Geochemistry and Geochronology of the Guajira Eclogites, northern Colombia: evidence of a metamorphosed primitive Cretaceous Caribbean Island-arc

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The chemical composition of eclogites, found as boulders in a Tertiary conglomerate from the Guajira Peninsula, Colombia suggests that these rocks are mainly metamorphosed basaltic andesites. They are depleted in LILE elements compared to MORB, have a negative Nb-anomaly and flat to enriched REE patterns, suggesting that their protoliths evolved in a subduction related tectonic setting. They show island-arc affinities and are similar to primitive island-arc rocks described in the Caribbean. The geochemical characteristics are comparable to low-grade greenschists from the nearby Etpana Terrane, which are interpreted as part of a Cretaceous intra-oceanic arc. These data support evidence that the eclogites and the Etpana terrane rocks formed from the same volcano-sedimentary sequence. Part of this sequence was accreted onto the margin and another was incorporated into the subduction channel and metamorphosed at eclogite facies conditions. ⁴⁰Ar-³⁹Ar ages of 79.2±1.1Ma and 82.2±2.5Ma determined on white micas, separated from two eclogite samples, are interpreted to be related to the cooling of the main metamorphic event. The formation of a common volcano-sedimentary protolith and subsequent metamorphism of these units record the ongoing Late Cretaceous continental subduction of the South American margin within the Caribbean intra-oceanic arc subduction zone. This gave way to an arc-continent collision between the Caribbean and the South American plates, where this sequence was exhumed after the Campanian.

KEYWORDS | Eclogites. Primitive island-arc. Geochronology. Guajira Peninsula. Colombia. Caribbean.

INTRODUCTION

High pressure rocks provide an important record of the geodynamic history of convergent margins. They enable the identification of extinct subduction zones and their tectonothermic history allows the characterization of the particular conditions of the tectonic environments of plate convergence (Ernst, 1988).

The geochemistry of eclogites can be used to constrain the tectonic setting in which the protoliths formed prior to being taken into the subduction path (Bocchio et al., 1990; Volkova et al., 2004; Unger et al., 2005), and understanding their origin can yield major insights as to the type of subduction or collisional setting (e.g. Tang et al., 2007). In addition, geochronological data can constrain the timing of the various stages of the tectonic evolution of these rocks (e.g. Stöckhert et al., 1995).

Different high-pressure metamorphosed oceanic and related continental units have been identified around the

circum-Caribbean areas. They represent a record of the evolution of intra-oceanic subduction or arc-continent collision between the front of the Caribbean and the North and South American plates (e.g. Sisson et al., 1997; García-Casco et al., 2008; Krebs et al., 2008). Of these, only three locations have been identified along the southern margin of the Caribbean. These are: the Cordillera de la Costa-Margarita belt in Venezuela (Stöckhert et al., 1995; Sisson et al., 1997), the Villa de Cura belt also in Venezuela (Smith et al., 1999; Unger et al., 2005) and the Guajira boulders in a conglomerate in northern Colombia (Lockwood, 1965; Green et al., 1968; Zapata et al., 2005; Weber et al., 2007) (Fig. 1).

In this paper we present new geochemical and geochronological results from studies of the eclogites, found as clasts within proximal Miocene conglomerates, in the Colombian-southern Caribbean region, and greenschists from the nearby Etpana Terrane (Lockwood, 1965; Green et al., 1968; Zapata et al., 2005; Weber et al., 2007) (Fig. 2). Their stratigraphic and tectonic position link them



FIGURE 1 | Present day tectonic framework of the Caribbean region and location of the Guajira Peninsula. The locations of the Cordillera de la Costa-Margarita-belt (CCM), the Villa de Cura belt (VC) and the Guajira (G) are enclosed in squares. Other high-pressure rocks localities are shown with black stars. Allochtonous basaltic provinces are shown in black. The inset shows the northern part of the Guajira Peninsula and the three Serranías. Adapted from Lidiak and Jolly (1996).



FIGURE 2 | Simplified geological map of the northern Guajira Peninsula, showing the three main Serranías and the Cabo de la Vela area. The Serranía de Jarara is highlighted. The Parashi granodiorite lies to the northwest of the Serranía. The Etpana and Jarara Terranes and the composite Late-Mesoproterozoic and Palaeozoic metamorphic domain (see text for details) are depicted. Modified from Lockwood (1965) and Gómez et al. (2007). A) The Cabo de la Vela Complex and B) the Parashi area are shown in more detail.

with the NW allocthonous Caribbean belt. Furthermore, similarities to other high-pressure occurrences within the Caribbean area, provide evidence as to the complexity of the convergence tectonics between the South American and Caribbean plates.

GENERAL GEOLOGY

The Guajira Peninsula, in north-easternmost Colombia (Fig. 2), is characterised by several isolated mountain ranges surrounded by broader flat lands and Cenozoic basins (Alvarez, 1967; Lockwood, 1965; MacDonald, 1964). Within these ranges, at least three main lithotectonic belts can be identified (Fig. 2). From southeast to northwest they include 1) a weakly deformed Mesozoic volcanosedimentary belt with a typical south American passive autochthonous margin record (Villamil, 1999), 2) an older metamorphic basement, with Proterozoic and Paleozoic rocks intruded by Jurassic granitoids, whose characteristics resemble basement domains of different segments of the Northern Andes (Alvarez, 1967; Aspden et al., 1987; Cordani et al., 2005; Cardona-Molina et al., 2006) and 3) several deformed low grade meta-volcano-sedimentary units that are interpreted as intra-oceanic arcs and subduction-accretion complexes, related to the Caribbean plate evolution, that were probably accreted during the Late Cretaceous (Weber et al., 2009). The northernmost of these units is the Etpana Terrane (elsewhere called Etpana Formation) that comprises low-grade greenschists, phyllites and quartzites, and interspersed serpentinites, rodingites and gabbros (MacDonald, 1964; Lockwood, 1965; Alvarez, 1967; Zuluaga et al., 2008).

