 ± 88 Ma (n = 8, MSWD = 49). Presuming the isochron age to be

201   accurate, the initial $^{187}Os/^{188}Os$ value (Os_i) of each sample is back-calculated. The reproducibility of Os_i

202   of individual samples in the Serra do Garrote shale (Table 1) suggests minimal post-depositional mobility

203   (Kendall et al., 2009). The Serra do Garrote date presented here is, admittedly, imprecise with a relatively

204   high MSWD value. However, the Os_i from the isochron regression falls between values of ~0.12

205   (chondritic/mantle compositions in the late Mesoproterozoic; Walker et al., 2002a, b) and 1.5 (riverine

206   inputs; Levasseur et al., 1999) that would reasonably be expected for seawater $^{187}Os/^{188}Os$. Such an

207   observation suggests that any post-depositional disturbance is relatively minor. The large uncertainty

208   (~5%) on the age may arise from changes in the initial Os isotopic composition of seawater during

209 deposition (data used to generate Fig. 4A come from samples spreading approximately 1.5 m of section).

210 The changing Os isotopic composition of the source water and minor open-system behavior may also

211 explain the relatively high MSWD value.

212   Rhenium and Os concentrations in the thick, organic-rich Morro do Calcário shale vary

213 substantially between the two sampled cores, which were drilled ~2.3 km apart. Samples from drill core

214 42-88 contain between ~0.30 and 0.85 ppb Re and between ~27 and 55 ppt Os, while those from drill core

215 134-86 are characterized by higher concentrations with ~1 to 23 ppb Re and ~40 to 700 ppt Os. The

216 differences are most likely related to environmental and facies variations, as metal abundances in the two

217 cores are broadly correlated with that of total organic carbon, suggesting sedimentary controls on their

218 distribution (Anbar et al., 2007). Sample sets from these two cores can be combined to yield a composite

219 isochron with an age of 1112 ± 50 Ma (n = 16, MSWD = 91; Fig. 4B). Although care was taken to

220 sample the two drill cores from roughly equivalent horizons, we cannot *a priori* assume that these

221 horizons are directly contemporaneous, particularly as the data plot in two distinct positions along the

222 isochron. Furthermore, the samples from drill core 42-88 have very low Re and Os abundances, and

223 therefore may be more readily contaminated by detrital components of the shale (Azmy et al., 2008).

224 Taking only the more metal enriched Morro do Calcário samples from drill core 134-86 results in an

225 imprecise isochron age of 1035 ± 200 Ma (n = 8, MSWD = 150; Fig. 4C) with scatter that is greater than

226 analytical uncertainties. Duplicate analyses of some samples gave minor to moderate differences in

227 $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ and likely reflect variable extents of powder heterogeneity. While neither the

228 composite isochron nor the drill core 134-86 isochron are strong enough to warrant a direct depositional

229 age assignment, it is worth noting that both are statistically identical to the Morro do Calcário

230 Formation's previously assigned Re-Os age (1100 ± 77 Ma; Azmy et al., 2008).

231   Samples from the thin Lapa Formation shale in core 134-86 have the lowest concentrations of

232 both Re and Os in this study (Table 1), and exhibit a very limited range in $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$.

233 Hence, these samples do not define an isochron, and we do not consider the Lapa Formation

234 measurements further.

235

4.2 C-S

Results for time-series C and S analyses from the Serra do Garrotte, Morro do Calcário and Lapa

formations sampled from drill core 134-86 and 42-88 are reported in Table 2 and illustrated in Figures 5

and 6. In core 134-86 (Fig. 5), where all three shale horizons were collected and analyzed, TOC

abundances range widely between 0 and 4 wt.% with highest overall (but variable) abundances in the

Morro do Calcário shale and in a singular peak within the Lapa shale. Carbon isotope compositions of

Serra do Garrotte samples range between -28 and -31‰, values similar to samples from the base of the

Morro do Calcário Formation. Stratigraphically higher in the Morro do Calcário, samples define a trend

of ^{13}C enrichment with δ^{13}C values reaching as high as -22‰. In contrast, organic matter in Lapa

Formation samples have relatively constant δ^{13}C values around -25‰. Sulfur isotope compositions in this

core were not measured for the Serra do Garrotte Formation. In the Morro do Calcário, sample δ^{34}S

values range from +10 to -15‰, becoming more depleted in ^{34}S up-section. In contrast, Lapa Formation

samples are notably enriched in ^{34}S, ranging from +10 to +35‰, defining a positive excursion that peaks

in the most organic-rich horizons.

Morro do Calcário samples from core 42-88 (Fig. 6) were previously studied for biomarker

distributions and organic carbon contents (Olcott et al., 2005). TOC abundances in these samples range

up to 3.5 wt.%, with most samples having δ^{13}C values near to -25‰, regardless of organic carbon content.

Sulfur contents are similar to those of organic matter, ranging up to 3 wt.%, but δ^{34}S values define a

significant positive excursion with a progressive 20‰ rise in the lower half of the section to values as

high as approximately +30‰, which fall back to around +10‰ in the upper half of the section.

256

4.3 Fe-speciation

Iron-speciation analyses were conducted on the Morro do Calcário samples from core 42-88 (Fig.

6; Table 3) in order to better understand the redox architecture of the depositional basin and for

260 comparison with environmental interpretations from the previously published biomarker results. Fe_{HR}/Fe_T

261 ratios can be used to distinguish oxic from anoxic water column depositional conditions, whereby values

262 >0.38 provide strong support for anoxic deposition, while values <0.22 suggest oxic depositional water

263 column conditions (Raiswell and Canfield, 1998; Poulton and Raiswell, 2002; Poulton and Canfield,

264 2011). For samples that show clear evidence for anoxic deposition, Fe-S/Fe_{HR} values >0.7-0.8 suggest

265 euxinic deposition, while values below this threshold suggest anoxic non-sulfidic depositional conditions

266 (Poulton et al., 2004b; Poulton and Canfield, 2011). Fe_{HR}/Fe_T ratios range widely through the formation

267 (Fig. 6). Notably high values for samples at depths <759 m, between 785 and 812 m, and >825 m provide

268 strong evidence for dominantly anoxic deposition across these intervals, perhaps with occasional

269 transitions to oxic deposition from 800-812 m (potentially a consequence of fluctuations in the depth of

270 the chemocline). In contrast, low Fe_{HR}/Fe_T from 759-785 m and 812-825 m depths suggests dominantly

271 oxic water column conditions for these samples, although periodically higher Fe_{HR}/Fe_T ratios suggest the

272 possibility of cycling between oxic and anoxic conditions. To distinguish anoxic non-sulfidic and euxinic

273 deposition, Fe-S/Fe_{HR} ratios are plotted on Fig. 6 for samples which show evidence of anoxic deposition

274 (i.e., Fe_{HR}/Fe_T >~0.38). In general, lower Fe-S/Fe_{HR} towards the top and bottom of the section implies

275 anoxic non-sulfidic depositional conditions, while higher values in the middle portion of the section

276 suggests dominantly euxinic conditions.

277

278 **5. Discussion**

279   Although the Re-Os isochron ages for upper Vazante shales determined previously (Azmy et al.,

280 2008) and in this study are imprecise, they are consistent with a late Mesoproterozoic to earliest

281 Neoproterozoic age assignment. This age for the Vazante Group contrasts with an earlier

282 chemostratigraphic age estimate (Azmy et al., 2001; 2006), which was in part based on the assumption

283 that all the glacial deposits must be from the Neoproterozoic Era.

