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MINERALOGY, PETROGRAPHY, GEOCHEMISTRY AND ECONOMIC POTENTIAL OF CARBONATE ROCKS OF SRI LANKA

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ABSTRACT

Sri Lanka comprises different paragenetic types of carbonate rocks such as Miocene limestone, crystalline limestone (marble), carbonatite and dyke like carbonate bodies. The purpose of this paper is to summarize documented studies on petrogenesis and economic potential of crystalline limestone, carbonatite and dyke-like carbonate bodies. Pure marbles, which are confined to the Highland Complex (HC) of the country are composed mainly of dolomite, while carbonatite occurrences at Eppawala consist mainly of calcite. Mono-mineralic calcite bodies with trace amounts impurities are found in the Southeastern part of the country. Detailed geochemical, stable isotope and petrological studies on marbles of HC have revealed that they have formed by granulite grade metamorphism of dolostones deposited in an open ocean. Pure marbles basically retain their primary isotopic signatures with only their $\delta^{18}\text{O}$ values amenable to alteration due to $^{18}\text{O}/^{16}\text{O}$ exchange with percolating waters. Over a limited distance, geochemistry of contact zones of the marbles has been changed significantly due to metamorphic geochemical alterations.

Eppawala carbonatites are unique among the other carbonatites in the world in terms of field setting, isotope and elemental geochemistry and textural features of carbonate minerals. Trace and rare earth element composition as well as stable isotope ratios from the Eppawala carbonatites are not comparable with most of carbonatites in the world. But they are within the broader range of carbonatitic rocks and do not show any meta-limestone signatures. Textural features and chemical composition of carbonate minerals suggest that present carbonatite bodies have been dislocated from the emplaced positions in the crust due to deformations experienced by the country rocks. Geochemically and petrographically the dyke-like carbonate bodies differ significantly from both carbonatites and crystalline limestone. Concentrations of Sr and Rare Earth Elements (REEs) of dyke-like bodies lie between those of carbonatites and marbles. However, the concentrations are much lower than those of carbonatites. Carbon and oxygen isotope compositions are similar to those of most meta-sedimentary carbonates suggesting that the carbonate dykes were formed as melts from marbles at crustal levels due to shearing and thrusting of HC and Vijayan Complex (VC) plates.

Laboratory experiments carried-out in the recent past were able to synthesize value-added products such as Precipitated Calcium Carbonate (PCC), magnesium hydroxide [$\text{Mg}(\text{OH})_2$], magnesium oxide (MgO), their nanoparticles, their polymer-nanocomposites, Amorphous Calcium Carbonate (ACC) and poly(acrylate)(PA-)-encapsulated $\text{Mg}(\text{OH})_2$; Hollow Calcium Carbonate (HCC), hydrophobic PCC and hydrophobic $\text{Mg}(\text{OH})_2$ from carbonate rocks of Sri Lanka. Results of those studies suggest that there is a high possibility to synthesize nanoparticles and nanocomposites of PCC, $\text{Mg}(\text{OH})_2$ and MgO using Sri Lankan carbonate rocks with appropriate quality to meet industrial requirements and to fulfill the current demand.

Keywords: *Marble, Carbonatite, Dykes, Dolomite, Calcite, Carbon and Oxygen isotopes*

INTRODUCTION

The major constituents of carbonate rocks are calcite and dolomite where their content range from 50 to 90% modal. The common carbonate rocks in the world are limestone, crystalline limestone (here after marble) and carbonatite. Other than these rocks, dyke-like carbonate rocks have rarely been found. Limestone and dolomitic limestone are sedimentary rocks composed of calcite and dolomite while marble has been recrystallized form of limestones by metamorphism. Carbonatites are formed from mantle-derived magmas, which are enriched in F, P, Sr, Nb, rare-earth elements (REEs), U, and Th, and have quite different stable and radiogenic isotope signatures with respect to limestones. Carbonate-rich dykes are formed from melts that originated from sedimentary limestone rocks (Liu *et al.*, 2006; Lentz, 1999). Although many researchers disagree on a possible melt origin, both field and laboratory studies have provided adequate evidence for such process (Bhowmik, *et al.*, 1995; Le Bas *et al.*, 2002, 2004; Liu *et al.*, 2006; Fanelli *et al.*, 1986; Santos *et al.*, 2013).

As marbles and carbonatites consist of coarse, interlocking dolomite and calcite grains, igneous and metamorphic carbonate rocks may be indistinguishable from one another as a result of subsolidus modification that obliterates primary textural and compositional characteristics (Barker, 1993). Both dolomite and calcite can crystallize or recrystallize with equilibrium polyhedral textures in the 300–700°C range and they produce variety of textures (Puhan, 1984; Mizuochi *et al.*, 2010) that may form in marble during metamorphism and in carbonatite during the cooling of the melt. Subsequently, textures of marble may be altered by multi-stage events related to contrasting fluid processes, which occur during the tectonic evolution of a region, and primary textures of carbonatite may be modified due to deuteric alteration (Morogan 1994; Zaitsev and Polezhaeva 1994; Keller and Zaitsev 2006). Furthermore, unlike silicate

minerals, carbonate minerals are highly sensitive to physico-chemical changes and can easily be deformed due to high crystal-plasticity even at very low P and T conditions (Burkhard, 1990).

Despite a large number of documented studies on carbonate rocks, only a few attempts have been made on textural characteristics of carbonate minerals (Chakhmouradian *et al.*, 2016; Pitawala and Lottermosser, 2012; Zaitsev and Polezhaeva, 1994; Madugalla *et al.*, 2017) However, interpretation of carbonate textures is a useful tool not only to interpret the petrogenesis of carbonate rocks but also to ore-body delineation and understanding industrial minerals potential. Further, the geochemical and stable isotope data of carbonate rocks along with textural characteristics of carbonate minerals provide valuable information on the origin, genesis, temperatures of mineralization, rock–fluid interaction and alteration processes of marbles and crystallization and emplacement history, as well as the post-emplacement history of carbonatites (Hogarth *et al.*, 1985; Barker and Nixon, 1989; Le Bas and Srivastava, 1989; Hornig-Kjarsgaard, 1998; Zaitsev and Chakhmouradian, 2002; Zheng and Hoefs, 1993; Cooper and Reid 1991; Zaitsev and Polezhaeva 1994; Mizuochi, *et al.*, 2010; Mposkos *et al.*, 2006).

