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Geochemistry of Marine Carbonates from Hole 1394, off the coast of Montserrat, IODP Expedition-340; Implications on provenance, paleoenvironment and Lesser Antilles arc migration

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Abstract

The marine carbonate sediment samples are subsampled and collected from various cores spanning from top depths 11.67 meters (core depth below sea floor; CSF) and 11.45 meters (CSF) up to the depth of 168.57 meters (CSF) respectively of U1394 A and B holes drilled to south east of Montserrat Volcanic Island during IODP Expedition 340. These thin horizons are characterised for major, minor, trace and rare earth elements, total carbon to decipher their mode of origin, provenance, implications on paleo-environment. The carbonate sediments show variation in major oxide contents in SiO₂ (11.4-35.5 wt.%), CaO (22.4-44.7 wt.%), CaCO₃ (3.6-76.6 wt.%), Fe₂O_{3T} (1.1-6.0 wt.%), MgO (2.9-4.0 wt.%) with very low K₂O, TiO₂ and P₂O₅ contents. Their Mg/Ca, reciprocals (Ca/Mg) and Sr/Ca ratios classify these sediments as dolomitic limestones. These sediments depict very low total organic carbon (TOC) contents compared to total inorganic carbon (T_{ic}) indicating their lithogenic origin. The PAAS normalised rare earth element and yttrium (REY) distribution patterns show slightly depleted LREE abundances relative to HREE with (La/Yb)_{SN} range between 0.3-0.7 indicating low degree of fractionation with varying Σ REE contents (35-105 ppm). Subchondritic to superchondritic Y/Ho (25.7-31.6), Ce/Ce* (0.2-0.5) and Pr/Pr* (1.0-1.3) indicate low magnitude negative anomalies, slight negative to positive anomalies. Eu/Eu* (0.9-1.6) point towards the minimal terrigenous input, varied nature of sediments and plagioclase addition. The studied sediments mimic the seawater REY distribution patterns indicating REY are sourced from the seawater. The major, minor, immobile element ratios and redox sensitive element proxies indicate that the studied carbonate sediments are derived from an intermediate to felsic source. These sediments deposited in a low saline, oxygen rich open ocean shallow water environment akin to an active continent margin affinity. It can also be stated that later to their dissolution in extinct arc zones (between the old and young arc) led to the re-deposition in favourable sites in the marine sediment column during middle Miocene period or later due to the submarine slope failures and debris avalanches.

Key words IODP Expedition-340 . Lesser Antilles Arc . Marine carbonates . Rare earth elements . Montserrat Volcanic Island

Introduction

The Integrated Ocean Drilling Program (IODP) undertook Expedition 340 with an objective to obtain drill cores from several sites of Lesser Antilles volcanic arc region (Fig.1). These cores are used to recover the information to establish records of volcanic eruptions, landslides and their impact on the marine sedimentary record. The drill site U 1394 A and B are first among all and located to ~ 24 km southeast of Montserrat volcanic island (Fig.1). The site U 1394 is at a water depth of 1115 meters and consists of hemipelagic muds, turbidite sequences, mafic volcanoclastics, volcanoclastic sands, tephra layers and carbonate muds as main lithologies (Fig.2).

Fig.1 Map of the study area (Inset: Red box is the location of Lesser Antilles Island Arc) showing volcanic islands and IODP Expedition 340 Drilling sites indicated by solid colour circles and squares. Studied borehole U1394 A and B are shown in the dotted line box (Modified after Le Friant et al. 2013).

The Lesser Antilles arc is an oceanic island arc located at the eastern boundary of Caribbean Plate under which the American plate is subducting (Macdonald et al.2000). The rate of subduction is reported to be 2 cm/year (Feuillet et al.2002 and references therein) with a highly curved subduction zone geometry which is tectonically bounded by two strike-slip faults towards north and south. Although, several minor and major events of volcanism are reported from Lesser Antilles, the recent report of a 2.36 Ma Plinian eruption from Guadeloupe volcanic island, with volcanic explosivity index ~6 is known to be the largest documented volcanic event in this region since time (Palmer et al. 2016). The Lesser Antilles arc, with active volcanism in the Caribbean Sea since 40 Ma (Soufriere Hills Volcano of Montserrat Volcanic Island) divided into two arcs to the north of Martinique (Germa et al. 2011). The east and west diverged two volcanic axes converges to single at Martinique island. The eastern segment also called as

the Limestone Caribbees is inactive and older than the young (~7 My ago) active western segment start with the volcanic chain islands from north to south Montserrat, Guadeloupe, Dominica, Martinique, St. Lucia, St. Vincent and Grenada (Nagle et al. 1976; Briden et al. 1979). The eastern segment consists of carbonate platform type sediment islands (such as Anguilla, St. Martin, Barbuda, Antigua etc., of eastern older arc) rested on the volcanic basement (Murray et al. 2016; Palmer et al. 2016; Garmon et al. 2017). Carbonate sediments mixed with pelagic and hemipelagic muds, clays are omnipresent in every marine stratigraphic column in modern as well as old settings. Such sediment horizons occurring in shallow marine conditions in a volcanic/intraoceanic arc tectonic regime in convergent margins record key information on the ocean red-ox conditions, sea-level changes, terrestrial input and paleodepocenters, depositional environments, diagenetic changes etc., (Dorobek, 2007; Hawkins et al. 1984). Although, such studies are not much in existence, they throw light on the geochemical and tectonic implications on the shallow marine carbonate systems in a convergent margin tectonic setting. Present study, deal with such shallow marine carbonate system encountered in holes U1394 A and B drill cores pertaining to the Soufriere Hills Volcano of Montserrat Volcanic Island along the Lesser Antilles Arc system to constrain the influence of siliciclastic and volcano-sedimentary inputs from active volcanism through major, trace and rare earth element (REE) geochemistry, total organic carbon content etc., Our studies indicate that these sediment horizons having varying carbonate contents are deposited in an oxygen rich environment under active continental margin tectonic setting.