Remnants of a mafic to intermediate island-arc to backarc are exposed immediately to the northwest in the Cabo de la Vela mafic-ultramafic complex (Fig. 2). This islandarc was active at least until ca. 77-74Ma, as indicated by K-Ar whole rock ages on basalt-andesite dikes (Weber et al., 2009). Together the Etpana Terrane and the Cabo de la Vela Complex have been interpreted as elements of the arccontinent collision between the Caribbean plate and the South American margin (Weber et al., 2009). The intrusion of the Parashi Granodiorite at ca. 50Ma defines the lower limit for metamorphism of the Etpana Terrane (Cardona et al., 2007).

Available paleomagnetic constrains have shown that the geologic units in northern South America must have undergone significant block rotation since the Late Jurassic (MacDonald and Opydike, 1974). During the eastern migration of the Caribbean plate in the Neogene, a complex strike-slip system developed in northeastern Colombia and transported tectonic fragments, including the Guajira blocks, from their original position towards the east (Macellari, 1995; Montes et al., 2005; Vence, 2008; Montes et al., 2009).

ANALYTICAL TECHNIQUES

Whole rock geochemistry

Whole rock chemical analyses were carried out at Acme Analytical Laboratories Ltd. in Vancouver, Canada. A 0.2g aliquot is weighed into a graphite crucible and mixed with 1.5g of LiBO₂ flux. The crucibles are placed in an oven and heated to 1050°C for 15 minutes. The molten sample is dissolved in 5% HNO₃. Calibration standards and reagent blanks are added to the sample sequence. Sample solutions are aspirated into an Inductively Coupled Plasma-Emission Spectrometer (ICP-ES) (Jarrel Ash Atom Comb 975) for determining major oxides and certain trace elements (Ba, Nb, Ni, Sr, Sc, Y & Zr) in the sample. For determination of the trace elements, including rare earth elements (REE), solutions are aspirated into an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Perkins-Elmer Elan 6000).

Sample EK-K2 was analysed using a Phillips PW-2400 X-ray Fluorescence (XRF) spectrometer at the GeoForschungsZentrum Potsdam (major and trace elements) and REE Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, VistaMPX) at the Geochemical Laboratory of the University of Potsdam.

Ar-Ar geochronology

Argon-Ar analyses were performed on two handpicked mica samples separated from eclogite samples MJ-033 and MJ-039 at the Geochronology Laboratory of the Departamento de Geología of the Centro de Investigación Científica y de Educación Superior de Ensenada, México. The argon isotope experiments were conducted on mineral grains with a coherent Ar-ion Innova 370 laser extraction system on line with a VG5400 mass spectrometer. All the samples and irradiation monitors were irradiated in the U-enriched research reactor of the University of McMaster in Hamilton, Canada, at position 5C in capsule CIC-66 for 10hr. To block thermal neutrons, the capsule was covered with a cadmium liner during irradiation. As irradiation monitors, aliquots of standard FCT-2 sanidine (27.84±0.04Ma) were irradiated alongside the samples and distributed among them to determine the neutron flux variations. Upon irradiation the monitors were fused in one step while the samples were step-heated. The argon isotopes were corrected for blank, mass discrimination, radioactive decay of ³⁷Ar, ³⁹Ar and atmospheric contamination. For the Ca neutron interference reactions, the factors given by Masliwec (1984) were used. In processing the data, the decay constants recommended by Steiger and Jäger (1977) were applied. The equations reported by York et al. (2004) were used in all the straight line fitting routines of the argon data reduction. The plateau age was calculated from the weighted mean of consecutive fractions that were in agreement within 1σ . The error in the plateau, and in the integrated and isochron ages includes the scatter in the irradiation monitors. The analytical precision is reported as one standard deviation (1σ). For each sample the relevant ⁴⁰Ar-³⁹Ar data for all the experiments is presented, and includes the results for the individual steps and the integrated ages. In the table, the fractions selected to calculate the plateau age are identified as well as the fractions ignored in the isochron age calculation. The preferred age is highlighted in bold typeface.

ECLOGITES

Various types of high-pressure rocks, including eclogites, white-mica schists and quartzites are found as rock-clasts up to 20cm in size within a Miocene conglomerate. Studies on the conglomerate have shown that the source of the clasts is proximal, possibly from the nearby Etpana Terrane (Zapata et al., 2010). Nevertheless, no in-situ outcrops of the eclogites and high-pressure metasediments have been found thus far. The eclogites were first described by Lockwood (1965) and preliminary geothermometry was undertaken by Green et al. (1968) and Weber et al. (2007). The selected samples have a variety of compositions and are similar to those described in previous studies, except for sample 2832 (J-291A) described by Green et al. (1968), which contains scapolite and calcite.

In general, all samples are different from one another in detail, but can be divided roughly into two groups: Samples that contain more than 99% omphacite + garnet + rutile (GM-2b, MJ-007B, MJ-043), and a second group of samples that, in addition to these minerals, also contain high proportions of other minerals such as clinozoisite \pm kyanite \pm mica \pm amphibole \pm quartz \pm sphene (GM-2c, MJ-033, MJ-039, MJ-040, EK-K2). Folded mesoscale banding of garnet-rich and garnet-poor domains is evident in three of the samples (MJ-007B, MJ-033, MJ-039). This suggests that some of the eclogites were formed from layered gabbros. All rocks contain compositionally zoned garnet, with orange cores and lighter coloured pink rims (Fig. 3A). Garnet zonation patterns show Fe-rich cores and Mg-rich rims (Weber et al., 2007).

In the first group, two samples have a porphyroblastic texture defined by garnet crystals within an omphacite matrix (GM-2b, MJ-043), and one sample has a granoblastic texture, with garnet-rich domains interspersed with scarce pyroxene-rich domains (MJ-007B) (Fig. 3B).

