

# **Manasseite, ferrohogbomite and amesite in mantle plume associated carbonatite: Implications for unplumbed ultra-hydrous nature of parental carbonatite magma**

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## **Abstract**

Study of solid and fluid inclusions in carbonatite is vital for understanding the nature of primary carbonatitic magma. In this study, biphasic fluid inclusions were observed in calcites and solid mineral inclusions were observed in accessory magnetite in Sung Valley carbonatite of NE India. This carbonatite is part of an Ultramafic-Alkaline-Carbonatite Complex (UACC), related to the Kerguelen Plume activity. All of the studied inclusions are primary in nature. Raman spectroscopy of these inclusions suggested that the biphasic inclusions hosted by calcite are essentially composed of water whereas, the solid mineral inclusions hosted by magnetite in the Sung Valley carbonatite are manasseite, ferrohogbomite and amesite. The extremely hydrous mineral inclusions occurring in the magnetite are not a product of hydrothermal alteration but represent the primary magmatic characteristics of the parental magma. Our observations suggest that the parental magma of the Sung Valley carbonatite was ultra-hydrous in nature, which can be attributed to metasomatism of the source carbonated peridotite. Our study also suggests that there is a strong possibility for more hydrous carbonatite melts to occur on a global scale.

**Keywords:** *Carbonatite; Fluid inclusions; Raman spectroscopy; Manasseite, Ferrohogbomite; Amesite; Sung Valley, NE India.*

## **Plain Language Summary**

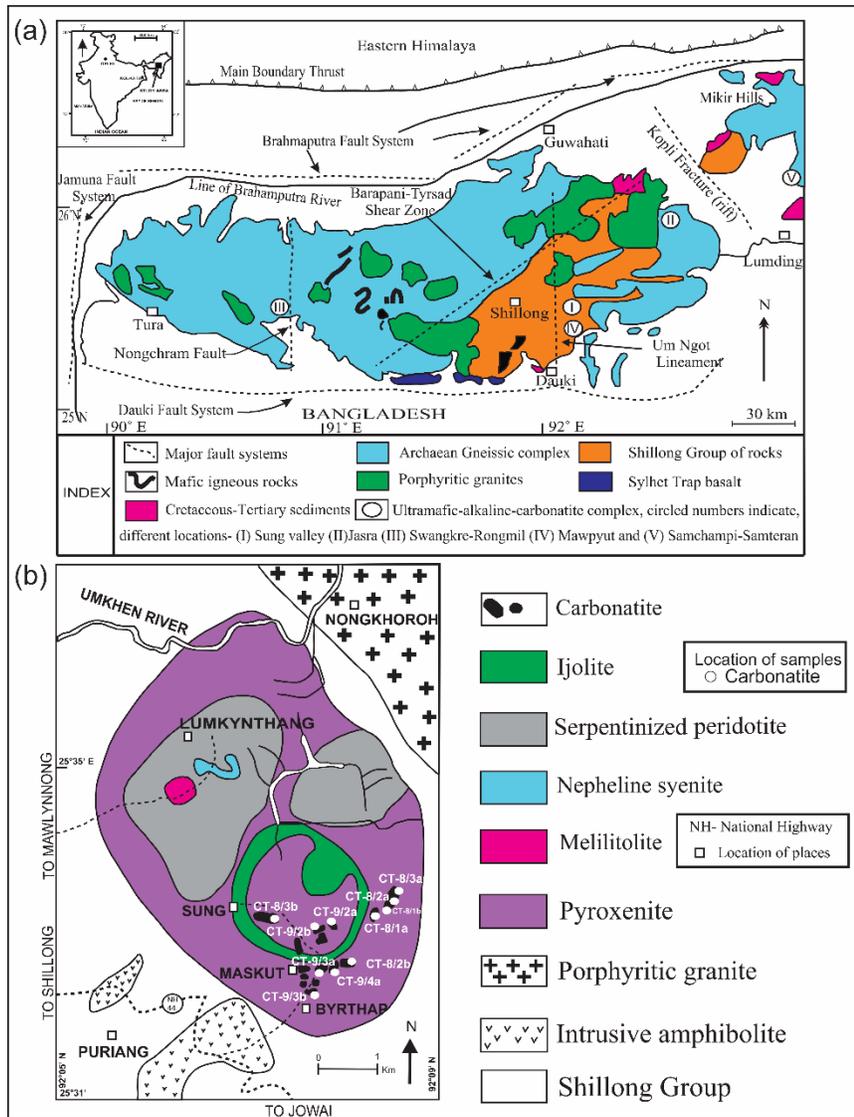
Primary solid inclusions of manasseite, ferrohogbomite and amesite and biphasic fluid inclusions of H<sub>2</sub>O were observed in magnetite and calcite respectively in Sung Valley carbonatite of northeast India. These carbonatites are related to the Kerguelen mantle plume. Solid and fluid inclusions, identified with the help of Raman spectroscopy, are all of hydrous nature and provide detailed information about the magma these carbonatites have crystallized from. Inclusion data suggests that the parental magma of these carbonatites had a significant amount of dissolved water. Such ultra-hydrous character of the parental magma could be acquired due to the exhaustion of hydrous minerals during low degree of partial melting of the source carbonated peridotite.