284

285 *5.1 Stratigraphic context for a Mesoproterozoic age of the upper Vazante Group*

286   Detrital zircons from the middle of the Serra do Garrote and the top of the Morro do Calcário

287   formations yield U-Pb ages varying from 1505 to 2521 Ma and 1109 to 2466 Ma, respectively; lower in

288   the Serra do Garrote detrital zircon ages vary from 1242 to 3409 Ma (Rodrigues et al., 2012). Taken as

289   maximum depositional ages, these former dates do not contradict the Re-Os ages but do require relatively

290   rapid unroofing and transportation of the zircons. In contrast, younger detrital zircon U-Pb ages from

291   formations of the Vazante Group below the shale horizons (Azmy et al., 2008; Rodriguez et al., 2012) do

292   appear to contradict our Re-Os age estimates. For example, the Rocinha Formation contains zircons as

293   young as 930 Ma and the St. Antônio do Bonito Formation contains zircons with ages as young as ~1000

294   Ma (Azmy et al., 2008; Rodrigues et al., 2012), suggesting a likely Neoproterozoic age for this part of the

295   succession. In support of this view, Sr isotope compositions of phosphorite samples from the Rocinha

296   Formation (Fig. 3D), with $^{87}Sr/^{86}Sr$ values of 0.70766 (Misi et al., 2007), match those of the

297   Neoproterozoic Bambuí Group to the east on the São Francisco craton. The cap carbonate at the base of

298   that succession is constrained by a Pb-Pb carbonate age of 740 ± 22 Ma (n = 11; MSWD = 0.66; Babinski

299   et al., 2007).

300   These paradoxical observations are resolved by the presence of a 40-45° oblique-slip reverse fault

301   beneath outcrops of *Conophyton metula Kirichenko* stromatolite in the Lagamar Formation (Fig. 3E).

302   The fault is identified in aerial photographs and in the field by the presence of brown to yellow clay-rich

303   and sandy mylonite overlying thickly bedded purple shale (Fig. 3F). This reverse fault appears to

304   subdivide the Vazante Group into two parts; older sediments assigned to the Vazante Group are thrust

305   above younger carbonates and phosphates in the Rocinha Formation and the St. Antônio do Bonito

306   Formation glacial diamictite (Misi et al., 2010; 2011). Notably, the Vazante Formation (now Group)

307   originally defined by Dardenne (1978) did not include the basal Santo Antônio do Bonito and Rocinha

308   because these units were severely faulted relative to overlying strata. This tectonic transposition explains

309   many of the conflicting chronometric constraints on the Vazante Group and should be expected given the

310   imbrication of thrust nappes to the west and south in highly metamorphosed terrains (Dardenne, 2000).

311   Movement along this reverse fault – initiated by collision of continental blocks during the late-

312   Neoproterozoic (*ca*. 600 Ma) Brasíliano orogeny – places older strata above younger and separates the

313   Vazante Group into at least two distinct tectonic and sedimentary domains. If this interpretation is

314   correct, the basal Vazante Group diamictite would likely be equivalent to the glacial deposits at the base

315   of the Neoproterozoic Bambuí Group, leaving the two glacial deposits above the thrust fault to be the only

316   radiometrically constrained glaciogenic deposits of the Mesoproterozoic Era. The possibility of

317   additional, yet unrecognized, reverse faults in the Vazante Group cannot be discounted, which may

318   explain the slightly younger U-Pb ages observed in detrital zircons in the lower part of the Serra do

319   Garrote Formation (Rodrigues et al., 2012).

320

321   *5.2 Regional and depositional setting of the Vazante Group*

322   Two different tectonic models have been proposed to explain the accumulation of Vazante Group

323   strata. In one, Vazante sediments are suggested to have been deposited in a rapidly subsiding foreland

324   basin initiated during collision of the BFB with the flat-lying São Francisco craton at *ca.* 790 Ma

325   (Dardenne, 2000). This suggests a Neoproterozoic age for the succession. However, accepting the Re-Os

326   and U-Pb detrital zircon age constraints, as well as the presence of a major reverse fault within the

327   Vazante succession, it is most likely that only the Rocinha Formation and St. Antônio do Bonito

328   diamictite are correlative with Neoproterozoic deposits on the São Francisco craton (Misi et al., 2010;

329   2011).

330   In contrast, upper Vazante Group strata that accumulated on a passive margin carbonate platform

331   are of Mesoproterozoic age and likely correlative with the Paranoá Group (Fig 1) consistent with the

332   interpreted model based on Nd isotopic measurements of detrital grains from a variety of formations

333   across the BFB (Pimentel et al., 2001). The Nd-isotope measurements suggest a likely source of

334   sediments to the Vazante Group was from either the São Francisco craton to the east (T_{DM} ranging from

335   ~2.3 to 1.7 Ga) or the off-shore Goiás Magmatic Arc to the west (T_{DM} ranging from ~1.0 to 1.3 Ga). The

336   initial Nd isotopic compositions of detrital grains from the Serra do Garrote and Serra do Poço Verde

337   formations are identical to those from the nearby Paranoá Group, supporting their direct equivalence

338   (Pimentel et al., 2001). The Paranoá Group lacks direct radiometric constraints but is broadly constrained

339   to between 1200 and 900 Ma (albeit based on stromatolite biostratigraphy; Dardenne et al., 1976). The

340   Paranoá Group sits stratigraphically below the Bambuí Group, and glacial deposits have also been

341   observed at its base (Dardenne, 2000). Carbonates in both the Vazante and Paranoá groups reveal

342   relatively little $\delta^{13}C$ variation (Santos et al., 2000; Azmy et al., 2001). The pattern of relatively muted

343   carbon isotope compositions through these successions stands in sharp contrast with Neoproterozoic

344   carbonates of the Bambuí Group which exhibit a striking upsection trend in $\delta^{13}C$ values progressing from

345   as low as -5‰ near its base in a cap carbonate lithofacies to near +15‰ at its top in bituminous

346   limestones (Misi et al., 2007).

347   Previous biomarker studies of the Morro do Calcário shale (Olcott et al., 2005) interpreted this

348   unit to be syn-glacial based on its appearance between thick carbonate diamictite and ample evidence of

349   ice rafted debris. We currently recognize this organic-rich shale as related to post-glacial transgression

350   with a stratigraphic placement between two carbonate diamictites of different age. Extractable

351   biomarkers (including n-alkanes, isoprenoids, steranes and hopanes from shale, carbonate and diamictite)

352   in the Morro do Calcário shale were interpreted to be indigenous to the sediments and reflect a complex

353   microbial ecosystem, including both phototrophic bacteria and eukaryotes living in a stratified ocean with

354   thin or absent sea ice, oxic surface waters and euxinic conditions within the photic zone (Olcott et al.,

355   2005). Our Fe-speciation and S isotope results from the Morro do Calcário shale are consistent with these

356   findings. The partitioning of Fe phases in these ancient sediments suggest that redox conditions in the

357   depositional environment fluctuated on relatively short timescales between anoxic, euxinic and oxic water

358   column conditions as the Morro do Calcário sediments accumulated, supporting the view of initial

359   progressive stratification of the water column followed by generally more expansive ventilation. The

360   dramatic enrichment in ^{34}S of pyrite in the lower part of the sampled interval may thus be interpreted in

361   terms of progressive sulfate-limitation as the water column became increasingly euxinic. Our re-

362   evaluation of this shale as a post-glacial (rather than syn-glacial) deposit, however, complicates our ability

363   to predict aspects of the ice age as they relate to biological productivity and diversity (*cf.* Olcott et al.,

364   2005; Corsetti et al., 2006).