In all samples garnet is euhedral. Samples GM-2b and MJ-007B show weakly foliated fabrics defined by the omphacite (Fig. 3B), whereas sample MJ-043 is isotropic. Two populations of pyroxene can be identified, a larger one with zonation shown by darker green cores compared to the edges, and a smaller one, that comprises the main matrix foliation (Fig. 3A). In addition to the main minerals, sample GM-2b contains <1% of white mica within the matrix. A small degree of retrogression to green amphibole, chlorite and sphene is evident in sample MJ-007B (Fig. 3B).

Of the second group, in which additional mineral phases are present, three samples contain Ky (MJ-033, MJ-039, EK-K2) as an important part of the assemblage (Fig. 3C). Other minerals present are quartz \pm clinozoisite \pm white mica \pm talc. In general the textures comprise porphyroblastic garnets in a weakly foliated matrix. Two samples display compositional banding (Fig. 3D): Sample MJ-039 has quartz-white mica bands intercalated with garnet + omphacite + amphibole bands (Fig. 3C), whereas sample MJ-033 has complex folded intercalations of garnet-rich, omphacite-rich, quartz-rich and kyanite-rich bands. Garnet in all samples is euhedral. Kyanite crystals are porphyroblasts, often with inclusion free cores and poikilitic rims that suggest two generations of crystal growth. Sample retrogression is evident in kyanite porphyroblasts that are almost totally replaced by a fine mass of white mica. Textures composed of white micas and quartz in sample MJ-039 suggest that they are pseudomorphs after a previous tabular mineral phase.

Sample GM-2c is a retrogressed eclogite with a heterogranular texture containing garnet + omphacite + rutile + quartz as the peak metamorphic assemblage. There is conspicuous evidence of two consecutive retrogression events. In the first event, poikilitic clinozoisite laths reaching 1.7cm along with colorless amphibole (Fig. 3E) are interpreted to have formed in the Guajira during the exhumation of these rocks (Weber et al., 2005). About 60% of the rock was replaced by this process. The second event is defined by the breakdown of garnet to form the assemblage to chlorite + white mica + amphibole + quartz, indicating that these rocks retrogressed through the amphibolite facies (Weber et al., 2005).

Sample MJ-040 is a heterogranular eclogite containing 15% of clinozoisite. Replacement textures in garnets and clinozoisite (Fig. 3F) suggest that omphacite grew after these two minerals crystallized.

⁴⁰Ar/³⁹Ar age determinations

White micas from two eclogite samples (MJ-033 and MJ-039) were selected for ⁴⁰Ar-³⁹Ar step heating analyses. Results are presented in Figure 4 and Tables 1A and 1B.

White mica from sample MJ-033 yields a well-defined plateau age spectra with about 70% of the released ³⁹Ar during three steps. The calculated plateau age of 79.2 \pm 1.1Ma is consistent with the isochron age of 77.3 \pm 1.5Ma (Fig. 4A). Ca/K ratios derived from the

³⁷Ar/³⁹Ar show that the obtained plateau may come from a relatively homogeneous reservoir, whereas in the last steps the ages become a little younger and fall away from the plateau. The high Ca/K ratios suggest the presence of a potential Ca-bearing phase, probably inclusions of



FIGURE 3 | Microphotographs from various eclogite samples from the Guajira location. A) Garnet idioblast in a foliated omphacite matrix. Zonation is shown by garnet, and the larger omphacite crystals. PPL. B) Compositional banding defined by garnet-rich and omphacite-rich domains. PPL. C) Compositional banding defined by quartz + mica-rich domains interspersed with omphacite + garnet-rich domains. PPL. D) Clinozoisite replacement in the matrix of one of the Guajira eclogite samples. XPL. E) Kyanite-bearing eclogite with garnet idioblasts and omphacite. F) Heterogranular eclogite sample. Note the irregular edges of the garnet and particularly the clinozoisite. PPL. Abbreviations (after Kretz, 1983); Czo: clinozoisite, Grt: garnet, Omp: omphacite, Qtz: quartz, Wmca: white mica.

minerals such as clinozoisite and sphene, which have been observed petrographically.

Muscovite from sample MJ-039 also shows an age spectra in which 85% of the ³⁹Ar was released in two intermediate stages (Fig. 4B). Ca/K ratios are also homogeneous, although in the other heating stages there is evidence of some mix with high Ca phases. The plateau age of 82.2 ± 2.5 Ma is close to the calculated isochron age of 81.6 ± 2.7 Ma (Fig. 4B).

Closure temperatures for white mica in the Ar-Ar system have conventionally been considered to lie between 325° and 375°C (McDougall and Harrison, 1999). Recent experiments have suggested that temperatures may be as high as 425°C (Harrison et al., 2009). In the case of the analysed micas from the Guajira eclogites, initial calculated temperatures are above 700°C (Weber et al., 2005), consequently the Ar-Ar ages are possibly related to

the cooling of the last metamorphic event, and therefore might be linked to the exhumation path.

Geochemistry

Seven samples were analysed for major and trace element geochemistry. Analyses are presented in Table 2.

Figure 5 shows variation diagrams of selected elements versus Zr. Zirconium has been plotted against other elements as it is accepted as immobile during alteration (Humphris and Thompson, 1978; Staudigel et al., 1996). In general, elements considered as compatible are well correlated with Zr, whereas elements such as K_2O , Ba and Rb, which are considered as incompatible, show some degree of scatter. Sample MJ-043 has high Zr contents and in general plots away from the overall trend, indicating possible differences in the chemistry of the protolith.



FIGURE 4 | White mica ⁴⁰Ar/³⁹Ar incremental step heating spectra for eclogite samples MJ-033 and MJ-039 from the Guajira area.