Materials and methods

The samples are collected from cores of holes U1394 A and B at different depth intervals (Table1). Based on the shipboard Carb., XRD data, the carbonate horizons are identified and sub sampled at IODP Gulf coast repository, Texas A & M University, College Station, U.S.A, at depths between top depth 11.67 meters core depth below sea floor A (hereafter CSF) and 11.45 meters CSF-B upto the bottom depth of 168.57 meters CSF of U1394 A and B holes. These samples are dried and further homogenised in an agate mortar and pestle until fineness. The sample quantities are very less, as they represent the working half cores and all the geochemical analytical methods are destructive in nature, care has been taken to provide sufficient amount of sample for each analysis. Thus the samples made to fine fraction of size <0.075 mm were stored in glass bottles labelled with all the details as per IODP sample curation protocol are subjected to carbonate, total carbon, major, minor oxides, loss on ignition, trace and REE determinations. For carbonate analyses, a 5 cm³ plug sample was taken and was freeze-dried for ~24 hours and pulverised manually using an agate mortar and pestle during sample preparation. Inorganic carbon concentrations were determined using a CO₂ coulometer available on board. 2 Molar HCl was added to around ~10 mg of dried, ground sediment and the liberated CO₂ was titrated to an end point determination using an on board photodetection cell. CaCO₃ weight percentage was calculated from the obtained inorganic carbon content, assuming that all evolved CO₂ was derived from calcium carbonate as follows: CaCO₃ (wt.%) = 8.33 × IC (wt.%), where IC = inorganic carbon. As this approach does not discriminate among carbonate minerals, all the evolved CO₂ is assumed to derived from CaCO₃.

Total carbon is determined using a ThermoElectron Corporation Flash EA 1112 CHNS elemental analyser available on board calibrated using the Thermo Soil Reference Material NC standard (338 40025 Lot N12A) using ~10–20 mg of dried, ground sediment. Total organic carbon content was estimated as the difference between inorganic carbon and total carbon. (for further details pl. refer to Expedition 340 Summary, Methods, 2013).

The loss on ignition (%LOI) was determined separately using a high temperature muffle furnace and pure silica crucibles at 1000°C for 60 minutes in muffle furnace. Sediment samples and standards (International reference materials such as GSR-5, (Shale, Chinese Geochemical Standard Reference Samples), JDO-1 (dolomite, JGS, Japan), JLS-1 (limestone, GSJ, Japan) were prepared as pressed pellets Major (SiO_2 , Al_2O_3 , $\text{Fe}_2\text{O}_3\text{T}$, MgO , CaO , K_2O , Na_2O) and minor elements (TiO_2 , MnO and P_2O_5) concentrations were determined by X-ray fluorescence spectrometry (XRF; Phillips MAGIX PRO Model 2440), on pressed pellets prepared from powdered whole-rock samples following the method of Krishna et al. (2007) at CSIR-NGRI, Hyderabad. Trace element contents and REE were determined by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) using international standard reference materials JDO-1 (dolomite, JGS, Japan), JLS-1 (limestone, GSJ, Japan). Satyanarayanan et al. (2018) is followed for analytical parameters and instrument calibration methods, for trace and REE determination. Sample digestion procedures are as given in Subramanyam et al. (2013). Analytical precision for major, minor oxides and trace elements should be less than 5% relative standard deviation (RSD) where as in the present case it is less than 2% (Table 1). REE data are normalised to the PAAS compositions after Taylor and MacLennan (1985). Major, minor trace and

REE analysis are presented in Table 1. For curator procedures, sample depth calculations, stratigraphic correlations, XRD, TOC, TIC, TC and carbonate analysis methods please see the Chapter Methods in Le Friant et al. (2013). Analytical precision of major, trace and REE are presented in Table 2).

Stratigraphy and Nature of sediments

The hole U 1394 A was drilled at latitude: 16°38.4259'N, longitude: 62°02.2822'W at a water depth 1114.9 (m), Seafloor depth (DRF in m): 1126.3, Cored interval (m): 244.5 having recovery 23% and generated 27 nos. of total cores. The hole U1394 B is drilled 20 meters north of hole A at latitude: 16°38.4375'N, longitude: 62°02.2819'W at water depth of 1114.2 (m), penetration depth DRF (m):181.4(m), cored interval (m): 181.4 having recovery 78% and generated 21 nos. of total cores. Both the holes are located off the tip of southeast coast of Montserrat volcanic island at an aerial distance of 24 km which have deposits of Soufriere Hills Volcano. Both the holes were drilled to target the debris avalanche deposits (DAD) to constrain the Soufriere Hills Volcanism of Montserrat volcanic Island. The subsampled points locations on the various cores are presented in Figure 2.

Fig.2 Core sections of U1354 A & B showing lithological horizons and sub-sample locations for the present study.

Results

Geochemistry

Major and minor oxides

Major oxide geochemistry of 17 sediment samples of U1394 A and B cores between top depth 11.6 meters (CSF-A) to 168.5 meters (CSF-A) indicate highly variable SiO₂ contents (11.4-35.5 wt.%), Al₂O₃ (2.9-10.4 wt.%), Fe₂O₃ (1.1-6.0 wt.%), MnO (0.1-0.3 wt.%), MgO (2.8-4.0 wt.%), CaO (24.7-44.6 wt.%), total alkalies (1.5-3.0 wt.%), TiO₂ (0.2-0.6 wt.%) and P₂O₅ (0.08-0.16 wt.%) and loss on ignition range between LOI (13.4-33.6 wt.%; Table 1). These sediments also vary widely in Mg/Ca (0.06-0.15 wt.%, except 0.26 in one sample) and the reciprocal Ca/Mg (3.8-14.8 wt.%, except 16.2 one sample) but very consistent in ratios such as (Na+Ca)/(Na+Ca+K) 0.96-0.99, (Si/Si+Al) 0.72-0.83, Sr/Ca (0.01-0.1) and Fe/Mn (11.5-24.5) classify them as dolomitic limestones as per the chemical criteria described by Todd (1966). The major oxide relationships of with other major, minor and trace elements are presented in Figure. 3.

Fig. 3 Major element and selected trace element cross plot relationships of studied marine carbonates of U 1394 A & B.

Trace Elements

The immobile elements contents (ppm) such as Th, Sc, Ti, Zr, Nb and Y are in the range of 0.6 to 3.2; (avg.1.7; PAAS-14.6), 3.9 to 23.7; (avg.9.0; PAAS-16), 779-7373; (avg.2314; PAAS-4916), 10.8-83.5; (avg.32.8; PAAS-201), 0.9 to 4.2 (avg.2.3; PAAS-15.4) and 8.7-23.5; (avg.14.4; PAAS-33, Table-1) respectively. The large ion lithophile elements such as Ba, Rb, Cs, K, Sr and U show abundances (ppm) in the range of 73.9 to 325.2; (avg.183.2, PAAS-551), 4.4 to 24.0; (avg.12.4, PAAS-163), 0.2 to 1.5 (avg.0.7, PAAS-), 0.2 to 0.7 (avg.0.48, PAAS-3.18), 250 to 2477 (avg.1473; PAAS-136) and 1.2 to 6.0 (avg.2.8; PAAS-2.9, Table-1). The PAAS normalised spidergram of selected trace elements show depletion of V, Cr, Ni, Cu, Sc, Y, Rb, Ba, Nb, Pb and Th whereas the Mn, Zn and Sr show enrichment characteristics (Fig.4a).