365

366   *5.3 The Vazante Group in the context of a late Mesoproterozoic world*

367   The upper part of the Vazante Group (as originally described by Dardenne, 2000) is thus far the

368   only radiometrically constrained Mesoproterozoic succession preserving lithological and geochemical

369   evidence of glaciation, so caution about its global significance is warranted. Other studies of late

370   Mesoproterozoic strata indicate that this was a period of a global greenhouse conditions marked by

371   eustatic highstand (Kah et al., 1999; 2012; Gilleaudeau and Kah, 2013). This conundrum may be

372   explained by one of three scenarios: 1) the diamictites of the upper section of the Vazante Group have

373   been mis-identified as glaciogenic; 2) the Re-Os system has been perturbed or mis-interpreted, and the

374   apparent isochron ages do not reflect the timing of deposition; or 3) the Vazante Group accurately

375   captures a previously unobserved component of the late Mesoproterozoic Earth.

376   There is strong evidence that units within these strata are the result of multiple discrete glacial

377   events. Glaciation is the most likely mechanism that unites the geology (faceted and striated dropstones

378   along with iron-formation), mineralogy (glendonite) and geochemistry (negative δ^{13}C excursions) of the

379   upper Vazante Group diamictites. Citing these lines of evidence, this study is not the first to have

380   interpreted glacial strata within the Vazante Group (*cf.* Dardenne, 2001; Azmy et al., 2001; Brody et al.,

381   2004; Olcott et al., 2005; Azmy et al., 2006; Misi et al., 2007). However, the Vazante Group diamictites

382   have commonly been interpreted as correlative with Neoproterozic "snowball Earth" deposits found atop

383   the São Francisco craton (Misi et al., 2005) and the conjugate Congo craton (Azmy et al., 2001; 2006). If

384   the Re-Os ages are correct, these correlations will need to be revised. These new data do not warrant

385   altering the interpretation of glacial episodes within the Vazante Group, merely their timing.

386   The Re-Os system in organic-rich shale has been shown to be fairly robust. It appears

387   unperturbed by low-grade metamorphism (Kendall et al., 2004) and hydrocarbon maturation and

388   expulsion (Creaser et al., 2002) but can be disturbed by surface weathering (Jaffe et al., 2002). The

389   Vazante Group has been exposed to only sub-greenschist faces metamorphism (Babinksi et al., 2005;

390   Azmy et al., 2008) in the outcrop region. Furthermore, we sampled from unweathered and well-preserved

391   cores (Azmy et al., 2006). While it is possible for detrital components of the shale to contaminate the

392   hydrogenous Re-Os signatures and thereby influence the isochron ages, we used the Cr^{VI}-H_2SO_4 digestion

393   medium that preferentially attacks the hydrogenous component of the shale over detrital input (Selby and

394   Creaser, 2003; Kendall et al., 2004). Hydrothermal fluid flow can disturb Re-Os systematics but

395   documented cases of remobilization of Re and Os under such conditions have resulted in erroneously

396   *younger*, not older, ages (Kendall et al., 2009). Therefore, even with hydrothermal perturbation, the Serra

397   do Garrote and Morro do Calcário glaciations would not be correlative with the younger, globally

398   distributed Neoproterozoic events.

399   If the detrital input includes organic matter – as suggested for the post-glacial shale of the Morro

400   do Calcário Formation (Marshall et al., 2009) – then preferential digestion of hydrogenous components

401   may result in mixing of authigenic and detrital components and complicated Re-Os systematics. It seems

402   unlikely, however, that such a mixing process would have a consistently wide-spread impact (both

403   temporally and spatially) and result in isochronous relationships. Moreover, the Vazante stata Re-Os

404   dates presented here are in stratigraphic agreement with one another, over a time scale of hundreds of

405   millions of years, and derived from cores drilled approximately three kilometers apart. Furthermore,

406   while the Morro do Calcário shale is clearly related to glacial phenomenon, the Serra do Garrote shale is

407   not and thus detrital organic matter contamination through weathering inputs (*cf.* Johnston et al., 2012)

408   should be considerably less significant.

409   The abundance and wide geographic spread of open marine and epicratonic carbonate platform

410   deposits from the Mesoproterozoic, including the Bangemall Group (Buick et al., 1995), the Turukhansk

411   Group (Knoll et al., 1995; Bartley et al., 2001), the Society Cliffs Formation (Kah et al., 2001) and the

412   Atar Group (Kah et al., 2012) support the view of a world with globally high sea levels. Notably, the

413   carbon isotope records of these successions are characterized by relatively little variation, predominantly

414   ranging between -4‰ and +4‰, with shifts generally not exceeding 5‰ (Kah et al., 1999; Bartley et al.,

415   2001; Bartley et al., 2007; Kah et al., 2012; Gilleaudeau and Kah, 2013). This record stands in stark

416   contrast to the succeeding Neoproterozoic when carbon isotope compositions of marine proxies reveal

417   significant overall ^{13}C enrichments and high amplitude variations (Knoll et al., 1986; Kaufman and Knoll,

418   1995; Kaufman et al., 1997; Prave et al., 2009; Halverson et al., 2010).

419   As mentioned above, carbon isotope compositions of marine carbonates in the Vazante Group

420   reveal a moderate spread in δ^{13}C values, largely falling within the range of -4‰ to +3‰ (Azmy et al.,

421   2006). This range is consistent with other late Mesoproterozoic successions lacking evidence for

422   glaciation (e.g. Kah et al., 1999). Stratigraphically coherent negative carbon isotope excursions in these

423   successions have recently been explained as a result of relative sea level highstands, which promote

424   anoxia and organic matter remineralization in epicratonic environment (Gilleaudeau and Kah, 2013). In

425   contrast, the upper Vazante Group displays two consistent basin-wide negative shifts of up to 8‰

426   immediately above the interpreted glacial units (Azmy et al., 2006). Furthermore, the positive S isotope

427   excursion captured in the lower Morro do Calcário shale, which occurs over just 20 meters of section

428   (Fig. 6) is similar in magnitude to an event recorded from late Mesoproterozoic bedded sulfates on Baffin

429   Island (Kah et al., 2004). This biogeochemical anomaly is best explained as the result of widespread

430   removal of sulfate (via bacterial sulfate reduction) from an ocean that was relatively sulfate-poor

431   (Canfield, 1998; Kah et al., 2004).

432   Given the uncertainties of the Re-Os ages presented here and previously (Azmy et al., 2008) and

433   lack of geochronometric constraints in most other late Mesoproterozoic basins, it seems possible that the

434   interval was environmentally variable or that there was a strong temperature gradient between the poles

435   and equator. Paleomagnetic reconstructions place the São Francisco craton at high southern latitudes (45

436   to over 60° S) in the late Mesoproterozoic (Weil et al., 1998; Tohver et al., 2006), allowing the possibility

437   that the glaciations of the Morro do Calcário and Serra do Garrote formations were local rather than

438   global in extent.

