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Manuscript Details

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Title	A Palaeoproterozoic dolomite (Vempalle Formation, Cuddapah Basin, India) showing Phanerozoic-type dolomitisation
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Abstract

The Palaeoproterozoic Vempalle Formation of the Cuddapah Basin, India, significantly adds to our understanding of the evolution of Precambrian marine carbonate systems and the redox state of the Earth's early oceans. A faciesmicrofacies-diagenetic-geochemical examination of samples from a 900-m long exposure in a freshly-cut canal section shows that 10 to 15 % of precursor limestone is still preserved in the Vempalle Formation in the form of remnant patches of calcimicrite and ooids with calcite spar cement. The ooids, preserving primary radial and concentric fabrics and radial fractures, are considered to have been originally precipitated as calcite, which may have been low-Mg. In places the preserved calcite spar, that is partially replaced by fabric-destructive dolomite, shows Type I calcite twin lamellae. Petrographic observations demonstrate that Vempalle Formation dolomite formed through very early precipitation, which in stromatolites preserved microbial filaments, as well as through fabric-destructive dolomitization during shallow to moderate burial. Vempalle Formation dolomite is characterized by micritic dolomite crystals which suggest rapid early dolomitization of lime mud and micritic calcite from a supersaturated Mg-Ca-rich solution, probably near-surface or during shallow burial. Depletion of Na and Sr contents of Vempalle Formation dolomite along with negative 180 values indicate dolomite recrystallisation during burial and further replacement. Dolomite 13C values of -0.5 to 2 ‰ are likely inherited original marine values. Geochemical proxies (trace elements and rare earths) imply that Cuddapah Basin seawater and dolomitizing fluids were anoxic and ferruginous but not euxinic. Geochemical analyses also indicate that the burial diagenetic fluids evolved from Eu-enriched seawater that probably resulted from continental rifting around 1.9 - 2.0 Ga. This probable ocean chemistry is in contrast with the anoxic, ferruginous and extremely high Mg/Ca "dolomite oceans" that prevailed during Proterozoic time. The Vempalle dolomite shows more similarities with dolomitised Phanerozoic platform carbonates than typical Precambrian dolomite with its well-preserved textures and burial dolospar cements.

Keywords	Dolomitization, Proterozoic carbonate rocks, redox, fluid chemistry
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Suggested reviewers	Alan Collins, Nic Beukes, Santanu Banerjee, Ian Somerville, Abhijit Basu

Submission Files Included in this PDF

File Name [File Type]

Cover_letter_27-3-19.doc [Cover Letter]

Reply to Reviewers_comments_27-3-19.doc [Response to Reviewers]

Revised_Manuscript_27-3-19.doc [Revised Manuscript with Changes Marked]

Highlights.doc [Highlights]

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To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given: all the data are given in Tables and Supplementary files

Dear Prof. Pease Editor, Precambrian Research

Thank you and the reviewers for their thoughtful comments and suggestions. Here in the revised draft we have taken into account all the suggestions and comments and modified the manuscript accordingly. All the modifications are highlighted in yellow in the revised draft, figure, table and supplementary files and outline every change made by us with line numbers. Please note that Section 4 is rewritten and abridged and Figs. 2 and 3 are added. The revised manuscript was checked by all the coauthors and they agreed about its content.

Also note that we have taken out the name of Marcin D. Syczewski from the author list. He helped one of the co-authors (MS) with SEM and according to MS it is not enough for a co-authorship.

Sincerely

Amlan Bangee.

Amlan Banerjee Geological Science Unit Indian Statistical Institute

Dear Dr. Banerjee,

Re: A Palaeoproterozoic dolomite (Vempalle Formation, Cuddapah Basin, India) showing Phanerozoic-type dolomitisation

Thank you for submitting your manuscript to Precambrian Research. I have received comments from two reviewers on your manuscript and they both enjoyed reading your manuscript. Nonetheless, some improvements can be made and your paper should become acceptable for publication after moderate revisions. In particular, please address the following points:

1. Better integrate the classical sedimentology (facies, facies associations, depositional environments) and dolomite geochemistry in the paper by discussing as a function of the facies/depositional environments. This may in fact work well with converting Table 1 into a facies-graphic.

Section 4 is rewritten and abridged (line number 194 – 267). New Table 1 and Figs. 2 and 3 are also added.

2. Clarify why the positive Eu anomaly and the relatively high Fe and Mn contents indicate dolomitization of Phanerozoic type rather than Precambrian type?

The argument that the VF dolomitization is more of Phanerozoic type rather than Precambrian type is based more on petrographic rather than geochemical analysis. Precambrian dolomites are generally characterised by very well-preserved fabrics of the original carbonate grains and early cements likely a reflection of seawater chemistry higher Mg/Ca ratio, higher partial pressure CO2 (pCO2), higher temperature, and lower SO42- (Tucker 1982, Hood and Wallace 2018), in addition, many Precambrian dolomites have drusy dolospar cements, precipitated during shallow to moderate burial (e.g. Tewari and Tucker, 2011), a feature rarely seen in Phanerozoic dolomites.

Petrographic analysis suggests that the VF carbonates originally precipitated as lime mud and calcimicrite and 10 to 15% of precursor limestone is still preserved in the Vempalle Formation in the form of remnant patches of calcimicrite and ooids with calcite spar cement. The ooids preserve primary radial and concentric fabrics and radial fractures, and are considered to have been originally precipitated as calcite. In places the preserved calcite spar, that is partially replaced by fabric destructive dolomite, shows Type I calcite twin lamellae. Petrographic observations suggest fabric destructive dolomitization in VF carbonate rocks (Tucker et al., 2002), and the mimetic to obliterated mosaic texture indicate progressive dolomite replacement (Braithwaite, 1991). It is likely that this was a time of calcite precipitation (a "calcite sea"), with anoxic, Eu anomaly and ferruginous conditions, and an elevated Mg/Ca ratio but not so high that either dolomite precipitation or very early fabric-retentive dolomitization of ooids and cements could take place, like those of the Beck Spring Dolomite (Tucker, 1983). On the other hand the occurrence of dolomitic micritic facies in the VF suggests that the dolomite crystals rapidly precipitated from a dolomite supersaturated fluid having high Mg/Ca ratio and low SO4-2 concentration as primary precipitates due to evaporation or due to microbial activity and as would be expected in the Proterozoic environments.

3. There is a notable lack of references to other Paleoproterozoic carbonate successions (e.g., Grotzinger on the Canadian shield and late Archean carbonate platform successions in South Africa and Australia with positive Eu anomalies of Kamber and Webb, 2001, Geochim Cosmochim Acta; Schier et al 2018, Precam Research; Eroglu et al., Precam Research, 2017).

We have added several references (six in numbers) of J.P Grotzinger and the references recording positive Eu anomalies from carbonate platform successions as suggested by the reviewer.

1.Grotzinger, J.P., 1989. Facies and evolution of Precambrian carbonate depositional systems: emergence of the modern platform archetype, in, SEPM Special Publication 44, p. 79-106 (line number 52; and 748-749)

2. Grotzinger, J. P., Read, J. F., 1983. Evidence for primary aragonite precipitation, lower Proterozoic (1.9 Ga) dolo- mite, Wopmay orogen, northwest Canada: Geology, v. 11, p. 710-713 (line number 52; and 750-751)

3. Grotzinger, J.P., Kasting, J. 1993. New constraints on Precambrian ocean composition. Journal of Geology, v. 101, p. 235-243 (line number 52; and 752-753)

4. Pope, M. C., Grotzinger, J. P., 2003. Paleoproterozoic Stark Formation, Athapuscow basin, northwest Canada: Record of cratonic-scale salinity crisis. Journal of Sedimentary Research, v. 73, p. 280-295. (77) (line number 49; and 901-903)

5. Saylor, B. Z., Grotzinger, J. P., Germs, J. B. 1995. Sequence stratigraphy and sedimentology of the Neoproterozoic Kuibis and Schwarzrand Subgroups (Nama Group), southwestern Namibia. Precambrian Research, v. 73, p. 153-171. (line number 48; and 935-937)

6. Kamber B. S., Webb, G. E., 2001. The geochemistry of late Archaean microbial carbonate: implications for ocean chemis- try and continental erosion history. Geochim. Cosmochim. Acta 65, 2509–2525. (line number 457; and 801-803)

7. Schier, K., Bau, M., Münker, C., Beukes, N., Viehmann, S., 2018. Trace element and Nd isotope composition of shallow seawater prior to the Great Oxidation Event: Evidence from stromatolitic bioherms in the Paleoproterozoic Rooinekke and Nelani Formations, South Africa. Precambrian Research 315, 92-102 (line number 472; and 939-942)

 Eroglu, S., van Zuilen, M.A., Taubald, H., Drost, K., Wille, M., Swanner, E.D., Beukes, N.J., Schoenberg, R., 2017, Depth-dependent δ13C trends in platform and slope settings of the Campbellrand-Malmani carbonate platform and possible implications for Early Earth oxygenation. Precambrian Research 302, 122-139. (line number 471; and 712-715) 4. Convert data Table 1 into a schematic strat column or a stylized facies cartoon/graphic.

See Fig. 2 and Fig. 3

5. Move data tables 2-6 into supplementary material.

See Supplementary section where Tables 1S to 5S are presented showing all the data (XRD; Ca excess and ordering; Major and Trace element concentrations in wt% and ppm; PAAS normalized REE values; and oxygen and carbon isotope values).

6. Add scale bars on all images in Figs 3 & 4.

Done

When resubmitting your manuscript, please carefully consider my comments above and the reviewers' comments, outline every change made by line number, and provide suitable rebuttals for any comments not addressed.

Reviewer 1

- This is a very well written manuscript.

<mark>Thank you</mark>

I have only two major concerns:

1. I do not follow the argument that the dolomitization is of Phanerozoic type rather than Precambrian type if you refer to the positive Eu anomaly and the relatively high Fe and Mn contents.

The argument that the VF dolomitization is more of Phanerozoic type rather than Precambrian type is based more on petrographic rather than geochemical analysis. Precambrian dolomites are generally characterised by very well-preserved fabrics of the original carbonate grains and early cements likely a reflection of seawater chemistry higher Mg/Ca ratio, higher partial pressure CO_2 (pCO₂), higher temperature, and lower SO_4^{2-} (Tucker 1982, Hood and Wallace 2018), in addition, many Precambrian dolomites have drusy dolospar cements, precipitated during shallow to moderate burial (e.g. Tewari and Tucker, 2011), a feature rarely seen in Phanerozoic dolomites.

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replaced by fabric destructive dolomite, shows Type I calcite twin lamellae. Petrographic observations suggest fabric destructive dolomitization in VF carbonate rocks (Tucker et al., 2002), and the mimetic to obliterated mosaic texture indicate progressive dolomite replacement (Braithwaite, 1991). It is likely that this was a time of calcite precipitation (a "calcite sea"), with anoxic, Eu anomaly and ferruginous conditions, and an elevated Mg/Ca ratio but not so high that either dolomite precipitation or very early fabric-retentive dolomitization of ooids and cements could take place, like those of the Beck Spring Dolomite (Tucker, 1983). On the other hand the occurrence of dolomitic micritic facies in the VF suggests that the dolomite crystals rapidly precipitated from a dolomite supersaturated fluid having high Mg/Ca ratio and low SO4-2 concentration as primary precipitates due to evaporation or due to microbial activity and as would be expected in the Proterozoic environments.

2. I miss references to other Paleoproterozoic carbonate successions for example as described by Grotzinger from the Canadian shield and late Archean carbonate platform successions in South Africa and Australia with positive Eu anomalies (refer for example to Kamber and Webb, 2001, Geochim Cosmochim Acta; Schier et al 2018, Precam Research; Eroglu et al., Precam Research, 2017).

We have added several references (six in numbers) of J.P Grotzinger and the references recording positive Eu anomalies from carbonate platform successions as suggested by the reviewer.

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2. Grotzinger, J. P., Read, J. F., 1983. Evidence for primary aragonite precipitation, lower Proterozoic (1.9 Ga) dolo- mite, Wopmay orogen, northwest Canada: Geology, v. 11, p. 710-713 (Line number 52; and 750-751)

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4. Pope, M. C., and Grotzinger, J. P., 2003. Paleoproterozoic Stark Formation, Athapuscow basin, northwest Canada: Record of cratonic-scale salinity crisis. Journal of Sedimentary Research, v. 73, p. 280-295. (77) (Line number 49; and 901-903)

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Reviewer 2

The manuscript submitted to Precambrian Research by Banerjee and co-authors is an interesting work contributing to a better knowledge of the evolution of ocean geochemistry in deep time, essentially to what concerns carbonate sediments. It is therefore a paper that adds new knowledge for Earth's history.

Thank you Prof. Pittet.

The manuscript is separated into 2 parts, one devoted to classical sedimentology (facies, facies associations, depositional environments) and one to dolomite geochemistry. The problem in the manuscript is that these 2 parts are not clearly linked together as dolomite geochemistry is not analysed as a function of the facies, or of the environments. It seems that dolomite sampling was done rather randomly, at a more or less constant step (15m). I wonder if these 2 parts should not be published separately. Alternatively, it is necessary to better relate these 2 parts to write a more integrative/homogenous paper. Another alternative possibility is to drastically reduce the facies analysis in the present manuscript to focus on dolomite geochemistry. I however think that the data presented are of importance, and should be published. I have made comments and corrections all along the pdf file -both for the text and the figures- that I will not repeat here

Thank you Prof. Pittet for the comments. Changes made based on your comments and suggestions in the text (including figures) are described below.

1. Corrected in line 76 and 77 deleted "a short" and "short"

2. Line 82 corrected "¹⁸O depleted"

3. Line 107, 109, change gradational in to "transitional"

4. The Facies section is re-written and abridged. Table 1 is added along with Fig. 3. Table 2 is modified. All the other tables are shifted to Supplementary section. See Supplementary section where Tables 1S to 5S are presented showing all the data (XRD; Ca excess and ordering; Major and Trace element concentrations in wt% and ppm; PAAS normalized REE values; and oxygen and carbon isotope values).

5. Line number 196 Fig 1a, b, c are now marked.

6. Line no. 244 the environment is "quiescent" is interpreted from the presence of stromatolite with low synoptic relief and parallel lamination. Probable interpretation is deposition in a relatively quiet-water protected area between two bars or in a relatively deeper-water environment.

7. Line number 285 reference added. Dolomite petrology of the formation is described depending on the dolomite classification system by Sibley and Gregg (1987, 1984) where they have designated mainly three types of dolomite depending on crystal size distribution and crystal boundary shape (preserved crystal face junction). Planar-e dolomites are described as euhedral crystals with intercrystalline boundaries filled by other minerals. Planar-s dolomites are subhedral to anhedral crystals with straight compromise boundaries and many crystal face junctions with low intercrystalline matrix. Nonplanar dolomites are defined by closely packed anhedral crystals with irregular intercrystalline boundaries and fewer (<30%) preserved crystal face junction.

8. Line 340-341, Figure 7 is modified and Fig. 7 d) and 7 e) added.

9. Line 347 (Table 3Sa, see Supplementary section) added.

10. Line 399 Tucker (1982) reference added.

11. Line 445 Fig. 7c corrected.

12. Fig. 1 the three figures are labeled a) b) and c); Fig. 2 is modified and New Fig 3 is added; in Figure 4 Planer-s explained in the text (see line no. 285); in Figure 5 captions heading e) and f) corrected.

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A Palaeoproterozoic dolomite (Vempalle Formation, Cuddapah Basin, India) showing Phanerozoic-type dolomitisation

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14 Abstract: The Palaeoproterozoic Vempalle Formation of the Cuddapah Basin, India, significantly adds to 15 our understanding of the evolution of Precambrian marine carbonate systems and the redox state of the 16 Earth's early oceans. A facies-microfacies-diagenetic-geochemical examination of samples from a 900-m 17 long exposure in a freshly-cut canal section shows that 10 to 15 % of precursor limestone is still preserved 18 in the Vempalle Formation in the form of remnant patches of calcimicrite and ooids with calcite spar 19 cement. The ooids, preserving primary radial and concentric fabrics and radial fractures, are considered to 20 have been originally precipitated as calcite, which may have been low-Mg. In places the preserved calcite 21 spar, that is partially replaced by fabric-destructive dolomite, shows Type I calcite twin lamellae. 22 Petrographic observations demonstrate that Vempalle Formation dolomite formed through very early precipitation, which in stromatolites preserved microbial filaments, as well as through fabric-destructive 23 24 dolomitization during shallow to moderate burial. Vempalle Formation dolomite is characterized by 25 micritic dolomite crystals which suggest rapid early dolomitization of lime mud and micritic calcite from 26 a supersaturated Mg-Ca-rich solution, probably near-surface or during shallow burial. Depletion of Na 27 and Sr contents of Vempalle Formation dolomite along with negative δ^{18} O values indicate dolomite 28 recrystallisation during burial and further replacement. Dolomite δ^{13} C values of -0.5 to 2 ‰ are likely 29 inherited original marine values. Geochemical proxies (trace elements and rare earths) imply that 30 Cuddapah Basin seawater and dolomitizing fluids were anoxic and ferruginous but not euxinic. 31 Geochemical analyses also indicate that the burial diagenetic fluids evolved from Eu-enriched seawater 32 that probably resulted from continental rifting around 1.9 - 2.0 Ga. This probable ocean chemistry is in 33 contrast with the anoxic, ferruginous and extremely high Mg/Ca "dolomite oceans" that prevailed during 34 Proterozoic time. The Vempalle dolomite shows more similarities with dolomitised Phanerozoic platform 35 carbonates than typical Precambrian dolomite with its well-preserved textures and burial dolospar 36 cements.

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- 39 Keywords: Dolomitization, Proterozoic carbonate rocks, redox, fluid chemistry
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45 **1. INTRODUCTION**

46 Carbonate ramps and rimmed platforms are a distinctive feature of Neoarchean to 47 Neoproterozoic deposition and in many cases the dolomite content of these ancient carbonate 48 platforms is high in comparison with those of the Mesozoic and Cenozoic (Saylor et al., 1995; 49 Holland and Zimmermann, 2000; Pope and Grotzinger, 2003). The processes of formation of 50 these ancient dolomites are still the subject of much debate. The Precambrian sedimentary record 51 to about 3.5 Ga includes dolomites and limestones that likely precipitated as primary aragonite and calcite (Grotzinger and Read, 1983; Grotzinger, 1989; Grotzinger and Kasting, 1993). 52 53 Palaeoproterozoic carbonate sedimentation was marked by less spectacular occurrences of 54 massively-precipitated aragonite and calcite (Grotzinger and Kasting, 1993). Precambrian 55 dolomites may have also formed by precipitation directly from seawater or by dolomitization 56 during very early diagenesis from fluids comparable with seawater (e.g., Veizer and Hoefs, 57 1976; Tucker, 1982, 1983; Hood and Wallace, 2018). Precambrian dolomites are generally 58 characterised by very well-preserved fabrics of the original carbonate grains and early cements, 59 leading to arguments over primary versus replacement dolomite (Tucker 1982, Hood and 60 Wallace 2018). In addition, many Precambrian dolomites have drusy dolospar cements, 61 precipitated during shallow to moderate burial (e.g. Tucker, 1983; Tewari and Tucker, 2011), a 62 feature rarely seen in Phanerozoic dolomites. In India, several Precambrian sedimentary basins 63 are reported to host dolomite successions several kilometres thick. The Palaeoproterozoic 64 Vempalle Formation (VF), located in the crescent-shaped intracratonic Cuddapah Basin (CB), 65 Eastern Dharwar craton, and a part of the Papaghni Group (Fig. 1), is characterized by the presence of $\frac{1}{a} \sim 1.9$ km-thick stromatolitic dolomite. The VF carbonate platform can be traced for 66 67 more than 1000 km without any significant physical break from the SE to the NW part of the 68 basin.

69

Zachariah et al. (1999) obtained a Pb-Pb age of 1756 ± 29 Ma for the VF dolomite. Taking into consideration the age of intruded sills (1817 ± 24 Ma; Bhaskar Rao et al., 1995) within VF carbonate rocks/Pulivendla quartzites and the age of VF dolomite (1756 ± 29 Ma), Zachariah et al. (1999) proposed 1756 ± 29 Ma as the time of dolomitization of the precursor VF limestone. Rai et al. (2015), based on a Pb–Pb (PbSL) age of VF dolomite and of the intruded sills of 1885 Ma (U-Pb and Ar-Ar methods; French et al., 2008; Anand et al., 2003), proposed that 76 dolomitization of VF limestone might have taken place within 100 My duration of time (from 77 1900-2000 Ma). This time duration of sedimentation and dolomitization is also reported from the 78 Wittenoom Formation and Carawine Dolomite of the Hamersley Group, Western Australia, 79 where the time between deposition, diagenesis and dolomitization is thought to be within 100-80 150 My (Jahn and Cuvellier, 1994; Jahn and Simson, 1995). On the other hand, Chakrabarti et al. (2011, 2014), using isotopic (δ^{13} C and δ^{18} O) and elemental (Mg, Ca, Fe, Mn, Sr and SO₄⁻²) data, 81 82 concluded that VF dolomite is primary in nature and precipitated either from $\frac{180}{180}$ depleted marine 83 water or from a geochemically distinct mixed fluid source. Based on collective geochemical 84 signatures, δ^{13} C and δ^{18} O isotopic values, flat REE patterns along with Ce, Eu and Gd anomalies, and chondritic to superchondritic Y/Ho ratios, Khelen et al. (2017) have recently 85 86 proposed that VF dolomite was precipitated from marine water having a hydrothermal signature. 87 These discrepancies in the plumbing mechanism(s) of VF dolomite warrant the need to revisit 88 the question about the origin of VF dolomite and related dolomite-precipitating fluids.

89

90 In this project we have used field and petrographic observations and various geochemical 91 proxies to understand the mechanism(s) of formation of the shallow-marine VF dolomite and to 92 assess the redox heterogeneity existing during its time of formation. Geochemical data, 93 integrated with petrology and tectonic history of the CB, help not only to infer the source of Mg-94 rich fluids but also to contribute to a better understanding of the redox conditions of this 95 Proterozoic shallow-water carbonate. In addition, as will be shown, this Palaeoproterozoic 96 dolomite has more features in common with dolomitised Phanerozoic platform carbonates, than 97 the typical Precambrian dolomite with well-preserved fabrics, likely a reflection of seawater 98 chemistry, redox and microbes.

99

100 2. GEOLOGICAL BACKGROUND

101 The Papaghni Group (~2110 m thick) represents the first sedimentary cycle of the 102 Cuddapah Supergroup (Patranabis-Deb et al., 2012) in the CB. The succession unconformably 103 overlies the basement granite, gneiss and greenstone complex of the Eastern Dharwar craton, 104 which in turn is unconformably overlain by the Chitravati Group (4975 m). The VF (~1900 m) 105 of the Papaghni Group constitutes the lowermost carbonate-dominated unit of the Cuddapah 106 Supergroup and overlies a basal siliciclastic unit, the Gulcheru Quartzite (~210 m), with a

107 transitional contact (Nagaraja Rao et al., 1987). The Gulcheru Quartzite constitutes a basal 108 conglomerate and immature sandstone unit, deposited in a fan-delta to prodelta setting, which 109 transitionally passes up into a mature quartz arenite unit, deposited in a shallow-shelf 110 environment (Majumder et al., 2015). The VF is represented mostly by thick stromatolitic 111 dolomite and minor limestone (10 to 15%). Near the transition zone to the Gulcheru Quartzite, 112 thin beds of splintery red mudstone alternate with siliciclastic and carbonate beds to form a 113 mixed siliciclastic-carbonate unit (Fig. 2). Tidal and storm currents played a major role in 114 sculpturing the sandstone bodies at this transition.