Rare Earth Elements

Rare earth elements along with yttrium abundances, Ce, Eu, La anomalies and other elemental ratios are presented in Table 1. Total REE concentrations (Σ REY) range from 35-102 (ppm) in the studied sediments. The PAAS normalised REY distribution patterns are smooth and coherent with progressive enrichment in the heavy REE (Fig.4b). This is due to the formation of trivalent REE and mono- and di-carbonate ion complexes in seawater, thus the filling of 4f electron shell along the series (Tostvien et al.2016 and references there in). The studied samples show the varying abundance of rare earth elements such as Ce in the range of 7.8-25.6 ppm (avg.15.6, PAAS Ce-82), La 5.2-14.0 ppm (avg.9.7, PAAS 38.8), Eu 0.4-1.0ppm (avg.0.6, PAAS 1.14), Y 8.7-23.5 (avg.14.4, PAAS 33), Σ REY 35-102 (avg.63.7, PAAS 216). The inverse relationship observed between CaCO_3 and Σ REY clearly indicate the role of seawater as a major source of REY in these samples (Fig.4c).

Fig. 4 **a** PAAS normalised selected trace elements distribution patterns of the studied samples showing depletion of V, Cr, Ni, Cu, Sc, Y, Rb, Ba, Nb, Pb and Th whereas the Mn, Zn and Sr show enrichment characteristics. **b** PAAS normalised selected rare earth element distribution patterns showing slightly depleted LREE relative to HREE with Ce negative and Eu positive anomalies. **c** Plot of Σ REY versus CaCO_3 showing negative relationship indicating the REY are sourced from seawater

Discussion

The major element ratios such as $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ are excellent proxies for the interpretation of sediment recycling and detrital input (Zaid 2013; Madhavaraju et al. 2016; Zaid et al. 2015; Tapia-Fernandez et al. 2017). If sediment recycling and detrital inputs are high in the depositional system $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is >6, similarly, the $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ ratio is >5 and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio is >1. The studied samples show $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.9-5.6), $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ (1.9-5.8, >5 only one sample) and

K₂O/Na₂O ratios (0.1-0.5) indicating no sediment recycling or detrital input in the studied samples. Further, Roser et al. (1996) have identified SiO₂ / Al₂O₃ ratio of sediments as a measure of maturity of sedimentary rocks where the ratio more than 5 is treated as resulted from mature chemical components of the rocks. SiO₂/Al₂O₃ ratio of the studied samples as mentioned above is very consistent except one sample recorded 5.6 indicating their low maturity. This is further supported by low K₂O/Na₂O and very consistent and low Al₂O₃/TiO₂ ratios. The distinct negative relationship obtained between SiO₂ and CaO indicate distinct origins of the two elements in the studied samples (Fig.3). Very clear carbonate dilution trends are obtained from the positive relationships of Fe₂O₃ when plotted against Al₂O₃, TiO₂, CaO and SiO₂ which is also resulted in high Sr and Ca in these samples (Table 3; Sawant et al.2017). SiO₂ when plotted against Fe₂O₃, Na₂O and TiO₂ show positive relationship suggesting that these sediments are derived from stable constituents of rocks showing low to moderate sediment maturity level (Fig.3).

Trace and rare earth element (REE) concentrations are shown in Table 1. The PAAS normalised (Taylor and McLennan, 1985) trace element distribution patterns (Fig. 4a) show extreme depletion in V, Sc, Y, Rb, Nb. Cr, Ni, Cu, Ba, Pb and Th whereas enrichment is observed in case of Mn, Zn and Sr relative to PAAS abundances and on the spidergram (Fig. 4a). The trace element pairs such as Zr-Hf, Nb-Ta, Cr-Ni, Ti-V and are compatible elements and behave identically in magmatic systems whereas in alteration-weathering-sedimentary systems these igneous pairs may be fractionated which is influenced by several weathering and depositional (marine/freshwater) conditions (Veizer, 1983). The studied marine sediments show positive covariation between Zr-Hf and Nb-Ta (Fig.5 a, b) indicating a significant role played by felsic or

intermediated sources which are weakly weathered and remain coupled till their deposition, whereas Cr-Ni and Ti-V which are mostly controlled by mafic-ultramafic sources are not correlated in present case (Fig.5 c,d). These element pairs might have been highly fractionated and decoupled before during their transportation to the site of deposition (Brand and Veizer, 1980; Veizer, 1983). Floyd et al.(1989) described a relationship between two most abundant end members of felsic (TiO_2) and mafic (Ni) systems to verify the provenance from which the sediments derived. The studied sediment samples having low Ni and low TiO_2 contents plot along the typical magmatic trend further containing their derivation from an acidic source (Fig.5e). Th/Sc versus Zr/SC relationship after McLennan et al.(1993) indicating that the sediments are derived from varied compositions due to igneous differentiation that is only possible in a an active continental margin setting (Fig.5f). The studied samples follow the trend of Th/Sc (incompatible/compatible elements in igneous chemical differentiation system) and clustered below the PAAS and UCC indicating their derivation from a differentiated felsic igneous source.

Fig. 5 **a** and **b** Relationship between felsic element pairs Zr versus Hf and Nb versus Ta showing positive covariance indicating their source rocks are felsic to intermediate. **c** and **d** where negative correlations between mafic element pairs Ni versus Cr and Ti versus V confirms the above felsic-intermediate source for the carbonaceous sediments in the present study. **e** Zr/Sc versus Th/Sc (after Floyd et al. 1989) indicating their derivation from rocks of magmatic differentiation, wherein all the studied samples following a typical trend of active continental margin tectonic affinity

Rare earth element (REE+Y) geochemistry in sedimentary systems offer proxies for weathering, depositional, diagenesis, source rock, oceanic paleoredox conditions. Yttrium behaves similar to REE due to their coherent geochemical properties, based on the ionic radii, yttrium is place between Dy and Ho which behaves like a HREE

(Nozaki et al.1997; Allwood et al.2010). Hence, such Y/Ho ratios indicate anomalous nature of sea water and marine sediments (Bau and Dulski, 1996; Quinn et al.2004). In addition to this the LREE/HREE, Eu/Eu*, Ce/Ce*,Pr/Pr* ratios as well as Er/Nd characteristics are discussed for the studied samples which offer excellent clues on the genesis of carbonate fraction as well as source of terrigenous contamination if any (Greaves et al.1999;Taylor and McLennan,1985). The pure carbonate facies record very low abundance of REY whereas the admixed terrigenous material along with seawater influence will increase the REE abundances (Piper, 1974; Bellanca et al.1997). Total REY (Σ REY) contents in the studied samples range from 35 to 105 ppm. PAAS (Post Archean Australian Shale) normalised REY distribution patterns show overall less fractionation (La/Yb_N ;0.3-0.7) with slight LREE depletion relative to flat HREE with slight negative to positive Ce (Ce/Ce^* 0.2-1.1; most of the samples record<1) and positive Eu (Eu/Eu^* 0.9 to 1.6; most of the samples record>1) anomalies. The studied samples exhibit modern sea water like REE distribution patterns with slight LREE depletion relative to HREE except positive Y-anomalies.