439   Re-Os age estimates from the Touirist and En Nesoar formations of the Atar Group are

440   statistically identical to the Morro do Calcário Formation (~1100 Ma; Rooney et al., 2010). The

441 similarity of these ages (and Os$_i$ values) as well as their carbon isotopic records have led to the suggestion

442 that these units were deposited coevally atop the West African and São Francisco cratons, respectively

443 (Rooney et al., 2010). Although some aspects of the geochemistry and radiometric constraints are

444 consistent with this hypothesis, the two successions were clearly deposited under conflicting climatic

445 conditions causing other researchers (Kah et al., 2012) to question this correlation. Alternatively, the

446 imprecise age for the Morro do Calcário (Azmy et al., 2008) allow the possibility that Vazante

447 glaciogenic units are younger than the Touirist and En Nesoar formations of the Atar Group. Given the

448 incision of the glacial units into the underlying carbonate platforms (Fig. 2), the Morro do Calcário and

449 Lapa formations may document more substantial sea-level falls following Mesoproterozoic highstands

450 captured elsewhere. Lacking a wider range of sedimentary units from this time period for comparison, it

451 may not be possible to reconcile the Atar Group and other contemporary basins with the Vazante Group

452 until more precise age constraints are available.

453

454 **6. Conclusions**

455   Based on our geological and radiometric study of Vazante Group strata in south-central Brazil,

456 we conclude that the upper 2/3 of the succession was deposited on a passive margin of the São Francisco

457 craton during the late Mesoproterozoic Era. The Re-Os radiometric ages for the Serra do Garrote (1345 ±

458 88 Ma; this study) and Morro do Calcário (1100 ± 77 Ma; Azmy et al., 2008) are consistent with previous

459 estimates for upper Vazante strata based on the U-Pb age distributions of detrital zircons. Paleontological

460 and carbon isotopic constraints also support a correlation of the upper section of the Vazante Group

461 (above the Lagamar fault) with the Paranoá Group (also atop the São Francisco Craton), but not the

462 Neoproterozoic Bambuí Group as suggested by earlier authors.

463   Evidence of two discrete glacial episodes in the upper part of the Vazante stratigraphy is

464 preserved as 1) discrete diamictite horizons bearing both angular and rounded, faceted and striated clasts,

465 sometimes preserved as dropstones in laminated shale; 2) the presence of the cold-water carbonate

466 mineral glendonite within one of the post-glacial shale horizons; 3) Fe-oxide cementation and local

467 accumulation of iron-formation; and 4) negative $\delta^{13}C$ excursion in carbonate overlying the diamictites.

468 Furthermore, we have identified map and field evidence for an oblique-slip reverse fault that

469 juxtaposes Neoproterozoic glaciogenic strata of the lower Vazante Group (Rocinha and St. Antônio do

470 Bonito) beneath late Mesoproterozoic formations of the upper Vazante Group, including the Serra do

471 Garrote, Morro do Calcário and Lapa units evaluated in this geochemical study. While the fault solves

472 the paradoxical U-Pb maximum depositional ages derived from detrital zircons and the stratigraphic

473 inversion, it also opens up the possibility of other, yet undiscovered, faults within the sequence which

474 may further complicate stratigraphic relationships.

475 The Vazante Group is unique in the late Mesoproterozoic in that it displays evidence of glaciation

476 in a period generally regarded as a time of greenhouse conditions and globally high sea levels. The

477 glaciations may be regional phenomena as paleo-reconstructions place the São Francisco craton at high

478 southern latitudes during the late Mesoproterozoic Era, but the general lack of open marine successions

479 from this time interval limits our current understanding of this ancient episode of Earth history.

480

489

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689

Captions

Figure 1: Geologic map of study area. The Vazante Group is elongated north to south within Brazil with ┼ indicating the approximate location of the drill cores examined here. Modified from Babinski et al. (2005).

Figure 2: Generalized stratigraphy of the Vazante Group with formation and member names highlighting sub-glacial valleys and post-glacial fill, the newly discovered reverse fault and geochronometric constraints discussed in the text. Modified after Dardenne (2000) with generalized C-isotope trends from Azmy et al. (2001; 2006). No vertical scale implied.

Figure 3: Photographs of A. carbonate ice-rafted debris in the organic-rich post-glacial shale of the Morro do Calcário Formation in drill core MASW-01; B. faceted cobble in silicified shale matrix of the Morro do Calcário Formation near Paracatu, MG, Brazil; C. *Conophyton* stromatolites from the basal Lagamar Formation above the thrust fault; D. phosphorite and high-Sr limestone from the Rocinha Formation located below the thrust fault and west of the Vazante mine; E. thrust fault trace with brown to mauve sandy mylonite to the left and bedded purple shale and siltstone of the upper Rocinha Formation to the right; F. Close up of clay and quartz-rich mylonite at thrust fault contact.

Figure 4: Re-Os isochrons for: A. Serra do Garrote Formation samples from drill core 134-86; B. Morro do Calcário Formation samples from drill core 42-88 and 134-86; C. Morro do Calcário Formation samples taken only from drill core 134-86.

Figure 5: Time-series elemental and stable isotope compositions of the Serra do Garrote, Morro do Calcário and Lapa Formations (shale intervals only) in the Mesoproterozoic Vazante Group, drill core 134-86 (data available in Table 2), where TOC = total organic carbon.

716   Figure 6: Time-series elemental and stable isotope compositions of the Morro do Calcário Formation

717   shale interval in the Mesoproterozoic Vazante Group, drill core 42-88 (data available in Tables 2 and 3),

718   where TOC = total organic carbon and S = sulfide-sulfur. Iron speciation data allows identification of

719   deposition from an oxic, anoxic non-sulfidic or euxinic (free sulfide) water column. FeHR = highly

720   reactive iron; FeT = total iron; FeS = pyrite iron. Euxinic conditions are interpreted from FeHR/FeT >

721   0.38 and FeS/FeHR > ~0.7; anoxic non-sulfidic conditions are recognized from FeHR/FeT > 0.38 and

722   FeS/FeHR < ~0.7; oxic conditions are demonstrated by FeHR/FeT < 0.22. Dashed lines are presented at

723   these threshold values. For all data points, the uncertainty on the measurement is smaller than the

724   symbol.

725

726   Table 1: Re and Os abundance and isotope data for black shale intervals in the Serra do Garrote, Morro do

727   Calcário and Lapa Formations. Os_i = initial $^{187}Os/^{188}Os$ ratio back-calculated using the isochron age in

728   Figure 4.

729

730   Table 2: Time-series total organic carbon (TOC) abundances in weight percent; carbon isotopic

731   composition of the organic carbon ($\delta^{13}C$); sulfur isotopic composition of the sulfide sulfur ($\delta^{34}S$); and

732   sulfide sulfur abundance in weight percent (S) of the Serra do Garrote, Morro do Calcário and Lapa

733   Formations in drill core 134-86 as well as the Morro do Calcário Formation of drill core 42-88.

734   Uncertainties do not exceed: TOC and S ± 10% of value; $\delta^{13}C$ ± 0.15‰; $\delta^{34}S$ ± 0.35‰. nd = not

735   detected.