115

116 Tepee structures, desiccation cracks filled with lime mud and sand and halite casts, are 117 common in the lower VF (Fig. 2). The upper part is dominated by bedded dolomite deposited in 118 a range of environments, starting from shallow shelf with intermittent exposure to fairly deep-119 water conditions below normal wave base. Stromatolite morphologies reflect environments 120 varying from intertidal to subtidal and facies cycles are the result of multiple rhythms of sea-121 level change (Patranabis-Deb et al., 2018). Demise of the carbonate platform is marked by the 122 deposition of thick brown shale with laterally persistent beds of chert. The common occurrence 123 of sills up to a metre or more thick and thinner dykes of basalt and/or dolerite in the upper part of 124 the VF succession indicates tectonic-magmatic activity (Anand et al., 2003). Conglomerate and 125 pebbly sandstone of the basal Chitravati Group, upon a sharp unconformity, mark the beginning 126 of the second sedimentary cycle. Clasts of chert with stromatolite, oolite, vein quartz, jasper and 127 volcanics, derived from the Papaghni Group, reflect subaerial exposure and erosion during the 128 formation of the unconformity between the two groups.

129

130 Rifting of the Eastern Dharwar craton and passive-margin sedimentation deposited the 131 Gulcheru fan-delta succession (Majumder et al., 2015) followed by deposition of the extensive 132 VF carbonate platform (Tripathy and Saha, 2008; Patranabis-Deb et al., 2018). Rai et al. (2015) 133 inferred a minimum age of 2000 Ma for the onset of sedimentation in the Cuddapah Supergroup 134 and this coincides with the onset of rifting of the supercontinent Columbia, as evidenced by widespread emplacement of mafic dykes in and around the CB during this period. The 135 136 intermittent occurrence of mafic flows, ash-fall tuffs and associated shallow-crustal intrusives in 137 the upper part of the VF (~1.88 Ga; Ravikant, 2010) is related to the second cycle of rifting that possibly represents the initial phase of fragmentation and separation of the south Indian craton from the North China craton (Ravikant, 2010). With continued passive subsidence, the CB evolved into a large epicontinental sea with a near-complete cessation of coarse clastic influx and deposition of the extensive shale–carbonate succession of the Chitravati Group. Tectonically, the CB is punctuated by multiple unconformities, major tectonic contacts, faults and various basic sills (Saha and Tripathy, 2012; Saha and Mazumder, 2012; Patranabis-Deb et al., 2012; Collins et al., 2015), which affected and shaped its sedimentary succession.

- 145
- **3. Methods**
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3.1. Sample collection for petrological analysis

149 Samples were collected at 5-15 m intervals up-section (Table 1) along a freshly cut canal 150 section, nearly 4 km long (hereafter referred as the 'canal section') that exposed the dolomite 151 beds of the VF (~1000 m thick dolomite unit, Fig. 2) near Parnapalle village (N14°32'58.3", 152 E77°58'09.9") in the Cuddapah district, Rayalaseema. Samples collected from the dolomite beds covered eight facies namely F1, F2, F4, F5, F7, F8, F9 and F10 (Table 1; Fig. 2). F3 and F11 are 153 intentionally avoided as they are mostly composed of shale, siltstone and dolomite (Table 2). 154 155 Thin-sections were made from twenty-nine selected dolomite samples for petrographic analysis. 156 Carbonate components (calcite, dolomite) were determined by staining the thin-sections with 157 Alizarin Red S.

158

159 **3.2.** *X-Ray diffraction*

Twenty-nine selected dolomite samples were powdered for X-ray diffraction analysis on
a Panalytical X'Pert Pro diffractometer, equipped with a Cu Ka X-ray source and an X'Celerator
detector, operating at the following conditions: 40 kV and 40 mA; range 5 – 80 deg 20; step size
0.017 deg 20; time per step 50.2 sec; fixed divergence slit, angle 0.5°; sample rotation 1 rev sec⁻¹.
The quantities of the mineral phases were determined using the Rietveld method.

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166 **3.3.** *Major and trace elements*

167 Forty-two selected dolomite samples were powdered for bulk major, trace and REE 168 analyses, undertaken at the Wadia Institute of Himalayan Geology. The elemental analysis was 169 performed using an ICP-MS PerkinElmer SCIEX ELAN DRC-e. Concentrations of REE + Y (n 170 = 42) were normalized to the Post-Archaean Australian Shale (PAAS) representing an estimate 171 for the composition of average terrigenous input to the oceanic environment. Specifically, REE 172 fractionation was calculated as Pr_{SN} / Yb_{SN} (SN, shale normalized) to avoid problems in case of 173 anomalous La and Ce concentrations. To avoid any anomalous behaviour of La, Ce, Eu and Gd, 174 the anomalies were calculated using the geometric equations of Lawrence and Kamber (2006) 175 and are given as Ce/Ce^{*}, Eu/Eu^{*}, Gd/Gd^{*} and La/La^{*}.

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3.4. Scanning electron microscopy with energy-dispersive spectroscopy

Thin-sections were examined under a scanning electron microscope (SEM) FE-SIGMA VP (Carl Zeiss Microscopy GmbH) with energy-dispersive (EDS) detector (Quantax XFlash 3|10, Bruker Nano GmbH). Thin-sections were placed on the mount with carbon conductive tape. Then, samples were coated with a 20 nm layer of carbon by vacuum coater (Quorum 150T ES). Furthermore, carbon tape bridges were made for each sample to avoid excessive accumulation of charge. Analyses were done with 120 µm aperture and 15 keV accelerationvoltage. Beam intensity was 2.5 nA and working distance was 7.5 mm.

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3.5. Oxygen and carbon stable isotope analysis

187 Thirty-five selected dolomite samples were analysed for bulk carbon and oxygen stable 188 isotopes at the Activation Laboratories Ltd., Canada. Samples were run on a DELTAPlus XL 189 stable isotope ratio mass spectrometer (IRMS) coupled with ConFlo III Interface and EA1110 190 elemental analyser. Standards NBS-19 ($\delta^{13}C = 1.95 \%$ and $\delta^{18}O = -2.20 \%$) and NBS-18 ($\delta^{13}C =$ 191 -5.05 ‰ and $\delta^{18}O = -23.1 \%$) were used for comparison. The results are expressed relative to the 192 Vienna Peedee Belemnite (VPDB).

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4. Sedimentation Pattern and Depositional Environment

The VF is well exposed along the south-western margin of the CB outcrop (Fig. 1a, b and c), represented by a \sim 1000-m thick succession of stromatolitic dolomite, dolomitic limestone and limestone (\sim 70%), with minor calcimicrite (\sim 20%), and \sim 10% siliciclastic sandstone and mudstone. Facies analysis reveals that the succession can be sub-divided into 11 distinct lithofacies (Table 1) which may be grouped into inner, mid and outer – ramp associations, 200 stacked in different orders as part of a major ramp-type carbonate platform (Fig. 3). The platform 201 maintained a shallow depth throughout its life, thus indicating a keep-up mode of deposition, that 202 is where the carbonate succession built up to sea level and kept pace with subsequent sea-level 203 changes, such that a balance was maintained with the generation of accommodation space. 204 Occasional storms and regular tides were important, distributing clastic sediments at particular 205 times, which hampered the growth of the platform in time and space. The depth-controlled 206 growth patterns of the stromatolites give clues to their depositional environment (Patranabis-Deb 207 et al., 2018), which in the canal section reflects a gradient from shallow-water with exposure to 208 shallow to moderate depths.

209

210 The VF succession in the canal section (Fig. 2) starts with a basal mixed unit, 211 representing the transition between the basal siliciclastic unit of the Gulcheru Formation and 212 carbonate rocks of the VF. It comprises mixed siliciclastic-dolomite (F1), bedded dolomite with 213 crinkled laminites (F2) and intraformational conglomerate (F9). The mixed siliciclastic-dolomite 214 beds are characterized by flaser bedding and lenticular bedding with preservation of desiccation cracks filled with lime mud and sand and halite casts within shale intervals, tepee structures and 215 216 fluid-escape structures. The presence of these sedimentary features, suggests intermittent exposure in a supratidal to upper intertidal flat, in an inner ramp setting. Palaeocurrent directions 217 218 measured from trough cross-stratification from the sandy units indicate east-north-easterly flow.

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220 The mixed siliciclastic unit passes upward to a thick succession of bedded dolomite with 221 crinkled laminites (F2), black dolomite with or without stromatolite (F4), dolomite-micrite 222 rhythmite (F5) and brown shale (F3), without any break. Steel grey to black coloured massive to 223 stromatolitic dolomite beds (F4) with isolated to laterally-linked mutually-aligned stromatolites 224 are observed, alternating with dolomite-micrite rhythmite (F5). Isolated occurrences of 225 stromatolite with low synoptic relief and parallel lamination in black dolomite (F4) indicate a 226 quiescent water environment. The close association of F4 and F5 also suggests their deposition 227 in a low-energy protected environment. Thick occurrences of F2 alternating with F5, with 228 signatures of intermittent exposure at different stratigraphic levels, suggest that they have 229 possibly formed a barrier, which imposed a rimmed-shelf profile to the platform, creating 230 lagoons on the shoreward side with an open shelf to seaward.

231 The mid-ramp association consists of oolite (F6), with intercalations of dolomite mud rhythmite (F5), columnar stromatolite (F7), conical stromatolite (F8) and thickly – bedded 232 233 dolomite (F10). The association starts with the occurrence of oolite (F6), as shoaling-up bars. 234 The oolites comprise well-rounded, well-sorted medium- to coarse-grained ooids, usually 235 preserving a concentric fabric with a clastic grain as the nucleus. Medium-to-fine-grained ooids 236 with a radial fabric (with or without a clastic grain in the centre) and superficial ooids are also 237 observed. Oolite beds are generally trough cross-stratified, showing NE and SW palaeocurrent 238 directions with bidirectional pattern. The abundance of siliciclastic grains as nuclei to ooids 239 indicates a ready source of clastics on the landward side. The oolite bank may have further acted 240 as a barrier with the seaward side being cut off from the coastal sediments so that ooids formed 241 without sand nuclei and a radial fabric. F6 is interbedded with small columnar stromatolites (4-14 cm in height). F7 suggests spatial and temporal variations in the intensity and fluctuations of 242 243 wave action (Swett and Knoll, 1989; Holland and Patzkowsky, 1998) in a lower intertidal to 244 upper subtidal environment. The rhythmite facies (F5) may have been deposited as interbars in a 245 relatively quiet-water protected area between two bars or in a relatively deeper-water 246 environment. Up-section the columns increase in number and size and coalesce to form a continuous biostromal structure (F7), many metres thick, commonly intercalating with parallel-247 248 stratified dolomite (F10).

249

250 Planar-parallel to wavy-parallel stratified and trough cross-stratified dolomite beds of F10 251 strongly suggest that this facies was deposited by traction currents. Gutter casts (Fig. 3d) and 252 pillow and ball structures within the dolomite beds suggest storm waves on a shallow shelf. 253 Changes of stromatolite type from shallow intertidal columnar to columnar biostromes, and a 254 conical type, indicate deposition on a low-gradient ramp where the distribution of microbialite 255 facies is distinctly depth-partitioned (Patrabanis-Deb et al., 2018). The gradual change in the 256 shape, size and synoptic relief of stromatolites also suggests balanced sedimentation, deposition 257 and accommodation space generation.

258

The top part of the VF is mainly characterized by F10 and F11, interpreted to be deposited in an outer ramp environment, below fair-weather wave base. The association comprises a rhythmic occurrence of plane-parallel laminated dolomite (F10) with interbedded green shale/siltstone and dolomite (F11), commonly interrupted by igneous intrusions. This depozone predominantly involved deposition from background suspension rarely interrupted by strong storm surges. Isolated gutter casts within the dolomite beds are thought to have been produced by storm-generated return flows (Fairchild and Herrington, 1989; Myrow, 1992). Chert and steatite nodules of various shapes and sizes (Fig. 3f) are common with iso-volumetric metasomatic alteration of dolomite to talc observed in the upper part of the VF.

268

269 **5. RESULTS**

270 **5.1.** *Petrography*

271 Petrographic analysis of the VF dolomite led to the identification of four microfacies: i) 272 dolo-micrite with few quartz and feldspar grains, ii) stromatolitic dolomite bindstone, iii) oolitic 273 grainstone (limestone and dolomite), and iv) calcimicrite with local limestone clasts. Micritic 274 dolomite is plane-parallel laminated, where laminae are defined by alternating light (micrite) and 275 dark (clay-rich) layers (Fig. 4a). Dolomicrite is commonly mixed with fine sand or silt-sized 276 grains of well-rounded to sub-rounded quartz and feldspar (Fig. 4b). Dolomicrite shows grain 277 enlargement due to recrystallization (Fig. 4c). Stromatolitic dolomite preserves crinkly to smooth 278 lamination defined by alternating dolomicrite and microbial filaments (Fig. 4d). Preservation of 279 the primary microbial texture suggests that this VF dolomite is either a very early mimetic 280 replacement of CaCO₃, preserving the original microbial filaments, or it is a primary microbial 281 dolomite precipitating directly from ancient seawater (Tucker, 1983, Corsetti et al., 2006, van 282 Smeerdijk Hood and Wallace, 2012). Good preservation of microbial structures also indicates 283 little or no recrystallization during diagenesis. The stromatolitic dolomite is characterized by 284 polymodal planar-e and subhedral to anhedral planar-s or non-planar micritic dolomite crystals 285 (see dolomite classification by Sibley and Gregg, 1984, Gregg and Sibley, 1987), with sharp 286 intercrystalline boundaries (Fig. 4e, f). Moreover, the SEM-EDS analysis of thin-sections did not 287 show any relics of calcite crystals.

288

The coarser carbonate facies include grainstone, mostly with spheroidal ooids, but also eye-shaped ooids. Stages of dolomitization are well-documented and recorded by the ooids (Fig. 5a-f). At one extreme, the ooids are composed entirely of calcite crystals having a radial fabric, such that a continuous sweep of the extinction is seen on stage rotation under crossed polars (Fig.

293 5a, b). Preserved calcite ooids show well-developed primary concentric, radial and radial-294 concentric fabrics; some have an outer silicified zone (cf. Tucker, 1984, 1985). Some of the 295 ooids are radially fractured as a result of compaction (Fig. 5a). These radial fractures crudely 296 coincide with the radial fabric which is probably a primary feature. Also the presence of primary 297 radial - concentric fabrics as observed within the unreplaced calcite ooids suggest its growth in a 298 mud-free environment whereas the radial fabric results from ooid growth in a relatively calm 299 environment with the presence of lime mud (Tucker, 1984). The good fabric preservation of the 300 ooids could suggest that they were originally composed of low-Mg calcite since this tends to 301 resist dolomitization; however, they could originally have been high-Mg calcite, with the Mg 302 leached out before dolomitisation (Tucker 1984, 1985). Some calcitic ooids have euhedral 303 rhombic dolomite crystals in the nucleus of the ooid (Fig. 5c). At the other extreme, the ooid 304 cortex is completely replaced by planar-e (euhedral) and subhedral to anhedral planar-s 305 (subhedral) or non-planar micritic dolomite crystals, with sharp but slightly ragged 306 intercrystalline boundaries, completely obliterating the internal fabric but still preserving the 307 shape of the ooids (Fig. 5f). In between there are ooids that show incomplete replacement 308 phenomena where the central part of the ooid is composed of coarse euhedral and mostly planar-309 e to planar-s dolomite crystals obliterating the internal fabrics, but the outer rim is composed of 310 calcite crystals still preserving the original radial-concentric fabrics (Fig. 5d). The primary radial 311 fabric of the ooid at the peripheral margin is commonly partially destroyed by replacement 312 micritic dolomite (Fig. 5e). Within massive dolomite there are still patches and lenses of 313 limestone that preserve the primary micritic calcite matrix and calcite spar (Fig. 6a); the latter 314 shows Type I calcite twin lamellae and it is partially replaced by dolomicrite destroying the 315 primary fabric (Fig. 6b). Thin-section evidence of fabric-destructive dolomite in VF carbonate 316 rocks indicates a replacement origin (Tucker et al., 2002), and the mimetic to obliterated mosaic 317 texture indicates progressive dolomite replacement (Braithwaite, 1991).

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5.2. X-ray diffraction

320 XRD analysis shows that dolomite is the dominant mineral in the samples analysed, with 321 subordinate quartz and minor K-feldspar (Table 1S, Supplementary section). Barring three 322 samples, calcite is absent in VF dolomite samples analysed. Trace amounts of talc, barite, mica, 323 chlorite and hematite were also detected. Calcium excess of VF dolomites is calculated using the formula: CaCO₃ mol% = $333.33*d_{104} - 911.99$ (Lumsden, 1979, where d_{104} is the peak position in angstrom units, Table 2S). VF dolomites have a nearly stoichiometric composition (mole % CaCO₃ = 49–51, mean 50) indicating an ideal composition of the dolomite (Mg:Ca = 1). Ordering of VF dolomite crystals ranges from 0.40 to 1.07 (average 0.56), according to the method described by Hardy and Tucker (1988). Only five samples had an ordering ratio <0.5 and >0.4.

- 330
- **5.3.** *Geochemistry*

332 Total iron content of VF dolomite varies from 19,235 ppm to 2170 ppm (average 5240 333 ppm); Mn ranges from 2040 ppm to 125 ppm (average 320 ppm), whereas Al varies from 19,955 334 ppm to 160 ppm (average 5475 ppm) (Table 3Sa,b). Average Fe/Mn and Fe/Al ratios are 19.6 335 and 3.4, respectively. Sodium and Sr concentrations range from 60 ppm to 735 ppm (average 290 336 ppm) and from 40 ppm to 420 ppm (average 85 ppm), respectively (Table 3Sa,b). Fe and Mn 337 concentrations show a positive correlation (Fig. 7a), whereas the Sr/Ca ratio versus Na₂O shows 338 a poor correlation (Fig. 7b). Mn and Fe concentrations versus the Mg/Ca ratio can be used to 339 explore modification of the carbonate chemistry during burial diagenesis (Gilleaudeau and Kah, 340 2013). Fe and Mn concentrations of VF dolomites are independent of the Mg/Ca ratio (Fig. 7d, 341 e). The Fe/Sr and Mn/Sr ratios can also be regarded as sensitive indicators of diagenetic 342 alteration as both of the elements Fe and Mn replace Sr during diagenesis (Veizer, 1983; Derry et 343 al., 1992). The Mn/Sr ratio is typically >2 (average 5.1; only five samples have Mn/Sr <2) and 344 the Fe/Sr versus Mn/Sr ratios show positive covariance (Fig. 7c).

345

346 V/(V+Ni) ratios vary from 0.6 to 0.9 (average 0.7), whereas the (Cu+Mo)/Zn ratios 347 (Hallberg, 1976; 1982) vary from 5.9 to 0.4 (Table 3Sa). The enrichment factors of redox-348 sensitive trace elements such as Mo, V and Co ($EF_X = (X_T/Al_T)/(X_{SN}/Al_{SN})$) can be calculated to 349 estimate their relative enrichment or depletion (Tribovillard et al., 2006). VF dolomite is 350 significantly enriched in Mo, V and Co (enrichment factor > 1) relative to PAAS.

351

The $\Sigma REEs$ (Table 4S) in dolomite samples range from 0.49 to 11.06 ppm (average 2.4 ppm; standard deviation, SD = 2.5 ppm). Dolomites have mostly homogeneous geochemical features (flat REE + Y patterns, Fig. 8; (La/Sm)_{SN} \approx 1, (Gd/Yb)_{SN} \approx 1, Fig. 9) with MREE 355 enrichment and a positive Eu anomaly (Eu/Eu* = 82.2 to 1.02, average Eu/Eu* = 8.25, SD = 356 15.6). The dolomite samples display a small negative Gd anomaly (0.8<Gd/Gd*<1.3, average 357 $Gd/Gd^* = 0.99$, SD = 0.09), a positive La anomaly (0.7<La/La*<2.08, average La/La* = 1.08, SD = 0.3) and a slightly positive Ce anomaly ($0.7 < Ce/Ce^* < 1.3$, average Ce/Ce* = 1.03, SD = 358 359 0.16). The Y/Ho ratios range between 0.94 and 1.46 (average 1.15, SD = 0.14) and the Pr/Yb 360 ratios range from 0.73 to 3.83 (average 1.32, SD = 0.59), respectively. Marine carbonate 361 sediments in general have a ΣREE range of 0.04 to 14 ppm (Turekian and Wedepohl, 1961). The 362 average ΣREE of typical marine carbonate is 28 ppm (Bellanca et al., 1997). The ΣREE of VF 363 dolomite samples, normalized to PAAS ranges from 11.06 to 0.49 ppm (average 2.4 ppm) and 364 does not show any positive correlation with the major elements (Fe, Mn, Al and Si).

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366

5.4. Oxygen and carbon isotopes

The whole–rock δ^{18} O and δ^{13} C values of VF dolomite range from -8.1 to -5.2 ‰ (average -6.8 ‰) and -0.35 to 2.0 ‰ (average 0.5 ‰), respectively (Table 5S), and they show an inverse correlation (Fig. 10). Most of the δ^{13} C values are near 0 ‰ (average 0.5 ‰), with six samples showing slightly depleted values (-0.35 ‰ < δ^{13} C < 0 ‰), and the majority with slightly elevated δ^{13} C, maximizing at 2‰.

372

373 **6. Discussion**

374

6.1. XRD mineralogy and petrography

375 The non-ferroan type dolomites (FeCO₃ < 2 mol%; Tucker and Wright, 1990) are nearly stoichiometric (mol% $CaCO_3 = 49$ to 51, mean 50, Lumsden, 1979) and they are relatively well 376 377 ordered (degree of order ranging from 0.4 to 1.0, mean 0.6, Hardy and Tucker, 1988). The near 378 stoichiometric and relatively well-ordered nature of the dolomite crystals could reflect slow 379 growth controlled by elevated temperature. This could be the result of dolomitization during 380 burial or burial recrystallization of earlier, near-surface-formed dolomite. Lithospheric stretching and crustal sagging associated with volcanic activity during the interval 1.8 - 2.0 Ga in the CB 381 382 (Anand et al., 2003; Ravikant et al., 2014) could have provided a higher than normal geothermal 383 gradient during burial.

384

385 Petrographic analysis of VF dolomite shows patches of remnant calcimicrite (Fig. 6a) and 386 calcite spar still preserving their primary fabrics like calcite twin-lamellae (Fig. 6b). The 387 presence of twin-lamellae in the precursor calcite suggests a minimum temperature of 170°C is 388 required for diagenetic deformation (Ferrill et al., 2004). Since the calcite ooids with original 389 internal fabrics and textures are primary, and there is no evidence of calcitised aragonite (cf. 390 Tucker, 1985), it is likely that the original lime mud (now calcimicrite) would have been calcitic 391 and this was probably the precursor sediment of VF dolomite. Planar-s dolomite crystals (mostly 392 5-15 µm) show cloudy centres (due to the presence of minute inclusions) and clear rims; this 393 could suggest either replacement of original limestone or recrystallization of an earlier 394 dolomicrite at depth. Petrographic study has shown that VF dolomite is characterized by the 395 presence of micritic dolomite crystals that commonly exhibit crystal enlargement 396 (recrystallization). The widespread occurrence of dolomitic micritic facies in the VF suggests 397 that the dolomite crystals precipitated rapidly from a dolomite-supersaturated fluid with a high Mg/Ca ratio and low SO₄-2 concentration, as would be expected in the Proterozoic compared to 398 399 typical Phanerozoic environments (Tucker, 1982), because of rapid nucleation and 400 crystallization in а supratidal/upper tidal-flat environment. Rapid dolomite 401 precipitation/replacement might also have been facilitated by fine-grained precursor carbonate 402 sediment that had a high reactive surface area to volume ratio and high density of nucleation sites 403 (Sibley and Gregg, 1987). Microbial influences within the sediment inducing suitable conditions 404 for dolomite precipitation may well have been involved as well (e.g. Bontognali et al., 2010; 405 Petrash et al., 2017; Perri et al., 2018).