Throughout the world, carbonate rocks are used as dimensional or decorative stones, as a refractory material, as a catalyst, in the production of lime, as a fertilizer and as an additive in glass, paper, plastics and rubber industries (Varela *et al.*, 2006; Rabaha and Ewais, 2009; Karatas *et al.*, 2013). Use of carbonate rocks in many industries depend mainly on their purity and chemical composition (Varela *et al.*, 2006). Grain size, textural characteristics and rheological properties of the rocks are also governing factors, if they are used for dimensional or decorative stones.

All types of carbonate rocks described above are found in Sri Lanka. These rocks have huge economic potential capable of significantly contributing to the country's social and economic development. These rocks have been mined from the historical period to the present day and produce several thousand tons of carbonate-based products per year in the manufacture of cement, chemical, lime and many other goods used in the construction industry. The high variability of chemical and mineralogical composition (Pitawala *et al.*, 2003), micro and macro scale fractures and higher quantities of impurities (Cooray, 1984; Madugalla *et al.*, 2013) of Sri Lankan marbles together with the coarse-grained nature make them unsuitable for most of the above applications. Hence, the current use of Sri Lankan marbles is limited to the lime industry, construction activities and the production of fertilizers (Mantilaka *et al.*, 2013a). However, their chemistry indicates that, these rocks have a higher potential for synthesis of chemical products such as precipitated calcium carbonate (PCC), magnesium hydroxide, magnesium oxide and their nanomaterials (Mantilaka *et al.*, 2013 a,b; Mantilaka *et al.*, 2014 a,b). Out of these products, PCC has a high economic potential and great demand from many industries such as paper, textile, rubber, plastic, paint, cosmetic, sealant, tooth paste and food stuff (Kim *et al.*, 2009; Price *et al.*, 2010). Currently the demand for PCC in Sri Lankan industries is fulfilled by importing such products from other countries at a high cost. Further, synthetization of PCC from Sri Lankan carbonate rocks by simple chemical processes is a timely need (Mantilaka *et al.*, 2013b; 2014 a).

The author has been studying carbonatites, marbles and dyke-like carbonate bodies of Sri Lanka since 1995. The present contribution is a concise account on petrographic observations, geochemical characteristics and stable isotope (C and O) composition of such rocks based on a broad spectrum of work carried out over the past two decades.

GEOLOGICAL OVERVIEW

The bulk of Sri Lankan basement is composed of Precambrian high-grade metamorphic rocks (Cooray, 1984; Kehelpannala, 2003; Kröner *et al.*, 2003). Miocene to recent sedimentary rocks occur in the Northern and Northwestern parts of Sri Lanka. Igneous rocks are rare and confined to local occurrences of few granites, granitic and syenitic pegmatites, dolerite dykes and carbonatites (Kehelpannala, 2004; Pitawala *et al.*, 2003; Pitawala *et al.*, 2008; Pitawala, 2009; Pitawala and Lottermoser, 2012). Based on the lithology, age and deformational features, the crystalline basement has been subdivided into four main units; (i) the Vijayan Complex (VC) in the East, (ii) the Highland Complex (HC) in the central part (iii) the Wannu Complex (WC) in the West and (iv) the Kadugannawa Complex (KC) towards the northwestern part of Kandy (KC) as shown in Fig.1.

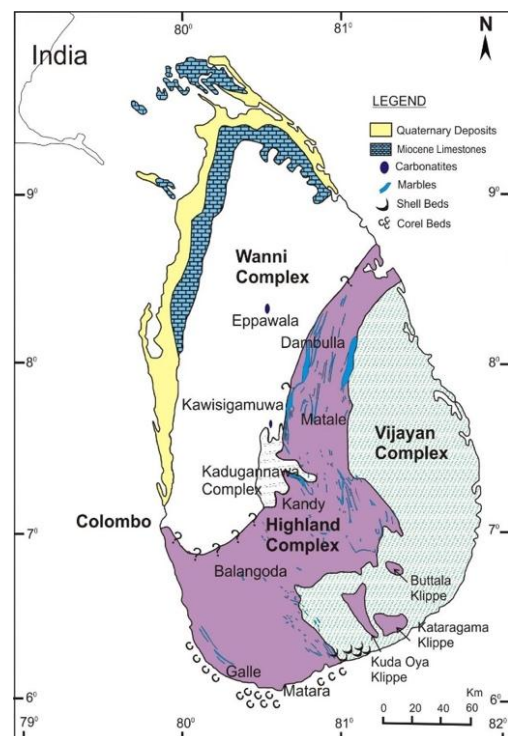


Fig. 1. Generalized geological and tectonic map of Sri Lanka showing occurrences of marbles, carbonatites, limestones and other carbonate rocks (after Cooray, 1984).

The isotopic data obtained for the Sri Lankan rocks suggest that the different complexes were assembled prior to the high-grade metamorphism (Kröner and Williams, 1993). The HC is predominantly made up of charnockitic and pelitic gneisses with various mineral assemblages, which are intercalated with quartzites, mafic granulites, marbles and calc-silicate gneisses. The WC comprises granitoid gneisses, migmatites, metasediments (garnet-cordierite gneisses, meta-quartzites, marbles) and charnockites. Both HC and WC have been metamorphosed to upper amphibolite- to granulite-facies conditions (Cooray, 1994). The boundary between the HC and the VC is a tectonic contact (e.g., Kriegsman, 1995), with evidence for shearing and thrusting, while the boundary between the HC and WC is not well determined yet (Kehelpannala, 2003; Kehelpannala and Ranaweera, 2007).

FIELD SETTING OF CARBONATE ROCKS

Marbles and calc-silicate gneisses are widely distributed in the central region of the HC (Fig. 1). These are found as layers or intercalations (10-20 km along strike) with pelitic gneiss, mafic granulite and charnockite (Cooray, 1984; Osanai *et al.*, 2000; Osanai *et al.*, 2016). In general, the marbles in the northeastern area of the island are massive and oriented in the NE direction. The marble layers in the southwestern area of Sri Lanka are trending northwesterly and show strong gneissose banding with regular interchange of silicate rich layers and pure marble layers (Fig. 2a). Almost all marbles of the country enclose decimeter- to few meter-sized mafic boudins. The dolomitic marbles are represented by three major varieties: (i) white to pale grey, massive, medium- to coarse-grained; (ii) white, massive, finely crystalline; and (iii) grey to dark grey, thinly-banded, finely crystalline marbles. The marbles have been deformed, metamorphosed and recrystallized under P-T conditions of the granulite facies,

which largely obliterated primary sedimentological features (Madugalla, 2015).