TABLE 1 | Geochemical data for Guajira samples

				<u> </u>			I		
Samplo		GM-2h	GM-2c	Eclogite	M 1033	M 1040	M 1043	GUA24A	CLIA24B
SiO	50 A	48.08	/0 16	101007B	53.84	17 15	17 17	54 77	50 51
	1 01	1 5 4	1 01	+0.00	1 07	0.77	9 50	0.91	1 1 0
	1.21	1.04	1754	1.17	1.37	15.05	15.00	10.01	1.12
	14.2	14.1	17.54	14.07	10.00	10.40	15.32	13.03	10.40
N=0	12.11	14.29	12.11	10	12.03	12.40	15.50	9.41	10.74
MaQ	0.155	0.21	0.15	0.4	0.22	0.27	0.14	0.17	0.2
NIGO	0.51	10.00	4.96	10.00	5.85	5.63	5.33	6.38	4.64
Na _o O	9.76	10.00	9.70	3.09	3.27	3.85	0.37 4.64	9.27	0.40 4 12
K ₀ O	0.03	0.04	0.34	0.00	0.13	0.00	0.01	1.05	0.42
P ₂ O ₂	0.00	0.04	0.04	*	0.10	0.02	0.32	0.14	0.42
Cr ₂ O ₂	0.1	0.02	0	0.008	0.018	0.016	0.052	0.022	0.20
101	1.31	0.1	0.3	0.7	0.1	0.3	0.6	3.6	28
Total	99.75	100.01	100	99 78	99 77	99 74	99.73	99 79	99.82
- Otal	00.70	100.01	100	00.70	00.11	00.71	00.70	00.70	00.02
Ba	53	72	77.8	28	36	27	11	203	57
Rb		0	8	0.6	3.5	0.6	0.5	20.3	7
Sr	37	37.2	258.8	19.3	85.6	525.7	1//.2	146	152.1
Cs		0	0.4	^ 	^	^ 	°	0.4	
Ga T-	14	15	17.7	10.9	16.4	13.1	20.5	14.2	15
1a Nh	4	0.2	0.1	0.3			1.9		
	4	3.3	1.7	5.4	2.1	1.0	24.7	1	1.4
ПI 7r	67	112.0	2.2	2.8	2.2	1.2	0.2	1.5	67.0
ZI V	22	113.2	00.3 27.7	CO 66 2	72.9	42.2 20.1	232.0	44.Z	24.9
ть	23	43.7	27.7	00.2	20	20.1	32.4 0.4	21.0	24.9
111		0.9	0.4	0.9	0.5	0.0	2.4	0.5	0.9
La/Nh	1 05	2.3	2.82	1 04	2.62	7 14	0.7	3.3	3.93
Cr	1.00	*	*	*	*	*	*	*	*
Ni	103	727	1407 5	42.6	48	9.6	194	22.5	23 1
Со	100	38.1	39.7	23.9	34.3	30.6	42.9	23.9	29.2
Sc	46.82	32	31	48	36	41	41	32	31
V		406	334	304	371	342	318	258	273
Cu		6.9	33.7	16.5	32.1	18.3	78.9	67.9	38.3
Pb		0.2	0.5	1	0.6	1.3	0.9	1.7	0.9
Zn	68	13	8	12	11	5	14	33	55
Bi		0	0	*	*	*	* *	k	*
Cd		0.1	0	*	*	*	*	0.1	*
Sn		1	1	1	*	*	2	k	*
W		0.6	0.3	*	2.8	2	2.7	k	*
Мо		0.4	0.7	*	0.7	0.9	1.2	0.2	0.3
Be		1	1	*	*	*	1 '	k	*
Au		0.8	0	2.4	1.6	1.3	0.9	2.8	0.6
Hg		0	0	*	*	*	* 1		*
As		0.5	1	1.1	*	*	* •		*
Se		0	0	*	0.5	*	0.8		*
Sb		0.1	0.1	0.1	*	*	* 1	•	*
La	4.21	7.6	4.8	5.6	5.5	5	22.4	3.3	5.5
Ce	11.07	20.3	13.2	11.8	13.1	12.2	51.8	9.3	15
Pr	1.6	3.29	2.15	1.82	2.26	1.89	6.94	1.53	2.22
Nd	8.16	16.2	11.7	9	11.7	9.4	30.5	8.2	11.7
Sm	2.91	4.5	3.5	2.17	3.18	2.62	7.22	2.74	3.43
Eu	1.11	1.52	1.22	0.68	1.19	0.95	2.51	0.92	1.18
Gd	3.66	4.98	4.12	4.09	3.94	3.14	7.66	3.43	4.14
Tb	0.55	0.89	0.74	1.15	0.74	0.57	1.26	0.64	0.75
Dy	4.11	6.81	4.86	8.53	4.39	3.32	6.51	3.89	4.67
Ho	0.89	1.48	0.98	2.25	0.94	0.72	1.25	0.82	0.97
Er	2.72	4.54	2.81	8.24	2.8	2.11	3.42	2.4	2.95
Tm	0.39	0.74	0.45	1.45	0.42	0.32	0.5	0.34	0.45
Yb	2.66	4.48	2.72	10.08	2.6	2.02	2.95	2.01	2.71
LU	0.4	0.68	0.43	1.63	0.4	0.31	0.43	0.3	0.41
∟a/Yb	1.58	1.7	1.76	0.56	2.12	2.48	7.59	1.64	2.03

* not analysed

Most eclogite samples from Guajira plot within the basaltic andesite field (Fig. 6) in the diagram proposed by Winchester and Floyd (1977), in a classification of volcanic rocks using less mobile (incompatible) element ratios, except for sample MJ-043, which plots in the alkali-basalts field. All the samples analysed are tholeiitic, except for sample MJ-043, which contains 3.58wt% TiO₂ and is an alkali basalt. The low to moderate MgO concentrations (4.65-6.5wt.%), the Mg# [Mg#=100Mg/ (Mg+Fetot)] between 21 and 35 for SiO₂ ranging from 45.35 to 54.77wt%, as well as Ni contents lower than 40ppm, indicate that the protoliths of most of the eclogites are unlikely to be primary melts of the upper mantle and therefore represent fairly fractionated melts of basaltic to andesitic composition that cannot have been in equilibrium with a mantle peridotite. The low concentrations of Nb (<5,5ppm), Zr (<80ppm) and light rare earth elements (LREE), in most samples, are also mentioned.