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407

6.2. Redox conditions

408 MREE enrichment (Haley et al., 2004) (Fig. 8), strong Europium anomalies (Bau, 1991) 409 (Fig. 8) and absence of negative Ce anomalies (Bau and Koschinsky, 2009) (Fig. 11) in VF 410 dolomite are compelling evidence suggesting its formation from anoxic marine-derived waters. 411 High Fe and Mn concentrations (>1000 ppm and >50 ppm, respectively) of dolomites indicate 412 that the fluids responsible for dolomite formation were iron-rich (Fe²⁺) and reducing in nature 413 (Budd, 1997). The Fe/Mn ratio of VF dolomite, correlated with the Fe/Al ratio, implies 414 insignificant sulphate reduction and pyrite precipitation during dolomite formation (Barnaby and 415 Read, 1992), and this is consistent with the petrographic observations, where little pyrite was

416 detected. The Fe/Al ratio (Anderson and Raiswell, 2004; Lyons and Severmann, 2006) of VF 417 dolomite also implies that the fluids responsible for dolomite formation were anoxic but not 418 euxinic. Had the palaeo-fluids been euxinic, Fe²⁺ and other metal ions would have preferred to 419 precipitate as sulphides (such as pyrite), and these were not observed. Hatch and Leventhal 420 (1992) suggested a V/(V+Ni) ratio greater than 0.84 for euxinic, 0.54–0.82 for anoxic, and 0.46– 421 0.60 for dysoxic conditions. The V/(V+Ni) values of VF dolomite vary from 0.6 to 0.88 (average 422 0.7) indicating chiefly anoxic waters of precipitation. The highest V/(V+Ni) ratio likely suggests 423 euxinic depositional conditions. Hallberg (1976, 1982) proposed that the (Cu+Mo)/Zn ratio can 424 also be used as a proxy to infer redox conditions. This ratio increases under reducing conditions 425 and decreases when the environment is oxidising. VF dolomite samples show that the 426 (Cu+Mo)/Zn ratio can be as high as 5.9 or as low as 0.37; this suggests dolomite formation 427 mostly under reducing conditions. The V/(V+Ni) and (Cu+Mo)/Zn ratios also indicate anoxic 428 depositional conditions. Molybdenum and vanadium are enriched in more reducing 429 environments (Crusius et al., 1996; Algeo and Maynard, 2004; Breit and Wanty, 1991; Wanty 430 and Goldhaber, 1992), whereas Co tends to be less soluble under reducing conditions (Algeo and 431 Maynard, 2004). The enrichment factors ($EF_X = (X_T/Al_T)/(X_{SN}/Al_{SN})$; Tribovillard et al., 2006) 432 of redox-sensitive trace elements (Mo, V and Co) show that dolomite samples are significantly 433 enriched in redox-sensitive trace elements relative to PAAS, suggesting reducing conditions 434 during dolomite precipitation.

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6.3. Post-depositional alteration

437 The flat REE patterns of VF dolomite could indicate very limited siliciclastic input to the 438 basin during carbonate deposition. The range of PAAS normalized ΣREE values (0.5 ppm-11.0 439 ppm) and average ΣREE value (2.4 ppm) of VF dolomite suggests that the precursor rock is 440 probably of marine origin (Turekian and Wedepohl, 1961; Bellanca et al., 1997) and the REE 441 contribution from non-carbonate fractions (Fe-Mn oxides and siliciclastic contamination) 442 appears to be minor (Fig. 12, Piper, 1974; Palmer, 1985). In addition, the Mn and Fe 443 concentrations are independent of the Mg/Ca ratio suggesting minimal post-depositional 444 alteration of VF dolomite (Nordeng and Sibley, 1994; Malone et al., 1996; Machel, 2004). 445 However, The Fe/Sr versus Mn/Sr plot (Fig. 7c) shows clustered data with moderate covariance, 446 suggesting that diagenesis could have altered the parent sediment geochemical signal. However,

447 elevated Mn/Sr ratios of VF dolomite (average 4.9) could be interpreted as a signature of 448 diagenetic alteration (following, for example, Derry et al., 1992, 1994; Kaufman and Knoll, 449 1995; Montañez et al., 1996), although on the other hand, this may not necessarily always be the 450 case (for an alternative view see Knoll et al., 1995; Lindsay and Brasier, 2000); it could be 451 related to the fluid chemistry (Yoshioka et al., 2003; Shen et al., 2005; Font et al., 2006; Hurtgen 452 et al., 2006; Nédélec et al., 2007). Also, Archean and Palaeoproterozoic dolomites on average 453 contain more Fe and Mn than younger carbonate rocks (Veizer et al., 1990), thus complicating 454 the application of the Mn/Sr ratio as an index of alteration. The low Y/Ho ratio (0.94-1.46; mean 455 1.15, SD = 0.14) and the Y/Ho and Ce/Ce* cross-plot (Fig. 13) probably indicate a variable 456 degree of contamination of the precursor carbonate by clay material, reflecting the depositional 457 setting in a shoreline or lagoonal environment (Kamber and Webb, 2001).

458

459 **6.4.** *Fluid source*

460 The PAAS-normalized REE profiles for VF dolomite show no LREE depletion, show MREE enrichment (cf. Haley et al., 2004) and have positive Eu and Y/Ho anomalies with a 461 462 weakly positive Ce anomaly. These observed REE characteristics are consistent with the 463 chemistry of anoxic marine basins (Bau and Möller, 1993), ferruginous lakes, marine 464 hydrothermal plumes and anoxic diagenetic waters (Johannesson and Zhou 1999; Sherrell et al., 465 1999; Haley et al., 2004; Wang et al., 2018). The weakly positive Gd anomaly present in VF 466 dolomite may reflect seawater precipitation (Bau, 1999). Eu is also normally enriched in 467 Archean seawater-precipitated carbonate too (Bolhar and Karnendonk, 2007), the source of 468 which can be either hydrothermal solutions derived from mid-ocean ridges and/or back-arc 469 spreading centres, or burial diagenetic fluids (Michard et al., 1983; Michard, 1989; Derry and 470 Jacobsen, 1990; German et al., 1990; Murray et al., 1991; Danielson et al., 1992; German et al., 471 1993; German et al., 1999; Douville et al., 1999; Kamber and Webb, 2001; Eroglu et al., 2017; 472 Schier et al., 2018). In VF dolomite significant positive correlation is observed between Eu/Eu* 473 and Ba content (Fig. 14) and this clearly indicates the influence of hydrothermal activity on the 474 studied carbonates (Khelen et al., 2017). Extensive volcanic activity in the CB around 1.9 to 2.0 475 Ga in a continental rift setting (Anand et al., 2003; Ravikant et al., 2014) could be the source for 476 Eu. However, diagenetic alteration of the precursor carbonate sediments is suggested by the

477 Fe/Sr versus Mn/Sr plot (Fig. 8c), low Y/Ho ratio (0.94-1.46; mean 1.15, SD = 0.14) and the 478 Y/Ho and Ce/Ce* plot (Fig. 13), and this could also have enhanced the Eu anomaly.

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480 Sodium content of dolomites can be used as an indicator of salinity of the fluid from 481 which the dolomites precipitated (Land and Hoops, 1973; Sass and Katz, 1982; Sass and Bein, 482 1988; Budd, 1997). The low Na concentrations (60-735 ppm, average 290 ppm) of VF dolomite 483 along with the poor correlation of Sr/Ca vs. Na₂O (Fig. 8b) rules out their hypersaline fluid 484 origin and probably suggests a diagenetic fluid source. Depletion in Na, however, can also be a 485 consequence of burial (Sachan, 1993), as successive episodes of dolomitization of limestone and 486 dolomite recrystallisation would reduce the levels of Na (Warren, 2000). Similarly, low 487 strontium concentrations (40-420 ppm, average 85 ppm; average Sr value of lithospheric 488 carbonate rocks is 610 ppm; Turekian and Wedepohl, 1961) of VF dolomite probably reflect a 489 Sr-depleted water-buffered diagenetic system (Budd, 1997; Warren, 2000; Azmy et al., 2001), 490 supporting a burial diagenetic effect (Sachan, 1993; Warren, 2000). Tucker (1983), from studies 491 of the Precambrian Beck Spring Dolomite, suggested that low concentrations of Na and Sr in 492 ancient dolomites excludes precipitation from marine fluids and warrants either fluid-mixing or 493 wet-recrystallization of an initially precipitated poorly-ordered calcian dolomite that drives out 494 Na and Sr.

495

The δ^{13} C values (- 0.4 ‰ to 2.0 ‰; average value 0.5 ‰) of dolomite samples probably reflect the carbon isotopic composition of the precursor carbonate precipitated from the Proterozoic seawater. Palaeoproterozoic carbonate successions are characterized by δ^{18} O values ranging from -6 to -12 ‰ (Tucker, 1982; Burdett et al., 1990; Veizer et al., 1992a; 1992b; Melezhik et al., 1997; Bekker et al., 2001; 2003a, b). The oxygen isotope range (-5.2 to -8.1 ‰) for VF dolomite is within this range and is consistent with precipitation (or recrystallization) during shallow to moderate burial (Sachan, 1993; Warren, 2000).

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504 **7. PROBABLE MECHANISM OF DOLOMITIZATION**

505 The field observations and petrographic features of the dolomites within the 506 Palaeoproterozoic VF can be interpreted in terms of early dolomitization of peritidal platform 507 carbonate sediment consisting of lime mud and calcimicrite. Preservation of microbial fabric 508 elements of the stromatolitic dolomite suggests that either VF dolomite associated with 509 microbial-laminites formed as primary precipitates due to microbial activity and minor 510 evaporation (Hird et al., 1987) or that they are very early, replacement mimetic dolomites. 511 During subsequent shallow sub-surface burial and diagenesis, fabric-destructive dolomitization 512 of the undolomitized oolitic grainstones and calcimicrite, along with recrystallization of the 513 early-formed peritidal dolomite happened as suggested by the petrographic textures. In terms of 514 seawater chemistry in the Palaeoproterozoic CB, it is likely that this was a time of calcite 515 precipitation (a "calcite sea"), with anoxic and ferruginous conditions, and an elevated Mg/Ca 516 ratio but not so high that very early fabric-retentive dolomitization of ooids and cements could 517 take place, like those of the Beck Spring Dolomite (Tucker, 1983). The lack of a very high 518 seawater Mg/Ca ratio could be related to the onset of rifting of supercontinent Columbia around 519 2.0 Ga that coincides with the VF carbonate sedimentation. Grotzinger (1989) proposed that 520 Precambrian seawater was oversaturated with respect to calcium carbonate that favoured abiotic 521 carbonate precipitation that gradually decreased the carbonate saturation through the Proterozoic 522 to Phanerozoic levels. This process, coupled with a fast rate of sea-floor spreading, would draw Mg²⁺ down producing a "calcite ocean" (Wilkinson and Algeo, 1989; Bots et al., 2011). This 523 524 ocean chemistry is in contrast to the anoxic, ferruginous and extremely high Mg/Ca conditions 525 that prevailed during Neoproterozoic time (Hood and Wallace, 2018). In addition, the coarse 526 replacement VF dolomite crystallized from a burial fluid that evolved from the europium-527 enriched anoxic seawater with a lower SO₄ content (Hood and Wallace, 2018), as marine water or its derivative is the only known infinite source of Mg²⁺ and Ca²⁺. The PAAS-normalized REE 528 529 profiles for VF dolomite are consistent with the chemistry of anoxic diagenetic waters. Low Na 530 and Sr concentrations of VF dolomite in and around Parnapalle also suggest their precipitation 531 (or early recrystallisation) during burial diagenesis (Veizer, 1983; Vahrenkamp and Stewart, 532 1990; Tucker and Wright, 1990; Banner, 1995; Budd, 1997; Warren, 2000; Azmy et al., 2001; 533 Balter et al., 2011; Sosdian et al., 2012); this is also supported by the stable isotope (δ^{18} O) values that fall within the range of the burial dolomite model (Warren, 2000; Machel, 2004). The δ^{13} C, 534 535 on the other hand, having 'marine' values, suggests that the original lime mud and/or micritic 536 calcite were derived from seawater (Tucker and Wright, 1990). The likely factor promoting 537 dolomite formation during early burial diagenesis could be the presence of an early, finely-538 crystalline, less well-ordered dolomite, as is being precipitated in modern tidal flats and

539 microbial mats in Abu Dhabi and Qatar (e.g., Bontognalli et al., 2010; Perri et al., 2018). These 540 early Ca-Mg precipitates could have provided the nuclei and substrates for continued dolomite 541 formation. The near-stoichiometric and relatively well-ordered VF dolomite crystals probably 542 would be the result of dolomite recrystallisation during burial, possibly promoted by an elevated 543 geothermal gradient from crustal thinning and mafic volcanic activity around 2.0 - 1.8 Ga 544 (Anand et al., 2003; Ravikant et al., 2014). Such tectonic-volcanic processes may have 545 diagenetically-modified the then seawater composition and be responsible for the positive Eu anomaly ($Eu/Eu^* = 89.33-1.03$) recorded in VF dolomite. 546

547

548 **8.** CONCLUSIONS

549 Combined field data and microscopic observations suggest that the Cuddapah Basin 550 carbonate rocks initially precipitated as fine lime mud and/or micritic calcite in tidal-flat and 551 associated shallow-marine environments. These sediments were replaced by dolomicrite during 552 early peritidal dolomitization. Petrographic observations also reveal fabric-retentive dolomite 553 textures, including filaments, in stromatolites, possibly reflecting microbial dolomite 554 precipitation-dolomitisation. During shallow sub-surface burial, fabric destructive dolomitization 555 of undolomitized oolitic grainstone and calcimicrite took place, along with recrystallization of 556 the early-formed peritidal dolomite. The δ^{18} O and δ^{13} C values of VF dolomite samples suggest 557 that these dolomites were either precipitated or recrystallised from burial diagenetic fluids that 558 evolved from Eu-enriched seawater. Burial diagenetic precipitation and recrystallisation of 559 dolomite are also supported by depleted Na and Sr contents. Ratios and contents of redox-560 sensitive metals (Cu, Co, Fe, Mn, Mo, Ni, V, Zn), REE distribution and high Fe_T/Al ratios imply 561 that dolomitizing fluids were anoxic and ferruginous but not euxinic. The positive Eu anomaly 562 could reflect a hydrothermal source and this may have been related to fluids connected to 563 continental rifting and volcanic activity within the CB around 1.9 - 2.0 Ga. The pattern of 564 diagenesis and dolomitisation recorded in the VF is more typical of Phanerozoic platform 565 carbonates than many Precambrian dolomites which show perfect preservation of original 566 textures (such as ooids and fibrous cements) and continued precipitation of dolomite in the burial 567 environment as a dolospar cement.

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- 569

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- 579
- 580

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HIGHLIGHTS

Field study shows that the exposed ~900 m outcrop of Vempalle Formation (VF) of the Cuddapah Basin (CB), India along the south-western margin of the basin is represented by a thick succession of stromatolitic dolomite, dolomitic limestone and limestone (~70%), with minor calcimicrite (~20%), and ~10% siliciclastic sandstone and mudstone. Facies analysis reveals that the succession can be sub-divided into 14 distinct lithofacies which can be grouped into five distinct facies associations, stacked in different orders as part of a major ramp-type carbonate platform.

Petrographic study shows preservation of 10 to 15 % of precursor limestone in the form of remnant patches of calcimicrite and ooids with calcite spar cement. Petrographic analysis suggests that the ooids, preserving primary radial and concentric fabrics and radial fractures, are considered to have been originally precipitated as calcite, which may have been low-Mg. In places the preserved calcite spar, that is partially replaced by fabric destructive dolomite, shows Type I calcite twin lamellae. Petrographic observations suggest that Vempalle Formation dolomite probably formed through very early precipitation, which in stromatolites preserved microbial filaments, as well as through fabric-destructive dolomitization during shallow to moderate burial. Vempalle Formation dolomite is characterized by micritic dolomite crystals that suggest rapid early dolomitization of lime mud and micritic calcite from a supersaturated Mg-Ca-rich solution, probably near-surface or during shallow burial.

Geochemical data suggest that depletion of Na and Sr contents along with negative δ^{18} O values indicate dolomite recrystallisation during burial and further replacement. Dolomite δ^{13} C values of -0.5 to 2 ‰ are likely inherited original marine values. Geochemical proxies (trace elements and rare earths) imply that Cuddapah Basin seawater and dolomitizing fluids were anoxic and ferruginous but not euxinic. Geochemical analyses also indicate that the burial diagenetic fluids evolved from Eu-enriched seawater that probably resulted from continental rifting around 1.9 - 2.0 Ga.

In terms of seawater chemistry in the Palaeoproterozoic CB, it is likely that this was a time of calcite precipitation (a "calcite sea"), with anoxic and ferruginous conditions, and an elevated Mg/Ca ratio but not so high that very early fabric-retentive dolomitization of ooids and cements could take place, like those of the Beck Spring Dolomite. The lack of a very high seawater Mg/Ca ratio could be related to the onset of rifting of supercontinent Columbia around 2.0 Ga that coincides with the VF carbonate sedimentation. This tectonic process with a fast rate of sea-floor spreading would draw Mg²⁺ down producing a "calcite ocean". This ocean chemistry is in contrast to the anoxic, ferruginous and extremely high Mg/Ca conditions that prevailed during Neoproterozoic time.

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A Palaeoproterozoic dolomite (Vempalle Formation, Cuddapah Basin, India) showing Phanerozoic-type dolomitisation

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14 Abstract: The Palaeoproterozoic Vempalle Formation of the Cuddapah Basin, India, significantly adds to 15 our understanding of the evolution of Precambrian marine carbonate systems and the redox state of the 16 Earth's early oceans. A facies-microfacies-diagenetic-geochemical examination of samples from a 900-m 17 long exposure in a freshly-cut canal section shows that 10 to 15 % of precursor limestone is still preserved 18 in the Vempalle Formation in the form of remnant patches of calcimicrite and ooids with calcite spar 19 cement. The ooids, preserving primary radial and concentric fabrics and radial fractures, are considered to 20 have been originally precipitated as calcite, which may have been low-Mg. In places the preserved calcite 21 spar, that is partially replaced by fabric-destructive dolomite, shows Type I calcite twin lamellae. 22 Petrographic observations demonstrate that Vempalle Formation dolomite formed through very early precipitation, which in stromatolites preserved microbial filaments, as well as through fabric-destructive 23 24 dolomitization during shallow to moderate burial. Vempalle Formation dolomite is characterized by 25 micritic dolomite crystals which suggest rapid early dolomitization of lime mud and micritic calcite from 26 a supersaturated Mg-Ca-rich solution, probably near-surface or during shallow burial. Depletion of Na 27 and Sr contents of Vempalle Formation dolomite along with negative δ^{18} O values indicate dolomite 28 recrystallisation during burial and further replacement. Dolomite δ^{13} C values of -0.5 to 2 ‰ are likely 29 inherited original marine values. Geochemical proxies (trace elements and rare earths) imply that 30 Cuddapah Basin seawater and dolomitizing fluids were anoxic and ferruginous but not euxinic. 31 Geochemical analyses also indicate that the burial diagenetic fluids evolved from Eu-enriched seawater 32 that probably resulted from continental rifting around 1.9 - 2.0 Ga. This probable ocean chemistry is in 33 contrast with the anoxic, ferruginous and extremely high Mg/Ca "dolomite oceans" that prevailed during 34 Proterozoic time. The Vempalle dolomite shows more similarities with dolomitised Phanerozoic platform 35 carbonates than typical Precambrian dolomite with its well-preserved textures and burial dolospar 36 cements.

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- 39 Keywords: Dolomitization, Proterozoic carbonate rocks, redox, fluid chemistry
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45 **1. INTRODUCTION**

46 Carbonate ramps and rimmed platforms are a distinctive feature of Neoarchean to 47 Neoproterozoic deposition and in many cases the dolomite content of these ancient carbonate 48 platforms is high in comparison with those of the Mesozoic and Cenozoic (Saylor et al., 1995; 49 Holland and Zimmermann, 2000; Pope and Grotzinger, 2003). The processes of formation of 50 these ancient dolomites are still the subject of much debate. The Precambrian sedimentary record 51 to about 3.5 Ga includes dolomites and limestones that likely precipitated as primary aragonite 52 and calcite (Grotzinger and Read, 1983; Grotzinger, 1989; Grotzinger and Kasting, 1993). 53 Palaeoproterozoic carbonate sedimentation was marked by less spectacular occurrences of 54 massively-precipitated aragonite and calcite (Grotzinger and Kasting, 1993). Precambrian 55 dolomites may have also formed by precipitation directly from seawater or by dolomitization 56 during very early diagenesis from fluids comparable with seawater (e.g., Veizer and Hoefs, 57 1976; Tucker, 1982, 1983; Hood and Wallace, 2018). Precambrian dolomites are generally 58 characterised by very well-preserved fabrics of the original carbonate grains and early cements, 59 leading to arguments over primary versus replacement dolomite (Tucker 1982, Hood and 60 Wallace 2018). In addition, many Precambrian dolomites have drusy dolospar cements, 61 precipitated during shallow to moderate burial (e.g. Tucker, 1983; Tewari and Tucker, 2011), a 62 feature rarely seen in Phanerozoic dolomites. In India, several Precambrian sedimentary basins 63 are reported to host dolomite successions several kilometres thick. The Palaeoproterozoic 64 Vempalle Formation (VF), located in the crescent-shaped intracratonic Cuddapah Basin (CB), 65 Eastern Dharwar craton, and a part of the Papaghni Group (Fig. 1), is characterized by the 66 presence of a ~1.9 km-thick stromatolitic dolomite. The VF carbonate platform can be traced for more than 1000 km without any significant physical break from the SE to the NW part of the 67 68 basin.

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Zachariah et al. (1999) obtained a Pb-Pb age of 1756 ± 29 Ma for the VF dolomite. Taking into consideration the age of intruded sills (1817 ± 24 Ma; Bhaskar Rao et al., 1995) within VF carbonate rocks/Pulivendla quartzites and the age of VF dolomite (1756 ± 29 Ma), Zachariah et al. (1999) proposed 1756 ± 29 Ma as the time of dolomitization of the precursor VF limestone. Rai et al. (2015), based on a Pb–Pb (PbSL) age of VF dolomite and of the intruded sills of 1885 Ma (U-Pb and Ar-Ar methods; French et al., 2008; Anand et al., 2003), proposed that 76 dolomitization of VF limestone might have taken place within 100 My duration of time (from 77 1900-2000 Ma). This time duration of sedimentation and dolomitization is also reported from the 78 Wittenoom Formation and Carawine Dolomite of the Hamersley Group, Western Australia, 79 where the time between deposition, diagenesis and dolomitization is thought to be within 100-80 150 My (Jahn and Cuvellier, 1994; Jahn and Simson, 1995). On the other hand, Chakrabarti et al. (2011, 2014), using isotopic (δ^{13} C and δ^{18} O) and elemental (Mg, Ca, Fe, Mn, Sr and SO₄⁻²) data, 81 82 concluded that VF dolomite is primary in nature and precipitated either from ¹⁸O depleted marine 83 water or from a geochemically distinct mixed fluid source. Based on collective geochemical 84 signatures, δ^{13} C and δ^{18} O isotopic values, flat REE patterns along with Ce, Eu and Gd anomalies, and chondritic to superchondritic Y/Ho ratios, Khelen et al. (2017) have recently 85 86 proposed that VF dolomite was precipitated from marine water having a hydrothermal signature. 87 These discrepancies in the plumbing mechanism(s) of VF dolomite warrant the need to revisit 88 the question about the origin of VF dolomite and related dolomite-precipitating fluids.

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90 In this project we have used field and petrographic observations and various geochemical 91 proxies to understand the mechanism(s) of formation of the shallow-marine VF dolomite and to 92 assess the redox heterogeneity existing during its time of formation. Geochemical data, 93 integrated with petrology and tectonic history of the CB, help not only to infer the source of Mg-94 rich fluids but also to contribute to a better understanding of the redox conditions of this 95 Proterozoic shallow-water carbonate. In addition, as will be shown, this Palaeoproterozoic 96 dolomite has more features in common with dolomitised Phanerozoic platform carbonates, than 97 the typical Precambrian dolomite with well-preserved fabrics, likely a reflection of seawater 98 chemistry, redox and microbes.