The carbonatite bodies in the country are found at Eppawala and Kawisigamuwa in the WC (Fig. 1). Based on field evidence and Rb-Sr and Sm-Nd isotopic data, the Eppawala carbonatite has been emplaced after the high-grade metamorphism of the surrounding country rocks during late Neoproterozoic times (550 Ma; Weerakoon *et al.*, 2001). The carbonatites form steeply dipping plugs and large dykes, ranging in thickness from 50 to 200 m and display a strike extension of a few meters to several hundreds of meters. Differential weathering of carbonatites has led to the formation of a hummocky topography. Occurrences of several small bodies of carbonatite are found in the vicinity of Kawisigamuwa village located in the Kurunegala District of Sri Lanka (Fig. 1). These bodies are relatively small, and no detailed studies have been carried out.

Dyke-like carbonate bodies mainly as calcite deposits cutting across the Precambrian basement in the Balangoda area in the HC are associated with marbles, close to the boundary between the HC and the VC (Fig. 2). They are located around Kalthota, Molamure, Ahulliyadda, Weligepola and Godakawela and are running from West to Southwest direction. They are 2-20 m wide and 20-150 m long lens shaped blue to yellowish brown bodies of almost pure calcite, which transect marble, pelitic-gneiss and charnockitic gneiss (Madugalla *et al.*, 2014a; Madugalla and Pitawala, 2014). Carbonate bodies commonly contain enclaves of charnockitic gneiss, mafic rocks and calc-silicate rocks of irregular shape.

MINERALOGICAL AND TEXTURAL CHARACTERISTICS

Marbles of Sri Lanka are composed more than 90% of dolomite and calcite except in the zones rich in silicate minerals. Common silicate minerals present in the marbles are forsterite, phlogopite, diopside and tremolite.

In most instances, marbles show granoblastic texture with medium- to coarse-grain size (1–10 mm). Dolomite is the predominant carbonate mineral in Sri Lankan marbles. They are mostly free from mineral inclusions, and occur as coarse to very coarse (~0.5 to 2 cm), subhedral to euhedral grains. Medium-grained calcite occurs along the grain boundaries of dolomite and micro-grained calcite occurs within coarse-grained dolomite. These calcites may be primary in origin and may have formed prior to the metamorphism. Often calcite (~ 55%) with lamellae or vermicular inclusions of dolomite dominates in zones rich in silicate minerals and along the contact zones with gneisses. They could be metamorphic in origin due to interaction of primary dolomite with silicate minerals (Bucher and Grapes, 2011; Madugalla, 2015; Pradeepkumar and Krishnanath, 2000; Satish-Kumar and Niimi, 1998).

Dolomite in such zones shows several types of morphologies similar to those observed in certain carbonatites (Zaitsev and Polezhaeva, 1994) and high-grade marbles (Kretz, 1988), and has been interpreted as possible products of Mg-metasomatism or pervasive exsolution of magnesian-calcite.

In the Eppawala carbonatites, calcite dominates (65 to 70 modal percent) the mineral assemblages and is accompanied by dolomite, magnesite, apatite, magnetite, ilmenite, forsterite, phlogopite and pyrite in varying proportions. Calcite commonly occurs as fine- to coarse-grained anhedral grains with sutured and interpenetrating grain boundaries with neighboring dolomite grains. In general, calcite grains are rich in fine-grained small dolomite inclusions. Both magmatic calcite (major constituent) and recrystallized calcite are present.

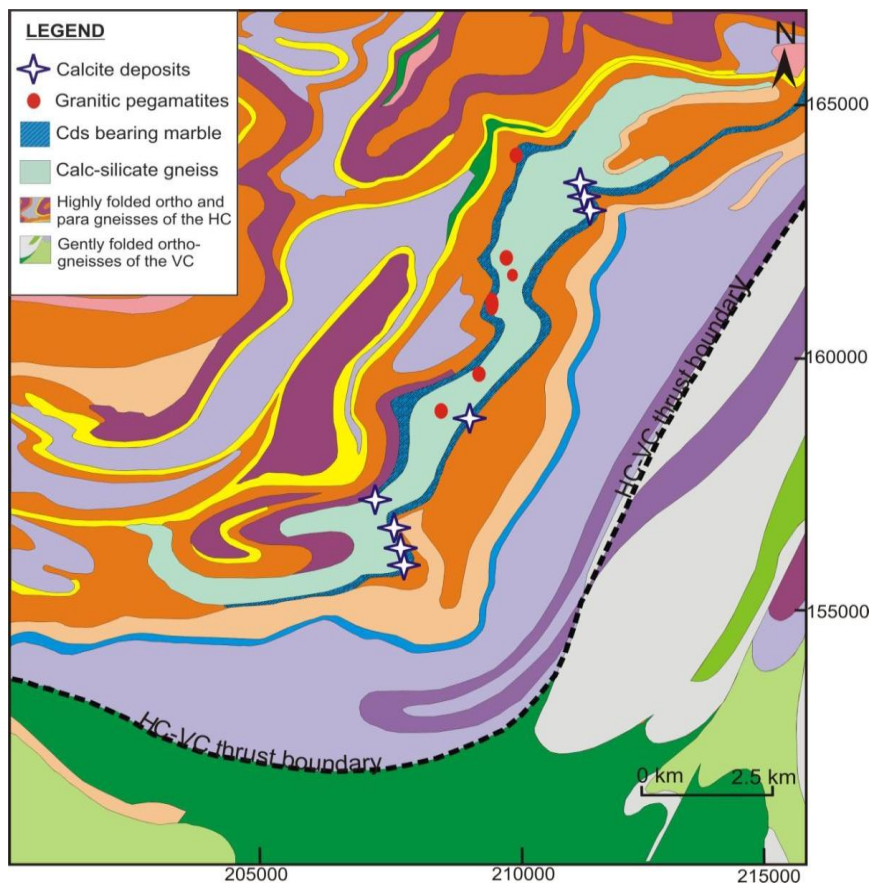


Fig. 2. Geological map of the Balangoda area showing the outcrop of calcite deposits, typical marble (Cds bearing marble), calc silicate rocks and pegmatite with highly deformed gneisses.