736

737   Table 3: Results from the analysis of the Morro do Calcário Formation shale interval in the

738   Mesoproterozoic Vazante Group, drill core 42-88. Iron speciation analyses: All concentrations are in

739   weight % (nd = not detected). FeT = total iron; Fecarb = carbonate iron; Fox = oxide iron; Femag =

740   magnetite iron; Fe-AVS = acid volatile sulfide iron; Fepy = pyrite iron; FeHR = highly reactive iron; Fe-S

741   = Fe-AVS + Fepy.

Fig. 1
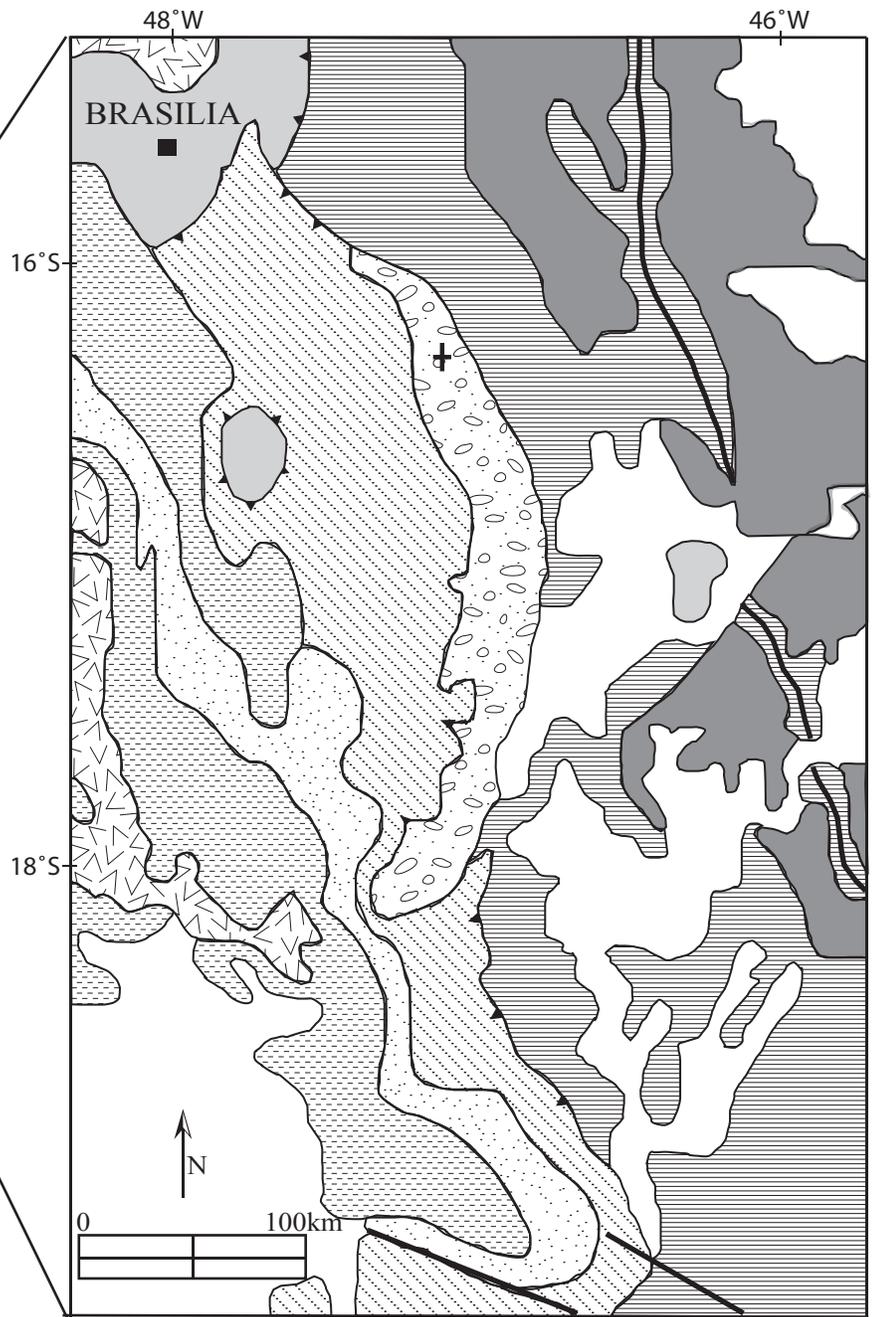
Phanerozoic Sediments

Bambuí Group
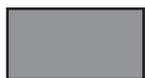
Três Marias Fm.
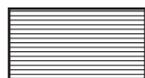
Paraopeba Subgroup

Brasília Fold Belt

Ibía Fm.
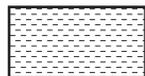
Araxá Group

Granulites

Vazante Group

Paranoá Group

Canastra Group

Fig. 2

Fig. 3

A

Serra do Garrote Fm.
Age = 1354±88 Ma
Initial $^{187}Os/^{188}Os$ = 0.13±0.34
MSWD = 49
(n = 8, Model 3 age)

G2 dup
G4
G2
G1 dup   G1
G5
G3
G3 dup

$^{187}Os/^{188}Os$

B

Morro do Calcario Fm., Composite
Age = 1112±50 Ma
Initial $^{187}Os/^{188}Os$ = 0.51± 0.16
MSWD = 91
(n = 16, Model 3 age)

MC7 dup
MC10
MC9   MC7
MC8 dup   MC8
MC6 dup   MC6
MC4
MC2
MC1 dup   MC4_dup
MC5   MC1
MC3 dup
MC3

$^{187}Os/^{188}Os$

C

Morro do Calcario Fm., Core 134-86
Age = 1035±200 Ma
Initial $^{187}Os/^{188}Os$ = 0.84±0.84
MSWD = 150
(n = 8, Model 3 age)