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100 2. GEOLOGICAL BACKGROUND

101 The Papaghni Group (~2110 m thick) represents the first sedimentary cycle of the 102 Cuddapah Supergroup (Patranabis-Deb et al., 2012) in the CB. The succession unconformably 103 overlies the basement granite, gneiss and greenstone complex of the Eastern Dharwar craton, 104 which in turn is unconformably overlain by the Chitravati Group (4975 m). The VF (~1900 m) 105 of the Papaghni Group constitutes the lowermost carbonate-dominated unit of the Cuddapah 106 Supergroup and overlies a basal siliciclastic unit, the Gulcheru Quartzite (~210 m), with a

107 transitional contact (Nagaraja Rao et al., 1987). The Gulcheru Quartzite constitutes a basal 108 conglomerate and immature sandstone unit, deposited in a fan-delta to prodelta setting, which 109 transitionally passes up into a mature quartz arenite unit, deposited in a shallow-shelf 110 environment (Majumder et al., 2015). The VF is represented mostly by thick stromatolitic 111 dolomite and minor limestone (10 to 15%). Near the transition zone to the Gulcheru Quartzite, 112 thin beds of splintery red mudstone alternate with siliciclastic and carbonate beds to form a 113 mixed siliciclastic-carbonate unit (Fig. 2). Tidal and storm currents played a major role in 114 sculpturing the sandstone bodies at this transition.

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116 Tepee structures, desiccation cracks filled with lime mud and sand and halite casts, are 117 common in the lower VF (Fig. 2). The upper part is dominated by bedded dolomite deposited in 118 a range of environments, starting from shallow shelf with intermittent exposure to fairly deep-119 water conditions below normal wave base. Stromatolite morphologies reflect environments 120 varying from intertidal to subtidal and facies cycles are the result of multiple rhythms of sea-121 level change (Patranabis-Deb et al., 2018). Demise of the carbonate platform is marked by the 122 deposition of thick brown shale with laterally persistent beds of chert. The common occurrence 123 of sills up to a metre or more thick and thinner dykes of basalt and/or dolerite in the upper part of 124 the VF succession indicates tectonic-magmatic activity (Anand et al., 2003). Conglomerate and 125 pebbly sandstone of the basal Chitravati Group, upon a sharp unconformity, mark the beginning 126 of the second sedimentary cycle. Clasts of chert with stromatolite, oolite, vein quartz, jasper and 127 volcanics, derived from the Papaghni Group, reflect subaerial exposure and erosion during the 128 formation of the unconformity between the two groups.

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130 Rifting of the Eastern Dharwar craton and passive-margin sedimentation deposited the 131 Gulcheru fan-delta succession (Majumder et al., 2015) followed by deposition of the extensive 132 VF carbonate platform (Tripathy and Saha, 2008; Patranabis-Deb et al., 2018). Rai et al. (2015) 133 inferred a minimum age of 2000 Ma for the onset of sedimentation in the Cuddapah Supergroup 134 and this coincides with the onset of rifting of the supercontinent Columbia, as evidenced by 135 widespread emplacement of mafic dykes in and around the CB during this period. The 136 intermittent occurrence of mafic flows, ash-fall tuffs and associated shallow-crustal intrusives in 137 the upper part of the VF (~1.88 Ga; Ravikant, 2010) is related to the second cycle of rifting that possibly represents the initial phase of fragmentation and separation of the south Indian craton from the North China craton (Ravikant, 2010). With continued passive subsidence, the CB evolved into a large epicontinental sea with a near-complete cessation of coarse clastic influx and deposition of the extensive shale–carbonate succession of the Chitravati Group. Tectonically, the CB is punctuated by multiple unconformities, major tectonic contacts, faults and various basic sills (Saha and Tripathy, 2012; Saha and Mazumder, 2012; Patranabis-Deb et al., 2012; Collins et al., 2015), which affected and shaped its sedimentary succession.

- 145
- **3. Methods**
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3.1. Sample collection for petrological analysis

149 Samples were collected at 5-15 m intervals up-section (Table 1) along a freshly cut canal 150 section, nearly 4 km long (hereafter referred as the 'canal section') that exposed the dolomite 151 beds of the VF (~1000 m thick dolomite unit, Fig. 2) near Parnapalle village (N14°32'58.3", 152 E77°58'09.9") in the Cuddapah district, Ravalaseema. Samples collected from the dolomite beds 153 covered eight facies namely F1, F2, F4, F5, F7, F8, F9 and F10 (Table 1; Fig. 2). F3 and F11 are 154 intentionally avoided as they are mostly composed of shale, siltstone and dolomite (Table 2). 155 Thin-sections were made from twenty-nine selected dolomite samples for petrographic analysis. 156 Carbonate components (calcite, dolomite) were determined by staining the thin-sections with 157 Alizarin Red S.

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- 159 **3.2.** *X*-*Ray diffraction*

Twenty-nine selected dolomite samples were powdered for X-ray diffraction analysis on
a Panalytical X'Pert Pro diffractometer, equipped with a Cu Ka X-ray source and an X'Celerator
detector, operating at the following conditions: 40 kV and 40 mA; range 5 – 80 deg 20; step size
0.017 deg 20; time per step 50.2 sec; fixed divergence slit, angle 0.5°; sample rotation 1 rev sec⁻¹.
The quantities of the mineral phases were determined using the Rietveld method.

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3.3. *Major and trace elements*

167 Forty-two selected dolomite samples were powdered for bulk major, trace and REE 168 analyses, undertaken at the Wadia Institute of Himalayan Geology. The elemental analysis was 169 performed using an ICP-MS PerkinElmer SCIEX ELAN DRC-e. Concentrations of REE + Y (n 170 = 42) were normalized to the Post-Archaean Australian Shale (PAAS) representing an estimate 171 for the composition of average terrigenous input to the oceanic environment. Specifically, REE 172 fractionation was calculated as Pr_{SN} / Yb_{SN} (SN, shale normalized) to avoid problems in case of 173 anomalous La and Ce concentrations. To avoid any anomalous behaviour of La, Ce, Eu and Gd, 174 the anomalies were calculated using the geometric equations of Lawrence and Kamber (2006) 175 and are given as Ce/Ce^{*}, Eu/Eu^{*}, Gd/Gd^{*} and La/La^{*}.

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3.4. Scanning electron microscopy with energy-dispersive spectroscopy

Thin-sections were examined under a scanning electron microscope (SEM) FE-SIGMA VP (Carl Zeiss Microscopy GmbH) with energy-dispersive (EDS) detector (Quantax XFlash 3|10, Bruker Nano GmbH). Thin-sections were placed on the mount with carbon conductive tape. Then, samples were coated with a 20 nm layer of carbon by vacuum coater (Quorum 150T ES). Furthermore, carbon tape bridges were made for each sample to avoid excessive accumulation of charge. Analyses were done with 120 µm aperture and 15 keV accelerationvoltage. Beam intensity was 2.5 nA and working distance was 7.5 mm.

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3.5. Oxygen and carbon stable isotope analysis

187 Thirty-five selected dolomite samples were analysed for bulk carbon and oxygen stable 188 isotopes at the Activation Laboratories Ltd., Canada. Samples were run on a DELTAPlus XL 189 stable isotope ratio mass spectrometer (IRMS) coupled with ConFlo III Interface and EA1110 190 elemental analyser. Standards NBS-19 ($\delta^{13}C = 1.95 \%$ and $\delta^{18}O = -2.20 \%$) and NBS-18 ($\delta^{13}C =$ 191 -5.05 ‰ and $\delta^{18}O = -23.1 \%$) were used for comparison. The results are expressed relative to the 192 Vienna Peedee Belemnite (VPDB).

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194 **4. Sedimentation Pattern and Depositional Environment**

The VF is well exposed along the south-western margin of the CB outcrop (Fig. 1a, b and c), represented by a ~1000-m thick succession of stromatolitic dolomite, dolomitic limestone and limestone (~70%), with minor calcimicrite (~20%), and ~10% siliciclastic sandstone and mudstone. Facies analysis reveals that the succession can be sub-divided into 11 distinct lithofacies (Table 1) which may be grouped into inner, mid and outer – ramp associations, 200 stacked in different orders as part of a major ramp-type carbonate platform (Fig. 3). The platform 201 maintained a shallow depth throughout its life, thus indicating a keep-up mode of deposition, that 202 is where the carbonate succession built up to sea level and kept pace with subsequent sea-level 203 changes, such that a balance was maintained with the generation of accommodation space. 204 Occasional storms and regular tides were important, distributing clastic sediments at particular 205 times, which hampered the growth of the platform in time and space. The depth-controlled 206 growth patterns of the stromatolites give clues to their depositional environment (Patranabis-Deb 207 et al., 2018), which in the canal section reflects a gradient from shallow-water with exposure to 208 shallow to moderate depths.

209

210 The VF succession in the canal section (Fig. 2) starts with a basal mixed unit, 211 representing the transition between the basal siliciclastic unit of the Gulcheru Formation and 212 carbonate rocks of the VF. It comprises mixed siliciclastic-dolomite (F1), bedded dolomite with 213 crinkled laminites (F2) and intraformational conglomerate (F9). The mixed siliciclastic-dolomite 214 beds are characterized by flaser bedding and lenticular bedding with preservation of desiccation 215 cracks filled with lime mud and sand and halite casts within shale intervals, tepee structures and 216 fluid-escape structures. The presence of these sedimentary features, suggests intermittent 217 exposure in a supratidal to upper intertidal flat, in an inner ramp setting. Palaeocurrent directions 218 measured from trough cross-stratification from the sandy units indicate east-north-easterly flow.

219

220 The mixed siliciclastic unit passes upward to a thick succession of bedded dolomite with 221 crinkled laminites (F2), black dolomite with or without stromatolite (F4), dolomite-micrite 222 rhythmite (F5) and brown shale (F3), without any break. Steel grey to black coloured massive to 223 stromatolitic dolomite beds (F4) with isolated to laterally-linked mutually-aligned stromatolites 224 are observed, alternating with dolomite-micrite rhythmite (F5). Isolated occurrences of 225 stromatolite with low synoptic relief and parallel lamination in black dolomite (F4) indicate a 226 quiescent water environment. The close association of F4 and F5 also suggests their deposition 227 in a low-energy protected environment. Thick occurrences of F2 alternating with F5, with 228 signatures of intermittent exposure at different stratigraphic levels, suggest that they have 229 possibly formed a barrier, which imposed a rimmed-shelf profile to the platform, creating 230 lagoons on the shoreward side with an open shelf to seaward.

231 The mid-ramp association consists of oolite (F6), with intercalations of dolomite mud 232 rhythmite (F5), columnar stromatolite (F7), conical stromatolite (F8) and thickly – bedded 233 dolomite (F10). The association starts with the occurrence of oolite (F6), as shoaling-up bars. 234 The oolites comprise well-rounded, well-sorted medium- to coarse-grained ooids, usually 235 preserving a concentric fabric with a clastic grain as the nucleus. Medium-to-fine-grained ooids 236 with a radial fabric (with or without a clastic grain in the centre) and superficial ooids are also 237 observed. Oolite beds are generally trough cross-stratified, showing NE and SW palaeocurrent 238 directions with bidirectional pattern. The abundance of siliciclastic grains as nuclei to ooids 239 indicates a ready source of clastics on the landward side. The oolite bank may have further acted 240 as a barrier with the seaward side being cut off from the coastal sediments so that ooids formed 241 without sand nuclei and a radial fabric. F6 is interbedded with small columnar stromatolites (4-242 14 cm in height). F7 suggests spatial and temporal variations in the intensity and fluctuations of 243 wave action (Swett and Knoll, 1989; Holland and Patzkowsky, 1998) in a lower intertidal to 244 upper subtidal environment. The rhythmite facies (F5) may have been deposited as interbars in a 245 relatively quiet-water protected area between two bars or in a relatively deeper-water 246 environment. Up-section the columns increase in number and size and coalesce to form a 247 continuous biostromal structure (F7), many metres thick, commonly intercalating with parallel-248 stratified dolomite (F10).

249

250 Planar-parallel to wavy-parallel stratified and trough cross-stratified dolomite beds of F10 251 strongly suggest that this facies was deposited by traction currents. Gutter casts (Fig. 3d) and 252 pillow and ball structures within the dolomite beds suggest storm waves on a shallow shelf. 253 Changes of stromatolite type from shallow intertidal columnar to columnar biostromes, and a 254 conical type, indicate deposition on a low-gradient ramp where the distribution of microbialite 255 facies is distinctly depth-partitioned (Patrabanis-Deb et al., 2018). The gradual change in the 256 shape, size and synoptic relief of stromatolites also suggests balanced sedimentation, deposition 257 and accommodation space generation.

258

The top part of the VF is mainly characterized by F10 and F11, interpreted to be deposited in an outer ramp environment, below fair-weather wave base. The association comprises a rhythmic occurrence of plane-parallel laminated dolomite (F10) with interbedded green shale/siltstone and dolomite (F11), commonly interrupted by igneous intrusions. This depozone predominantly involved deposition from background suspension rarely interrupted by strong storm surges. Isolated gutter casts within the dolomite beds are thought to have been produced by storm-generated return flows (Fairchild and Herrington, 1989; Myrow, 1992). Chert and steatite nodules of various shapes and sizes (Fig. 3f) are common with iso-volumetric metasomatic alteration of dolomite to talc observed in the upper part of the VF.

268

269 **5. RESULTS**

270 **5.1.** *Petrography*

271 Petrographic analysis of the VF dolomite led to the identification of four microfacies: i) 272 dolo-micrite with few quartz and feldspar grains, ii) stromatolitic dolomite bindstone, iii) oolitic 273 grainstone (limestone and dolomite), and iv) calcimicrite with local limestone clasts. Micritic 274 dolomite is plane-parallel laminated, where laminae are defined by alternating light (micrite) and 275 dark (clay-rich) layers (Fig. 4a). Dolomicrite is commonly mixed with fine sand or silt-sized 276 grains of well-rounded to sub-rounded quartz and feldspar (Fig. 4b). Dolomicrite shows grain 277 enlargement due to recrystallization (Fig. 4c). Stromatolitic dolomite preserves crinkly to smooth 278 lamination defined by alternating dolomicrite and microbial filaments (Fig. 4d). Preservation of 279 the primary microbial texture suggests that this VF dolomite is either a very early mimetic 280 replacement of CaCO₃, preserving the original microbial filaments, or it is a primary microbial 281 dolomite precipitating directly from ancient seawater (Tucker, 1983, Corsetti et al., 2006, van 282 Smeerdijk Hood and Wallace, 2012). Good preservation of microbial structures also indicates 283 little or no recrystallization during diagenesis. The stromatolitic dolomite is characterized by 284 polymodal planar-e and subhedral to anhedral planar-s or non-planar micritic dolomite crystals 285 (see dolomite classification by Sibley and Gregg, 1984, Gregg and Sibley, 1987), with sharp 286 intercrystalline boundaries (Fig. 4e, f). Moreover, the SEM-EDS analysis of thin-sections did not 287 show any relics of calcite crystals.

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The coarser carbonate facies include grainstone, mostly with spheroidal ooids, but also eye-shaped ooids. Stages of dolomitization are well-documented and recorded by the ooids (Fig. 5a-f). At one extreme, the ooids are composed entirely of calcite crystals having a radial fabric, such that a continuous sweep of the extinction is seen on stage rotation under crossed polars (Fig.

293 5a, b). Preserved calcite ooids show well-developed primary concentric, radial and radial-294 concentric fabrics; some have an outer silicified zone (cf. Tucker, 1984, 1985). Some of the 295 ooids are radially fractured as a result of compaction (Fig. 5a). These radial fractures crudely 296 coincide with the radial fabric which is probably a primary feature. Also the presence of primary 297 radial - concentric fabrics as observed within the unreplaced calcite ooids suggest its growth in a 298 mud-free environment whereas the radial fabric results from ooid growth in a relatively calm 299 environment with the presence of lime mud (Tucker, 1984). The good fabric preservation of the 300 ooids could suggest that they were originally composed of low-Mg calcite since this tends to 301 resist dolomitization; however, they could originally have been high-Mg calcite, with the Mg 302 leached out before dolomitisation (Tucker 1984, 1985). Some calcitic ooids have euhedral 303 rhombic dolomite crystals in the nucleus of the ooid (Fig. 5c). At the other extreme, the ooid 304 cortex is completely replaced by planar-e (euhedral) and subhedral to anhedral planar-s 305 (subhedral) or non-planar micritic dolomite crystals, with sharp but slightly ragged 306 intercrystalline boundaries, completely obliterating the internal fabric but still preserving the 307 shape of the ooids (Fig. 5f). In between there are ooids that show incomplete replacement 308 phenomena where the central part of the ooid is composed of coarse euhedral and mostly planar-309 e to planar-s dolomite crystals obliterating the internal fabrics, but the outer rim is composed of 310 calcite crystals still preserving the original radial-concentric fabrics (Fig. 5d). The primary radial 311 fabric of the ooid at the peripheral margin is commonly partially destroyed by replacement 312 micritic dolomite (Fig. 5e). Within massive dolomite there are still patches and lenses of 313 limestone that preserve the primary micritic calcite matrix and calcite spar (Fig. 6a); the latter 314 shows Type I calcite twin lamellae and it is partially replaced by dolomicrite destroying the 315 primary fabric (Fig. 6b). Thin-section evidence of fabric-destructive dolomite in VF carbonate 316 rocks indicates a replacement origin (Tucker et al., 2002), and the mimetic to obliterated mosaic 317 texture indicates progressive dolomite replacement (Braithwaite, 1991).

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319

5.2. X-ray diffraction

320 XRD analysis shows that dolomite is the dominant mineral in the samples analysed, with 321 subordinate quartz and minor K-feldspar (Table 1S, Supplementary section). Barring three 322 samples, calcite is absent in VF dolomite samples analysed. Trace amounts of talc, barite, mica, 323 chlorite and hematite were also detected. Calcium excess of VF dolomites is calculated using the formula: CaCO₃ mol% = $333.33*d_{104} - 911.99$ (Lumsden, 1979, where d_{104} is the peak position in angstrom units, Table 2S). VF dolomites have a nearly stoichiometric composition (mole % CaCO₃ = 49–51, mean 50) indicating an ideal composition of the dolomite (Mg:Ca = 1). Ordering of VF dolomite crystals ranges from 0.40 to 1.07 (average 0.56), according to the method described by Hardy and Tucker (1988). Only five samples had an ordering ratio <0.5 and >0.4.

- 330
- **5.3.** *Geochemistry*

332 Total iron content of VF dolomite varies from 19,235 ppm to 2170 ppm (average 5240 333 ppm); Mn ranges from 2040 ppm to 125 ppm (average 320 ppm), whereas Al varies from 19,955 334 ppm to 160 ppm (average 5475 ppm) (Table 3Sa,b). Average Fe/Mn and Fe/Al ratios are 19.6 335 and 3.4, respectively. Sodium and Sr concentrations range from 60 ppm to 735 ppm (average 290 336 ppm) and from 40 ppm to 420 ppm (average 85 ppm), respectively (Table 3Sa,b). Fe and Mn 337 concentrations show a positive correlation (Fig. 7a), whereas the Sr/Ca ratio versus Na₂O shows 338 a poor correlation (Fig. 7b). Mn and Fe concentrations versus the Mg/Ca ratio can be used to 339 explore modification of the carbonate chemistry during burial diagenesis (Gilleaudeau and Kah, 340 2013). Fe and Mn concentrations of VF dolomites are independent of the Mg/Ca ratio (Fig. 7d, 341 e). The Fe/Sr and Mn/Sr ratios can also be regarded as sensitive indicators of diagenetic 342 alteration as both of the elements Fe and Mn replace Sr during diagenesis (Veizer, 1983; Derry et 343 al., 1992). The Mn/Sr ratio is typically >2 (average 5.1; only five samples have Mn/Sr <2) and 344 the Fe/Sr versus Mn/Sr ratios show positive covariance (Fig. 7c).

345

346 V/(V+Ni) ratios vary from 0.6 to 0.9 (average 0.7), whereas the (Cu+Mo)/Zn ratios 347 (Hallberg, 1976; 1982) vary from 5.9 to 0.4 (Table 3Sa). The enrichment factors of redox-348 sensitive trace elements such as Mo, V and Co ($EF_X = (X_T/Al_T)/(X_{SN}/Al_{SN})$) can be calculated to 349 estimate their relative enrichment or depletion (Tribovillard et al., 2006). VF dolomite is 350 significantly enriched in Mo, V and Co (enrichment factor > 1) relative to PAAS.

351

The Σ REEs (Table 4S) in dolomite samples range from 0.49 to 11.06 ppm (average 2.4 ppm; standard deviation, SD = 2.5 ppm). Dolomites have mostly homogeneous geochemical features (flat REE + Y patterns, Fig. 8; (La/Sm)_{SN} \approx 1, (Gd/Yb)_{SN} \approx 1, Fig. 9) with MREE 355 enrichment and a positive Eu anomaly (Eu/Eu* = 82.2 to 1.02, average Eu/Eu* = 8.25, SD = 356 15.6). The dolomite samples display a small negative Gd anomaly (0.8<Gd/Gd*<1.3, average 357 $Gd/Gd^* = 0.99$, SD = 0.09), a positive La anomaly (0.7<La/La*<2.08, average La/La* = 1.08, SD = 0.3) and a slightly positive Ce anomaly ($0.7 < Ce/Ce^* < 1.3$, average Ce/Ce* = 1.03, SD = 358 359 0.16). The Y/Ho ratios range between 0.94 and 1.46 (average 1.15, SD = 0.14) and the Pr/Yb 360 ratios range from 0.73 to 3.83 (average 1.32, SD = 0.59), respectively. Marine carbonate 361 sediments in general have a ΣREE range of 0.04 to 14 ppm (Turekian and Wedepohl, 1961). The 362 average ΣREE of typical marine carbonate is 28 ppm (Bellanca et al., 1997). The ΣREE of VF 363 dolomite samples, normalized to PAAS ranges from 11.06 to 0.49 ppm (average 2.4 ppm) and 364 does not show any positive correlation with the major elements (Fe, Mn, Al and Si).

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366

5.4. Oxygen and carbon isotopes

The whole–rock δ^{18} O and δ^{13} C values of VF dolomite range from -8.1 to -5.2 ‰ (average -6.8 ‰) and -0.35 to 2.0 ‰ (average 0.5 ‰), respectively (Table 5S), and they show an inverse correlation (Fig. 10). Most of the δ^{13} C values are near 0 ‰ (average 0.5 ‰), with six samples showing slightly depleted values (-0.35 ‰ < δ^{13} C < 0 ‰), and the majority with slightly elevated δ^{13} C, maximizing at 2‰.

372

373 **6. Discussion**

374

6.1. XRD mineralogy and petrography

375 The non-ferroan type dolomites (FeCO₃ < 2 mol%; Tucker and Wright, 1990) are nearly stoichiometric (mol% $CaCO_3 = 49$ to 51, mean 50, Lumsden, 1979) and they are relatively well 376 377 ordered (degree of order ranging from 0.4 to 1.0, mean 0.6, Hardy and Tucker, 1988). The near 378 stoichiometric and relatively well-ordered nature of the dolomite crystals could reflect slow 379 growth controlled by elevated temperature. This could be the result of dolomitization during 380 burial or burial recrystallization of earlier, near-surface-formed dolomite. Lithospheric stretching 381 and crustal sagging associated with volcanic activity during the interval 1.8 - 2.0 Ga in the CB 382 (Anand et al., 2003; Ravikant et al., 2014) could have provided a higher than normal geothermal 383 gradient during burial.