Dolomite (~20 vol. %) is the second most common carbonate mineral found in the carbonatites, with five morphological types (Madugalla *et al.*, 2017): (i) coarse-grained dolomite (type-1), (ii) rod-shaped or vermicular dolomite micro-crysts within the type-1 calcite (type-2), (iii) inclusions of dolomite within the type-1 calcite forming plug- or wedge-shaped arrangements (type-3), (iv) dolomite micro-crysts along the grain boundaries of type-1 calcite (type-4) and (v) clusters of dolomite crosscutting the type-1 calcite (type-5). In addition, some of the dolomites are found in association with calcite, forsterite and diopside. Syn- to post-magmatic processes in carbonatites can modify the grain-size, shape, orientation and the modal proportions of carbonate minerals significantly (Chakhmouradian *et al.*, 2016; Zaitsev and Polezhaeva, 1994). Different textures of carbonate minerals in the Eppawala carbonatites indicate that they have undergone multiple stages of crystallization/re-crystallization and geochemical modification.

The carbonatite body having emplaced within the crust initially has experienced post-magmatic cooling yielding exsolution of primary magmatic calcite. Subsequently squeezing of the carbonatite body to the upper crust has taken place resulting in recrystallization and rearrangement of carbonate minerals (Madugalla *et al.*, 2017).

Dyke-like carbonate bodies in the country are composed entirely of calcite crystals and those do not show any signs of metamorphic overprint. They are different from typical marbles in terms of texture, grain size and mineralogical composition. Grain sizes of calcite crystals vary from about 4 to 12 cm. Such large calcite grains are also found in hydrothermally altered zones in calc-silicate rocks of the country. In these monomineralic rocks, four distinct zonations with different colours of calcite of yellow, white, ash and blue are found. X-ray Diffraction (XRD) analysis indicates that the crystallinity of these calcites is different from that of typical

marble in the country. Calcites are generally very clear and free from mineral inclusions. However, calcite grains along the contact zones of both enclaves and host rocks contain dark coloured fine to medium grained mineral inclusions.

GEOCHEMICAL SIGNATURES

Whole rock geochemistry of Sri Lankan marbles shows that many marble bands of Sri Lanka are relatively pure rocks containing a limited amount of SiO₂ and Al₂O₃ and are almost devoid of Na₂O and K₂O (Pitawala, 1999). Marbles intercalated with layers and lenses of silicate rocks are relatively enriched in SiO₂ and Al₂O₃ as well as in other major elements common to gneissic rocks of the country. Mg/Ca ratios of the marbles range between 0.32 and 0.72, most of which are higher than that for stoichiometric dolomite (0.62). Variations in the Mg/Ca ratios of marbles are controlled mainly by calcite produced by metamorphic process. Compositional variation of marble bands with depth is not considerable (Madugalla, 2015). The pure marbles are low in trace elements and they do not show correlations with major elements (Ca and Mg). The impure marbles are rich in trace elements compared to pure marbles. The majority of the trace elements correlate positively with the silica content of the impure marbles, indicating the controlling role of silicate minerals on trace elements distribution. Therefore, the detected elements may have come only from carbonate sources (precipitate origin). The Al/Si ratios of pure marbles are low indicating negligible influence of terrigenous materials. High Si in some marble may be derived from another source (biogenic chert) besides clay minerals. Similarly, these marbles are low in terms of REEs as well. The measured total content of REE ranges from 0.6 to 10.7 ppm (Pitawala, 1999). Marble in the contact zones is low in MgO and high in CaO. The concentrations of REEs are high compared to pure marble (Fig.3).

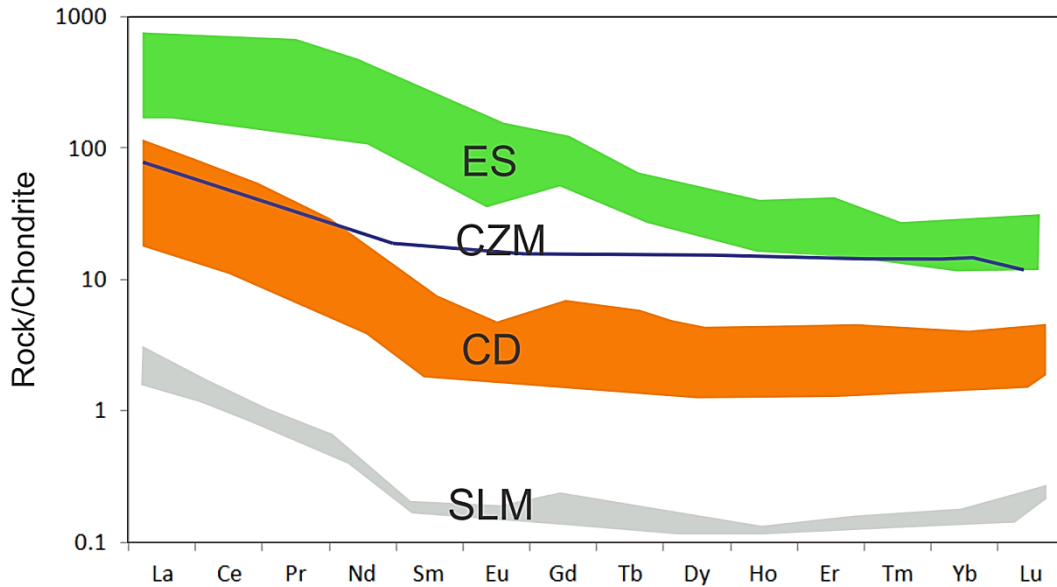


Fig. 3. Chondrite-normalized REE abundance diagram for Eppawala carbonatites (EC), marbles of contact zones (CZM), carbonatite dykes (CD) and marbles of Sri Lanka (SLM). Chondrite values are from McDonough and Sun (1995).

Marbles associated with meta-sediments are widespread around the world (Katz, 1971; Pradeepkumar and Krishnanath, 1996; Satish-Kumar and Niimi, 1998; Satish-Kumar *et al.*, 2008 and references therein). Presence of high content of dolomite indicates that Sri Lankan marbles may have been derived from metamorphism of pre-existing dolostones occurred in Paleoproterozoic era (Madugalla, 2015). Further, the low concentrations of Al_2O_3 and REEs of Sri Lankan marbles suggest that the source materials of the latter may have deposited in an open ocean basin as shown by Zhang *et al.*, 2017. Mineral assemblage of forsterite + calcite \pm diopside \pm dolomite in Sri Lankan marble indicates that those have been subjected to high grade metamorphism. Presence of exsolved dolomite in these calcites indicates a potential later stage cooling. Furthermore, diopside and tremolite bearing assemblages most likely formed during retrogressive metamorphism.