### **1. Introduction**

Carbonatitic magmas show very high solubilities of many elements, which are rare in silicate magmas, and these melts also have very high melt capacities for dissolving water and other volatile species like halogens at lower pressures (Jones et al., 2013). These magmas have very low viscosity, which enables them

to not only migrate easily through the mantle but also react with it (Green & Wallace, 1988; Hammouda & Laporte, 2000). The efficiency of transportation of carbon from the mantle to the crust is also controlled up to a greater extent by these carbonatitic magmas (Jones et al., 2013). Redistribution and recycling of carbon at mantle depth are also significantly controlled by hydrous carbonate melts and these melts also play an important role in global carbon cycle (Dasgupta, 2013; Poli, 2015; Kelemen & Manning, 2015; Schettino & Poli, 2020). The presence of water enhances the process of melting at shallower depths compared to anhydrous systems in not only the simple carbonate compositions (Wyllie & Boettcher, 1969) but also in complex carbonated subducted lithologies (Poli, 2015; Dasgupta, 2018; Schettino & Poli, 2020). During such melting processes, water strongly partitions into carbonate magmas (Sokol et al., 2013) and these magmas carry almost four times more water compared to the alkali silicate melts at depth (Keppeler, 2003). Numerous experimental studies suggest that carbonatitic magmas derive from carbonated peridotite through dry solidus melting at higher pressure (5 to 10 GPa) in Earth's mantle (Dalton & Presnall, 1998; Dasgupta & Hirschmann, 2006, 2007; Novella, 2014). Hydrated carbonatitic magma can be derived through the partial melting of  $\text{CO}_2\text{-H}_2\text{O}$  enriched peridotite, that is, carbonated peridotite (Sifre and Gaillard 2012). The hydration of the carbonatitic magma significantly increases the mobility of these melts in the upper mantle (Ritter et al., 2020). Carbonatite are generally believed to be originated through the residual melts after fractionation of carbonated nephelinite or melilitite (Gittins, 1989; Gittins & Jago, 1998), fractionation of immiscible melt fractions of  $\text{CO}_2$ -saturated silicate melts (Church & Jones, 1995; Lee & Wyllie 1997; Dawson, 1998; Halama et al., 2005; Brooker & Kjarsgaard, 2011) and primary mantle melts generated through partial melting of carbonated peridotite (Wallace & Green, 1988; Sweeney, 1994; Harmer & Gittins, 1998; Harmer et al., 1998; Ying et al., 2004).

Sung Valley ultramafic-alkaline-carbonatite complex (UACC) is derived from the Kerguelen plume (Veena et al., 1998; Ray et al., 1999, 2000; Srivastava et al., 2005; Srivastava et al., 2019) (Figure 1).



**Figure 1.** (a) Geological map of the Shillong plateau. (b) Geological map of Sung Valley, Meghalaya, NE India with sample locations. (a, b) Modified after Srivastava & Sinha (2004).

Petrogenetic studies carried out on the Sung Valley carbonatite suggest that these rocks are a product of primary carbonate magma, which was generated through low degree partial melting of a metasomatised mantle peridotite (carbonated peridotite) at 2.5 GPa pressure (Srivastava & Sinha, 2004; Melluso et al., 2010). Stable isotopic analyses of carbon (C) and oxygen (O) also suggest that these carbonatite contain inorganic carbon from the lithospheric mantle

(Ray et al., 1999; Srivastava et al., 2005; Choudhary et al., 2020).