384

385 Petrographic analysis of VF dolomite shows patches of remnant calcimicrite (Fig. 6a) and 386 calcite spar still preserving their primary fabrics like calcite twin-lamellae (Fig. 6b). The 387 presence of twin-lamellae in the precursor calcite suggests a minimum temperature of 170°C is 388 required for diagenetic deformation (Ferrill et al., 2004). Since the calcite ooids with original 389 internal fabrics and textures are primary, and there is no evidence of calcitised aragonite (cf. 390 Tucker, 1985), it is likely that the original lime mud (now calcimicrite) would have been calcitic 391 and this was probably the precursor sediment of VF dolomite. Planar-s dolomite crystals (mostly 392 5-15 µm) show cloudy centres (due to the presence of minute inclusions) and clear rims; this 393 could suggest either replacement of original limestone or recrystallization of an earlier 394 dolomicrite at depth. Petrographic study has shown that VF dolomite is characterized by the 395 presence of micritic dolomite crystals that commonly exhibit crystal enlargement 396 (recrystallization). The widespread occurrence of dolomitic micritic facies in the VF suggests 397 that the dolomite crystals precipitated rapidly from a dolomite-supersaturated fluid with a high 398 Mg/Ca ratio and low SO₄-2 concentration, as would be expected in the Proterozoic compared to 399 typical Phanerozoic environments (Tucker, 1982), because of rapid nucleation and 400 supratidal/upper tidal-flat crystallization in а environment. Rapid dolomite 401 precipitation/replacement might also have been facilitated by fine-grained precursor carbonate 402 sediment that had a high reactive surface area to volume ratio and high density of nucleation sites 403 (Sibley and Gregg, 1987). Microbial influences within the sediment inducing suitable conditions 404 for dolomite precipitation may well have been involved as well (e.g. Bontognali et al., 2010; 405 Petrash et al., 2017; Perri et al., 2018).

406

407

6.2. Redox conditions

408 MREE enrichment (Haley et al., 2004) (Fig. 8), strong Europium anomalies (Bau, 1991) 409 (Fig. 8) and absence of negative Ce anomalies (Bau and Koschinsky, 2009) (Fig. 11) in VF 410 dolomite are compelling evidence suggesting its formation from anoxic marine-derived waters. 411 High Fe and Mn concentrations (>1000 ppm and >50 ppm, respectively) of dolomites indicate 412 that the fluids responsible for dolomite formation were iron-rich (Fe²⁺) and reducing in nature 413 (Budd, 1997). The Fe/Mn ratio of VF dolomite, correlated with the Fe/Al ratio, implies 414 insignificant sulphate reduction and pyrite precipitation during dolomite formation (Barnaby and 415 Read, 1992), and this is consistent with the petrographic observations, where little pyrite was

416 detected. The Fe/Al ratio (Anderson and Raiswell, 2004; Lyons and Severmann, 2006) of VF 417 dolomite also implies that the fluids responsible for dolomite formation were anoxic but not 418 euxinic. Had the palaeo-fluids been euxinic, Fe²⁺ and other metal ions would have preferred to 419 precipitate as sulphides (such as pyrite), and these were not observed. Hatch and Leventhal 420 (1992) suggested a V/(V+Ni) ratio greater than 0.84 for euxinic, 0.54–0.82 for anoxic, and 0.46– 421 0.60 for dysoxic conditions. The V/(V+Ni) values of VF dolomite vary from 0.6 to 0.88 (average 422 0.7) indicating chiefly anoxic waters of precipitation. The highest V/(V+Ni) ratio likely suggests 423 euxinic depositional conditions. Hallberg (1976, 1982) proposed that the (Cu+Mo)/Zn ratio can 424 also be used as a proxy to infer redox conditions. This ratio increases under reducing conditions 425 and decreases when the environment is oxidising. VF dolomite samples show that the 426 (Cu+Mo)/Zn ratio can be as high as 5.9 or as low as 0.37; this suggests dolomite formation 427 mostly under reducing conditions. The V/(V+Ni) and (Cu+Mo)/Zn ratios also indicate anoxic 428 depositional conditions. Molybdenum and vanadium are enriched in more reducing 429 environments (Crusius et al., 1996; Algeo and Maynard, 2004; Breit and Wanty, 1991; Wanty 430 and Goldhaber, 1992), whereas Co tends to be less soluble under reducing conditions (Algeo and 431 Maynard, 2004). The enrichment factors ($EF_X = (X_T/Al_T)/(X_{SN}/Al_{SN})$; Tribovillard et al., 2006) 432 of redox-sensitive trace elements (Mo, V and Co) show that dolomite samples are significantly 433 enriched in redox-sensitive trace elements relative to PAAS, suggesting reducing conditions 434 during dolomite precipitation.

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6.3. Post-depositional alteration

437 The flat REE patterns of VF dolomite could indicate very limited siliciclastic input to the 438 basin during carbonate deposition. The range of PAAS normalized ΣREE values (0.5 ppm-11.0 439 ppm) and average ΣREE value (2.4 ppm) of VF dolomite suggests that the precursor rock is 440 probably of marine origin (Turekian and Wedepohl, 1961; Bellanca et al., 1997) and the REE 441 contribution from non-carbonate fractions (Fe-Mn oxides and siliciclastic contamination) 442 appears to be minor (Fig. 12, Piper, 1974; Palmer, 1985). In addition, the Mn and Fe 443 concentrations are independent of the Mg/Ca ratio suggesting minimal post-depositional 444 alteration of VF dolomite (Nordeng and Sibley, 1994; Malone et al., 1996; Machel, 2004). 445 However, The Fe/Sr versus Mn/Sr plot (Fig. 7c) shows clustered data with moderate covariance, 446 suggesting that diagenesis could have altered the parent sediment geochemical signal. However,

447 elevated Mn/Sr ratios of VF dolomite (average 4.9) could be interpreted as a signature of 448 diagenetic alteration (following, for example, Derry et al., 1992, 1994; Kaufman and Knoll, 449 1995; Montañez et al., 1996), although on the other hand, this may not necessarily always be the 450 case (for an alternative view see Knoll et al., 1995; Lindsay and Brasier, 2000); it could be 451 related to the fluid chemistry (Yoshioka et al., 2003; Shen et al., 2005; Font et al., 2006; Hurtgen 452 et al., 2006; Nédélec et al., 2007). Also, Archean and Palaeoproterozoic dolomites on average 453 contain more Fe and Mn than younger carbonate rocks (Veizer et al., 1990), thus complicating 454 the application of the Mn/Sr ratio as an index of alteration. The low Y/Ho ratio (0.94-1.46; mean 455 1.15, SD = 0.14) and the Y/Ho and Ce/Ce* cross-plot (Fig. 13) probably indicate a variable 456 degree of contamination of the precursor carbonate by clay material, reflecting the depositional 457 setting in a shoreline or lagoonal environment (Kamber and Webb, 2001).

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6.4. Fluid source

460 The PAAS-normalized REE profiles for VF dolomite show no LREE depletion, show MREE enrichment (cf. Haley et al., 2004) and have positive Eu and Y/Ho anomalies with a 461 462 weakly positive Ce anomaly. These observed REE characteristics are consistent with the 463 chemistry of anoxic marine basins (Bau and Möller, 1993), ferruginous lakes, marine 464 hydrothermal plumes and anoxic diagenetic waters (Johannesson and Zhou 1999; Sherrell et al., 465 1999; Haley et al., 2004; Wang et al., 2018). The weakly positive Gd anomaly present in VF 466 dolomite may reflect seawater precipitation (Bau, 1999). Eu is also normally enriched in 467 Archean seawater-precipitated carbonate too (Bolhar and Karnendonk, 2007), the source of 468 which can be either hydrothermal solutions derived from mid-ocean ridges and/or back-arc 469 spreading centres, or burial diagenetic fluids (Michard et al., 1983; Michard, 1989; Derry and 470 Jacobsen, 1990; German et al., 1990; Murray et al., 1991; Danielson et al., 1992; German et al., 471 1993; German et al., 1999; Douville et al., 1999; Kamber and Webb, 2001; Eroglu et al., 2017; 472 Schier et al., 2018). In VF dolomite significant positive correlation is observed between Eu/Eu* 473 and Ba content (Fig. 14) and this clearly indicates the influence of hydrothermal activity on the 474 studied carbonates (Khelen et al., 2017). Extensive volcanic activity in the CB around 1.9 to 2.0 475 Ga in a continental rift setting (Anand et al., 2003; Ravikant et al., 2014) could be the source for 476 Eu. However, diagenetic alteration of the precursor carbonate sediments is suggested by the

477 Fe/Sr versus Mn/Sr plot (Fig. 8c), low Y/Ho ratio (0.94-1.46; mean 1.15, SD = 0.14) and the 478 Y/Ho and Ce/Ce* plot (Fig. 13), and this could also have enhanced the Eu anomaly.

479

480 Sodium content of dolomites can be used as an indicator of salinity of the fluid from 481 which the dolomites precipitated (Land and Hoops, 1973; Sass and Katz, 1982; Sass and Bein, 482 1988; Budd, 1997). The low Na concentrations (60-735 ppm, average 290 ppm) of VF dolomite 483 along with the poor correlation of Sr/Ca vs. Na₂O (Fig. 8b) rules out their hypersaline fluid 484 origin and probably suggests a diagenetic fluid source. Depletion in Na, however, can also be a 485 consequence of burial (Sachan, 1993), as successive episodes of dolomitization of limestone and 486 dolomite recrystallisation would reduce the levels of Na (Warren, 2000). Similarly, low 487 strontium concentrations (40-420 ppm, average 85 ppm; average Sr value of lithospheric 488 carbonate rocks is 610 ppm; Turekian and Wedepohl, 1961) of VF dolomite probably reflect a 489 Sr-depleted water-buffered diagenetic system (Budd, 1997; Warren, 2000; Azmy et al., 2001), 490 supporting a burial diagenetic effect (Sachan, 1993; Warren, 2000). Tucker (1983), from studies 491 of the Precambrian Beck Spring Dolomite, suggested that low concentrations of Na and Sr in 492 ancient dolomites excludes precipitation from marine fluids and warrants either fluid-mixing or 493 wet-recrystallization of an initially precipitated poorly-ordered calcian dolomite that drives out 494 Na and Sr.

495

The δ^{13} C values (- 0.4 ‰ to 2.0 ‰; average value 0.5 ‰) of dolomite samples probably reflect the carbon isotopic composition of the precursor carbonate precipitated from the Proterozoic seawater. Palaeoproterozoic carbonate successions are characterized by δ^{18} O values ranging from -6 to -12 ‰ (Tucker, 1982; Burdett et al., 1990; Veizer et al., 1992a; 1992b; Melezhik et al., 1997; Bekker et al., 2001; 2003a, b). The oxygen isotope range (-5.2 to -8.1 ‰) for VF dolomite is within this range and is consistent with precipitation (or recrystallization) during shallow to moderate burial (Sachan, 1993; Warren, 2000).

503

504 **7. PROBABLE MECHANISM OF DOLOMITIZATION**

505 The field observations and petrographic features of the dolomites within the 506 Palaeoproterozoic VF can be interpreted in terms of early dolomitization of peritidal platform 507 carbonate sediment consisting of lime mud and calcimicrite. Preservation of microbial fabric 508 elements of the stromatolitic dolomite suggests that either VF dolomite associated with 509 microbial-laminites formed as primary precipitates due to microbial activity and minor 510 evaporation (Hird et al., 1987) or that they are very early, replacement mimetic dolomites. 511 During subsequent shallow sub-surface burial and diagenesis, fabric-destructive dolomitization 512 of the undolomitized oolitic grainstones and calcimicrite, along with recrystallization of the 513 early-formed peritidal dolomite happened as suggested by the petrographic textures. In terms of 514 seawater chemistry in the Palaeoproterozoic CB, it is likely that this was a time of calcite 515 precipitation (a "calcite sea"), with anoxic and ferruginous conditions, and an elevated Mg/Ca 516 ratio but not so high that very early fabric-retentive dolomitization of ooids and cements could 517 take place, like those of the Beck Spring Dolomite (Tucker, 1983). The lack of a very high 518 seawater Mg/Ca ratio could be related to the onset of rifting of supercontinent Columbia around 519 2.0 Ga that coincides with the VF carbonate sedimentation. Grotzinger (1989) proposed that 520 Precambrian seawater was oversaturated with respect to calcium carbonate that favoured abiotic 521 carbonate precipitation that gradually decreased the carbonate saturation through the Proterozoic 522 to Phanerozoic levels. This process, coupled with a fast rate of sea-floor spreading, would draw Mg²⁺ down producing a "calcite ocean" (Wilkinson and Algeo, 1989; Bots et al., 2011). This 523 524 ocean chemistry is in contrast to the anoxic, ferruginous and extremely high Mg/Ca conditions 525 that prevailed during Neoproterozoic time (Hood and Wallace, 2018). In addition, the coarse 526 replacement VF dolomite crystallized from a burial fluid that evolved from the europium-527 enriched anoxic seawater with a lower SO₄ content (Hood and Wallace, 2018), as marine water or its derivative is the only known infinite source of Mg²⁺ and Ca²⁺. The PAAS-normalized REE 528 529 profiles for VF dolomite are consistent with the chemistry of anoxic diagenetic waters. Low Na 530 and Sr concentrations of VF dolomite in and around Parnapalle also suggest their precipitation 531 (or early recrystallisation) during burial diagenesis (Veizer, 1983; Vahrenkamp and Stewart, 532 1990; Tucker and Wright, 1990; Banner, 1995; Budd, 1997; Warren, 2000; Azmy et al., 2001; 533 Balter et al., 2011; Sosdian et al., 2012); this is also supported by the stable isotope (δ^{18} O) values that fall within the range of the burial dolomite model (Warren, 2000; Machel, 2004). The δ^{13} C, 534 535 on the other hand, having 'marine' values, suggests that the original lime mud and/or micritic 536 calcite were derived from seawater (Tucker and Wright, 1990). The likely factor promoting 537 dolomite formation during early burial diagenesis could be the presence of an early, finely-538 crystalline, less well-ordered dolomite, as is being precipitated in modern tidal flats and

539 microbial mats in Abu Dhabi and Qatar (e.g., Bontognalli et al., 2010; Perri et al., 2018). These 540 early Ca-Mg precipitates could have provided the nuclei and substrates for continued dolomite 541 formation. The near-stoichiometric and relatively well-ordered VF dolomite crystals probably 542 would be the result of dolomite recrystallisation during burial, possibly promoted by an elevated 543 geothermal gradient from crustal thinning and mafic volcanic activity around 2.0 - 1.8 Ga 544 (Anand et al., 2003; Ravikant et al., 2014). Such tectonic-volcanic processes may have 545 diagenetically-modified the then seawater composition and be responsible for the positive Eu anomaly ($Eu/Eu^* = 89.33-1.03$) recorded in VF dolomite. 546

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548 **8.** CONCLUSIONS

549 Combined field data and microscopic observations suggest that the Cuddapah Basin 550 carbonate rocks initially precipitated as fine lime mud and/or micritic calcite in tidal-flat and 551 associated shallow-marine environments. These sediments were replaced by dolomicrite during 552 early peritidal dolomitization. Petrographic observations also reveal fabric-retentive dolomite 553 textures, including filaments, in stromatolites, possibly reflecting microbial dolomite 554 precipitation-dolomitisation. During shallow sub-surface burial, fabric destructive dolomitization 555 of undolomitized oolitic grainstone and calcimicrite took place, along with recrystallization of 556 the early-formed peritidal dolomite. The δ^{18} O and δ^{13} C values of VF dolomite samples suggest 557 that these dolomites were either precipitated or recrystallised from burial diagenetic fluids that 558 evolved from Eu-enriched seawater. Burial diagenetic precipitation and recrystallisation of 559 dolomite are also supported by depleted Na and Sr contents. Ratios and contents of redox-560 sensitive metals (Cu, Co, Fe, Mn, Mo, Ni, V, Zn), REE distribution and high Fe_T/Al ratios imply 561 that dolomitizing fluids were anoxic and ferruginous but not euxinic. The positive Eu anomaly 562 could reflect a hydrothermal source and this may have been related to fluids connected to 563 continental rifting and volcanic activity within the CB around 1.9 - 2.0 Ga. The pattern of 564 diagenesis and dolomitisation recorded in the VF is more typical of Phanerozoic platform 565 carbonates than many Precambrian dolomites which show perfect preservation of original 566 textures (such as ooids and fibrous cements) and continued precipitation of dolomite in the burial 567 environment as a dolospar cement.

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Fig. 1. (a) Distribution of the major Proterozoic basins in India. The red, dashed, outlined rectangle demarcates the Cuddapah Basin; (b) Outline sketch of the Cuddapah Basin showing four sub-basins (after Ramam and Murty, 1997). The red, outlined rectangle demarcates the study area in the Papaghni sub-basin, Cuddapah Basin; (c) General geological map of the south-western part of the Papaghni sub-basin showing the different lithostratigraphic units of formation status. The study area is located near Parnapalle village (N14°32'58.3", E77°58'09.9").



Fig. 2. Representative litho-log showing the vertical arrangement of facies, at a canal-cut section exposing ~ 1000 m of the Vempalle Formation.




Fig. 3. Field photographs showing different features of the Vempalle Formation, referred in the interpretative block diagram showing the VF depositional environment. a) Mixed siliciclastic dolomite (sandstone-mudstone heterolith, F1); b) Mixed siliciclastic dolomite (laminated calcareous mudstone with siliciclastic input, F1); c) Bedded dolomite with crinkled laminites (F2) characterized by flat or wavy lamination; d) Dolomite-micrite rhythmite (F5) characterized by buff-coloured dolomite alternating with green or brown shale; e) Thick occurrence of brown shale (F3), where the bed-sets (~1.5 m) laterally persist more than 10 m; f) Black dolomite with chert nodules (F4); g) Tabular biostromes of laterally-linked domes of stromatolite (F7); h) Planar- and trough-stratified oolitic grainstone beds (F6); i) Tabular biostromes of columnar stromatolites; j) Tabular biostromes of conical stromatolites (F9); k) Tabular beds of parallel stratified dolomite (F10) alternating with buff-coloured marl and green shale (F11) with steatite (talc) interbeds; l) Schematic representation of the palaeogeography of the VF. The hammer in photograph a, c is 32.5 cm in length. The hammer in photograph b is 28.5 cm and the scale in other photographs (marked by black coloured line) is 1.6 m long.



Fig. 4. a) Mixed siliciclastic-carbonate with >10% of terrigenous material characterized mostly by sub-rounded to well-rounded quartz with minor feldspar (XPL). b) Lithic fragments of quartz (centre) and feldspar (upper right). c) Non-planar polymodal relatively coarse-crystalline dolomite completely replaced the calcimicrite matrix. Note the curved crystal faces and undulose extinction of the non-planar dolomite (XPL). d) Stromatolitic dolomite showing alternate occurrence of fine- and coarse- crystalline dolomite and microbial laminae (PPL). e) Polymodal non-planar dolomite crystals from the coarse-crystalline layers of the stromatolitic dolomite. Note the preservation of crystal-face junctions in the non-planar dolomite crystals from the dolomite polymodal planar-s to non-planar dolomite crystals from the stromatolitic dolomite crystals from the dolomite layers of the stromatolitic dolomite crystals from the non-planar dolomite crystals from the dolomite (XPL).



Fig. 5. a) **Ooids** of different sizes showing concentric rims and radial cracks (PPL); b) Ooids composed of calcite crystals, showing radial fabric (XPL) c) Presence of euhedral rhombic dolomite crystals at the nucleus of the ooid. Radial fabric is clearly visible showing sweeping extinction (XPL); d) Partially replaced ooid grain preserving concentric rims and radial fabric at the outer margin. Dolomite replacement at the inner part of the ooid completely destroyed the primary fabric. Also note presence of silica rim at the margin of the ooid (PPL); e) Partial destruction of the primary radial fabric of the ooid at the peripheral margin by micritic dolomite crystals during replacement (XPL); f) ooid cortex is completely replaced by planar-e, planar - s and non-planar micritic dolomite crystals completely obliterating the internal fabric but still preserving the shape of the ooids.



Fig. 6. Photomicrograph of massive VF dolomite from the upper part of the formation. a) Still preserved unreplaced calcimicrite with medium-grained, polymodal calcite microspar (XPL). b) Calcite spar showing lamellae engulfing dolomite crystals (XPL).



Fig. 7. Cross-plots of a) Mn vs Fe, b) Sr/Ca vs Na₂O, and c) Fe/Sr vs Mn/Sr d) Mg/Ca vs Fe and e) Mg/Ca vs Mn from VF dolomite samples (oxide percent is converted in to ppm: oxide percent x conversion factor x 10000).



Fig. 8. Example of the typical PAAS-normalized REE patterns of Vempalle Formation dolomite samples. A red dashed-line represents an average of a chosen data-set and shows a pronounced positive Eu anomaly.



Fig. 9. Distribution of PAAS-normalised $(Gd/Yb)_{SN}$ vs $(La/Sm)_{SN}$ of Vempalle Formation dolomite samples.



Fig. 10. Cross-plot of oxygen vs carbon isotope values obtained from the Vempalle Formation dolomites showing an inverse correlation.



Fig. 11. Plot of Ce_{SN} and Pr_{SN} anomalies for the Vempalle Formation dolomites shows a wide range of anomalies from large positive Ce anomalies to moderately negative anomalies. Fields after Bau and Dulski (1996).



Fig. 12. The PAAS-normalized low Σ REE of the Vempalle Formation dolomites suggests that the precursor rock is probably of marine origin and the REE contribution from non-carbonate fractions (Fe-Mn oxides and siliciclastic contamination) appears to be minor.



Fig. 13. Correlation between Y/Ho versus Ce/Ce* of the Vempalle Formation dolomites suggests variable contamination of the precursor carbonate sediments.



Fig. 14. Strong correlation between Ba (ppm) versus PAAS normalized Eu of the VF dolomites clearly indicates the signature of hydrothermal activity.