The low Si (maximum 1.15%), high P (up to 21.73%) and high Sr content (2700 – 6819 ppm) as well as the significant quantities of light rare earth elements (LREEs) such as Ce

(124 – 1026 ppm), Nd (33 – 493 ppm) and La (51 – 574 ppm) in Eppawala carbonatite critically argue for the carbonatitic origin (Fig 2). The REE fractionation of these rocks is pronounced, and La/Yb ratios vary between 14 and 43. As for single minerals, both apatite and calcite show markedly elevated Sr-levels (up to 0.6%). The Sr/Mn and Ce/La ratios in the apatite are ~ 40 and ~ 2 , respectively (Pitawala, 1999). The mineral chemistry and isotope signatures of the carbonatites are consistent with an igneous origin (Mantilake *et al.*, 2007; Pitawala *et al.*, 2003, 2012). Compared to most carbonatites, the Eppawala rocks are generally depleted in selected trace elements, particularly Ba, Nb, Th, V, U and Zr. This depletion may be due to either a primary infertility of the parent magma with regard to such trace elements, or due to secondary removal as a result of mineral separations during the crystallization process. The markedly high REE concentrations in the bulk chemistry of the rocks have been shown to be mainly controlled by the content of phosphate minerals. Most carbonatites are associated with mafic or alkaline rocks, and theories of genesis include fractional

crystallization and liquid immiscibility. Absence of observable alkaline complexes in the periphery of the Eppawala occurrence argues against the involvement of liquid immiscibility process during its genesis. Field data and petrochemistry of carbonatite suggest that the parental magma of Eppawala carbonatite was primary, and was generated from a low degree of partial melting of carbonated source rocks. Primary carbonatite magmas can be generated from either carbonated peridotite or carbonated eclogite (Mantilake *et al.*, 2007; Pitawala *et al.*, 2003).

Dyke-like carbonate bodies are characterized by the highest content of CaO (~ 54 wt.%) and lowest content of MgO (<1 wt.%) with respect to the other carbonate rocks of the country. Concentrations of Fe, Mn, Sr, Na and K of the rocks are higher than that of marbles in the island (Madugalla, 2015). Concentrations of Sr and REEs of the rocks are higher than that of typical marbles but lower than that of Eppawala carbonatites. However, the REE contents are similar to those in calcite formed by melting of marbles (Liu *et al.*, 2006).

C-AND O-ISOTOPE COMPOSITIONS

The carbon isotopic compositions of marbles, carbonatites and dyke-like carbonate bodies of Sri Lanka are presented graphically as a $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ cross-plot (Fig. 4). The marbles of Sri Lanka are clearly distinguished from the Eppawala carbonatites using their isotopic composition, coming fairly close to common marine carbonates. The $\delta^{13}\text{C}$ values of carbon marbles usually fall close to the zero permil line, with a scatter field of 1 – 2‰ on either side [Schidlowski *et al.*, (1975); Veizer *et al.*, (1980) have defined ranges of $0.4 \pm 2.7\text{‰}$ and $0.5 \pm 2.6\text{‰}$ (PDB), respectively]. Hence, marbles have been derived from marine carbonates. It has been shown that marble beds basically retain their primary isotopic signatures where undergoing regional metamorphism, with only their $\delta^{18}\text{O}$ values amenable to alteration due to $^{18}\text{O}/^{16}\text{O}$ exchange

with percolating waters. In general, marbles with $\delta^{18}\text{O} < 20\text{‰}$ (SMOW) are likely to have interacted with significant quantities of external fluids during progressive metamorphism (Valley, 1986). The fact that the $\delta^{18}\text{O}$ values of majority of our marbles lie well above 20‰ can be taken as evidence that these rocks had never effectively interacted with external fluids during their metamorphic reconstitution.

The stable isotope ratios from the Eppawala carbonatites ($\delta^{13}\text{C}_{\text{PDB}}$ -2.2 to -3.4‰; $\delta^{18}\text{O}_{\text{SMOW}}$ 7.7 - 16.4‰) do not plot within the defined “mantle carbonatite box”, but lie within the broader range of carbonatitic rocks. The heavier isotope values are attributed to isotope fractionation processes during magma formation. Generally, postmagmatic processes did not contribute significantly to the enrichment of both ^{13}C and ^{18}O isotopes. However, the increased $\delta^{18}\text{O}$ values found in some samples appear to be the result of a postmagmatic phenomenon that can be ascribed to an interaction with meteoric waters.

The dyke-like carbonate bodies show $\delta^{13}\text{C}$ values ranging from -0.8 to +0.3, most of them being within the prescribed range for marine carbonates ($0 \pm 2\text{‰}$ Burdett *et al.*, 1990; $0.5 \pm 2.6\text{‰}$ Veizer *et al.*, 1980). Most of the dolomite samples in the area show negative $\delta^{13}\text{C}$ values (-1.4 to -0.6). The $\delta^{18}\text{O}$ values for both rock types are in a narrow range from 21.2 to 23.5. The isotope values of carbonate dykes are more similar to those of marble in the country and different from the carbonates derived from the hydrothermal processes (Simmons *et al.*, 2000). Further, the carbon isotope composition of vein graphite originated from hydrothermal process is more negative and in the range of -7.9 and -10.4 ‰ (Touzain *et al.*, 2010).

Calcite can be deposited from vapor saturation from CO_2 -rich, steam-heated water generated from hydrothermal systems that occur along the HC-VC boundary (Dissanayake and