Europium anomalies (Eu/Eu*)

The $(Eu/Eu^*)_{SN}$ values are presented in the Table 3. The shale normalised Eu anomalies range between 0.9-1.6 indicating their varied nature in the sediment column. Michard et al.(1983) and German et al.(1993) attributed Eu anomalies due to the effect of hydrothermal solutions, intense diagenesis of sediments (Murray et al.1991a; MacRae et al.1992), variations in plagioclase contents (Nath et al.1992) whereas Elderfield (1988) speculated about the aeolian input into the sediment column up to 50 meters. Hence, it is imperative to verify the Eu relationship with immobile trace elements such as Zr, Y and Th and found the positive correlations indicating non-diagenetic origin of Eu (Fig.6 a,b,c). Further, the regional influence of aeolian input

and hydrothermal effects on Eu positive anomalies have been negated by the poor correlation between the Eu when plotted against Na/Al and K/Al (Murray et al. 1991b; Fig. 6 d,e). Thus, the influence of plagioclase addition in the sediments played a role for positive Eu anomalies in the studied samples.

Fig. 6 a-c Eu (ppm) plotted against immobile trace elements Zr, Th, Zr display positive relationship indicating non-diagenetic origin of Eu (Murray et al. 1991a; MacRea et al. 1992; Nath et al. 1992). **d) and e)** are showing no correlations between Eu and major element ratios such as Na/Al and K/Al, indicating thus the influence of aeolian input is negated (Murray et al. 1991b).

Cerium anomalies (Ce/Ce*)

Ce/Ce* ratios are calculated using the technique of Bau and Dulski (1996; modified after Webb and Kamber 2000; $3\text{Ce}/(2\text{La} + \text{Nd})_{\text{SN}}$). Trivalent cerium from seawater can undergo oxidation to the highly insoluble tetravalent state. This is mainly a change in the ionic state of Ce as a function of oxidation state of the medium. Its scavenging from seawater and adsorption to the particulate matter is considered as distinctive depletion of Ce in well-oxygenated seawater. Nagarajan et al. (2011) compiled the reasons of anomalous cerium values in the marine system due to the following process

1. biologically mediated oxidation of Ce (III) to Ce (IV) in coastal and open ocean (Sholkovitz et al. 1994),
2. Ce (III) to Ce (IV) redox shift across anoxic/oxic interfaces in the water columns of marine basins (German and Elderfield, 1989; Sholkovitz et al. 1992) and
3. Due the development of largest Ce anomalies in rivers with the highest pH (Goldstein and Jacobsen, 1988).

Hence, Ce/Ce* parameter is very helpful to determine the redox conditions prevalent in the water column at the time of the REE uptake by these phases. (Elderfield and Greaves, 1982; German and Elderfield, 1990; Bellanca et al. 1997; Moller and Bau, 1993; Balaram et al. 2012 and references therein). Ce/Ce* values of the normal seawater range from < 0.1 to 0.4 (Elderfield and

Greaves, 1982; Wang et al.1986; Piepgras and Jacobsen, 1992) while in average shale Ce/Ce* is 1 (Haskin and Haskin, 1966; Murray et al.1991a). A low magnitude Ce-negative anomalies (Ce/Ce*=0.2-1.1; 04 samples show ≥ 1.0) are observed for the studied samples on the PAAS normalised REE patterns (Fig.4b) indicating inherited sea water compositions (Tostevin et al. 2016).

Er/Nd ratios

REE enrichment or depletion (LREE relative to HREE or vice-versa) depends on the redox potentials of the depositional system as well as their abundance in sea water. Fractionation of REE in marine sediments is also possible due to burial and diagenesis. Hence, the Er(HREE)/Nd(LREE) ratios are indicators of diagenetic changes, seawater contribution and the redox process operative during deposition. Er/Nd ratio of normal seawater is 0.27 (de Baar et al.1988) whereas, the high Er/Nd ratios >0.1 of the limestones reflect the seawater signature retained by the marine carbonates (Bellanca et al 1997). The Er/Nd ratios tend to decrease below 0.1 in case of addition of detrital input in the marine carbonate system. This is due to the preferential absorption of Nd over Er on to the particle surfaces (De Baar et al.1988; German and Elderfield, 1989; Bellanca et al.1997, Nagarajan et al.2011). In the studied samples Er/Nd ratios range between 0.12-0.18 representing the pristine nature of carbonates with very little detrital input into a few samples which show Er/Nd ~ 0.12 . Another important LREE/HREE ratio namely the (Nd/Yb)_{SN} ratios are good indicators of contamination. The studied samples show (Nd/Yb)_{SN} ratios in the range of 5-8, which are well below the shale values (PAAS-11.4) but much above the ratios for 50m water depth of normal ocean waters ~ 0.205 to 0.497 (Zhang and Nozaki, 1996; De

Baar et al.1985). The LREE depletion characteristics are responsible for such high ratios in the present samples. Relative HREE enrichment when compared to LREE prompted us to see the HREE/HREE ratios such as the $(Dy/Yb)_{SN}$ which are well constrained with the studied samples showing 1.4-1.8; whereas PAAS values are 1.6 and the modern seawater (~0.8–1.1) ratios are slightly low. Shields and Stille (2002) reported similar range of ratios recorded for Early Cambrian phosphorites (1.1-2.0) of South China and the same ratios are as low as 0.8-1.0 as reported by Hein et al. (1999), Siegmund (1995) and Kawabe et al.(1991), which are similar to the lower range of near surface modern and open Pacific seawater (Zhang and Nozaki, 1996; Nothdurft, 2001; Webb and Kamber,2000).