MC7 dup
MC10
MC7
MC9
MC8
MC6 dup   MC8 dup
MC6

$^{187}Os/^{188}Os$

$^{187}Re/^{188}Os$

Fig. 5

Serra do Garrote, Morro do Calcário and Lapa Fm. Shale in Drillcore 134-86
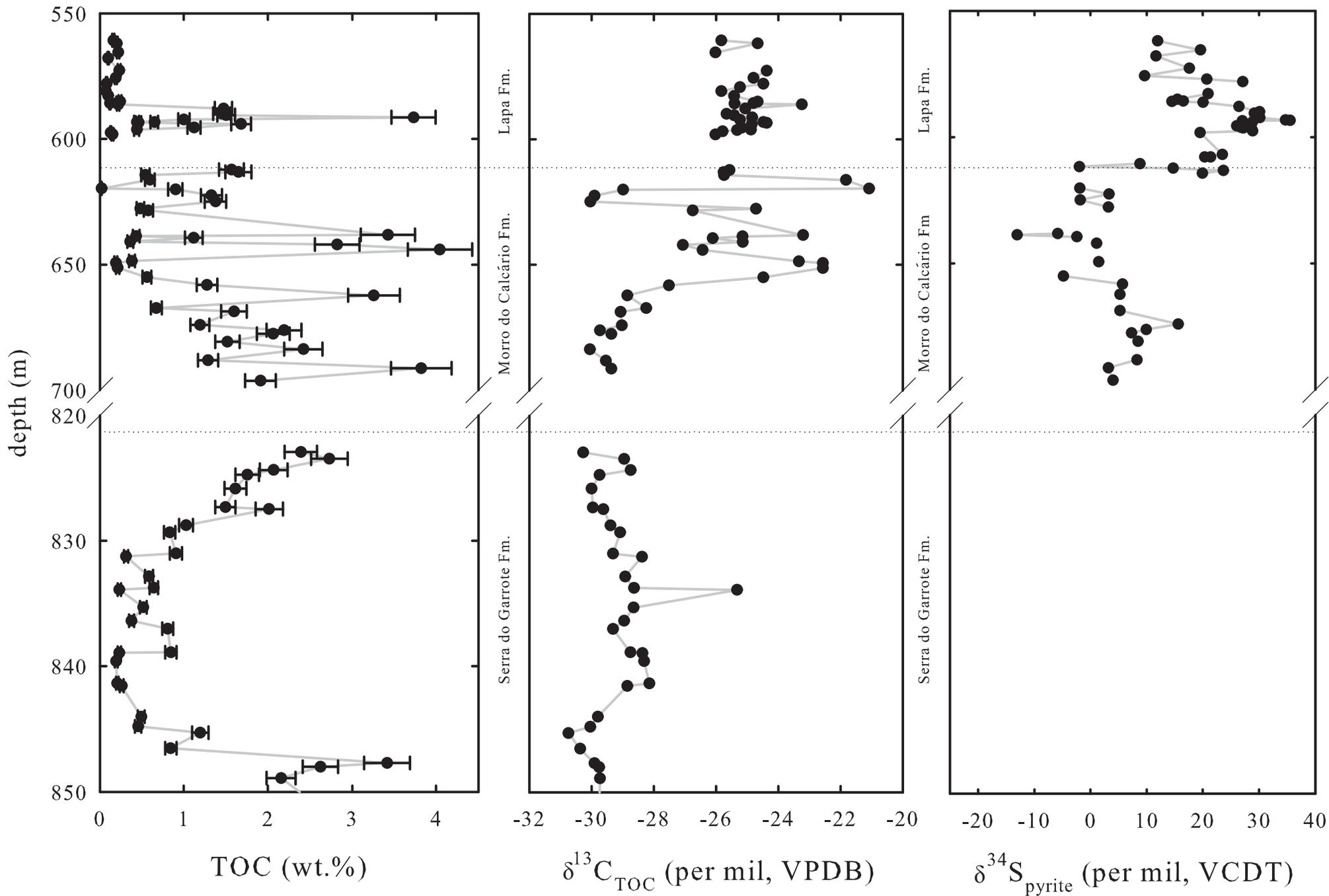
Fig. 6
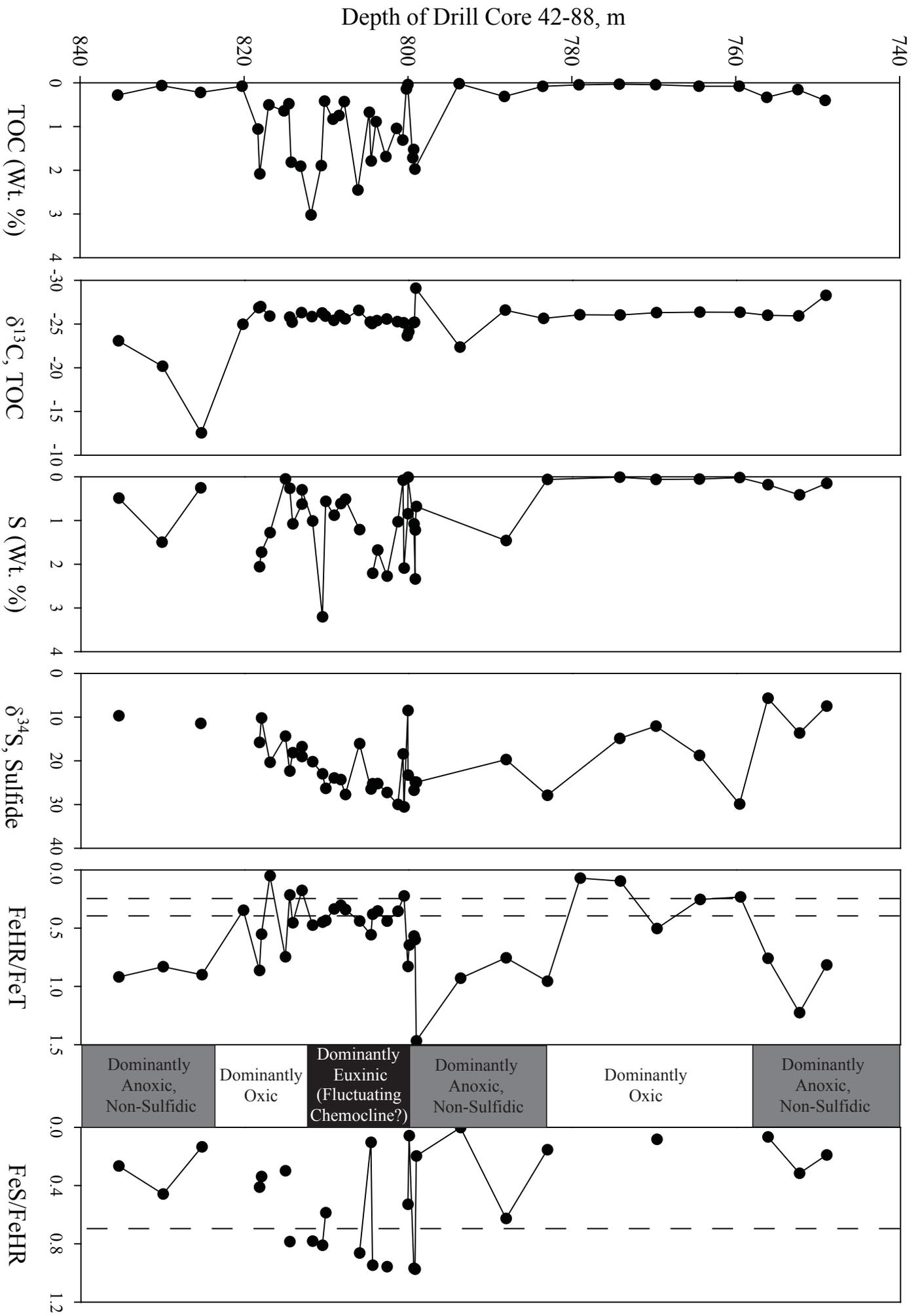
Table 1