On the Th-Hf-Nb representative geochemical discrimination diagram (Fig. 7A), the Guajira samples show consistent overlap, and plot within the destructive plate-margin basalt field. As expected, sample MJ-043 plots in the E-MORB or within-plate basalt field, away from the overall array.

In order to discriminate between volcanic-arc tholeiites and MOR or back-arc basin basaltic rocks, samples were plotted on the discrimination diagram of Shervais (1982) (Fig. 7B). In general The Guajira rocks fall within the MORB- back-arc basin field, and only sample MJ-043 falls within the ocean-island or alkali basalt field.

Multi-element diagrams

MORB-normalized multi-element diagrams are presented in Figure 8 (after Pearce, 1983). Eclogite samples show a similar trend (Fig. 8A) with the exception of samples MJ-043 and MJ-007B, which are plotted separately (Fig. 8B).

Some samples plotted on Figure 8A and those plotted on Figure 8B are notably depleted in Large Ion Lithophile Elements (LILE) K, Rb, Sr, and Ba, when compared to MORB. Sample MJ-043 is enriched in High Field Strength Elements when compared to MORB, whereas sample MJ-007B has a similar pattern. The LILE are scattered, possibly due to some degree of element migration during ocean floor alteration and metamorphism (Aguirre, 1988; Volkova et al., 2009). All samples have High Field Strength Elements patterns similar to N-MORB, and a strong negative Nb anomaly. Also, three of the four samples have a slightly negative Ti anomaly, the exception being sample MJ-033. La/Nb ratios range from 1.05 to 7.14. Samples MJ-007B and MJ-043 have no evident negative Nb anomaly and Y and Yb are scattered.

REE-diagrams

Chondrite normalized REE diagrams are presented in Figure 9. Eclogite samples are plotted in Figure 9A, and samples MJ-043 and MJ-007B are plotted separately, in Figure 9B. Eclogite samples from the Guajira region, except MJ-043 and MJ-007B, show a strong consistency

TABLE 2 | 40Ar-39Ar data for white micas from two eclogite samples. The preferred age is highlighted in bold typeface

A, sample MJ-033 muscovite											
Pwr	F ³⁹ Ar	⁴⁰ Ar*/ ³⁹ Ar _K	t (Ma)	% ⁴⁰ Ai	* ⁴⁰ Ar/ ³⁶	Ar ³⁷ Ar _{Ca} / ³⁹ /	Ar _K t _i (Ma)	t _p (Ma)	t _c (Ma)	(⁴⁰ Ar/ ³⁶ Ar) _i	MSWD/n
0.20	0.0018	13.86 ± 6.98	77.2 ± 38.1	17.1	0 356.	1.49	2				
0.65	0.0038	13.99 ± 3.69	78.0 ± 20.1	32.8	6 440.	11 < 0.00)1				
1.00	0.0526	13.70 ± 0.26	76.4 ± 1.4	86.0	4 2117.4	44 < 0.00)1				
1.30	0.1457	14.12 ± 0.36	78.7 ± 1.9 §	92.9	8 4208.	72 < 0.00)1				
1.50	0.2373	14.21 ± 0.23	79.2 ± 1.3 §	95.8	5 7127.4	44 < 0.00)1				
1.80	0.3025	14.28 ± 0.23	79.5 ± 1.2 §	96.9	9523.	56 0.004	4				
2.10	0.0842	13.32 ± 0.27	74.3 ± 1.5	96.1	4 7663.4	45 0.024	4				
2.10	0.1721	13.57 ± 0.18	75.7 ± 1.0	95.5	5 6642.	92 0.11	2 78.0 ± 1.4	79.2 ± 1.1	77.3 ± 1.5	293 ± 32	2.2/8
B, sample MJ-039 muscovite											
Pwr	F ³⁹ Ar	⁴⁰ Ar*/ ³⁹ Ar _K	t (Ma)	9	6 ⁴⁰ Ar* 40	۲/ ³⁶ Ar ³⁷ Ar	_{Ca} / ³⁹ Ar _K t _i (Ma) t _p (Ma)	t _c (Ma)	(⁴⁰ Ar/ ³⁶ Ar) _i	MSWD/n
0.20	0.0021	149.25 ± 21.83	696.5 ± 84.5		15.60	350.12	0.242				
0.41	0.0027	-4.58 ± 8.95	-26.3 ± 51.7	+	- 4.21	283.56 <	0.001				
0.80	0.0122	12.25 ± 1.40	68.4 ± 7.7	Ť	35.98 4	461.59 <	0.001				
1.10	0.0196	12.22 ± 0.55	68.3 ± 3.0	t	66.58 8	384.19	0.053				
1.50	0.3537	14.66 ± 0.66	81.6 ± 3.6	ş	93.37 44	454.26 <	0.001				
1.80	0.4607	14.87 ± 0.58	82.7 ± 3.2	Ş	96.82 93	303.17 <	0.001				
2.00	0.0463	12.57 ± 0.23	70.2 ± 1.3	†	91.50 34	175.70	0.033				
3.00	0 1026	1343 + 021	749 + 12	+	95.03 59	47 88	0.054 81.8 + 2	2 822+25	816+27	345 ± 10	01/3

Pwr: laser power in Watts applied to release argon; t age of individual fraction, it does not include the uncertainty in J; t, integrated age; t_o plateau age calculated with the weighted mean of the fractions selected; t_c isochron age; § fractions used to calculate the plateau age; † fractions ignored in the isochron age calculation; all errors are given to 1σ level. Corresponding J for all the samples: 0.003157 ± 0.000050. Preferred age is highlighted in bold typeface.

independent of fabric and metamorphic retrogression. REEs are largely more than 10 times that of chondrite. The samples have slightly enriched LREE patterns, with La/Yb between 1.7 and 2.48. The high heavy rare earth elements (HREE) concentrations and relatively low La/Yb ratios indicate a lack of residual garnet in the source, therefore suggesting that melting in the spinel-lherzolite stability field is more likely. The alkali-basalt sample MJ- 043 (Fig. 9B) shows the most LREE enriched pattern with a La/Yb ratio of 7.59. HREE values overlap those of the other eclogite samples, also indicating that the source region does not contain relic garnet.