Age of the carbonates

The present study deals with samples recovered from south eastern part of Montserrat volcanic island (MVI) from the drilled cores of U-1394 A and B holes which intersected debris of mass wasting events of Soufriere Hills volcano of Monserrat Island located along the Bouillante-Montserrat Graben. Young et al. (1998) studied the heightened volcano-seismic activity of Soufriere Hills volcano during 18th July 1995 to next three years till 1998. The authors further reported that the phreatic explosions have continually erupted juvenile andesitic lavas built a lava dome during November 1995. The collapse of eastern flank occurred followed by an explosive eruption on 17th September 1996 sustained till June 1997. The volcano has vented pyroclastic material on 22 and 23 March, 2012 just after we completed the drilling of U 1396 site. The Sofriere Hills pyroclast flows of quantity $2 \times 10^6 \text{ m}^3$, which occupied the shallow shelf area around the MVI mostly as proximal lobes and rest as distal turbidites (Trofimovs et al.2006). Trofimovs et al. (2010) argued about the large submarine slope failure of

378 carbonate platform and rapid raise of sea level in Lesser Antilles around Soufriere Hills
379 volcano of MVI during the last 26 kyr as well as the age the occurrence of mass flow
380 was 14 ka. Further, along the south eastern segment of MVI, the Bouillante-
381 Montserrat Graben where numerous piston cores, vibracore samples are studied prior
382 to and during IODP Exp. 340, resulted in a better understanding of the dynamic
383 evolution of volcanic island, mass flow deposits, erosional surfaces, Tsunami genesis
384 and failure of carbonate platforms due to seismogenesis. Wall-Palmer et al. (2014
385 and references there in) dated the sediments intersected in hole U1396 C located
386 towards the southwest of MVI using a combination of parameters such as high-
387 resolution oxygen isotope stratigraphy, AMS radiocarbon dating, biostratigraphy of
388 foraminifera, calcareous nanofossils, clast componentry and established five major
389 events since 250 Ka to present. Further, the authors established laterally correlatable
390 stratigraphic horizons across the drill holes on the south west and south east of
391 Montserrat (U 1396 A, B and C with U 1394 A and B) and identified high intensity
392 erosive density-currents that travelled at least 33 km offshore of Montserrat having
393 heterogeneously distributed in space. Coussens et al. (2016) characterised three
394 important age peaks (0.93 to 0.90, 0.81-0.76 and 0.19 to 0.12 Ma) mass wasting (flank
395 collapse) and high volcanic instability that are coinciding with Soufriere Hills volcanic
396 activity. The authors have shown excellent lateral stratigraphic correlations upto 15
397 meters depth. Debris Avalanche Deposits (DAD) 1,2,4,8 are located to the
398 southeastern part of Montserrat (Wall-Palmer, 2014; Coussens et al.2016). However,
399 earlier workers used shallow cores of various expeditions to constrain the evolutionary
400 history and volcanism around MVI but the carbonate horizons which are very important
401 in terms of their location along with the packet of hemipelagic and pelagic muds are
402 not studied. Trofimovs et al. (2013) alternatively argued two possible hypotheses for

the collapse of carbonate platforms. 1. Subjected to mass wasting of 12-14 ka non-volcanic carbonate shelf of Antigua and Rodanda reached till Montserrat. 2. The Sofriere Hills flank collapse related DAD 1 which also have triggered the collapse of carbonate shelf.

Coussens et al. (2016) studied DAD 2 from U 1394B drill hole intersected at depth of around 11.0 to 19.0 meters (CSF) assigned an age of 130 ka and these data sets are limited to 15 meters. The samples from depths 11.6 to 14.6 meters (CSF) studied in the present investigation characterise the DAD 2 having very little carbonate content and dominated by siliceous sediments. Wall-palmer et al. (2014) also studied the cores up to 5.9 meters and constrained age up to 246 ka events having done the lateral correlations up to 4.75 meters (mbsf) only. Since the studied samples are recovered from depths starting from 11.6 up to 168.5 meters (CSF) upper part samples (11.6 to 14.6 meters) can be speculated for age correlations since the drilled cores JR123-5V, JR123-6V and U-1394B are very closely spaced. Hence, it is speculated that the samples in the present study are recovered from the buried DADs 2,4,8 located along the Bouillante-Montserrat Graben (Figs.1 and 11 in Wall-Palmer et al.2014).

Deposit boundaries ages are determined using marine isotope stage (MIS) (Coussens et al.2016) which have been studied at core depths 28.31, 35.93 and 43.84 meters (CSF) from U 1395 B drill cores indicate ages of 191, 243, 300 Ka respectively. These ages can be well correlated with U 1394 B which is very closely spaced with U 1395 B drill hole at a slightly shallower depth i.e., 24.1, 31.6 and 39.6 meters (CSF; upper surface of Deposit 2 is located 4.2 meters shallower in U 1394 B than in U 1395 B).

These age boundaries do not reflect any significant changes in the studied geochemical parameters. Thus above aspects combined with the results of present study indicate episodic failures of platformal carbonates linked to the volcanic event of MVI.

Depth wise variation in Geochemical parameters

It can be interpreted from the depth profiles of studied geochemical parameters of carbonates that high Al and Fe contents are compensating the CaCO_3 and TOC contents at carbonate barren zones from 22 to 78 metres (CSF; Fig.7). From 78 to 168 meters (CSF) small numerous carbonate horizons show low Al, Fe and V/Cr ratios with moderate Mg contents. An increase in Sr (250-2477 ppm) from 20 meters to 98 meters (CSF) along with concomitant increase in Al_2O_3 and Fe, depletion in Mg, Ca and V/Cr indicate influence of redox conditions below the Deposit 2 assign an age older than 130 ka as well as increase in dolomitisation downward (Sr/Ca ratios discussed elsewhere). Mg content ranges from 2.7 to 4.7 (wt.%) having high values at 120 meters (CSF) show almost very consistent downward trends, where Fe, Al also show their peaks at 120 meters (CSF) but V/Cr record a very low ratio indicating a redox influence during >1Ma (Fig.7).

Fig. 7 Down the depth profiles of various geochemical parameters showing three major peaks w.r.t. red-ox sensitive elements (Sr, Mg, Fe, V/Cr, Fe/Mn and Mg).