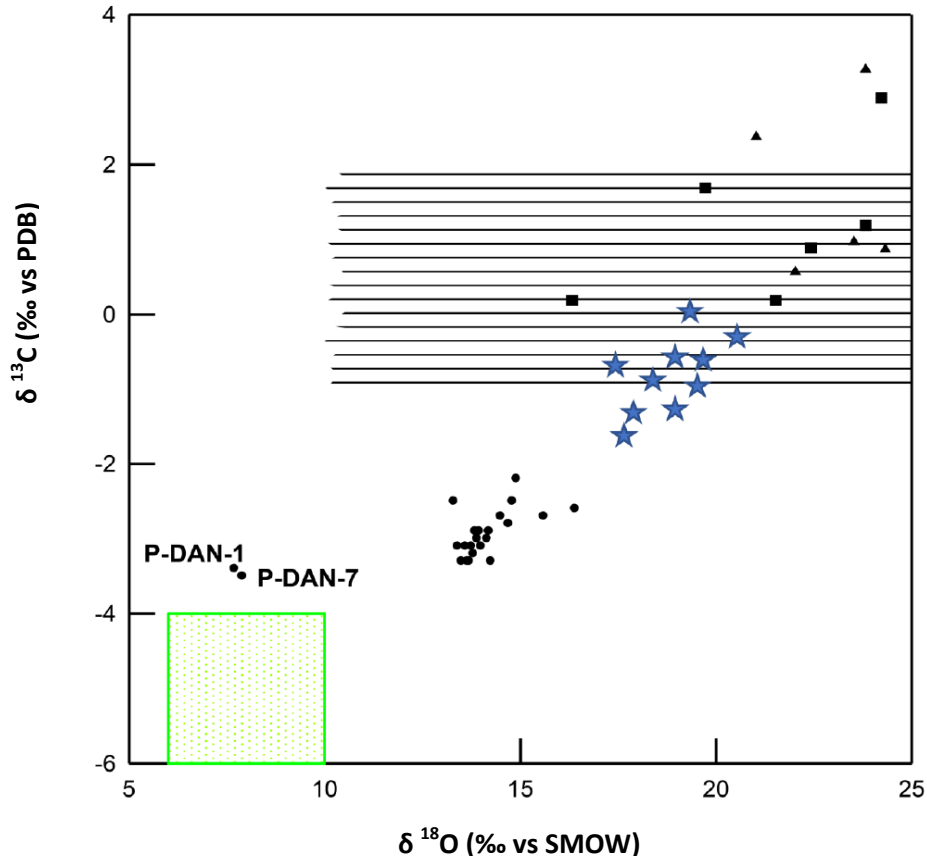


Fig. 4. Plot of $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ for Eppawala carbonatites (dots), dyke-like carbonate bodies (stars) and Sri Lankan marbles (other symbols). The data shows a general correlation among them.

Jayasena, 1988). High concentrations of dissolved ions such as HCO_3^- , Na, K and Ca are present in hydrothermal waters of Sri Lanka. Therefore, there is the possibility for formation of calcite from the saturated hydrothermal water. However, the chemical composition of Balangoda calcite argues against this assumption. Further, the O-isotope values of water from hydrothermal springs is more negative ($\delta^{18}\text{O}$; -5.9 to -4.9 , see Chandrajith *et al.*, 2013) and do not fall closer to the values of calcite formations. Therefore, it can be assumed that these carbonate dykes resulted from melting and fractional crystallization of marble melt.

INDUSTRIAL PRODUCTS FROM SRI LANKAN CARBONATE ROCKS

There are several commercially exploited marble deposits in Sri Lanka, many of those are located in the central part of the country.

Since the rocks are mainly made up of dolomite, their use is limited to a few industries. However, they can be used as one of the best options to replace expensive and consumable high-grade calcitic rocks to synthesize amorphous calcium carbonate (ACC) nanoparticles with optimum quality to meet with industrial requirements (Mantilaka *et al.* 2014a). In the last few years, several synthesis routes and methods have been proposed to produce precipitated calcium carbonate using Sri Lankan marbles (Mantilaka *et al.*, 2013a; Mantilaka *et al.*, 2014d). Studies have been performed to improve existing methods and/or develop innovative routes to synthesize well-controlled shapes and sizes of nanometer-to-submicrometer precipitated calcium carbonate particles. The spherical particles of Precipitated Calcium Carbonate (PCC) nanoparticles obtained are in the size range of 20-53 nm. The PCC/PMMA nanocomposite

shows specific properties of acid resistance and greater dispersibility in organic phases (Mantilaka *et al.*, 2013a). Hollow PCC with novel bone-like morphology is fabricated on novel PAA/Acetyl-trimethyl-ammonium chloride template (Mantilaka *et al.*, 2014c). Novel PA-encapsulated $Mg(OH)_2$ stable colloidal composite and $Mg(OH)_2$ nanoparticles are obtained using above $MgCl_2$ solution. MgO nanoparticles prepared by heating $Mg(OH)_2$ nanomaterials at 500 °C have the capability of adsorbing over 93% of methylene blue dye from effluents (Mantilaka *et al.*, 2013a; Mantilaka *et al.*, 2014b). The synthesized PCC and $Mg(OH)_2$ nanoparticles are modified with fatty acids to synthesize hydrophobic materials. Naturally occurring pure calcite at Balangoda, Sri Lanka is used to synthesize anticorrosive polyaniline (PANI)/PCC nanocomposites for the first time (Senarathna *et al.*, 2014). In this composite, unstable vaterite form of PCC has been stabilized by PANI. Fine-grade PCC shows a significant improvement in physical parameters of end product materials when used as a filler compared to other grades of carbonates such as limestones and marbles used as ground calcium carbonates, which typically display a broader and irregular particle size distribution. Balangoda carbonate rocks and Sri Lankan carbonatites are the most suitable sources for the synthesis of PCC since they are rich in calcite and low in silica content. However, the final product from Eppawala carbonatite contains some amount of strontianite ($SrCO_3$), which hinders its applications in bio-medical and pharmaceutical fields. Nevertheless, apatite and magnesium in the residue can also be obtained as byproducts of the PCC synthesis process. Hence, fresh carbonatites in the Eppawala ore body has a greater economic potential for PCC synthesis and the production of high quality multi-source fertilizer (Madugalla *et al.*, 2014b).

CONCLUSIONS

The protoliths of the Sri Lankan marbles are marine carbonates deposited in an open ocean. Despite having been subjected to granulite grade metamorphism, the marbles have inherited their depositional carbon signature, trace element and REEs composition and contain minor calcite relics.

Geochemical alterations associated with metamorphism are common along the contacts between dolomitic marbles and silicate rocks, where, over a limited distance, major and trace element as well as REEs compositions have been modified significantly.

Trace and REE composition as well as stable isotope ratios from the Eppawala carbonatites are not comparable with those of most carbonatite bodies around the world. But they are within the broader range of carbonatitic rocks. Textural features and mineralogical composition of carbonate minerals suggest that present carbonatite bodies have been re-localized after major phase of crystallization due to deformations experienced by the country rocks.

Dyke like carbonate rocks within the Precambrian basement of Sri Lanka occur near the contact between the Highland Complex and the Vijayan Complex. Field, geochemical, isotopic, and petrological evidence have suggested to us that these carbonate rocks resulted from marbles remobilized probably during shearing and thrusting between the two plates.

Despite many studies many gaps in knowledge remain in our understanding of the petrogenesis of carbonate rocks of Sri Lanka. However, Sri Lankan carbonate rocks shed light to understand origins of carbonate rocks, their relationships to silicate rocks and to the deep mantle magma and carbon recycling in the earth crust and mantle.

Carbonate rocks of Sri Lanka can be used to synthesize PCC nanoparticles and $Mg(OH)_2$

with high purity. The morphology and size of synthesized products from carbonate rocks are varied according to used organic and inorganic additives, solution concentration and temperatures of the synthesized medium.