In contrast, sample MJ-007B is the only LREE depleted example, with a La/Yb ratio <1. The high chondrite-



FIGURE 5 | Zr vs. selected major and trace elements. Zr is considered to be an immobile element, unmodified by alteration. Filled symbols are Group I eclogites and white symbols are Group II eclogites.



FIGURE 6 Nb/Y - Zr/TiO_2 diagram of Winchester and Floyd (1977), for the Guajira eclogite and Etpana Terrane samples. Legend as in Figure 5.

normalized HREE concentration is possibly due to a cumulate origin within a layered magmatic protolith.

Caribbean realm

Within the Caribbean realm, metabasic rocks generally underwent various degrees of metamorphism, mainly during subduction and/or accretion processes which were driven by tectonic forces related to the west to east migration of the Caribbean during the Cretaceous, the passage of which left behind fragments accreted onto continental margins (Burke, 1988). Primary basaltic rocks within the Caribbean realm are considered to have originated from four igneous sources (Donnelly and Rogers, 1980; Donnelly et al., 1990): 1) N-MORB that formed during the North America-South America plate separation after their break-up in the Jurassic 2) Ocean plateau-type rocks which originated as part of the Colombian Caribbean Plateau in Albian-Aptian times 3) Primitive intra-oceanic island-arc or island-arc tholeiites (IAT) forming first in the Early Cretaceous and 4) More evolved calc-alkaline volcanic rocks formed as the island-arcs evolved in the Late Cretaceous (Albian-Campanian) to Early Oligocene. The two later arc building phases have been related to the growth of a single great Caribbean arc (Burke, 1988; Pindell, 1993), although this concept has been questioned recently by various authors (Iturralde-Vinent and Lidiak, 2006; Wright and Wyld, in press).

The geochemical characteristics from most of the Guajira eclogites, such as the negative Nb-Ta anomalies and LREE enrichment relative to HREE, indicate that most of these rocks are more likely to have been formed in an island-arc tectonic setting, and therefore preclude formation from N-MORB sources or the Colombian-

Caribbean plateau. In addition, the concentrations of Nb below 5.5ppm, Zr below 75ppm and TiO_2 below 1.5wt% support the interpretation that these rocks are derived from an island-arc protolith (e.g. Verma, 2006).

LILE are tracers of either slab components, as they mobilize during dehydration of the subducting slab, or crustal contamination (e.g. Verma, 2006). Their slight enrichment or depletion in the Guajira rocks precludes large influence of continental contamination and slabinduced fluids. Furthermore, the depletion in LILE relative to MORB is inconsistent with a simplistic islandarc model. The subducted oceanic plate, that dehydrated and triggered magma genesis, must have been extremely depleted in LILE.

Of the Caribbean island-arc series, the calc-alkaline series basalts are characterized by the high LILE compared to High Field Strength Elements (HFSE), as well as high values of K_2O , Ba, Rb and Sr. Also present is an



FIGURE 7 A) Th-Hf/3-Nb/16 discrimination diagram (Wood, 1980) for the Guajira eclogites and the Etpana Terrane rocks. B) Ti/100 vs. V discrimination diagram (Shervais, 1982) for the Guajira eclogites and the Etpana Terrane. Legend as in Figure 5.

enrichment of LREE compared to HREE. In contrast, basalts from the Cretaceous primitive intra-oceanic island-arc series are only slightly enriched in LILE relative to high field strength elements, and the REE patterns are rather flat compared to the calc-alkaline. Figure 10A shows a comparative MORB-normalized multi-element geochemical plot between the Guajira data and the Cretaceous Washikemba Formation of Bonaire, believed to be an Aptian (~96Ma) intraoceanic arc sequence (Beets et al., 1984; Thompson et al., 2004). Also shown is data from the Aruba Batholith (White et al., 1999), which represents a major calcalkaline intrusion emplaced in the Late Cretaceous. The relatively flat patterns of the Guajira samples are



FIGURE 8 A) and B) Multi-element patterns normalized to MORB for Guajira Eclogites. C) Multi-element patterns normalized to MORB for Etpana Terrane greenschist-facies rocks. Legend as in Figure 5. Normalization values from Pearce.



FIGURE 9 | A) and B) REE patterns normalized to chondrite for Guajira eclogites. C) REE patterns normalized to chondrite for Etpana Terrane greenschist-facies rocks. Normalization values from Nakamura (1974).

similar to the Washikemba Formation, whereas the Aruba Batolith rocks have a higher LREE/HREE ratio.

These considerations indicate that most of the Guajira eclogites belong to a primitive intra-oceanic island-arc type series. The primitive intra-oceanic island-arc series has been considered to have been confined to the Aptian-Albian times (Donnelly and Rogers, 1980; Donnelly et al., 1990), but it is now realised that primitive intra-oceanic island-arc rock sources were still active during most of the Cretaceous (Iturralde-Vinent and Lidiak, 2006 and references therein). Examples are the Téneme Formation in Cuba (Proenza et al., 2006), active in the Late Cretaceous, and the Cabo de la Vela rocks in the Guajira Peninsula, which have K-Ar whole rock ages of 74Ma (Weber et al., 2009). Comparison with the Cabo de la Vela samples is shown in Figure 10C, and it is evident that both have similar REE and multielement patterns, indicating that

they might have formed from similar magma sources and processes, linked to comparable tectonic scenarios.