Source weathering and alteration characteristics

Goldberg and Humayun (2010) concluded that CIA should not be used for carbonate rich sediments having >30% carbonate content which should be treated by acetic acid prior to analysis to remove the carbonate content. Having very small sample size, the

authors could not perform such pre-treatment to eliminate the CaCO_3 , but as an alternative to this the CIW values are calculate (similar to CIA except K) which are in the range of 34.7-3.4 taking CaO corrected for Ca in apatite only, thus removing the carbonate fraction from non-silicate part (whole anhydrous Ca from anhydrous $\text{CaO} = \text{anhydrous CaO} / 56.077$, this many moles of oxide is calculated for apatite Ca by moles of oxide Ca—(moles of oxide P x (10/3); Harnois,1988, Fedo et al.1995). These values when plotted on the A-CN-K trilinear diagram after Nesbitt and Young (1982, Fig.8a), the studied samples occupying the CN apex indicating the clinopyroxene and hornblende weathering in the provenance; they show a parallel trend with the A-CN line inconsistent with the trends published by Nesbitt and Young (1982) indicating multiple factors involved in the weathering and suggest more influence on the composition of the rock than metamorphism and diagenetic process (McLennan et al.1993). Further, the ideal weathering trend would be parallel to the A-CN side, whereas the rocks which have not suffered strong weathering occupy the left bottom apex of the diagram below the plagioclase-K-feldspar joining line (Hu et al.2015). Diagenetic alteration of carbonates increases Mn at the extent of Sr (Nagarajan et al.2011). In the studied samples such relationship is obscure (Fig.8b) indicating that the samples have not undergone significant diagenetic alteration.

Contamination and diagenetic alterations

Lack of correlation between CaO and $\sum \text{REY}$ (Fig.8c) indicate that the REE are derived from either sea water or from the mildly admixed terrigenous material. Such anomalies on the REY distribution diagram are relative to adjacent element abundances whereas Pr/Pr* versus Ce/Ce* relationship indicate the studied samples plot in the modern sea

water field with negative Ce anomaly (Fig.8d). Similar REE distribution patterns are described for carbonate sediments in late Devonian Reefal carbonates by Nothdurft et al.(2004).

The Y/Ho ratios (20.7-31.5; average 28.0; Chondritic Y/Ho = 28; Sun and McDonough, 1989; Kamber and Webb, 2001) of the studied samples are subchondritic to superchondritic. Y/Ho ratio of modern sea water is strongly superchondritic (40-90; Bau, 1996; Global ocean waters 90-162; Johannesson et al.2006). Hence, the studied samples mimic the Y/Ho ratios of volcanic ash or minimal terrestrial sediment inputs (Y/Ho=28; Bau and Dulski, 1996; Nothdurft et al.2004). Feeble positive correlation of Σ REY with Al_2O_3 (Fig.8e), negative correlation of Σ REE and CaO (Fig.8c) and very significant negative correlation between Al_2O_3 with CaO (Fig.8f) along with limited variation in Y/Ho ratios indicate that the carbonate sediments are not affected by terrigenous input.

Fig. 8 a Ternary plot of molecular proportions of [$Al_2O_3/(Al_2O_3 + CaO + Na_2O)$] with the Chemical Index of Weathering (CIW) calculated after (Harnois, 1982; Fedo et al. 1995) plotted on alteration scale shown on the left after Nesbit and Young (1982). Also plotted are selected idealised igneous sedimentary minerals. **b** Sr versus Mn **c** Σ REY versus CaO **d** Plot of Ce/Ce* vs. Pr/Pr* after Bau and Dulski (1996) to identify La and Ce anomalies of carbonaceous sediments indicating negative Ce and positive La anomalies and occupying the zone of modern seawater (upper 50 m of water column) for which the data collected from different locations of the Pacific and Indian Oceans (Nagarajan et al. 2011 and references there in) **e** Σ REY versus Al_2O_3 relationships showing no correlations **f** Negative correlations between Al_2O_3 and CaO indicating that the carbonates are not effected by terrigenous input

Temperate (cool water) versus Tropical (warm water) carbonates

Winefield et al. (1996) have discriminated the carbonates precipitated from temperate (cooler waters) and tropical (warm waters) seawaters from both ancient and modern sediments based on elemental geochemistry such as Sr, Mg, Mn and Na contents.

Using 600 bulk samples studied from temperate Cenozoic limestones of New Zealand, the authors reported that low Mg and Sr contents and relatively higher Na, Fe and Mn contents than tropical (warm water) carbonates which are very consistent with the temperature effects on the carbonate dissolution. Moreover, such studies are rare other than few Tasmanian examples and eastern Iran (Azizi et al.2014).

The samples in the present study have recorded average values for Mn, 1278 ppm; Sr, 1433 ppm; Na,13814 ppm; Mg, 20339 ppm; and Fe, 24161 ppm much higher in abundance than the average contents of New Zealand Cenozoic limestones. These five elements are of most important to discriminate between the tropical and temperate carbonates (Winefield et al.1996).

The Sr/Na ratios and Mn contents in carbonates very well discriminate the carbonate sediments of temperate (cool water) zones from their tropical (warm water) counterparts of both modern and ancient occurrences (Rao,1991; Winefield et al.1996). The tropical (hot water) carbonate sediments of modern settings will have low Mn and High Sr/Na ratios (3-5), in contrary to this the modern temperate (cool water) carbonates will have high Mn and low Sr/Na ratios (~1). In the studied samples the Mn contents and Sr/Na are less than 1, (0.06-0.25 ppm; avg. 0.128) and (0.02-0.2; avg. 0.11) respectively.

On the binary discrimination of Sr-Na and Sr-Mg and Sr-Mn (Fig.9) for the studied samples plot along with the Cenozoic New Zealand carbonates (but on the higher side of the Mn, Mg and Na) indicating their genesis in a temperate cooler waters but in actual condition the MVI (Lesser Antilles) is located in the zone of tropics which is a

known latitudinal tectonic setting. Here we report a deviation from the general observation of Winefield et al.(1996); Rao (1991), Hood et al.(2004) and Azizi et al. (2014) on the temperate limestones, although the geochemical parameters and ratios as mentioned above satisfy the discrimination. The authors also suggested that the regional generalisations can be made limited to the skeletal differences, diagenetic process involved etc., Based on the above and analysed data sets of the studied samples, the net effect of volcanogenesis, carbonate dilution and dissolution play an important role in discriminating the carbonates of tropical origins. The failure of carbonate platforms and later events might have also modified the chemical character of the studied samples. Bouden et al. (2007) reported that the MVI has recorded more than 47 volcanic events where as 15 of them have occurred during the last 12 kyrs. These observations have been fairly matching with the DAD 2 where we have seen an age of 130 ka and mass flow of debris are observed at 14 ka due to submarine landslides and due to slope failures during rapid sea level changes (Trofimovs et al.and references there in, 2010). Bowles and Fleischer (1985) reported enhanced Amazon and Orinoco sediment influx to the eastern Caribbean during interglacial periods and at times of higher sea levels. Although, the authors speculated about the sediment dispersals and terrigenous dilution produced the reversals of carbonate trends as well as high accumulation rates of sediments during glacial periods around Aves Ridge (located south west to the MVI), the high amounts of cool water mixing into the Lesser Antilles and the increased production of cool water carbonates caused by upwelling cannot be ruled out. Further studies on these samples are warranted using stable isotope systematics to unravel the growth and destruction of shelf carbonates of Lesser Antilles to further substantiate the present findings.