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REFERENCES

- Barker, D.S., (1993) Diagnostic magmatic features in carbonatites: implications for the origins of dolomite- and ankerite-rich carbonatites. *South African Journal of Geology*, 96 (3): 131 – 138.
- Barker, D.S., Nixon, P.H., (1989) High-Ca, low-alkali carbonatite volcanism at Fort Portal, Uganda. *Contributions to Mineralogy and Petrology*. 103 (2): 166–177.
- Burdett, J.W., Grotzinger, J.P., Arthur, M.A., (1990) Did major changes in stable isotope compositions of seawater occur?. *Geology*, 18: 227-230.
- Burkhard, M., (1990) Ductile deformation mechanisms in micritic limestones naturally deformed at low temperatures (150–350 °C). In: Knipe RJ, Rutter EH (eds) *Deformation Mechanisms, Rheology and Tectonics*. Geological Society of London, Special Publications. 54: 241–257.
- Bucher, K., Grapes, R., (2011) Metamorphism of Dolomites and Limestones. *Petrogenesis of Metamorphic Rocks*. 225-255.
- Bhowmik, S.K., Dasgupta, S., Hoernes, S., Bhattacharva, P.K., (1995) Extremely high-temperature calcareous granulites from the Eastern Ghats, India: evidence for isobaric cooling, fluid buffering, and terminal channelized fluid flow. *European Journal of Mineralogy*, 7: 689-703.
- Chakhmouradian, A.R., Reguir, E.P., Zaitsev, A.N., (2016) Calcite and dolomite in intrusive carbonatites. I. Textural variations, Mineralogy and Petrology, 2–3: 333–360.
- Chandrajith, R., Barth, J.A.C., Subasinghe, N.D., Merten, D., Dissanayake, C.B., (2013) Geochemical and isotope characterization of geothermal spring waters in Sri Lanka: Evidence for steeper than expected geothermal gradients. *Journal of Hydrology*, 476: 360–369.
- Cooper, A.F., Reid, D.L., (1991) Textural evidence for calcite carbonatite magmas, Dicker Willem, southwest Namibia. *Geology*, 19: 1193-1196.
- Cooray, P.G., (1984) An introduction to the Geology of Sri Lanka (Ceylon) 2nd edition, pp. 81-104 & 183-188. National Museum, Colombo, Sri Lanka.
- Cooray, P.G., (1994) The Precambrian of Sri Lanka: A historical review. *Precam Research*, 66: 3-18.
- Dissanayake, C.B., Jayasena, H.A.H., (1988) Origin of geothermal systems of Sri Lanka. *Geothermics*, 17, 657–669.
- Fanelli, M.F., Cava, N., Wyllie, P.J., (1986) Calcite and dolomite without portlandite at a new eutectic in CaO-MgO-CO₂-H₂O, with applications to carbonatites, in *Morphology and phase equilibria of minerals: Proceedings of the 13th general meeting of the International Mineralogical Association: Sofia, Bulgarian Academy of Science*, 313–322.
- Hogarth, D.D., Hartree R., Solberg, T.N., (1985) Rare-earth element minerals in four carbonatites near Gatineau. Quebec. *American Mineralogy*, 70: 1135– 1142.
- Ingrid H.K., (1998) Rare earth elements in Sövitic Carbonatites and their mineral phases. *Journal of Petrology*, 39 (11-12): 2105–2121.
- Karatas, H., Olgun, H., Akgun, F., (2013) Coal and coal and calcined dolomite gasification experiments in a bubbling fluidized bed gasifier under air atmosphere. *Fuel Processing Technology*, 106: 666–672.
- Katz, M.B., (1971) The Precambrian metamorphic rocks of Ceylon. *Geologische Rundschau*, 60 (4): 1523-1549.
- Keller, J., Zaitsev A.N., (2006) Calciocarbonatite dykes at Oldoinyo Lengai, Tanzania: The fate of natrocarbonatite, *The Canadian Mineralogist*, 44(4): 857-876.
- Kriegsman, L.M., (1995) The Pan–African even in East Antarctica a view from Sri Lanka and the Mozambique. *Precambrian Research*, 75(3): 263-277.