TABLES

Table 1. Sample list of Vempalle Formation rocks from the Papaghni Group. < - Sample analyzed; -- - sample not analyzed

Sample No.	<mark>Color of Rock</mark> Sample	Lithology	Facies	<mark>Height</mark>	<mark>Major</mark> oxide	Trace element	REE	XRD	<mark>Isotope</mark>
V _T 1/12	Light Grey, 5Y 6/1	Locally algal laminated fine grained dolomicrite	F1	<mark>3.56m</mark>	✓	-		✓	
V _T 2/12	Grayish pink (5R 8/2) with elongated patches of grayish purple	Laminated Fine grained dolomicrite	F1	<mark>14.4m</mark>	<mark>✓</mark>	<mark>✓</mark>	<mark>✓</mark>	✓	
V _T 3A/12	Grayish pink (5R 8/2) with banding of grayish purple	Fine grained dolomicrite	F1	<mark>26.72m</mark>	<mark>✓</mark>	<mark>✓</mark>	<mark>✓</mark>	 ✓ 	
V _T 3B/12	Very light gray (N8) colored clast in a Grayish pink (5R 8/2) colored cement	Intraformational Conglomerate (Large, elongated limestone clasts in dolomite cement)	F1	<mark>29.92m</mark>	<mark>✓</mark>	<mark>✓</mark>	<mark>~</mark>	~	
V _T 4/12	Grayish Pink, 5R <mark>8/2</mark>	Algal laminated Fine grained dolomicrite	F1	<mark>44.3m</mark>	✓	✓	 ✓ 	 	
			<mark>97.85n</mark>	n Unexposed					
M1	Medium gray, N5	Fine grained dolomicrite	F1	228.35m	✓	✓	✓	✓	 ✓
M5	Dark gray, N3	Fine grained black dolomite	F4	251.85m	✓	✓	✓		
M7	Medium dark gray, N4	Fine grained black dolomite	<mark>F4</mark>	<mark>257.65m</mark>	 ✓ 	<mark>✓</mark>	✓	 ✓ 	
M11	Very light gray, <mark>N8</mark>	Fine grained black dolomite	<mark>F4</mark>	<mark>287.7m</mark>	 ✓ 	 ✓ 	 ✓ 		
M15	Light Gray, N7	Algal laminated bedded dolomite	F2	306.88m	 ✓ 	✓	✓	 ✓ 	
<mark>M17</mark>	Medium gray, N5	Fine grained black dolomite	<mark>F4</mark>	<mark>317.63m</mark>	 ✓ 	<mark>✓</mark>	 ✓ 		
<mark>M18</mark>	Medium light gray, N6	Fine grained dolomite	F5	<mark>324.92m</mark>		 ✓ 		✓	
<mark>M19</mark>	Grayish black, N2	Medium grained black dolomite	F4	<mark>334.62m</mark>	✓	✓	✓		
M20	Pale brown, 5YR 5/2	Algal laminated fine- grained bedded dolomite	F2	<mark>345.69m</mark>	✓	✓	<mark>✓</mark>	✓	<mark></mark>
M22	Grayish black, N2	Medium grained black dolomite with stromatolite	<mark>F4</mark>	<mark>364.14m</mark>	 ✓ 	 ✓ 	 ✓ 	 ✓ 	
			25m	unexposed					
<mark>V1/12</mark>	Light Gray, N7	Fine grained dolomite	F5	<mark>389.83m</mark>		✓	✓	✓	

V4/12	Grayish black, N2	Fine grained black dolomite	F4.	<mark>402.69m</mark>		-			 ✓
<mark>V7/12</mark>	Light Gray, N7	Fine grained dolomite	F5	<mark>415.2m</mark>		-			 ✓
<mark>V9/12</mark>	Grayish black, N2	Fine grained black dolomite	F4.	<mark>423.82m</mark>		-			 ✓
<mark>V10/12</mark>	White, N9	Fine grained dolomite	F5	<mark>428.25m</mark>	 ✓ 	✓	✓	 ✓ 	
V12/12	Grayish black, N2	Fine grained dolomite	F5	<mark>436.73m</mark>		-			✓
<mark>V14/12</mark>	Medium gray, N5	<mark>Stromatolitic black</mark> dolomite	F7	<mark>480.33m</mark>		-			<mark>✓</mark>
<mark>V15/12</mark>	<mark>Medium light</mark> gray, N6	Fine grained dolomite	F5	<mark>501.66m</mark>	<mark>✓</mark>	<mark>✓</mark>	✓	✓	
V17/12	Light Gray, N7	Stromatolitic dolomite	F7	<mark>533.04m</mark>	✓	✓	✓	✓	<mark>✓</mark>
<mark>V19/12</mark>	<mark>Medium light</mark> gray, N6	Fine grained dolomicrite	F10	<mark>557.03m</mark>	 ✓ 	✓	✓		<mark>✓</mark>
V21/12	Medium light gray, N6	Fine grained dolomite	F5	<mark>580.83m</mark>	✓	✓	✓	✓	✓
V23/12	Pale yellowish brown, 10YR 6/2	Very fine-grained dolomite	F5	<mark>604.02m</mark>	 ✓ 	-			
V26/12	Medium dark gray, N4	Stromatolitic dolomite	F8	<mark>633.75m</mark>	✓	✓	✓	 ✓ 	 ✓
V28/12	Medium dark gray, N4	Stromatolitic dolomite	F7	<mark>644.53m</mark>	 ✓ 	✓	✓		-
<mark>V29/12</mark>	Light Gray, N7	Stromatolitic dolomite	F7	<mark>650.54m</mark>		✓	✓		
V30/12	Light Gray, N7	Stromatolitic dolomite	F7	<mark>655.74m</mark>	✓	✓	✓	 ✓ 	
V32/12	Light Gray, (N7) with medium dark gray (N4) colored banding	<mark>Stromatolitic dolomite</mark>	F7	<mark>666.4m</mark>	<mark>√</mark>	✓	~		
V35/12	Very light gray, N8	Fine grained dolomite	F5	<mark>682.2m</mark>	✓	✓	✓	✓	<mark>✓</mark>
V36/12	Medium light gray, N6	Fine grained dolomite	F5	<mark>687.65m</mark>	✓	✓	✓		
V37/12	Grayish red purple (5RP 4/2) with dark reddish brown (10R 3/4) laminites in between	Dolomicrite	F5	<mark>695.67m</mark>	√	~	~	~	
V39/12	Pale yellowish brown, 10YR 6/2	Fine grained dolomite	F5	<mark>706.8m</mark>	✓	✓	✓	✓	

V42/12	Grayish pink, 5R 8/2	Stromatolitic dolomite	F7	730.93m	✓	 ✓ 	✓	✓	 ✓
<mark>V44/12</mark>	Medium gray, N5	Stromatolitic dolomite	F7	<mark>752.63m</mark>	 ✓ 	 ✓ 	 ✓ 	 ✓ 	
V44/12	Cream/white	oolite	<mark>F8</mark>	<mark>752.81m</mark>	✓	-	✓		-
<mark>V46/12</mark>	Medium light gray, N6	Fine grained dolomite	F5	<mark>775.16m</mark>	 ✓ 	 ✓ 	 ✓ 		
<mark>V47/12</mark>	Grayish black, N2	<mark>Stromatolitic black</mark> dolomite	F7	<mark>786.01m</mark>		-			 ✓
V48/12	Pale yellowish brown (10YR 6/2) colored large clasts in black (N1) colored cement	Intraformational Conglomerate (Large, elongated limestone clasts in dolomicrite)	F9	804.32m	<mark>✓</mark>	<mark>✓</mark>	<mark>✓</mark>	~	
<mark>V49/12</mark>	Alternate layering of medium gray (N5) and grayish black (N2) color	<mark>Stromatolitic dolomite</mark>	F7	<mark>814.72m</mark>		<mark>-</mark>		~	
V50/12	Grayish black, N2	Stromatolitic dolomite	F7	825.72m	✓	✓	✓	✓	<mark>></mark>
V51/12	Medium gray, N5	Stromatolitic dolomite	<mark>F7</mark>	<mark>835.92m</mark>	<mark>✓</mark>	✓	✓		-
<mark>V52/12</mark>	Pale brown, 5YR 5/2	Stromatolitic dolomite	F7	<mark>846.92m</mark>	<mark>✓</mark>	✓	✓		
<mark>V53/12</mark>	Pale yellowish brown, 10YR 6/2	Stromatolitic dolomite	F7	<mark>857.92m</mark>	✓	 ✓ 	<mark>✓</mark>	✓	
V54/12	Medium dark gray, N4	Stromatolitic dolomite	F7	868.07m	✓	 ✓ 	✓		
V55/12	Medium dark gray, N4	Stromatolitic dolomite	F7	<mark>878.79m</mark>	 ✓ 	 ✓ 	<mark>✓</mark>	✓	 ✓
<mark>V56/12</mark>	Medium dark gray, N4	Stromatolitic dolomite	F7	889.09m	 ✓ 	 ✓ 	 ✓ 	✓	
V57/12	Alternate layering of light gray (N7) and black (N1) color	Stromatolitic dolomite	F7	<mark>900.09m</mark>	 ✓ 	<mark>✓</mark>	<mark>✓</mark>	✓	

Table 2. Facies descriptions of Vempalle Formation rocks from the Papaghni Group.

Facies	Description	Interpretation
F1: Mixed siliciclastic- dolomite	Dolomite-sandstone-mudstone heterolithic beds, occupying ~100 m of the lowermost part of the succession Planar to wavy-parallel laminated or trough cross stratified 2-14 cm thick medium to fine-grained sandstone alternating with either reddish brown or local green mudstone or 5-25 cm, massive or planar parallel laminated tabular dolomite beds. Locally sandstones amalgamate to form 20-30 cm thick beds with ripple drift lamination, flaser bedding and graded bedding. Birds-eye structure (fenestral fabric, now filled with silica), locally developed breccias, tepee antiform structures, buckled margins of saucer-like megapolygons and chert nodules are common in the dolomites. Well-rounded, very coarse to coarse sand inter-layers or intraclastic conglomerate with sand matrix are also common.	The heterolith with flaser bedding, syneresis cracks strongly support a supratidal to upper intertidal zone of deposition for the sediments. Tepee structures, fluid-escape structures along with breccias indicate subaerial exposure in a tropical to subtropical climate; and back-beach or back-barrier deposition. Flat parallel laminae of the dolomites suggest supratidal to intertidal deposition with gentle waves.
F2: Bedded dolomite with crinkled laminites (bindstone)	Laterally-persistent, 50-80 cm thick, tabular beds (amalgamated up to 1.5 m) of grey fine-grained dolomite characterized by flat or wavy beds, 2-5 cm thick, light colored dolomite, separated by brown colored mm thin laminae. Crinkled lamination with sharp angular kinks (relict ripple marks), and mud drapes. Randomly distributed, irregularly-shaped fenestrae, parallel to bedding and soft-sediment deformation with microfaults.	Crinkle lamination and fenestrae suggesting tidal flat.
F3: Brown shale/ mudstone	Thin-bedded (0.5-2 cm), reddish brown, plane-parallel to wavy-parallel laminated mudstone. Individual beds laterally pinch out within a meter, but bed-sets, \sim 1.5 m thick, can be traced laterally up to 10 m. Wrinkle marks (adhesion ripples) and dolomite-filled polygonal cracks common on top surfaces of beds.	Thin-bedded parallel-laminated mudrock reflects low-energy sedimentation. The brown colour suggests well-drained, relatively oxidizing conditions.
F4: Black dolomite with or without stromatolite (wackestone)	Characterized by tabular, laterally persistent 40-60 cm thick (maximum 1.2 m) steel grey to black colored stromatolitic dolomite beds within brown, green or grey stripped shale. Stromatolite bed boundaries sharp with convex-up upper surface forming isolated bioherms or laterally-linked mutually-aligned biostromes with 3-15 cm high columns. Internal laminae of stromatolites closely packed, smooth convex up with low synoptic relief. Cm-scale slump structures and dolomite or silica filled irregularly shaped laminoid fenestrae. Chert nodules restricted to dolomite beds. Some dolomite beds massive in nature, either microbialites reworked or not developed.	Laterally-persistent stromatolitic dolomite beds within variegated colored shale indicates quiet conditions with fluctuating sea level and/or sediment supply. Small slumps and broken stromatolites suggest occasional storms. Transitional zone between subtidal to intertidal is suggested, where high sedimentation rate favored massive carbonate and a lower rate permitted stromatolite growth.
F5: Dolomite-micrite rhythmite (wackestone-mudstone)	Alternating grey to buff colored massive, normally graded to plane-parallel laminated fine-grained dolomite (2-25 cm bed thickness) and green to brown colored plane to wavy parallel-laminated calcareous mudstone (1-5 cm beds). Symmetrical ripples on bed upper surfaces. Dolomite-filled polygonal cracks, salt pseudomorphs, rain-drop prints at several horizons.	Fine grain-size and plane-parallel lamination suggests low energy in a shallow shelf/lagoon. Normal grading, rip-up clasts and symmetrical ripples point to occasional storms. Polygonal cracks, salt pseudomorphs, rain-drop prints indicate emergence in intertidal area of the shallow coast. Predominance

		of mud indicates restricted environment,
F6: Cross-stratified oolite (grainstone)	Oolite of well-rounded, well-sorted medium to coarse ooids as linear positive relief bodies, mostly forming shoaling-up bars and banks. Successive 10-70 cm thick wavy lenticular or pinch and swale beds separated by 1-2 cm thin mud layers constitute a shoreline barrier structure. Beds generally trough cross- stratified with subordinate planar cross-stratification, with a NE or SE palaeocurrent direction and a small component towards the SW. Local herringbone cross-stratification. Bed tops show symmetrical ripples with NE-SW ripple axis, straight, rounded crests and tuning-fork bifurcation. Ooids generally preserve a concentric fabric with clastic grains in the core. Medium to fine-grained ooids with a radial fabric and some superficial ooids.	Oolite beds with planar or trough cross- stratification deposited by migrating 2D and 3D subaqueous dunes in high-energy subtidal to intertidal shoals. Presence of herringbone cross-stratification and bidirectional palaeocurrents suggests a tidal influence in association with wave action. Oolite deposition with concentric fabric and clastic core points to an environment with high salinity and wave-agitated shoreline. Sand free ooids with radial fabric may be deposited in relatively quiet water.
F7: Columnar stromatolite (bindstone)	Laterally persistent biostromes and bioherms of columnar stromatolite. 2 types: (a) Tabular biostromes (0.7-2 m height), with erect, locally inclined, cylindrical columns, convex up, closely-spaced, linked smooth to wavy internal laminae with low synoptic relief. (b) Biostromes of laterally-linked domes (1.5-2 m width and 25-80 cm height) with crinkly to smooth laminae parallel to the dome surface. Intraformational conglomerates at the head part of stromatolites locally present.	Smooth lamination indicates quiet water. Large sizes suggest growth in deep water. Intraformational conglomerates reflect frequent storm events.
F8: Conical stromatolite (bindstone)	Biostromes and bioherms of conical stromatolites, embedded within calcareous mudstone. Individual stromatolites isolated to partially linked with open spacing ranging between 5-30 cm and sharp apical angle varying between $20^{\circ}-40^{\circ}$ with moderate to high synoptic relief, closely packed, smooth internal laminae. Biostromes laterally persistent and vary in height from 15-55 cm, bounded by sharp upper and lower surfaces.	Conical shape with high apical angle suggests deep water below wave base, where microbes need to grow fast with maximum apex reaching the light in a deep subtidal environment.
F9: Intraformational conglomerate (grainstone/packstone)	 2 types of conglomerate, occurring concurrently in the succession. (a) 3.2-30.8 cm thick, planar tabular beds of matrix-supported, massive ungraded to inversely-graded beds of intraformational conglomerate Poorly-sorted, sub-rounded clasts of stromatolite, lime mud and oolite with various shapes (lensoid, elongated, spherical, sinusoidal) and sizes (0.5-17 cm) embedded in a calcareous matrix Conglomerates alternate with beds of same lithology as the clasts. Small-scale slumps and fluid-escape structures common. Large (30-41 cm) cabbage-shaped oncoids present. Laterally-persistent, 0.4-1.5 m thick, grey to buff colored, planar, tabular, normally-graded beds of intraformational conglomerate. Conglomerates occur as thin layers (14-32 cm thick) mainly in the lower parts of beds, upon a sharp erosional surface, and grade upward to grey colored fine-grained dolomite. Conglomerates comprise clasts (0.6-9 cm) of lime mud and/or shale, in a micritic matrix. 	Conglomerates are event beds from mass flow and/or break-up of stromatolites either by local earthquakes or strong storms. Laterally-persistent graded beds suggest deposition by strong storm events. Presence of oncoids indicates wave reworking during storms.

F10: Parallel-stratified dolomite with isolated bioherms (packstone)	5-40 cm thick (amalgamated up to 1.2 m), planar, tabular dark grey colored dolomite beds with sharp to slightly uneven lower and upper bounding surfaces. Internally, plane-parallel to wavy-parallel laminated. Trough cross- stratification, pillow and ball structure and gutter casts common. Isolated bioherms with domal morphology (width 45 cm, height 26 cm) and interspaces filled with muddy carbonate in some restricted dolomite beds. Abundant chert and steatite nodules of various shapes (kidney-bean shaped, lensoid, spherical) and sizes (long axis of 3-26 cm and short axis of 2.5-14 cm). Dolomite beds commonly alternating with mm to 6 cm thick calcareous mudstone.	Plane-parallel stratification attributed to tractional deposition by waves with high near-bottom orbital velocities. Trough cross-stratification suggests 3D dune migration. Gutter casts from storm events. Isolated bioherms indicate quiet conditions, without regular wave and current activity. Chert and steatite nodules from later diagenetic event/s.
F11: Interbedded green shale/siltstone and dolomite (wackestone-mudstone)	1-2 cm thin laterally pinching out, plane-parallel laminated green to dark green colored shale /siltstone alternating with laterally persistent, 1-5 cm thick, plane to wavy-parallel or ripple cross- laminated buff to light grey colored very fine-grained dolomite.	Plane-parallel laminated shale deposited by suspension fall-out below storm wave base. Green colour from reducing environment.

TABLES

ID	Dolomite	Calcite	Quartz	K-feldspar	Mica	Talc	Chlorite	Barite	Hematite	Total
VT1/12	80.4	0	9.3	4.2	6.1	0	0	0	0	100
VT2/12	90.4	0	4.7	4.9	0	0	0	0	0	100
VT3A/12	93.2	0	6	0.8	0	0	0	0	0	100
VT4/12	83.9	0	9.1	7	0	0	0	0	0	100
M1	83.3	0	15.7	1	0	0	0	0	0	100
M7	97.1	0	2.9	0	0	0	0	0	0	100
M15	99.6	0	0.4	0	0	0	0	0	0	100
M20	88.7	0	8.6	2.7	0	0	0	0	0	100
M18	87.9	1.1	7.4	0	0	0	0	3.6	0	100
M22	100	0	0	0	0	0	0	0	0	100
V1/12	86	0	9.3	0	0	0	0	4.7	0	100
V10/12	40.9	0	20.4	0	0	38.7	0	0	0	100
V15/12	82.5	4.3	11.8	0	0	1.3	0	0	0	99.9
V17/12	82.6	4.4	11.7	0	0	1.3	0	0	0	100
V21/12	99.8	0	0.2	0	0	0	0	0	0	100
V26/12	100	0	0	0	0	0	0	0	0	100
V30/12	96.1	0	3.9	0	0	0	0	0	0	100
V35/12	84.8	0	12.5	0	0	0	0	2.7	0	100
V37/12	83.3	0	7.1	7.7	0	0	1	0	0.8	99.9
V39/12	85.9	0	8.1	0.5	0	0	0	5.4	0	99.9
V42/12	95.1	0	3.4	1.5	0	0	0	0	0	100
V44/12	83.4	0	16.6	0	0	0	0	0	0	100
V48/12	86	0	12.9	1.1	0	0	0	0	0	100
V49/12	71.5	0	28.5	0	0	0	0	0	0	100
V50/12	93.8	0	3.7	2.5	0	0	0	0	0	100
V53/12	87.3	0	10	2.7	0	0	0	0	0	100
V55/12	82.7	0	16.1	1.2	0	0	0	0	0	100
V56/12	71	0	28.1	0.9	0	0	0	0	0	100
V57/12	90.5	0	8.3	1.1	0	0	0	0	0	99.9

 Table 1S. Modal percentage of mineral phases identified in Vempalle Formation dolomites using the bulk XRD method.

Table 2S. Calculated calcium (Ca) excess (Lumsden, 1979) and ordering of Vempalle Formation dolomite crystals (Tucker 1995).

ID	mole % MgCO ₃	mole % CaCO ₃	Order
VT 1/12	44	50	0.4
VT 2/12	44	50	0.57
VT 3A/12	44	50	0.57
VT 4/12	43	50	0.51
M1	43	50	0.46
M7	45	49	1.07
M15	44	50	0.55
M20	44	50	0.57
M18	44	50	0.46
M22	44	50	0.57
V1/12	44	50	0.47
V10/12	44	50	0.58
V15/12	44	50	0.57
V17/12	44	50	0.57
V21/12	43	50	0.47
V26/12	44	49	0.56
V30/12	44	50	0.56
V35/12	44	50	0.56
V37/12	43	51	0.58
V39/12	44	50	0.56
V42/12	44	50	0.56
V44/12	43	50	0.56
V48/12	43	50	0.56
V49/12	44	49	0.56
V50/12	44	49	0.56
V53/12	43	50	0.56
V55/12	44	50	0.56
V56/12	44	49	0.56
V57/12	44	50	0.56

Table 3Sa. Major and trace element concentrations (n = 42) from Vempalle Formation dolomites. The major element concentrations are in wt% whereas Sr concentration is in ppm.