	Sample	Drill Hole	Core Depth	Re (ppb)	Os (ppt)	$^{187}Re / ^{188}Os$	$^{187}Os / ^{188}Os$	Os_i
Lapa Fm.	L1	134-86	587.84	0.322 ± 0.008	35.0 ± 0.4	53.34 ± 1.19	1.709 ± 0.003	N/A
	L2	134-86	589.90	0.288 ± 0.008	33.4 ± 0.4	50.73 ± 1.53	1.838 ± 0.007	N/A
	L3	134-86	590.50	0.138 ± 0.008	26.1 ± 0.4	30.4 ± 1.8	1.59 ± 0.01	N/A
	L4	134-86	591.34	0.366 ± 0.008	52.3 ± 0.5	39.05 ± 0.92	1.358 ± 0.006	N/A
Morro do Calcário Fm.	MC1	42-88	803.89	0.435 ± 0.009	31.6 ± 0.1	80.7 ± 1.8	1.86 ± 0.01	0.33
	MC1_dup	42-88	803.89	0.360 ± 0.007	31.5 ± 0.1	67.2 ± 1.5	1.88 ± 0.01	0.6
	MC2	42-88	804.00	0.690 ± 0.014	42.5 ± 0.1	100.0 ± 2.2	2.352 ± 0.003	0.46
	MC3	42-88	804.43	0.334 ± 0.007	31.6 ± 0.1	59.5 ± 1.3	1.46 ± 0.01	0.34
	MC3_dup	42-88	804.43	0.303 ± 0.006	26.9 ± 0.1	65.7 ± 1.4	1.79 ± 0.01	0.54
	MC4	42-88	804.48	0.858 ± 0.017	50.5 ± 0.2	107.0 ± 2.4	2.549 ± 0.01	0.53
	MC4_dup	42-88	804.48	0.831 ± 0.017	62.9 ± 0.2	78.2 ± 1.7	1.911 ± 0.009	0.44
	MC5	42-88	804.50	0.387 ± 0.008	33.5 ± 0.1	67.6 ± 1.5	1.82 ± 0.01	0.54
	MC6	134-86	676.05	3.498 ± 0.014	131.1 ± 0.4	195.2 ± 1.2	4.159 ± 0.004	0.46
	MC6_dup	134-86	676.05	3.485 ± 0.014	132.9 ± 0.4	194.4 ± 1.2	4.323 ± 0.006	0.64
	MC7	134-86	677.40	8.702 ± 0.035	244.4 ± 0.7	296.2 ± 1.8	5.744 ± 0.005	0.21
	MC7_dup	134-86	677.40	8.030 ± 0.032	227.7 ± 0.7	306.8 ± 1.8	6.365 ± 0.009	0.63
	MC8	134-86	680.78	6.137 ± 0.025	213.5 ± 0.6	217.5 ± 1.3	4.539 ± 0.005	0.47
	MC8_dup	134-86	680.78	5.871 ± 0.023	212.3 ± 0.6	207.1 ± 1.2	4.417 ± 0.005	0.54
	MC9	134-86	683.60	4.070 ± 0.016	129.0 ± 0.4	258.3 ± 1.5	5.581 ± 0.006	0.68
	MC10	134-86	691.23	6.570 ± 0.026	184.9 ± 0.6	300.6 ± 1.8	5.993 ± 0.004	0.35
Serra do Garrote Fm.	G1	134-86	824.37	16.02 ± 0.07	578.7 ± 1.2	222.5 ± 1.5	5.257 ± 0.003	0.19
	G1_dup	134-86	824.37	15.63 ± 0.07	588.7 ± 1.2	212.7 ± 1.4	5.209 ± 0.005	0.19
	G2	134-86	824.42	11.56 ± 0.06	370.1 ± 0.7	274.9 ± 2.1	6.468 ± 0.006	0.20
	G2_dup	134-86	824.42	11.72 ± 0.06	356.8 ± 0.7	300.4 ± 2.3	7.017 ± 0.006	0.17
	G3	134-86	824.76	1.093 ± 0.012	60.6 ± 0.1	116.2 ± 1.5	2.724 ± 0.003	0.07
	G3_dup	134-86	824.76	1.038 ± 0.012	80.2 ± 0.2	76.31 ± 1.00	1.844 ± 0.002	0.10
	G4	134-86	825.83	11.97 ± 0.07	355.4 ± 0.7	305.3 ± 2.3	6.892 ± 0.006	-0.07
	G5	134-86	825.86	5.650 ± 0.028	223.5 ± 0.4	189.8 ± 1.3	4.38 ± 0.005	0.06

Table 2

Core 134-86

Formation	Depth (m)	TOC (Wt. %)	$\delta^{13}C$, TOC	$\delta^{34}S$, Sulfide
Lapa Fm.	560.70	0.161	-25.83	nd
	561.82	0.2	-24.66	11.91
	565.40	0.22	-26.02	19.58
	567.83	0.1	--	11.67
	572.64	0.23	-24.37	17.59
	575.60	0.19	-24.80	9.62
	576.93	nd	nd	20.69
	577.92	0.08	-24.48	27.09
	579.27	--	-25.23	nd
	580.83	0.07	-25.83	nd
	582.74	0.1	-25.42	20.93
	585.00	0.24	-24.66	15.49
	585.60	0.21	-24.80	16.5
	585.80	0.12	-25.40	14.48
	586.20	0.22	-23.24	19.99
	587.84	1.47	-25.06	26.4
	589.90	1.45	-25.66	30.07
	590.50	1.5	-25.42	29.13
	591.34	3.73	-24.84	nd
	592.23	1	-25.23	30.1
	593.20	0.44	-24.48	34.69
	593.28	0.65	--	35.52
	593.47	0.46	-24.37	27.02
	594.04	1.68	-24.85	28.81
	595.42	1.12	-25.18	26
	596.20	0.44	-24.88	26.85
	596.33	--	-25.32	27.18
	596.85	--	-25.79	28.7
	597.43	0.13	--	28.86
	598.10	0.15	-26.02	19.52
Morro do Calcário Fm.	606.80	nd	nd	23.48
	607.78	nd	nd	20.33
	607.84	nd	nd	21.38
	608.70	nd	nd	nd
	610.52	nd	nd	8.77
	611.58	nd	nd	-1.97
	612.23	1.57	-25.56	14.72
	613.13	1.65	-25.76	23.66
	614.27	0.543	-25.74	19.9
	616.20	0.596	-21.82	nd
	619.69	0.021	-21.08	nd
	620.09	0.9	-28.99	-1.89
	622.46	1.33	-29.90	3.29
	624.86	1.38	-30.04	-1.83
	627.72	0.484	-24.71	3.2
	628.43	0.578	-26.75	nd
	638.17	3.43	-23.20	-5.84
	638.69	0.431	-25.15	-13.03
	639.38	1.12	-26.11	-2.46
	640.89	0.364	-25.14	nd
	642.05	2.82	-27.07	1.1
	644.05	4.04	-26.43	nd
	648.61	0.382	-23.34	nd
	649.32	0.191	-22.57	1.45
	651.31	0.214	-22.56	nd
	655.02	0.56	-24.48	-4.82
	658.16	1.27	-27.51	5.7
	662.25	3.26	-28.85	5.25
	667.29	0.672	-28.24	nd
	668.73	1.6	-29.07	5.25
	674.09	1.19	-29.03	15.61
	676.12	2.19	-29.73	9.88
	677.55	2.06	-29.37	7.32
	680.82	1.52	--	8.45
	683.69	2.42	-30.06	nd
	688.14	1.29	-29.54	8.26
	691.32	3.82	-29.37	3.15
	696.27	1.91	--	4.01