Fig. 9 Binary plots with fields demarcated for modern warm-water, Tasmanian cool water shelf carbonates as well as Ordovician Tasmanian subtropical shelf carbonates along

with the carbonates of under present study (red solid circles; Data and Figures after Winefield et al. 1996) plotted along with the Cenozoic New Zealand carbonates of Temperate waters for the Sr-Mn and Sr-Na relationships. On the Sr-Mg binary plot the same samples plot along the tropical (warm water) fields with overlap.

Th/U ratios

Th/U whole-rock ratios of the studied samples (0.3-2.0; predominantly most of the samples show <1.0) suggest that these are much below the upper continental crust igneous values (3.5-4.0; McLennan et al.1993). During weathering these values will increase much further whereas the low values as obtained in the present case are indicative of active continent margin values (pl. see the Th versus Th/U relationship Fig.10a). U enrichment in sedimentary process lead to lower ratios of Th/U. McLennan et al.(1993) suggested that low Th/U (U enrichment) in sedimentary processes commonly seen in active margin sediments also reflects geochemically depleted mantle sources of the arc provenance (pl. also refer to Hofer et al.2013). The high Th contents are generally added to sediments from continental sources as detrital material which is also a measure of sediment maturity. U enrichment is generally believed to be due to its binding or trapping with organic materials in the marine system. Thus low Th/U values also indicate immature or less mature nature of the studied samples.

Paleo-Redox Characteristics

Along with REE such as Ce and Eu (LREE), the trace elements and their ratios such as V, Cr, Ni, Co, Cu, Zn, U, Th etc., are also considered as good proxies for paleo-redox characteristics of marine sediments since these cationic metals possess more than one oxidation states by losing electrons except Zn and Th have single oxidation states II and IV respectively. These elements are also named redox sensitive

587 elements (ROS) in Marine Geochemistry (Jones and Manning, 1994; Cullers, 2002;
588 Kato et al.2002; Swanner et al.2014; Godlberg and Humayun, 2016, Altrin et al. 2015).
589 The redox mechanism aquatic systems operates based on the available oxidizable
590 and reducible metallic compounds. In other words, it is the balance between the
591 atmospheric oxygen supply and the oxygen consumption by microbial decomposition
592 of organic matter (Drever, 1997).

593

594 Ni/Co ratio is a strong indicator of paleo-redox conditions of aquatic systems. Ni/Co
595 <5 and >5 are considered to represent oxic and anoxic conditions respectively. The
596 studied samples consistently show the ratio in the range of 0.1-4.3 except one samples
597 showing 5.6). Similarly, the V/Cr ratio is a good indicator of paleo-redox conditions.
598 V/Cr ratio more than >4.5 is considered as anoxic, whereas <2 is considered as oxic
599 condition (Jones and Manning, 1994). The studied samples show a range of V/Cr
600 ratios from 0.4-4.9 (in which 5 samples show V/Cr>2.0). Further, Goldberg and
601 Humayun (2016) reported Cu/Zn ratio as a good indicator of paleo-redox conditions.
602 If this ratio is >1, it is considered as anoxic when it is <1 representing oxic conditions.
603 All the studied samples are in the range of 0.1-0.5 confirming to the prevalence of oxic
604 conditions during their deposition. Authigenic uranium (non-detrital fraction; derived
605 from $U_{au}=U_{Tot}-Th/3$) precipitates under reducing conditions being carried as uranyl
606 carbonates in solution (Langmuir, 1978). It is the difference between the total uranium
607 (measured) and detrital uranium. Detrital uranium can be taken as Th/3, since the
608 Th/U ratio in normal mudstone is 3; where the U is considered to be derived entirely
609 of detrital origin is 3 (Wignall and Myers, 1988). The studied samples show a range
610 of ratios 0.5-4.9 of U_{au} suggesting oxic depositional conditions wherein the values

between 5-12 and >12 suggest oxic and suboxic to anoxic depositional conditions respectively.

Total carbon and Carbonate content

The studied samples show highly variable CaCO_3 contents between 3.6-76.6 (wt.%). These sediments depict total carbon (TC) contents vary in a wide range from 0.46-9.89 (wt.%) whereas the inorganic carbon (T_{ic}) shows similar variation from 0.43-9.2 (wt.%). Total organic carbon is generally very low (Frimmel 2009, Hofer et al. 2013) obtained is very less (0.02 to 1.17 wt.%) when compared to the inorganic carbon which is a general case for many marine carbonate sediments indicating the samples are lithogenic. The positive relationship between TOC (wt.%) versus CaCO_3 (wt.%) (Fig.10c) for the carbonates indicate their deposition in oxic and a high rate of sedimentation (Nioti et al.2013).

Fig. 10 **a** Plot of Th/U versus Th (after McLennan et al. 1993) indicating the carbonaceous sediments occupy the region of active continental margin sediments also indicating that these sediments are unaltered and unweathered since these are well below the Th/U of upper crustal igneous rocks (3.5-4) which is characteristic of PAAS (shales) **b** $\text{K}_2\text{O}/\text{Na}_2\text{O}$ versus $\text{SiO}_2/\text{Al}_2\text{O}_3$ major oxide based tectonic discrimination diagram after Roser and Korsch (1986) discriminating the marine carbonates into A1 to A2 fields (A1= arc setting, basaltic and andesitic detritus; A2 = evolved arc setting, felsitic-plutonic detritus) **c** TOC (wt.%) versus CaCO_3 (wt.%) showing a slightly weak positive anomaly indicating oxic depositional environment d) Active and passive margin discrimination diagram based on log transformed major and selected trace element compositional data effectively discriminating the studied marine carbonates with active continental margin affinity

Shifting of platform carbonates to deep ocean: evidence from Ce and La (Pr/Pr^*) anomalies

The slight relative depletion of LREE compared to HREE on shale normalised patterns slight positive La, Eu, Gd and Y anomalies, Ce negative anomalies, superchondritic Y/Ho ratios are proxies for retention of seawater characteristics in sediments (Zhang