		1												
VT1/12 0.054 1.6.55 1.10 10 0.04 0.28 2.6.95 0.058 0.031 0.42 55.48 36.41 418 VT21/2 0.049 18.55 3.76 9.01 0.43 2.43 27.36 0.11 0.081 1.45 58.06 9.01 81.0 VT3B/12 0.045 18.02 1.35 7.84 0.31 6.057 1.08 0.070 0.071 1.08 58.05 81.06 1.31 59.07 1.00 0.010 0.010 0.019 0.012 51.09 60.10 0.012 0.012 0.012 1.01 0.01 0.010 0.010 0.012 0.012 0.012 0.012 1.01 1.01 0.01 0.012 0.005 0.044 0.42 53.49 42.27 52 M1 0.013 2.175 0.02 0.01 0.01 0.010 0.03 0.01 0.03 0.01 0.03 0.03 0.02 0.31 0.02 5.143 </td <td>ID</td> <td>Na₂O</td> <td>MgO</td> <td>Al_2O_3</td> <td>SiO₂</td> <td>P_2O_5</td> <td>K₂O</td> <td>CaO</td> <td>TiO₂</td> <td>MnO</td> <td>Fe₂O₃</td> <td>SUM</td> <td>LOI</td> <td>Sr</td>	ID	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	SUM	LOI	Sr
VT2/12 0.049 18.55 3.76 9.01 0.43 2.43 27.36 0.113 0.081 1.48 63.26 39.00 81 VT3A/12 0.033 18.02 1.35 7.84 0.31 2.33 28.49 0.079 0.071 1.48 59.87 38.06 93 VT3B/12 0.040 17.15 1.45 12.16 0.21 27.60 0.03 0.067 1.06 61.91 37.29 95 M1 0.032 1.840 1.30 12.15 0.01 0.04 3.09 0.005 0.048 0.42 54.51 41.61 45 M5 0.012 21.75 0.02 0.02 6.01 0.01 0.03 0.14 0.01 0.03 0.47 71.61 31.58 56 M1 0.043 1.74 0.46 6.29 0.01 0.026 0.44 0.25.64 4.56 4.52 51.77 41.76 43 M20 0.055	VT1/12	0.054	16.55	1.10	10	0.04	0.28	26.95	0.058	0.031	0.42	55.48	36.41	418
VT3A/12 0.033 18.02 1.35 7.84 0.31 2.33 28.49 0.079 0.071 1.34 59.87 38.06 93 VT3B/12 0.045 18.06 2.34 10.57 0.06 1.54 36.95 0.103 0.067 1.06 61.91 37.29 95 M1 0.036 18.40 1.30 0.21 2.76 0.010 0.067 1.02 50.40 0.067 1.08 6.021 0.05 0.048 0.42 53.49 42.27 52 M1 0.043 15.78 1.19 27.75 0.02 0.01 0.01 0.03 0.047 71.61 31.58 56 M17 0.012 21.07 0.09 1.18 0.00 0.03 0.01 0.03 0.39 52.96 42.24 58 M18 0.041 17.48 0.46 6.29 0.01 0.05 0.33 0.22 27.34 0.08 0.03 0.22 0.08 <td>VT2/12</td> <td>0.049</td> <td>18.55</td> <td>3.76</td> <td>9.01</td> <td>0.43</td> <td>2.43</td> <td>27.36</td> <td>0.113</td> <td>0.081</td> <td>1.48</td> <td>63.26</td> <td>39.00</td> <td>81</td>	VT2/12	0.049	18.55	3.76	9.01	0.43	2.43	27.36	0.113	0.081	1.48	63.26	39.00	81
VT3B/12 0.045 18.06 2.34 10.57 0.06 1.54 36.55 0.100 0.090 1.98 71.735 39.39 50 VT4/12 0.040 17.15 1.45 12.16 0.21 2.766 0.031 0.055 1.09 60.85 38.46 128 M5 0.012 2.125 0.12 1.50 0.01 0.44 30.09 0.005 0.048 0.42 53.49 42.27 52 M7 0.015 20.75 0.20 0.01 0.01 0.01 0.011 0.033 0.44 71.61 31.58 56 M15 0.008 21.73 0.03 0.12 0.007 0.03 0.02 0.036 0.04 0.059 42.2 58 M18 0.041 17.48 0.46 6.29 0.01 0.05 0.054 0.54 52.77 1.76 43 M20 0.055 18.62 2.40 12.56 0.00 0.01	VT3A/12	0.033	18.02	1.35	7.84	0.31	2.33	28.49	0.079	0.077	1.34	59.87	38.06	93
VT4/12 0.040 17.15 1.45 12.16 0.21 2.07 27.60 0.13 0.067 1.06 61.91 37.29 95 M1 0.036 18.40 1.30 12.15 0.01 0.02 0.05 0.09 0.055 1.09 60.85 38.46 128 M5 0.012 21.25 0.12 1.05 0.01 0.14 29.71 0.012 0.04 6.25 54.3 1.161 46 M11 0.043 15.78 1.19 27.75 0.02 0.02 26.30 0.011 0.03 0.47 71.61 31.58 56 M15 0.008 21.07 0.09 1.18 0.00 0.03 30.14 0.027 0.38 53.37 79.99 269 M19 0.009 21.60 0.36 0.00 0.32 0.006 0.42 0.45 52.77 41.76 43 M20 0.055 18.62 2.40 12.56	VT3B/12	0.045	18.06	2.34	10.57	0.06	1.54	36.95	0.100	0.090	1.98	71.735	39.39	50
M1 0.036 18.40 1.30 12.13 0.02 0.12 27.66 0.031 0.055 1.09 60.85 38.46 128 M5 0.012 21.25 0.12 1.50 0.01 0.04 30.09 0.005 0.048 0.42 53.49 42.27 52 M7 0.035 20.75 0.20 0.01 0.01 20.02 0.63 0.011 0.03 0.47 1.61 31.88 56 M15 0.008 21.73 0.03 0.12 0.00 0.01 30.14 0.007 0.36 0.39 52.96 42.24 58 M18 0.001 17.48 0.46 6.29 0.01 0.02 0.026 0.45 52.77 41.76 43 M20 0.055 18.62 2.40 12.56 0.30 0.22 7.34 0.024 0.54 52.59 44.16 46 V10/12 0.049 2.56 0.45 51.47	VT4/12	0.040	17.15	1.45	12.16	0.21	2.07	27.60	0.103	0.067	1.06	61.91	37.29	95
M5 0.012 21.25 0.12 1.50 0.01 0.04 30.09 0.005 0.048 0.42 53.49 42.27 52 M7 0.015 20.75 0.20 3.01 0.01 0.14 29.71 0.012 0.044 0.62 54.53 41.61 46 M11 0.043 15.78 1.03 0.12 0.00 0.01 10.19 0.033 0.026 0.44 52.56 42.69 56 M17 0.012 21.07 0.09 1.18 0.00 0.03 30.14 0.007 0.36 0.39 52.96 42.24 58 M18 0.041 17.48 0.46 6.29 0.01 0.05 8.02 0.05 8.33.7 39.95 49 M20 0.015 18.62 2.40 12.56 0.03 0.22 7.34 0.82 0.58 0.54 51.47 4.14 46 V10/12 0.048 25.68 0.45 <	M1	0.036	18.40	1.30	12.13	0.02	0.12	27.66	0.031	0.055	1.09	60.85	38.46	128
M7 0.015 20.75 0.20 3.01 0.01 2.14 2.9.71 0.012 0.064 0.62 54.53 41.61 46 M11 0.043 15.78 1.19 27.75 0.02 0.02 26.30 0.011 0.033 0.47 71.61 31.58 56 M15 0.008 21.77 0.09 1.18 0.00 1.003 30.14 0.007 0.036 0.39 52.96 42.24 58 M18 0.041 1.748 0.46 6.29 0.01 0.05 30.20 0.006 0.42 0.45 52.77 41.76 43 M20 0.055 18.62 2.40 12.56 0.03 0.22 27.34 0.082 0.054 0.54 52.59 44.16 46 V1012 0.009 12.12 0.02 0.01 30.12 10.01 0.01 10.02 0.024 0.35 70.23 30.21 149 V15/12 0.009 </td <td>M5</td> <td>0.012</td> <td>21.25</td> <td>0.12</td> <td>1.50</td> <td>0.01</td> <td>0.04</td> <td>30.09</td> <td>0.005</td> <td>0.048</td> <td>0.42</td> <td>53.49</td> <td>42.27</td> <td>52</td>	M5	0.012	21.25	0.12	1.50	0.01	0.04	30.09	0.005	0.048	0.42	53.49	42.27	52
M11 0.043 15.78 1.19 27.75 0.02 0.02 26.30 0.011 0.033 0.47 71.61 31.58 56 M15 0.008 21.73 0.03 0.12 0.00 0.01 30.19 0.003 0.026 0.44 52.56 42.64 58 M18 0.041 17.48 0.46 6.29 0.01 0.05 28.34 0.027 0.867 0.35 53.37 39.99 269 M19 0.005 18.62 2.40 12.56 0.03 0.22 27.34 0.82 0.036 1.05 62.39 39.56 49 M20 0.055 18.62 2.40 12.56 0.01 14.07 0.001 0.024 0.79 92.55 2.089 39 V17/12 0.099 19.21 0.23 14.36 0.01 0.11 4.07 0.021 0.31 0.01 0.33 0.021 0.31 0.021 0.31 0.021 0.31	M7	0.015	20.75	0.20	3.01	0.01	0.14	29.71	0.012	0.064	0.62	54.53	41.61	46
M15 0.008 21.73 0.03 0.12 0.00 0.01 30.19 0.003 0.026 0.44 52.56 42.64 55 M17 0.012 21.07 0.09 1.18 0.00 0.03 30.14 0.007 0.036 0.39 52.96 42.24 58 M18 0.041 17.48 0.46 6.29 0.01 0.05 8.34 0.07 0.087 0.58 53.37 39.99 269 M19 0.009 21.60 0.05 0.36 0.00 0.01 0.05 0.54 62.39 34.16 46 M20 0.055 18.62 2.40 12.56 0.00 0.01 30.25 0.001 0.54 52.59 20.89 39 V15/12 0.099 19.21 0.23 14.36 0.01 30.13 0.001 0.014 27.97 0.024 0.35 70.23 30.21 149 V17/12 0.009 21.73 1.32 <td>M11</td> <td>0.043</td> <td>15.78</td> <td>1.19</td> <td>27.75</td> <td>0.02</td> <td>0.02</td> <td>26.30</td> <td>0.011</td> <td>0.033</td> <td>0.47</td> <td>71.61</td> <td>31.58</td> <td>56</td>	M11	0.043	15.78	1.19	27.75	0.02	0.02	26.30	0.011	0.033	0.47	71.61	31.58	56
M17 0.012 21.07 0.09 1.18 0.00 0.03 30.14 0.007 0.036 0.39 52.96 42.24 58 M18 0.041 17.48 0.46 6.29 0.01 0.05 28.34 0.027 0.087 0.58 53.37 39.99 269 M19 0.009 21.60 0.05 0.36 0.00 0.05 30.20 0.066 0.042 0.45 52.77 41.76 43 M20 0.055 18.62 2.40 12.56 0.00 0.01 30.25 0.005 0.054 0.54 52.59 44.16 46 V10/12 0.048 25.68 0.45 51.47 0.01 0.01 14.07 0.001 0.01 0.021 0.01 0.024 0.54 52.57 44.16 68 V10/12 0.059 14.73 1.32 28.73 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01	M15	0.008	21.73	0.03	0.12	0.00	0.01	30.19	0.003	0.026	0.44	52.56	42.69	56
M18 0.041 17.48 0.46 6.29 0.01 0.05 28.34 0.027 0.087 0.58 53.37 39.99 269 M19 0.009 21.60 0.05 0.36 0.00 0.05 30.20 0.006 0.42 0.45 52.77 41.76 43 M20 0.055 18.62 2.40 12.56 0.03 0.22 27.34 0.024 0.45 52.59 44.16 46 V10/12 0.048 25.68 0.45 51.47 0.01 0.01 14.07 0.001 0.038 0.47 62.78 36.73 80 V17/12 0.059 14.73 1.32 28.73 0.02 0.021 0.038 0.47 62.78 36.21 14.94 V19/12 0.009 21.72 0.07 0.39 0.00 0.01 24.97 0.022 0.024 0.55 71.2 41.34 44 V23/12 0.003 17.97 1.78 <td< td=""><td>M17</td><td>0.012</td><td>21.07</td><td>0.09</td><td>1.18</td><td>0.00</td><td>0.03</td><td>30.14</td><td>0.007</td><td>0.036</td><td>0.39</td><td>52.96</td><td>42.24</td><td>58</td></td<>	M17	0.012	21.07	0.09	1.18	0.00	0.03	30.14	0.007	0.036	0.39	52.96	42.24	58
M19 0.009 21.60 0.05 0.36 0.00 0.05 30.20 0.006 0.42 0.45 52.77 41.76 43 M20 0.055 18.62 2.40 12.56 0.03 0.22 27.34 0.082 0.036 1.05 62.39 39.56 49 M22 0.011 21.24 0.08 0.40 0.00 0.01 30.25 0.005 0.54 0.54 52.59 44.16 46 V10/12 0.048 25.68 0.45 51.47 0.01 0.01 14.07 0.001 0.24 0.79 92.55 20.89 39 V15/12 0.099 14.71 1.32 28.73 0.02 0.01 28.36 0.011 0.313 0.005 0.21 0.41 52.77 41.94 48 V21/12 0.008 22.99 0.11 4.48 0.00 0.04 27.50 0.016 0.016 0.50 57.12 41.34 44	M18	0.041	17.48	0.46	6.29	0.01	0.05	28.34	0.027	0.087	0.58	53.37	39.99	269
M20 0.055 18.62 2.40 12.56 0.03 0.22 27.34 0.082 0.036 1.05 62.39 39.56 49 M22 0.011 21.24 0.08 0.40 0.00 0.01 30.25 0.005 0.054 0.54 52.59 44.16 46 V10/12 0.048 25.68 0.45 51.47 0.01 0.01 14.07 0.001 0.024 0.79 92.55 20.89 39 V15/12 0.099 19.21 0.23 14.36 0.01 0.01 24.97 0.022 0.024 0.35 70.23 30.21 149 V19/12 0.008 22.29 0.11 4.48 0.00 0.04 29.67 0.005 0.019 0.55 51.12 41.34 44 V23/12 0.037 17.97 1.78 15.80 0.01 30.19 0.055 0.02 0.73 52.93 44.38 56 V28/12 0.017	M19	0.009	21.60	0.05	0.36	0.00	0.05	30.20	0.006	0.042	0.45	52.77	41.76	43
M22 0.011 21.24 0.08 0.40 0.00 0.01 30.25 0.005 0.054 0.54 52.59 44.16 46 V10/12 0.048 25.68 0.45 51.47 0.01 0.01 14.07 0.001 0.024 0.79 92.55 20.89 39 V15/12 0.099 19.21 0.23 14.36 0.01 0.01 28.36 0.001 0.038 0.47 62.78 36.73 80 V17/12 0.099 14.73 1.32 28.73 0.02 0.01 30.13 0.005 0.014 52.77 41.94 68 V21/12 0.008 22.29 0.11 4.48 0.00 0.04 29.67 0.050 0.019 0.50 57.12 41.34 44 V26/12 0.012 21.33 0.07 0.56 0.00 0.11 30.19 0.020 0.73 52.93 44.38 56 V28/12 0.017 17.49	M20	0.055	18.62	2.40	12.56	0.03	0.22	27.34	0.082	0.036	1.05	62.39	39.56	49
V10/12 0.048 25.68 0.45 51.47 0.01 14.07 0.01 0.024 0.79 92.55 20.89 39 V15/12 0.099 19.21 0.23 14.36 0.01 28.36 0.001 0.038 0.47 62.78 36.73 80 V17/12 0.059 14.73 1.32 28.73 0.02 0.01 24.97 0.022 0.024 0.35 70.23 30.21 149 V19/12 0.009 21.72 0.07 0.39 0.00 0.01 30.13 0.005 0.01 0.41 52.77 41.94 68 V21/12 0.008 22.29 0.11 4.48 0.00 0.04 25.67 0.005 0.01 0.41 52.77 41.34 44 V23/12 0.017 17.97 1.78 15.80 0.01 0.03 29.53 0.016 0.02 0.73 52.93 44.38 56 V28/12 0.017 17.04	M22	0.011	21.24	0.08	0.40	0.00	0.01	30.25	0.005	0.054	0.54	52.59	44.16	46
V15/12 0.099 19.21 0.23 14.36 0.01 0.01 28.36 0.001 0.038 0.47 62.78 36.73 80 V17/12 0.059 14.73 1.32 28.73 0.02 0.01 24.97 0.022 0.024 0.35 70.23 30.21 149 V19/12 0.009 21.72 0.07 0.39 0.00 0.01 30.13 0.005 0.01 0.41 52.77 41.94 68 V21/12 0.008 22.29 0.11 4.48 0.00 0.04 29.67 0.05 0.01 0.55 57.12 41.34 44 V23/12 0.037 17.97 1.78 15.80 0.01 0.14 27.30 0.046 0.016 0.76 63.86 38.51 64 V26/12 0.017 19.49 0.81 6.85 0.01 0.03 29.53 0.016 0.023 0.77 55.07 38.41 289 V30/12 0.010 21.34 0.05 0.97 0.00 0.07 30.07 0.026	V10/12	0.048	25.68	0.45	51.47	0.01	0.01	14.07	0.001	0.024	0.79	92.55	20.89	39
V17/12 0.059 14.73 1.32 28.73 0.02 0.01 24.97 0.022 0.024 0.35 70.23 30.21 149 V19/12 0.009 21.72 0.07 0.39 0.00 0.01 30.13 0.005 0.021 0.41 52.77 41.94 68 V21/12 0.008 22.29 0.11 4.48 0.00 0.04 29.67 0.055 0.016 0.76 63.86 38.51 64 V23/12 0.037 17.97 1.78 15.80 0.01 0.14 27.30 0.046 0.016 0.76 63.86 38.51 64 V26/12 0.012 21.33 0.07 0.56 0.00 0.01 30.19 0.005 0.020 0.73 52.93 44.38 56 V28/12 0.037 17.04 0.61 23.37 0.01 0.03 29.53 0.016 0.023 0.77 53.31 41.92 42 V30/12 0.010 21.34 0.05 0.97 0.00 0.07 30.07 0.026	V15/12	0.099	19.21	0.23	14.36	0.01	0.01	28.36	0.001	0.038	0.47	62.78	36.73	80
V19/12 0.009 21.72 0.07 0.39 0.00 0.01 30.13 0.005 0.021 0.41 52.77 41.94 68 V21/12 0.008 22.29 0.11 4.48 0.00 0.04 29.67 0.005 0.019 0.50 57.12 41.34 44 V23/12 0.037 1.797 1.78 15.80 0.01 0.14 27.30 0.046 0.016 0.76 63.86 38.51 64 V26/12 0.012 21.33 0.07 0.56 0.00 0.01 30.19 0.005 0.020 0.73 52.93 44.38 56 V28/12 0.037 17.04 0.61 23.37 0.01 0.04 27.50 0.007 0.019 0.59 69.22 37.04 66 V30/12 0.077 19.49 0.81 6.85 0.01 0.03 29.53 0.016 0.023 0.77 53.31 41.92 42 V35/12 0.051 16.54 0.18 10.47 0.01 20.17 10.022 0.32	V17/12	0.059	14.73	1.32	28.73	0.02	0.01	24.97	0.022	0.024	0.35	70.23	30.21	149
V21/12 0.008 22.29 0.11 4.48 0.00 0.04 29.67 0.005 0.019 0.50 57.12 41.34 44 V23/12 0.037 17.97 1.78 15.80 0.01 0.14 27.30 0.046 0.016 0.76 63.86 38.51 64 V26/12 0.012 21.33 0.07 0.56 0.00 0.01 30.19 0.005 0.20 0.73 52.93 44.38 56 V28/12 0.037 17.04 0.61 23.37 0.01 0.04 27.50 0.007 0.019 0.59 69.22 37.04 66 V30/12 0.077 19.49 0.81 6.85 0.01 0.03 29.53 0.016 0.023 0.77 53.31 41.92 42 V35/12 0.051 16.54 0.18 10.47 0.01 27.71 0.022 0.32 0.75 55.77 38.41 289 V35/12 0.051 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.36	V19/12	0.009	21.72	0.07	0.39	0.00	0.01	30.13	0.005	0.021	0.41	52.77	41.94	68
V23/12 0.037 17.97 1.78 15.80 0.01 0.14 27.30 0.046 0.016 0.76 63.86 38.51 64 V26/12 0.012 21.33 0.07 0.56 0.00 0.01 30.19 0.005 0.020 0.73 52.93 44.38 56 V28/12 0.037 17.04 0.61 23.37 0.01 0.04 27.50 0.007 0.019 0.59 69.22 37.04 66 V30/12 0.010 21.34 0.05 0.97 0.00 0.07 30.07 0.026 0.77 53.31 41.92 42 V35/12 0.051 16.54 0.18 10.47 0.01 27.71 0.022 0.023 0.75 55.77 38.41 289 V36/12 0.072 15.75 3.29 23.02 0.37 1.50 26.08 0.202 0.263 2.63 73.18 34.66 62 V37/12 0.062 16.56 3.77 24.71 0.06 1.38 25.69 0.054 0.028 0.68 <td>V21/12</td> <td>0.008</td> <td>22.29</td> <td>0.11</td> <td>4.48</td> <td>0.00</td> <td>0.04</td> <td>29.67</td> <td>0.005</td> <td>0.019</td> <td>0.50</td> <td>57.12</td> <td>41.34</td> <td>44</td>	V21/12	0.008	22.29	0.11	4.48	0.00	0.04	29.67	0.005	0.019	0.50	57.12	41.34	44
V26/12 0.012 21.33 0.07 0.56 0.00 0.01 30.19 0.005 0.020 0.73 52.93 44.38 56 V28/12 0.037 17.04 0.61 23.37 0.01 0.04 27.50 0.007 0.019 0.59 69.22 37.04 66 V30/12 0.017 19.49 0.81 6.85 0.01 0.03 29.53 0.016 0.023 0.77 57.60 41.51 64 V32/12 0.010 21.34 0.05 0.97 0.00 0.07 30.07 0.026 0.77 53.31 41.92 42 V35/12 0.051 16.54 0.18 10.47 0.01 0.01 27.71 0.022 0.032 0.75 55.77 38.41 289 V36/12 0.062 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.036 2.75 74.91 34.81 64 V39/12 0.066 14.07 1.13 23.07 0.03 0.16 25.69 0.054 0.28	V23/12	0.037	17.97	1.78	15.80	0.01	0.14	27.30	0.046	0.016	0.76	63.86	38.51	64
V28/12 0.037 17.04 0.61 23.37 0.01 0.04 27.50 0.007 0.019 0.59 69.22 37.04 66 V30/12 0.077 19.49 0.81 6.85 0.01 0.03 29.53 0.016 0.023 0.77 57.60 41.51 64 V32/12 0.010 21.34 0.05 0.97 0.00 0.07 30.07 0.026 0.77 53.31 41.92 42 V35/12 0.051 16.54 0.18 10.47 0.01 27.71 0.022 0.32 0.75 55.77 38.41 289 V36/12 0.062 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.036 2.75 74.91 34.81 64 V39/12 0.066 14.07 1.13 23.07 0.03 0.16 25.69 0.054 0.28 0.68 64.98 32.87 271 V42/12 0.019 20.38 0.21 4.87 0.01 24.87 0.005 0.026 0.40 76.4	V26/12	0.012	21.33	0.07	0.56	0.00	0.01	30.19	0.005	0.020	0.73	52.93	44.38	56
V30/120.07719.490.816.850.010.0329.530.0160.0230.7757.6041.5164V32/120.01021.340.050.970.000.0730.070.0050.0260.7753.3141.9242V35/120.05116.540.1810.470.010.0127.710.0220.0320.7555.7738.41289V36/120.07215.753.2923.020.371.5026.080.2020.2632.6373.1834.6662V37/120.06216.563.7724.710.061.3825.360.2260.0362.7574.9134.8164V39/120.06614.071.1323.070.030.1625.690.0540.0280.6864.9832.87271V42/120.01920.380.214.870.010.4429.350.0380.0240.7256.0643.8544V44/12Grey0.06113.650.8536.760.010.0124.870.0050.0260.4076.6423.2757V44/12Cream0.02718.600.4614.510.000.0728.430.0100.0250.5461.6439.4751V46/120.05115.831.0527.620.010.0126.370.0180.3156.2639.5046V50/120.02319.560.1	V28/12	0.037	17.04	0.61	23.37	0.01	0.04	27.50	0.007	0.019	0.59	69.22	37.04	66
V32/12 0.010 21.34 0.05 0.97 0.00 0.07 30.07 0.005 0.026 0.77 53.31 41.92 42 V35/12 0.051 16.54 0.18 10.47 0.01 0.01 27.71 0.022 0.032 0.75 55.77 38.41 289 V36/12 0.072 15.75 3.29 23.02 0.37 1.50 26.08 0.202 0.263 2.63 73.18 34.66 62 V37/12 0.062 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.036 2.75 74.91 34.81 64 V39/12 0.066 14.07 1.13 23.07 0.03 0.16 25.69 0.054 0.028 0.68 64.98 32.87 271 V42/12 0.019 20.38 0.21 4.87 0.01 24.87 0.005 0.026 0.40 76.64 23.27 57 V44/12Grey 0.061 13.65 0.85 36.76 0.01 0.01 26.37 0.020 0.	V30/12	0.077	19.49	0.81	6.85	0.01	0.03	29.53	0.016	0.023	0.77	57.60	41.51	64
V35/12 0.051 16.54 0.18 10.47 0.01 0.01 27.71 0.022 0.032 0.75 55.77 38.41 289 V36/12 0.072 15.75 3.29 23.02 0.37 1.50 26.08 0.202 0.263 2.63 73.18 34.66 62 V37/12 0.062 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.036 2.75 74.91 34.81 64 V39/12 0.066 14.07 1.13 23.07 0.03 0.16 25.69 0.054 0.028 0.68 64.98 32.87 271 V42/12 0.019 20.38 0.21 4.87 0.01 0.44 29.35 0.038 0.024 0.72 56.06 43.85 44 V44/12Grey 0.061 13.65 0.85 36.76 0.01 0.01 24.87 0.005 0.026 0.40 76.64 23.27 57 V44/12Cream 0.027 18.60 0.46 14.51 0.00 0.07 28.43 <	V32/12	0.010	21.34	0.05	0.97	0.00	0.07	30.07	0.005	0.026	0.77	53.31	41.92	42
V36/12 0.072 15.75 3.29 23.02 0.37 1.50 26.08 0.202 0.263 2.63 73.18 34.66 62 V37/12 0.062 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.036 2.75 74.91 34.81 64 V39/12 0.066 14.07 1.13 23.07 0.03 0.16 25.69 0.054 0.028 0.68 64.98 32.87 271 V42/12 0.019 20.38 0.21 4.87 0.01 0.44 29.35 0.038 0.024 0.72 56.06 43.85 44 V44/12Grey 0.061 13.65 0.85 36.76 0.01 0.01 24.87 0.005 0.026 0.40 76.64 23.27 57 V44/12Cream 0.027 18.60 0.46 14.51 0.00 0.07 28.43 0.010 0.020 0.62 62.75 24.89 45 V46/12 0.051 15.83 1.05 27.62 0.01 0.01 26.37 <t< td=""><td>V35/12</td><td>0.051</td><td>16.54</td><td>0.18</td><td>10.47</td><td>0.01</td><td>0.01</td><td>27.71</td><td>0.022</td><td>0.032</td><td>0.75</td><td>55.77</td><td>38.41</td><td>289</td></t<>	V35/12	0.051	16.54	0.18	10.47	0.01	0.01	27.71	0.022	0.032	0.75	55.77	38.41	289
V37/12 0.062 16.56 3.77 24.71 0.06 1.38 25.36 0.226 0.036 2.75 74.91 34.81 64 V39/12 0.066 14.07 1.13 23.07 0.03 0.16 25.69 0.054 0.028 0.68 64.98 32.87 271 V42/12 0.019 20.38 0.21 4.87 0.01 0.44 29.35 0.038 0.024 0.72 56.06 43.85 44 V44/12Grey 0.061 13.65 0.85 36.76 0.01 0.01 24.87 0.005 0.026 0.40 76.64 23.27 57 V44/12Cream 0.027 18.60 0.46 14.51 0.00 0.07 28.43 0.010 0.020 0.62 62.75 24.89 45 V46/12 0.051 15.83 1.05 27.62 0.01 0.01 26.37 0.012 0.036 0.50 71.49 30.34 52 V48/12 0.042 18.39 1.80 13.09 0.02 0.39 27.27 <t< td=""><td>V36/12</td><td>0.072</td><td>15.75</td><td>3.29</td><td>23.02</td><td>0.37</td><td>1.50</td><td>26.08</td><td>0.202</td><td>0.263</td><td>2.63</td><td>73.18</td><td>34.66</td><td>62</td></t<>	V36/12	0.072	15.75	3.29	23.02	0.37	1.50	26.08	0.202	0.263	2.63	73.18	34.66	62
V39/120.06614.071.1323.070.030.1625.690.0540.0280.6864.9832.87271V42/120.01920.380.214.870.010.4429.350.0380.0240.7256.0643.8544V44/12Grey0.06113.650.8536.760.010.0124.870.0050.0260.4076.6423.2757V44/12Cream0.02718.600.4614.510.000.0728.430.0100.0200.6262.7524.8945V46/120.05115.831.0527.620.010.0126.370.0120.0360.5071.4930.3452V48/120.04218.391.8013.090.020.3927.270.0710.0250.5461.6439.4751V50/120.02319.560.126.310.010.6029.270.0450.0180.3156.2639.5046V51/120.04617.302.2718.530.010.0726.680.0570.0180.4165.3936.7344V52/120.03918.240.5413.240.000.0227.840.0080.0280.4960.4535.0946V53/120.03918.131.8513.120.020.2327.310.0530.0240.6061.3737.6649V54/120.05020.	V37/12	0.062	16.56	3.77	24.71	0.06	1.38	25.36	0.226	0.036	2.75	74.91	34.81	64
V42/120.01920.380.214.870.010.4429.350.0380.0240.7256.0643.8544V44/12Grey0.06113.650.8536.760.010.0124.870.0050.0260.4076.6423.2757V44/12Cream0.02718.600.4614.510.000.0728.430.0100.0200.6262.7524.8945V46/120.05115.831.0527.620.010.0126.370.0120.0360.5071.4930.3452V48/120.04218.391.8013.090.020.3927.270.0710.0250.5461.6439.4751V50/120.02319.560.126.310.010.6029.270.0450.0180.3156.2639.5046V51/120.04617.302.2718.530.010.0726.680.0570.0180.4165.3936.7344V52/120.03918.240.5413.240.000.0227.840.0080.0280.4960.4535.0946V53/120.03918.131.8513.120.020.2327.310.0530.0240.6061.3737.6649V54/120.05020.420.285.520.010.2729.320.0200.0190.3656.2638.2941	V39/12	0.066	14.07	1.13	23.07	0.03	0.16	25.69	0.054	0.028	0.68	64.98	32.87	271
V44/12Grey 0.061 13.65 0.85 36.76 0.01 0.01 24.87 0.005 0.026 0.40 76.64 23.27 57 V44/12Cream 0.027 18.60 0.46 14.51 0.00 0.07 28.43 0.010 0.020 0.62 62.75 24.89 45 V46/12 0.051 15.83 1.05 27.62 0.01 0.01 26.37 0.012 0.036 0.50 71.49 30.34 52 V48/12 0.042 18.39 1.80 13.09 0.02 0.39 27.27 0.071 0.025 0.54 61.64 39.47 51 V50/12 0.023 19.56 0.12 6.31 0.01 0.60 29.27 0.045 0.018 0.31 56.26 39.50 46 V51/12 0.046 17.30 2.27 18.53 0.01 0.07 26.68 0.057 0.018 0.41 65.39 36.73 44 V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 <td< td=""><td>V42/12</td><td>0.019</td><td>20.38</td><td>0.21</td><td>4.87</td><td>0.01</td><td>0.44</td><td>29.35</td><td>0.038</td><td>0.024</td><td>0.72</td><td>56.06</td><td>43.85</td><td>44</td></td<>	V42/12	0.019	20.38	0.21	4.87	0.01	0.44	29.35	0.038	0.024	0.72	56.06	43.85	44
V44/12Cream 0.027 18.60 0.46 14.51 0.00 0.07 28.43 0.010 0.020 0.62 62.75 24.89 45 V46/12 0.051 15.83 1.05 27.62 0.01 0.01 26.37 0.012 0.036 0.50 71.49 30.34 52 V48/12 0.042 18.39 1.80 13.09 0.02 0.39 27.27 0.071 0.025 0.54 61.64 39.47 51 V50/12 0.023 19.56 0.12 6.31 0.01 0.60 29.27 0.045 0.018 0.31 56.26 39.50 46 V51/12 0.046 17.30 2.27 18.53 0.01 0.07 26.68 0.057 0.018 0.41 65.39 36.73 44 V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 0.008 0.028 0.49 60.45 35.09 46 V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.0	V44/12Grey	0.061	13.65	0.85	36.76	0.01	0.01	24.87	0.005	0.026	0.40	76.64	23.27	57
V46/12 0.051 15.83 1.05 27.62 0.01 0.01 26.37 0.012 0.036 0.50 71.49 30.34 52 V48/12 0.042 18.39 1.80 13.09 0.02 0.39 27.27 0.071 0.025 0.54 61.64 39.47 51 V50/12 0.023 19.56 0.12 6.31 0.01 0.60 29.27 0.045 0.018 0.31 56.26 39.50 46 V51/12 0.046 17.30 2.27 18.53 0.01 0.07 26.68 0.057 0.018 0.41 65.39 36.73 44 V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 0.008 0.028 0.49 60.45 35.09 46 V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.053 0.024 0.60 61.37 37.66 49 V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 <td>V44/12Cream</td> <td>0.027</td> <td>18.60</td> <td>0.46</td> <td>14.51</td> <td>0.00</td> <td>0.07</td> <td>28.43</td> <td>0.010</td> <td>0.020</td> <td>0.62</td> <td>62.75</td> <td>24.89</td> <td>45</td>	V44/12Cream	0.027	18.60	0.46	14.51	0.00	0.07	28.43	0.010	0.020	0.62	62.75	24.89	45
V48/12 0.042 18.39 1.80 13.09 0.02 0.39 27.27 0.071 0.025 0.54 61.64 39.47 51 V50/12 0.023 19.56 0.12 6.31 0.01 0.60 29.27 0.045 0.018 0.31 56.26 39.50 46 V51/12 0.046 17.30 2.27 18.53 0.01 0.07 26.68 0.057 0.018 0.41 65.39 36.73 44 V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 0.008 0.028 0.49 60.45 35.09 46 V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.053 0.024 0.60 61.37 37.66 49 V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 0.019 0.36 56.26 38.29 41	V46/12	0.051	15.83	1.05	27.62	0.01	0.01	26.37	0.012	0.036	0.50	71.49	30.34	52
V50/12 0.023 19.56 0.12 6.31 0.01 0.60 29.27 0.045 0.018 0.31 56.26 39.50 46 V51/12 0.046 17.30 2.27 18.53 0.01 0.07 26.68 0.057 0.018 0.41 65.39 36.73 44 V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 0.008 0.028 0.49 60.45 35.09 46 V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.053 0.024 0.60 61.37 37.66 49 V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 0.019 0.36 56.26 38.29 41	V48/12	0.042	18.39	1.80	13.09	0.02	0.39	27.27	0.071	0.025	0.54	61.64	39.47	51
V51/12 0.046 17.30 2.27 18.53 0.01 0.07 26.68 0.057 0.018 0.41 65.39 36.73 44 V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 0.008 0.028 0.49 60.45 35.09 46 V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.053 0.024 0.60 61.37 37.66 49 V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 0.019 0.36 56.26 38.29 41	V50/12	0.023	19.56	0.12	6.31	0.01	0.60	29.27	0.045	0.018	0.31	56.26	39.50	46
V52/12 0.039 18.24 0.54 13.24 0.00 0.02 27.84 0.008 0.028 0.49 60.45 35.09 46 V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.053 0.024 0.60 61.37 37.66 49 V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 0.019 0.36 56.26 38.29 41	V51/12	0.046	17.30	2.27	18.53	0.01	0.07	26.68	0.057	0.018	0.41	65.39	36.73	44
V53/12 0.039 18.13 1.85 13.12 0.02 0.23 27.31 0.053 0.024 0.60 61.37 37.66 49 V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 0.019 0.36 56 26 38 29 41	V52/12	0.039	18.24	0.54	13.24	0.00	0.02	27.84	0.008	0.028	0.49	60.45	35.09	46
V54/12 0.050 20.42 0.28 5.52 0.01 0.27 29.32 0.020 0.019 0.36 56.26 38.29 41	V53/12	0.039	18.13	1.85	13.12	0.02	0.23	27.31	0.053	0.024	0.60	61.37	37.66	49
	V54/12	0.050	20.42	0.28	5.52	0.01	0.27	29.32	0.020	0.019	0.36	56.26	38.29	41
V55/12 0.051 17.03 1.98 17.49 0.01 0.01 26.55 0.031 0.016 0.44 63.61 34.49 45	V55/12	0.051	17.03	1.98	17.49	0.01	0.01	26.55	0.031	0.016	0.44	63.61	34.49	45
V56/12 0.036 19.08 1.26 11.15 0.01 0.17 28.01 0.033 0.027 0.36 60.13 36.43 42	V56/12	0.036	19.08	1.26	11.15	0.01	0.17	28.01	0.033	0.027	0.36	60.13	36.43	42
V57/12 0.035 19.51 0.97 9.28 0.01 0.26 28.51 0.037 0.031 0.42 59.06 38.53 42	V57/12	0.035	19.51	0.97	9.28	0.01	0.26	28.51	0.037	0.031	0.42	59.06	38.53	42