Hawkesworth et al. (1993a, b), subdivided islandarc basalts into two groups on the basis of LREE/HREE, using La-Yb ratios to discriminate between predominantly intra-oceanic arcs (La/Yb>5) and arcs developed in the proximity of continental margins (La-Yb>5). On the La-Yb variation diagram (Fig. 11) the Guajira eclogites fall within the low-LREE/Yb island-arc basalt field and are similar to the Central Puerto Rican phase I lavas (Jolly et al., 2001, Jolly et al., 2006) and the Late Cretaceous Cabo de la Vela basaltic units (Weber et al., 2009). Data from the Téneme Formation in eastern Cuba (Proenza et al., 2006) are also shown for comparison.

The different geochemical characteristics of sample MJ-043 indicate that, although the primitive intra-



FIGURE 10 | A) and B) Multi-element patterns normalized to MORB and REE patterns normalized to chondrite plots for the Guajira samples compared to the Washikemba Formation of Bonaire (Thompson et al., 2004) and the Aruba batholith (White et al., 1999). C) and D) Multi-element patterns normalized to MORB and REE patterns normalized to chondrite plots for the Guajira samples compared to the Cabo de la Vela intrusions (Weber et al., 2009). Sample conventions as in previous figures.

oceanic island-arc-like source predominates in the Guajira eclogites, other mafic protoliths were also integrated into the subduction zones and underwent high-pressure metamorphism.

ETPANA TERRANE

The Cretaceous Etpana Terrane crops out on the northwestern part of the Guajira Peninsula (Fig. 2). First described as the Etpana Formation, Lockwood (1965) divided this unit into six lithologic varieties: finely laminated phyllites, coarsely laminated quartzose phyllites, coarsely bedded quartzites, albite-epidotechlorite schists, albite-epidote-biotite schists and "complex" zones of mixed phyllite and serpentinite. Recently, this latter unit has been described as a mélange comprising a metapelite-matrix that contains exotic blocks of serpentinite and microgabbro (Zuluaga et al., 2008).

The maximum age of the Etpana Terrane is constrained by zircon provenance analyses at 116.1 ± 7.6 Ma (U-Pb in zircon) (Weber et al., 2010). The upper limit is defined by the Parashi Stock, a hornblende-biotite granodiorite intrusive that has been dated at ca. 45-48Ma (K/Ar in hornblende and biotite) (Lockwood, 1965; Cardona et al., 2007).

The assemblage of the two analysed samples of the Etpana Terrane consists of Ep+Alb+Act+Ttn. One of the samples (GUA 24A) is foliated, the schistosity being defined by actinolite and chlorite, with epidote and feldspar porphyroblasts (Fig. 12A). Inclusion trails in the porphyroclasts indicate syntectonic growth. The unfoliated sample is more albite and chlorite rich. The euhedral shape of these minerals seen in some samples suggests that they might represent phenocrystal pseudomorphs, relict from an original igneous rock (Fig. 12B).

Geochemistry

Two samples from greenschists of the Etpana Terrane were analysed for major and trace element geochemistry. Analyses are presented in Table 8. Selected elements versus Zr are plotted in Figure 5. In the compatible element diagrams, the two samples overlap in the first group of eclogites, whereas there is a considerable scatter among incompatible elements.

Figure 6 shows that both samples are classified as basaltic andesites in the Winchester and Floyd (1977) volcanic rock classification diagram, and plot within the destructive plate-margin basalt field in the Th-Hf-Nb discrimination diagram.

In the V-Ti discrimination diagram (Fig. 7B) of Shervais (1982) these samples fall in the MORB-BABB field, similar to most of the Guajira eclogites.

Multi-element diagrams

The two samples from the Etpana Terrane are plotted in a N-MORB normalized multi-element diagram (Fig. 8C). Both samples are enriched in Sr, K_2O , Rb and Ba, compared to N-MORB and have a pronounced Nb and a slightly less pronounced TiO₂ negative anomaly. The overall High Field Strength Elements pattern is similar to MORB. La/Nb ratios are 3.30 and 3.93. The Etpana Terrane pattern overlaps that of the Guajira eclogite samples, except for notable differences in the abundance of mobile elements.

REE-diagrams

The two samples from the Etpana Terrane (Fig. 9C) are somewhat LREE enriched, with La/Yb ratios of 1.64 and 2.03. Both are slightly (10 times) more enriched than chondrite, and in general have similar patterns to those shown by the Guajira eclogite samples. However, the Etpana Terrane samples exhibit a slight negative Eu-anomaly not seen in the Guajira eclogite samples, indicating probable plagioclase fractionation during the crystallization of the protolith.

Comparison between the geochemical characteristics of the geenschists from the Etpana Terrane and the eclogite boulders suggests that both have protoliths that formed in similar tectonic scenarios. There are some differences in mobile elements such as K₂O, Ba and Rb, but these can be



FIGURE 11 | La vs. Yb for Guajira eclogites and Etpana Terrane rocks (SiO₂<55) in intraoceanic and continental margin settings, after Hawkesworth et al. (1993a, b). CPR indicates central Puerto Rico samples (Jolly et al., 2006). Legend as in Figure 5.

explained by mobility during alteration and metamorphism (Aguirre, 1988; Volkova et al., 2009).

TECTONOMETAMORPHIC RECORD

Within the most accepted plate tectonic model for the evolution of the circum-Caribbean, the migration of the Caribbean during the Cretaceous took place after the Triassic-Jurassic breakup of Pangea and the formation of an oceanic rift that formed the proto-Caribbean ocean floor, between the separating North and South American plates (Pindell, 1994; Pindell et al., 2005; Pindell and Keenan, 2009). Plate motion during the mid- to Late Cretaceous resulted in the subduction of the proto-Caribbean beneath the east-west migrating Caribbean plate, and the formation of a complex island-arc setting. Parts of these island-arcs interacted with the South American continent, which resulted in the formation of subduction-accretion complexes at the Caribbean-South American and North American plate boundaries.