640 and Nozaki, 1996; De Baar et al.1985; Zhang and Nozaki, 1998; Bau, 1996; Elderfield
641 and Greaves, 1982; Piepgras and Jacobsen, 1992) respectively. Although, some
642 deviations to the above mentioned criteria observed in the later studies due to addition
643 of detrital material from adjacent continents, addition of biogenic sedimentation to the
644 ocean basins, changes in Eh, Ph conditions of the seawater modified due to the above
645 contamination that have operated at depth, varying temperatures, salinity conditions
646 as well as authigenic removal (scavenging) of rare earths and early diagenesis and
647 chemical alteration of sediments (Nagarajan et al. 2011 and references there in). The
648 above mentioned conditions may dilute the original seawater characteristics retained
649 by the marine carbonates resulting in a non-seawater like patterns of REE due to the
650 addition contaminants such as Fe-Mn oxyhydroxides, phosphatic sediments, non
651 carbonates, siliceous sediments etc., Since the rare earth element distribution patterns
652 of studied carbonate sediments have grossly retained the seawater characteristics
653 except yttrium-positive anomaly whereas Y/Ho values are near chondritic (range of
654 present study 20.7-31.5; average 28.0; Chondritic Y/Ho = 28; Sun and McDonough,
655 1989; Kamber and Webb, 2001). Lawrence and Kamber (2006) suggested that the
656 Y/Ho ratios vary as a function of salinity of sweater. Similar Y/Ho values and lack of
657 Y anomalies in most of the carbonate sediments, in spite of no shale contamination
658 obtained by Frimmel (2009). The authors attributed such lacking of Y anomaly as a
659 primary feature of precipitating water. Further, Lawrence et al. (2006) reported that
660 the freshwater influence and sediment load admixed by rivers on the marine sediments
661 may generate such low magnitude Y anomalies. While considering these aspects
662 along with the PAAS normalised Ce/Ce* versus Pr/Pr* discrimination diagram (Fig. 7d;
663 modified after Bau and Dulski, 1996) which discriminates the studied carbonate
664 samples into a tight cluster having negative Ce and positive La anomalies which are

in perfect agreement with modern open oceanic surface water. The demarcated area shown by a field enclosed in Figure 7d is an average of modern seawater samples (upper 50 m of water column) for which the data collected from different locations of the Pacific and Indian Oceans (Nagarajan et al.2011 and references there in). This observation gave a chance of speculation about the origin of the carbonates in an open ocean setting in between the younger and older arc towards north-western margin (located on the overriding plate) of Lesser Antilles volcanic arc as a carbonate platform which are also known as intra arc carbonates. These carbonate platforms due to the Lesser Antilles volcanism and associated tectonics slumped onto the ocean floor in the form of a collapsed carbonate platform as a debris avalanche deposit. Doborek et al. (2008) explained the growth of such thin shallow marine carbonate platforms in an active volcanic front such as the present case, which are effected by differential tectonic subsidence, uplift, relative sea-level changes and paleoclimate variations. The present day examples are Grenadine Islands, Lesser Antilles, where intra-arc carbonate facies form a submerged and incipiently drowned carbonate platform (the Grenadine Bank) that is currently at 20–40 m water depths (D'Anglejan and Mountjoy, 1973; Dey and Smith, 1989). Soja (1996) described such worldwide platformal carbonates related to the island-arc settings, their dissolution in extinct arc zones and deposition in favourable sites in the marine sediment column. Further, Soja (1996) explained the mechanism by which the carbonate platforms descend to deep marine conditions developed during the intermittent phase of volcanism.

Tectonic setting

Carbonaceous sediments may be accumulated at various sites in passive and active margin setting (Dorobek, 2007). The Lesser Antilles volcanic arc is an oceanic island

690 arc with active margin conditions wherein American plate is being subducted below
691 the Caribbean plate given rise to a chain of volcanic islands in an arcuate shape (Le
692 fraint et al.2013, Macdonald et al.2000). Based on the geochemical characteristics
693 of the studied sediments, the tectonic setting in which their deposition took place is
694 although known to be an active continental margin setting, a verification has been
695 made by using major oxide ratios K_2O/Na_2O versus SiO_2/Al_2O_3 proposed by Roser
696 and Korsch (1986; Fig. 10b). These discrimination diagrams have been used by many
697 workers for texturally dissimilar rocks (coarse grained sandstones to med grained
698 greywackes to fine grained shales/mudstones) which are derived from complex active
699 margins including material derived from continental margin magmatic arcs (and
700 deposited in a variety of basin settings including trench, fore-arc, intra-arc, and back-
701 arc). On the other side when these discrimination diagrams were used for modern
702 sediments which are chemically distinctive such as trailing-edge and forearc muds,
703 but compositions of continental margin arc, strike-slip, and back-arc muds overlapped
704 considerably. The studied carbonaceous samples when plotted on the K_2O/Na_2O
705 versus SiO_2/Al_2O_3 diagram (Fig.10b) occupy the field of A1–A2 (A1= arc setting,
706 basaltic and andesitic detritus; A2 = evolved arc setting, felsitic-plutonic detritus) very
707 similar to the results obtained by various other geochemical ratios of the present study
708 (Fig. 10b). Further, an online computer programme known as APM Disc (Active and
709 Passive Margin Discrimination diagrams) for the discrimination of active and passive
710 margins was written in Java using the framework ZK developed and published by
711 Verma and Altrin (2016) is used for the studied samples. The compositional data of
712 major oxides and trace elements (DF A-P MT) for the studied samples have been
713 processed using the excel sheets and discrimination diagrams are obtained. Figure.9c
714 show that all the studied samples effectively discriminated with active margin affinity.

Since the drilled core samples are collected from Lesser Antilles arc (a known active tectonic setting), the samples with <30 wt.% SiO₂ are also included during data processing (out of 20 samples 14 have SiO₂ contents less than <30%) for APM Disc programme, as the authors (Verma and Altrin; 2016, who also supported the idea during personnel communication) have considered only samples having >30% SiO₂ contents under this discrimination scheme.

Conclusions

1. The studied marine carbonates of drilled core samples from the off coast of Montserrat volcanic island of Lesser Antilles arc retain seawater REE characteristics showing slight LREE depletion relative to HREE, Negative Ce and positive Eu-anomalies.

2. Various geochemical proxies and total organic carbon contents indicate that the rare earth elements and yttrium are sourced from seawater whereas carbonates are lithogenic.

3. These marine carbonates are deposited in an open ocean, shallow water predominantly oxic environment devoid of any terrigenous or detrital contamination.

4. These sediments are immature to slightly mature and derived from intermediate to felsic nearby provenance.

5. Our studies indicate that the carbonates are platform type formed in a shallow seawater environment subsequently have undergone dissolution prior to their deposition in to the present deeper marine sediment column located on the overriding plate of the Lesser Antilles subduction system.

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