- Kehelpannala, K.V.W., (2003) Structural evolution of the middle to lower crust in Sri Lanka – a review. *Journal of Geological Society of Sri Lanka*, 11: 45–85.
- Kehelpannala, K.V.W., Ranaweera, L., (2007) Structural and kinematic evolution of a possible Pan-African suture zone in Sri Lanka. *International Association of Gondwana Research Conference Series*, 4: 83–88.
- Kehelpannala, K.V.W., (2004) Arc accretion around Sri Lanka during the assembly of Gondwana. *Gondwana Research*, 7(4S): 41-46.
- Kim, J.A., Han, G., Lim, M., You, K., Ryu, M., (2009) Effect of hydraulic activity on crystallization of Precipitated Calcium Carbonate (PCC) for eco-friendly paper. *International Journal of Molecular Science*, 10: 4954-4962.
- Kriegsman, L.M., (1995) The Pan-African event in East Antarctica: a view from Sri Lanka and the Mozambique belt. *Precambrian Research*, 75(3–4): 263-277.
- Kröner, A., Agramonte, Y.R., Kehelpannala, K.V.W., Zacka, T., Hegnerd, E., Genge, H.Y., Wonge J., Bartha, M., (2013) Age, Nd–Hf isotopes, and geochemistry of the Vijayan Complex of eastern and southern Sri Lanka: A Grenville-age magmatic arc of unknown derivation. *Precambrian Research*, 234: 288-321.
- Kröner, A., Williams, I. S., (1993) Age of metamorphism in the high-grade rocks of Sri Lanka. *The Journal of Geology*, 101 (4): 513-521.
- Kretz, R., (1988) SEM study of dolomite microcrystals in Grenville marble. *American Mineralogist*, 73: 619-631.
- Le Bas, M.J., Srivastava, R.K., (1989) The mineralogy and geochemistry of the Mundwara carbonatite dykes, Sirohi District Rajasthan, India. *Neues Jahrbuch für Mineralogie Abhandlungen*, 160: 207–227.
- Le Bas, M.J., Subbarao, K.V., Walsh, J.N., (2002). Metacarbonatite or marble? the case of the carbonate, pyroxenite, calcite-apatite rock complex at Borra, Eastern Ghats, India. *Journal of Asian Earth Sciences*, 20 (2): 127-140.
- Le Bas, M.J., Ba-bttat, M.A.O., Taylor, R.N., Milton, J.A., Windley, B.F., Evins, P.M., (2004) The carbonatite-marble dykes of Abyan Province, Yemen Republic: the mixing of mantle and crustal carbonate materials revealed by isotope and trace element analysis. *Mineralogy and Petrology*, 82: 105–135.
- Lentz, D.R., (1999) Carbonatite genesis: A reexamination of the role of intrusion-related pneumatolytic skarn processes in limestone melting. *Geology*, 27 (4): 335-338.
- Liu, Y., Berner, Z., Massonne, H.J., Zhongd, D., (2006) Carbonatite-like dykes from the eastern Himalayan syntaxis: geochemical, isotopic, and petrogenetic evidence for melting of metasedimentary carbonate rocks within the orogenic crust. *Journal of Asian Earth Sciences*, 26: 105–120.
- McDonough, W.F., Sun, S.S., (1995) The composition of the earth. *Chemical Geology*, 120, 223-253.
- Madugalla, T.B.N.S., Pitawala, A., Karunaratne, D.G.G.P., (2014) Marble or carbonatite? calcite deposits in marbles in Balangoda, Sri Lanka. Abs. 3rd annual international conference on geological and earth sciences, Singapore.
- Madugalla, T.B.N.S., Pitawala, H.M.T.G.A., (2015) Calcite deposits associated with marble in the Balangoda area, Sri Lanka. *Recent contribution to the Geology of Sri Lanka-Excursion Guide*, 10: 25-29.
- Madugalla, T.B.N.S., Mantilaka, M.M.M.G.P.G., Karunaratne, D.G.G.P., Rajapakse R.M.G., Pitawala, H.M.T.G.A., (2013) Effect of magnesium ions on synthesis of precipitated calcium carbonate: focused to Sri Lankan dolomitic marble. *Journal of Geological Society of Sri Lanka*, 15: 85-92.
- Madugalla, T.B.N.S., Pitawala, H.M.T.G.A., Manthilake, M.A.G., (2017) Primary and secondary textures of dolomite in Eppawala carbonatites, Sri Lanka: Implications for the petrogenetic history. *Journal of Geosciences*, 62: 187–200.
- Madugalla, T.B.N.S., Pitawala, A., Karunaratne, D.G.G.P., (2014) Use of Carbonatites in the production of precipitated calcium carbonate: A case study from Eppawala, Sri Lanka, *Natural Resources Research*, 23 (2): 217-229.
- Madugalla, T.B.N.S., (2015) Petrographical and geochemical characteristics of Sri Lankan marbles and carbonatites: implications for their genesis and economic potential, Ph.D. thesis,

- Postgraduate Institute of Science, University of Peradeniya.
- Manthilake, M.A.G.M., Sawada, Y., Sakai, S., (2008) Genesis and evolution of Eppawala carbonatites, Sri Lanka. *Journal of Asian Earth Science*, 32: 66-75.
- Mantilaka, M.M.M.G.P.G., Karunaratne, D.G.G.P., Rajapakse, R.M.G., Pitawala, H.M.T.G.A., (2013a) Precipitated calcium carbonate/poly (methyl methacrylate) nanocomposite using dolomite: Synthesis, characterization and properties. *Powder Technology*, 235: 628-632.
- Mantilaka, M.M.M.G.P.G., Pitawala, H.M.T.G.A., Rajapakse, R.M.G., Karunaratne, D.G.G.P., (2013b) Nanomaterials from Sri Lankan marble: A novel approach for value-added products, 29th Annual Technical Sessions of the Geological Society of Sri Lanka, Kandy, Sri Lanka, 28 February 2013.
- Mantilaka, M.M.M.G.P.G., Rajapakse, R.M.G., Karunaratne, D.G.G.P., Pitawala, H.M.T.G.A., (2014a) Preparation of amorphous calcium carbonate nanoparticles from impure dolomitic marble with the aid of poly (acrylic acid) as a stabilizer. *Advanced Powder Technology*, 25: 591-598.
- Mantilaka, M.M.M.G.P.G., Pitawala, H.M.T.G.A., Karunaratne, D.G.G.P., Rajapakse, R.M.G., (2014b) Nanocrystalline magnesium oxide from dolomite via poly(acrylate) stabilized magnesium hydroxide colloids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 443: 201-208.
- Mantilaka, M.M.M.G.P.G., Pitawala, H.M.T.G.A., Rajapakse, R.M.G., Karunaratne, D.G.G.P., Wijayantha, K.G.U., (2014c) Formation of hollow bone-like structures of calcium carbonate on surfactant/polymer templates. *Journal of Crystal Growth*, 392: 52-59.
- Mantilaka, M.M.M.G.P.G., Wijesinghe, W.P.S.L., Rajapakse, R.M.G., Karunaratne, D.G.G.P., Pitawala, H.M.T.G.A., (2014d) Surfactant-assisted synthesis of pure calcium carbonate nanoparticles from Sri Lankan dolomite. *Journal of the National Science Foundation*, 43: 237-244.
- Mizuochi, H., Satish-Kumar, M., Motoyoshi, Y., Michibayashi, K., (2010) Exsolution of dolomite and application of calcite-dolomite solvus geothermometry in high-grade marbles: an example from Skallevikshalsen, East Antarctica. *Journal of metamorphic Geology*, 28: 509-526.
- Mposkos, E., Baziotis, I., Proyer, A., Hoinkes, G., (2006) Dolomitic marbles from the ultra-high pressure metamorphic Kimi complex in Rhodope, N.E. Greece, *Mineralogy and Petrology* 88: 341-362.
- Morogan, V., (1994) Ijolite versus carbonatite as sources of fenitization *Terra Nova* 6(2): 166 - 176.
- Osanai, Y., Ando, K.T., Miyashita, Y., Kusachi, I., Yamasaki, T., Doyama, D., Prame, W.K.B.N., Jayatilake, S., Mathavan, V., (2000) Geological field work in the southwestern and central parts of the Highland Complex, Sri Lanka during 1998-1999, special reference to the highest grade metamorphic rocks. *Journal of Geoscience, Osaka City University*, 43: 227-247.
- Osanai, Y., Sajeev, K., Nakano, N., Kitano, I., Kehelpannala, K.V.W., Kato, R., Adachiand, T., Malaviarachchi, S.P.K., (2016) UHT granulites of the Highland Complex, Sri Lanka I: Geological and petrological background. *Journal of Mineralogical and Petrological Sciences*, 111: 145-156.