ID	Ni	Cu	Со	Zn	Pb	Li	Cd	Мо	Ga	Sb	V	Rb	Ba
VT 2/12	16	7	12.9	20	10.8	13	0.082	0.4	4.4	0.34	33	28	170
VT 3B/12	12	7	15.9	17	6.8	9	0.074	0.4	7.5	0.22	26	22	464
VT 4/12	9	101	19.8	17	6.5	6	0.068	0.4	3.9	0.24	47	22	141
VT 34/12	12	8	13.4	17	6.2	8	0.09	0.4	4.4	0.24	35	18	216
M.1	8	7	9.7	12	8.4	20	0.069	0.3	70.8	0.19	17	6	9550
M.5	4	24	6.1	12	4.5	18	0.109	0.4	1.8	0.33	16	2	86
M.7	5	9	9.9	9	8.2	11	0.067	1.2	0.7	0.12	13	2	30
M.11	4	8	8.8	10	2.6	12	0.004	0.2	7.1	0.12	11	2	520
M.15	6	11	7.8	10	7.1	33	0.053	0.3	56	0.12	23	11	7389
M.17	5	10	7.8	18	6.7	5	0.03	0.4	30.5	0.1	14	1	4044
M.18	6	9	17.8	15	6.7	11	0.028	0.4	366	0.2	21	2	51515
M.19	4	19	12.5	9	5.6	3	0.023	1.3	2	0.12	11	1	146
M.20	10	74	15.9	15	9.7	28	0.17	0.5	17.6	0.24	26	15	2218
M.22	3	6	35.6	10	7.2	5	0.072	0.3	1.8	0.09	14	2	81
V 1/12	5	10	13.3	12	6	14	0.032	0.6	465	0.1	17	7	64776
V.10/12	5	8	5.4	12	6.3	27	0.026	0.4	3.1	0.12	13	1	189
V 15/12	4	6	15.1	10	6.1	10	0.021	0.2	2.4	0.16	9	0.3	169
V.17/12	4	20	14.7	15	5.5	35	0.19	0.2	170	0.17	15	5	21793
V 19/12	4	7	4.8	11	6.2	8	0.027	0.2	11.7	0.1	18	1	857
V.21/12	5	8	5.8	11	11.5	4	0.115	0.4	1.2	0.12	12	1	71
V 26/12	5	5	4.1	8	4.8	4	0.03	0.6	13	0.08	11	1	1786
V 28/12	6	14	11.8	15	5.2	10	0.135	0.5	14.8	0.17	9	2	1903
V 29/12	4	12	5.1	11	9.5	5	0.09	0.3	2	0.15	11	5	123
V.32/12	8	8	10.3	12	10	4	0.049	2.9	2.1	0.16	13	4	130
V 35/12	6	6	12	9	4.5	5	0.013	0.2	264	0.09	14	1	36249
V 36/12	20	38	19.4	22	5.5	16	0.06	0.7	28	0.29	45	49	3183
V.37/12	19	17	15.6	24	5.6	99	0.145	0.5	49	0.36	38	42	6312
V 39/12	5	25	12.4	14	6	6	0.152	0.6	501	0.16	11	4	70163
V 42/12	6	16	8.1	13	4.6	4	0.105	0.2	2.5	0.19	17	7	151
V 46/12	4	6	25.5	9	4.7	4	0.013	0.3	0.7	0.07	8	1	41
V 48/12	6	24	8.3	21	8.7	53	0.044	0.5	4.9	0.2	18	17	280
V 51/12	4	7	10	12	8	25	0.09	0.3	3.6	0.14	21	13	154
V 52/12	5	21	17	12	6.6	4	0.129	0.2	1.4	0.16	15	2	67
V 53/12	8	10	7.8	15	8.9	17	0.036	0.3	5.9	0.16	16	12	385
V 55/12	6	19	18.7	17	8.3	25	0.168	0.4	2.4	0.23	11	10	116
V 56/12	4	8	11	13	7.5	17	0.038	0.2	1.5	0.12	12	9	57
V 57/12	5	16	11.4	19	9.7	22	0.199	0.3	2.2	0.18	13	9	100
V.44/12	4	9	37.2	10	3.6	5	0.014	0.2	2.7	0.12	30	2	86
V.44/12	4	13	9.1	7	2.9	20	0.008	0.4	1.9	0.12	14	4	94
V.54/12	3	11	4.8	9	4.1	5	0.016	0.2	1.8	0.13	10	5	114
V.30/12	4	7	6.3	7	2.4	3	0.003	0.2	38.4	0.11	11	1	5220
VT.3A/12	10	9	12.3	13	3.7	7	0.052	0.3	4	0.23	30	17	209
V.50/12	3	13	8.4	16	5.1	18	0.018	0.1	2.8	0.18	17	10	126

Table 3Sb. The trace element concentrations (n = 43, in ppm) obtained from Vempalle Formation dolomites.

Elemen	ıt	M.1	M.5	M.7	M.11	M.1	15 N	1.17	M.18	M.19	M.20	M.22	VT 2/12
La		0.147	0.081	0.055	0.037	7 0.08	86 0.	.034 (0.084	0.037	0.126	0.047	0.183
Ce		0.155	0.072	0.057	0.036	5 0.08	84 0.	.038 (0.093	0.034	0.133	0.041	0.202
Pr		0.147	0.057	0.057	0.034	l 0.0′	79 0.	.034 (0.102	0.034	0.136	0.045	0.193
Nd		0.150	0.059	0.053	0.035	5 0.09	91 0.	.035 (0.109	0.032	0.150	0.038	0.212
Sm		0.211	0.068	0.070	0.043	0.13	37 0.	.049 (0.182	0.040	0.222	0.041	0.261
Eu		1.407	0.083	0.074	0.176	5 1.0	19 0.	.574 (6.213	0.074	0.491	0.065	0.333
Gd		0.195	0.067	0.073	0.043	0.1	18 0.	.047 (0.142	0.039	0.197	0.043	0.247
Tb		0.194	0.078	0.078	0.039	0.12	29 0.	.039 (0.155	0.026	0.220	0.039	0.233
Dy		0.190	0.060	0.071	0.041	0.1	15 0	.041 (0.139	0.028	0.207	0.034	0.212
Y		0.181	0.059	0.085	0.044	0.10	07 0.	.048 (0.130	0.033	0.204	0.041	0.211
Но		0.182	0.050	0.071	0.040	0.10	01 0.	.040	0.121	0.030	0.202	0.030	0.202
Er		0.172	0.060	0.067	0.035	5 0.09	98 0.	.039 (0.116	0.021	0.196	0.028	0.189
Tm		0.173	0.049	0.074	0.025	5 0.09	99 0.	.025	0.123	0.025	0.198	0.025	0.173
Yb		0.138	0.043	0.043	0.032	2 0.08	89 0.	.028	0.089	0.014	0.163	0.021	0.163
Lu		0.162	0.046	0.046	0.023	0.09	92 0.	.046 (0.139	0.023	0.162	0.023	0.162
∑REE		3.804	0.932	0.972	0.683	3 2.44	46 1	.117 ′	7.935	0.490	3.006	0.562	3.176
Element	VT3	B/12 V	T 4/12 V	Г 34/12 V	/ 1/12 V	.10/12	V 15/12	2 V.17/1	2 V 19/	12 V.21/1	2 V 26/	12 V 28/1	2 V 29/12
La	0.1	20 (0.120	0.141 ().092 ().246	0.113	0.063	0.07	6 0.050	0.03	9 0.031	0.065
Ce	0.1	26 (0.132	0.155 ().097 (0.165	0.079	0.062	0.05	8 0.048	0.03	9 0.029	0.054
Pr	0.1	13 (0.125	0.147 (0.102 ().136	0.068	0.057	0.05	7 0.045	0.043	5 0.034	0.057
Nd	0.1	12 (0.136	0.150 ().103 (0.127	0.065	0.059	0.05	0 0.047	0.044	4 0.029	0.053
Sm	0.1	42 (0.180	0.177 ().214 (0.132	0.070	0.085	0.05	0 0.056	0.05	9 0.036	0.054
Eu	0.2	2.59 (0.241	0.259	7.824 (0.167	0.111	2.824	0.23	1 0.074	0.28	7 0.287	0.093
Gd	0.1	.44 (0.163	0.180 ().155 (0.142	0.073	0.073	0.05	4 0.054	0.054	4 0.034	0.056
Tb	0.1	55 (0.168	0.181 ().168 (0.116	0.065	0.065	0.05	2 0.052	0.052	2 0.039	0.052
Dy	0.1	45 (0.177	0.167 ().162 ().088	0.053	0.068	0.04	1 0.047	0.05	1 0.028	0.051
Y	0.1	48 (0.156	0.163 ().152 ().096	0.063	0.067	0.04	8 0.056	0.05	5 0.030	0.063
Но	0.1	51 (0.161	0.172 ().151 (0.071	0.050	0.071	0.04	0 0.040	0.040	0.030	0.050
Er	0.1	.44 (0.168	0.158 ().140 ().067	0.049	0.070	0.03	9 0.039	0.04	5 0.028	0.053
Tm	0.1	73 (0.198	0.173 ().148 ().049	0.049	0.074	0.02	5 0.025	0.049	9 0.025	0.049
Yb	0.1	42 (0.163	0.135 ().124 (0.035	0.035	0.064	0.02	8 0.032	0.032	2 0.021	0.039
Lu	0.1	.62 (0.139	0.139 ().185 ().046	0.046	0.092	2 0.02	3 0.023	0.02	3 0.023	0.046
∑REE	2.2	237 2	2.427	2.496	9.817	.682	0.990	3.792	2 0.872	2 0.686	6 0.91	7 0.705	0.835

Table 4S. The PAAS-normalized REE concentrations (ppm) of samples from Vempalle Formation dolomites.

Table 4S.	contd.
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Element	V.32/12	V 35/12	V 36/12	V.37/12	V 39/12	V 42/12	V 46/12	V 48/12	V 51/12	V 52/12	V 53/12
La	0.092	0.060	0.270	0.243	0.071	0.058	0.060	0.139	0.086	0.050	0.115
Ce	0.088	0.067	0.299	0.234	0.065	0.060	0.058	0.127	0.092	0.048	0.114
Pr	0.091	0.079	0.283	0.215	0.057	0.068	0.057	0.125	0.091	0.057	0.125
Nd	0.088	0.083	0.330	0.230	0.065	0.065	0.059	0.127	0.100	0.056	0.124
Sm	0.103	0.157	0.523	0.306	0.137	0.086	0.072	0.155	0.141	0.072	0.151
Eu	0.102	4.926	1.065	1.250	9.806	0.139	0.083	0.194	0.176	0.083	0.241
Gd	0.094	0.127	0.487	0.303	0.088	0.079	0.071	0.144	0.131	0.062	0.133
Tb	0.090	0.155	0.530	0.336	0.090	0.078	0.065	0.142	0.129	0.065	0.129
Dy	0.071	0.143	0.491	0.323	0.085	0.075	0.058	0.137	0.135	0.060	0.120
Y	0.070	0.144	0.441	0.337	0.096	0.085	0.063	0.133	0.148	0.056	0.119
Но	0.061	0.131	0.464	0.323	0.091	0.071	0.061	0.121	0.131	0.050	0.111
Er	0.056	0.119	0.456	0.326	0.098	0.074	0.053	0.123	0.123	0.046	0.123
Tm	0.049	0.123	0.469	0.346	0.099	0.074	0.049	0.123	0.123	0.049	0.123
Yb	0.039	0.096	0.379	0.291	0.071	0.053	0.043	0.110	0.124	0.035	0.099
Lu	0.046	0.139	0.370	0.323	0.139	0.046	0.046	0.115	0.115	0.046	0.115
∑REE	1.140	6.549	6.857	5.386	11.058	1.111	0.896	2.015	1.845	0.835	1.943

Element	V 55/12	V 56/12	V 57/12	V.44/12	V.44/12	V.54/12	V.30/12	VT.3A/12	V.50/12
La	0.230	0.089	0.092	0.045	0.052	0.063	0.031	0.136	0.063
Ce	0.190	0.084	0.080	0.039	0.052	0.053	0.024	0.148	0.055
Pr	0.147	0.091	0.079	0.045	0.057	0.057	0.023	0.136	0.057
Nd	0.153	0.088	0.080	0.038	0.053	0.050	0.024	0.147	0.062
Sm	0.142	0.112	0.094	0.040	0.074	0.058	0.032	0.175	0.074
Eu	0.167	0.130	0.120	0.056	0.102	0.083	0.769	0.259	0.093
Gd	0.146	0.105	0.092	0.043	0.069	0.056	0.028	0.167	0.073
Tb	0.129	0.116	0.103	0.039	0.078	0.065	0.026	0.168	0.065
Dy	0.115	0.109	0.096	0.036	0.068	0.053	0.019	0.160	0.066
Y	0.130	0.137	0.122	0.041	0.070	0.067	0.030	0.170	0.081
Но	0.101	0.111	0.101	0.030	0.061	0.050	0.020	0.151	0.061
Er	0.126	0.112	0.098	0.028	0.056	0.049	0.021	0.154	0.070
Tm	0.123	0.123	0.099	0.025	0.049	0.049	0.025	0.173	0.074
Yb	0.096	0.099	0.089	0.021	0.046	0.046	0.014	0.138	0.060
Lu	0.092	0.115	0.092	0.023	0.046	0.046	0.023	0.139	0.069
∑REE	2.089	1.623	1.438	0.548	0.933	0.845	1.108	2.423	1.023

ID	δ ¹³ C (‰ PDB)	δ ¹⁸ O (‰ PDB)
R1	0.71	-6.53
R2	0.635	-6.44
R3	0.57	-6.6
R4	0.74	-6.48
R5	0.58	-7.07
R6	0.54	-6.55
R7	0.65	-8.08
R8	0.5	-7
R9	0.33	-7.13
R10	0.35	-7.68
R11	0.14	-7.38
M1	0.835	-5.82
M15	2	-5.2
M20	0.55	-7.05
V1/12	1.3	-6.8
V4/12	0.25	-8.11
V7/12	-0.24	-7.91
V9/12	-0.21	-7.93
V12/12	0.18	-6.99
V14/12	0.46	-7.07
V17/12	0.68	-6.31
V19/12	-0.26	-7.43
V21/12	-0.25	-7.11
V23/12	0.6	-6.7
V26/12	0.54	-6.85
V30/12	1.35	-6.7
V35/12	0.35	-7.24
V39/12	0.7	-6.6
V42/12	-0.19	-6.12
V44/12	0.3	-6.2
V47/12	-0.355	-6.35
V50/12	0.26	-6.55
V53/12	1	-6.45
V55/12	0.34	-5.52
V57/12	1	-6.1

Table 5S. The δ^{18} O and δ^{13} C values of Vempalle Formation dolomites.