In the Guajira region, the distribution of high-pressure boulders is limited to the basal conglomerate of a Tertiary sedimentary sequence to the north-west of the Serranía de Jarara (Lockwood, 1965) (Fig. 2). Their eroded source has been shown to be in the adjacent Etpana Terrane (Zapata et al., 2010). This suggests that the in-situ high-pressure rocks were located towards the Caribbean plate, whereas the lower grade greenschist-facies rocks are located to the south, towards the South American continent. Farther northwest, the unmetamorphosed dikes of the ca. 77Ma Cabo de la Vela mafic-ultramafic complex have similar geochemical patterns to the Guajira eclogites and the greenschists of the Etpana Terrane. Associated with the Cabo de la Vela complex is the presence of a positive Bouguer anomaly, extending 100km offshore to the northwest and 30km, onshore to the southeast, but with no continuity into the Serranía de Jarara (Kellogg et al., 1991).

In addition, previous studies have argued that the deposition of the associated high-pressure metasedimentary rocks from within the Tertiary conglomerate and the Etpana Terrane metasediments occurred in a common paleogeographic configuration, due to the virtually identical provenance of zircon populations in their sedimentary protolith (Weber et al., 2010).

The spatial relationship between the eclogites and greenschists of the Etpana Terrane, geological and gravimetric constraints, the similarities of their geochemical characteristics and their common paleogeographic configuration are strong evidence that the volcanosedimentary sequence that formed the Etpana Terrane also formed high-pressure rocks found in conglomerate, and that these rocks are remnants of an allocthonous island-arc of a primitive nature. This arc was partially metamorphosed to eclogite facies conditions, whereas other parts attained greenschist-facies metamorphism.

According to the models proposed, the subduction of the proto-Caribbean beneath the migrating Caribbean resulted in the formation of a multistage single volcanic arc on the front of the moving plate. However, other models suggest the existence of a multiple-arc and microplate setting in Late Cretaceous times (Iturralde-Vinent and Lidiak, 2006 and references therein), including the formation of a major arc in the southern margin of the Caribbean plate (Wright and Wyld, in press). Although it is still necessary to determine the protolith ages of the Guajira eclogites, the



FIGURE 12 | Microphotographs from samples of the Etpana Terrane. A) Foliated sample where the epidote and albite porphyroclasts are shown. PPL. B) Unfoliated sample, note the euhedral feldspar crystal in the centre of the photograph. PPL. Abbreviations (after Kretz, 1983); Act: actinolite, Chl: chlorite, Ep: epidote, Fld: feldspar.

data presented here and the existence of the Cabo de La Vela in the Guajira region (Weber et al., 2009) suggest that the scenario of a multiple-arc system is very likely.

The 82.2 ± 2.5 and 79.2 ± 1.1 Ma ages obtained from one of the Guajira eclogites, plus a 75.88 ± 0.15 Ma Ar-Ar age obtained from a high-pressure white mica schist boulder in the same conglomerate (Tobón et al., 2009), suggest that subduction was active before and during the formation of the Cabo de la Vela island-arc. Furthermore, sedimentary provenance studies of these high-pressure metasedimentary rocks and the Etpana Terrane also suggest that this arc was already approaching the continental margin, and material with South American and arc sources was deposited and continued to be incorporated into the collisional wedge until up to ~71Ma (Cardona et al., 2009; Weber et al., 2009).

The presence of Turonian to Maastrichtian fossils in the Etpana Terrane (Lockwood, 1965) also confirms that the sediments forming the accretionary wedge were deposited and metamorphosed during its advance. Throughout the convergence of this arc, it is probable that the upper plate was incorporated into the subduction zone due to subduction-erosion, and continental subduction may have started until the final continental arc collision. Due to the presence of a significant amount of continental material, the high-pressure rocks followed an alpine-type P-T-t path that indicates the involvement of a continental margin, triggering the final collision (Cloos et al., 2005; Agard et al., 2009, Guillot et al., 2009).

Other high-pressure locations in the southern Caribbean include the Villa de Cura Group and Cordillera de la Costa-Margarita high-pressure belts. The highpressure metamorphism event of the Juan Griego Group in Margarita is constrained by the intrusion of the nonmetamorphosed El Salado granite, dated at 86Ma (U-Pb in zircon). Phengites from the Juan Griego high-pressure schists that yield ages between 90-80Ma (Stöckhert et al., 1995). Ar-Ar ages of 92.4±0.5Ma in amphibole and 86.5±0.2Ma on mica were obtained by Sisson et al. (2005), which are interpreted as the Late Cretaceous cooling age for this belt. In the same study, an Ar-Ar age of 88.5Ma on white mica was obtained for the nearby low-grade Los Robles Formation.

Estimated ages range from 96.3 ± 0.4 Ma on amphibole to 79.8 ± 0.4 Ma on mica (Smith et al., 1999) in the highpressure Villa de Cura belt, thought to represent a metamorphosed primitive intra-oceanic island-arc (Unger et al., 2005). Sisson et al. (2005) suggested that due to the similar metamorphic peak ages of both belts, the Villa de Cura and Los Robles may have formed in the same subduction system, but from different protoliths. Although correlation between the Guajira and Venezuela occurrences remains to be determined, their timing, nature of the protolith and in some instances type of metamorphism indicate that they are all part of a regional scale convergent system that put the Caribbean arc close to the continental margin (Pindell et al., 2005). A major question that remains open is whether these high-pressure belts represent a continuous subduction zone through time, or are part of multiple subduction zones that were modified by a strike slip system during their approach to the margin (Maresch et al., 2009).

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