Core 134-86

Formation	Depth (m)	TOC (Wt. %)	$\delta^{13}C$, TOC
Serra do Garrote Fm.	822.93	2.39	-30.27
	823.45	2.73	-28.95
	824.35	2.07	-28.74
	824.73	1.75	-29.74
	825.83	1.61	-30.00
	827.32	1.49	-29.96
	827.47	2.01	-29.62
	828.75	1.03	-29.39
	829.32	0.832	-29.08
	831.00	0.906	-29.31
	831.25	0.312	-28.38
	832.83	0.585	-28.92
	833.73	0.643	-28.63
	833.88	0.234	-25.32
	835.29	0.518	-28.64
	836.36	0.375	-28.95
	837.00	0.806	-29.31
	838.87	0.845	-28.75
	838.92	0.234	-28.37
	839.58	0.195	-28.31
	841.35	0.208	-28.14
	841.55	0.26	-28.85
	844.00	0.494	-29.80
	844.79	0.455	-30.04
	845.29	1.19	-30.74
	846.53	0.844	-30.37
	847.69	3.42	-29.90
	848.00	2.62	-29.76
	848.90	2.16	-29.73
	850.12	2.4	-29.75
	851.15	2.53	-30.12
	850.12	2.4	-29.75
	851.15	2.53	-30.12

Core 42-88

Formation	Depth (m)	TOC (Wt. %)	$\delta^{13}C$, TOC	S (Wt. %)	$\delta^{34}S$, Sulfide
Morro do Calcário Fm.	749.03	0.404	-28.3	0.15	7.49
	752.35	0.156	-25.9	0.42	13.7
	756.20	0.333	-26.0	0.18	5.69
	759.55	0.0797	-26.3	0.017	29.9
	764.47	0.0788	-26.4	0.052	18.8
	769.75	0.0440	-26.3	0.061	12.1
	774.20	0.0336	-26.0	0.0087	14.9
	779.10	--	--	--	--
	783.10	0.0484	-26.1	0.061	27.9
	788.15	0.0827	-25.6	1.5	19.7
	793.70	0.314	-26.6	0.68	24.9
	799.10	1.98	-29.1	2.3	24.9
	799.25	1.53	-25.2	1.1	26.7
	799.39	1.72	-25.2	0.0087	23.3
	799.97	0.0410	-24.1	0.85	8.51
	800.12	0.142	-23.6	2.1	30.6
	800.60	1.31	-25.1	0.078	18.4
	801.34	1.05	-25.3	1.0	30.0
	802.67	1.69	-25.6	2.3	27.3
	803.82	0.890	-25.4	1.7	25.2
	804.43	1.79	-25.1	2.2	25.3
	804.63	0.675	-25.2	--	26.5
	806.02	2.45	-26.6	1.2	16.1
	807.75	0.431	-25.6	0.51	27.7
	808.32	0.750	-26.0	0.61	24.3
	809.12	0.831	-25.4	0.88	23.9
	810.15	0.420	-25.9	0.56	26.3
	810.55	1.90	-26.3	3.2	23.0
	811.75	3.03	-25.8	1.0	20.2
	813.05	1.91	-26.3	0.63	16.8
	814.17	1.82	-25.2	1.1	18.2
	814.53	0.479	-25.8	0.27	22.4
	815.08	0.643	--	0.050	14.4
	816.95	0.507	-25.9	1.3	20.4
	818.00	2.09	-27.0	1.7	10.2
	818.23	1.06	-26.9	2.1	15.8
	820.20	0.0802	-25.0	nd	nd
	825.25	0.221	-12.5	0.25	11.5
	830.00	0.0650	-20.2	1.5	--
	835.40	0.282	-23.1	0.49	9.70

Table 3

	Depth (m)	FeT	Fecarb	Feox	Femag	Fe-AVS	Fepy	FeHR	FeHR/FeT	Fe-S/FeHR
Morro do Calcário Fm.	749.03	1.521	0.655	0.196	0.154	nd	0.236	1.241	0.816	0.190
	752.35	2.369	0.856	0.268	0.179	nd	0.601	1.904	0.804	0.316
	756.20	3.116	1.442	0.463	0.305	0.002	0.155	2.365	0.759	0.066
	759.55	2.235	0.324	0.063	0.062	nd	0.072	0.521	0.233	0.138
	764.47	2.132	0.302	0.104	0.061	0.004	0.075	0.542	0.254	0.146
	769.75	2.243	0.725	0.194	0.116	nd	0.094	1.129	0.503	0.083
	774.20	2.221	0.077	0.075	0.030	nd	0.031	0.213	0.096	0.146
	779.10	2.015	0.077	0.038	0.023	nd	0.005	0.143	0.071	0.035
	783.10	0.944	0.527	0.145	0.093	0.002	0.137	0.902	0.956	0.154
	788.15	3.169	0.608	0.129	0.157	nd	1.499	2.393	0.755	0.626
	793.70	0.502	0.359	0.082	0.025	nd	0.001	0.467	0.930	0.002
	799.10	2.301	1.032	0.220	0.307	nd	0.384	1.943	0.844	0.198
	799.25	3.564	0.012	0.031	0.011	nd	2.077	2.131	0.598	0.975
	799.39	2.442	0.011	0.025	0.008	nd	1.344	1.388	0.568	0.968
	799.97	1.717	0.600	0.178	0.265	nd	0.064	1.107	0.645	0.058
	800.12	1.199	0.322	0.079	0.067	nd	0.526	0.994	0.829	0.529
	800.60	4.938	0.007	0.023	0.007	nd	1.069	1.106	0.224	0.967
	801.34	1.542	0.004	0.020	0.007	nd	0.517	0.548	0.355	0.943
	802.67	2.133	0.008	0.027	0.005	nd	0.899	0.939	0.440	0.957
	803.82	3.392	0.118	0.041	0.043	nd	0.996	1.198	0.353	0.831
	804.43	2.521	0.023	0.027	0.001	nd	0.908	0.959	0.380	0.947
	804.63	3.416	1.128	0.245	0.337	0.004	0.193	1.903	0.557	0.104
	806.02	2.174	0.068	0.036	0.026	nd	0.824	0.954	0.439	0.864
	807.75	3.483	0.381	0.101	0.145	nd	0.561	1.188	0.341	0.472
	808.32	2.961	0.160	0.040	0.048	nd	0.653	0.901	0.304	0.725
	809.12	3.319	0.178	0.080	0.064	nd	0.793	1.115	0.336	0.711
	810.15	1.739	0.184	0.069	0.059	nd	0.443	0.755	0.434	0.587
	810.55	4.605	0.233	0.085	0.074	nd	1.674	2.066	0.449	0.810
	811.75	1.802	0.088	0.054	0.044	nd	0.668	0.854	0.474	0.782
	813.05	3.071	0.208	0.072	0.095	nd	0.168	0.543	0.177	0.309
	814.17	2.329	0.148	0.063	0.033	nd	0.814	1.058	0.454	0.769
	814.53	1.858	0.032	0.041	0.013	nd	0.314	0.400	0.215	0.785
	815.08	3.138	1.102	0.291	0.256	0.006	0.693	2.342	0.746	0.298
	816.95	2.082	0.018	0.022	0.002	nd	0.064	0.106	0.051	0.604
	818.00	2.353	0.563	0.128	0.169	nd	0.439	1.299	0.552	0.338
	818.23	0.836	0.278	0.075	0.079	0.007	0.290	0.722	0.864	0.411
	820.20	6.482	0.247	0.076	0.044	nd	1.878	2.245	0.346	0.837
	825.25	0.700	0.381	0.107	0.057	nd	0.085	0.630	0.900	0.135
	830.00	2.768	0.862	0.188	0.196	nd	1.056	2.302	0.832	0.459
	835.40	0.850	0.407	0.088	0.078	nd	0.208	0.781	0.919	0.266