In the present study, we present some extremely rare hydrous phases occurring as solid inclusions in accessory magnetite and aqueous biphasic fluid inclusions in calcite of these Sung Valley carbonatite (Figure 1b). Since magnetite ( $\text{Fe}_3\text{O}_4$ ) is one of the most common accessory minerals in magmatic rocks, it can preserve some pristine signatures (as inclusions/ trace elements) of the parental magmas it has crystallized from. Raman spectroscopy of solid inclusions in magnetite and fluid inclusions in calcite provides a unique opportunity to understand the parental melt characteristics of carbonatite through these entrapped phases. Our study suggests that the parental magma of the Sung Valley carbonatite was extremely hydrous in nature. This melt was derived from low degree partial melting of carbonated peridotite and some rare hydrous phases such as manasseite, amesite and ferrohobomite occurring as mineral inclusions in magnetite and aqueous biphasic fluid inclusions in calcite attest to this inference. Exhaustion of hydrous minerals such as phlogopite and amphibole from carbonated peridotite during low degree partial melting of the source resulted in the formation of these hydrous minerals, which are preserved as mineral inclusions hosted by magnetite. Our results also demonstrate that such ultra-hydrous nature with an abundance of dissolved water can significantly contribute towards lowering the viscosity of carbonatitic magmas.

## 1. Geological background

Sung valley ultramafic-alkaline-carbonatite complex (UACC) is an oval-shaped plutonic complex, which is associated with the Kerguelen plume igneous activity (Veena et al., 1998; Ray et al., 1999, 2000). Sung valley UACC intrudes the Proterozoic Shillong Group of rocks from horst like feature called the Shillong Plateau of Meghalaya in north-eastern India (Figure 1a). The Kopali fracture zone, trending NW-SE and Jamuna fault system trending N-S bound the Shillong plateau in East and West respectively (e.g. Evans, 1964; Desikachar, 1974, Nandy, 1980; Acharyya et al., 1986; Gupta & Sen, 1988; Sarma & Dey, 1996; Sengupta & Agarwal, 1998). Several alkalic intrusive bodies including the Sung valley UACC are contained by an N-S trending Um-Notog lineament, which cuts across the Shillong plateau (Kumar et al., 1996). The southern part of Shillong plateau bears the exposure of Sylhet traps, which are a part of Rajmahal-Sylhet flood basalt province associated with the Kerguelen mantle plume (Storey et al., 1992; Kent et al., 1997, 2002). The emplacement age of Sung Valley UACC has been dated to 105–107 Ma (Srivastava & Sinha, 2004). However, more precise  $^{40}\text{Ar}/^{39}\text{Ar}$  analysis of carbonatite gave an age of  $107.2\pm 0.8$  Ma (Ray & Pande, 2001). In a recent work the U-Pb age of perovskite in peridotite, ijolite and un-compahgrite are dated to  $109.1\pm 1.6$ ,  $104.0\pm 1.3$  and  $101.7\pm 3.6$  Ma respectively, while zircons from nepheline-syenite gave an age of  $106.8\pm 1.5$  Ma (Srivastava & Sinha, 2019). Sung valley UACC comprises, serpentinized peridotite, pyroxenite, melilitolite, ijolite, nepheline syenite and carbonatite (Krishnamurthy, 1985; Viladkar et al., 1994; Srivastava & Sinha, 2004) (Figure 1b). The pyroxenites from Sung Valley also host chalcopyrites, which are low-temperature (c. 400°C)

reequilibrated sulfides of high-temperature MSS (Choudhary et al., 2021). For detailed geology of the area please see Ray et al. (1999), Srivastava & Sinha (2004), Srivastava et al. (2005), Melluso et al. (2010), Basu & Murty (2015) and Srivastava et al. (2019).

The carbonatite are exposed mainly around Maskut area, in the southern part of the Sung valley UACC (Figure 1b). These rocks occur as small dykes, veins and oval-shaped bodies within pyroxenite and ijolite. The Sung valley carbonatite are considered to have formed by the last pulses of magmatism of the Rajmahal–Bengal–Sylhet flood basalt province (Ray et al., 1999). Intrusive relationships of carbonatite with other silicate rocks in Sung valley UACC indicate that carbonatite is the youngest member of the complex (Srivastava & Sinha, 2004). These carbonatitic bodies vary in size from 20–125 m in length and 10–40 m in width. The Sung valley carbonatite are mainly calciocarbonatite in nature, where more than 90% of the carbonate is calcite. However, a few occurrences of dolomite-bearing calcite carbonatite are also observed. These carbonatite are coarse-grained and show hypidiomorphic texture.

## 1. Analytical techniques

### (a) Optical Microscopy

Optical microscopy was carried out on thin rock wafers in transmitted and reflected light with Nikon Eclipse LV 100N POL microscope in Wadia Institute of Himalayan Geology, Dehradun, India. NIS elements software was used for the image analyses. The microscope is equipped with 100X short working distance lens, which was used at the time of small size solid and fluid inclusion petrography. For the present research, eleven thin sections were examined.

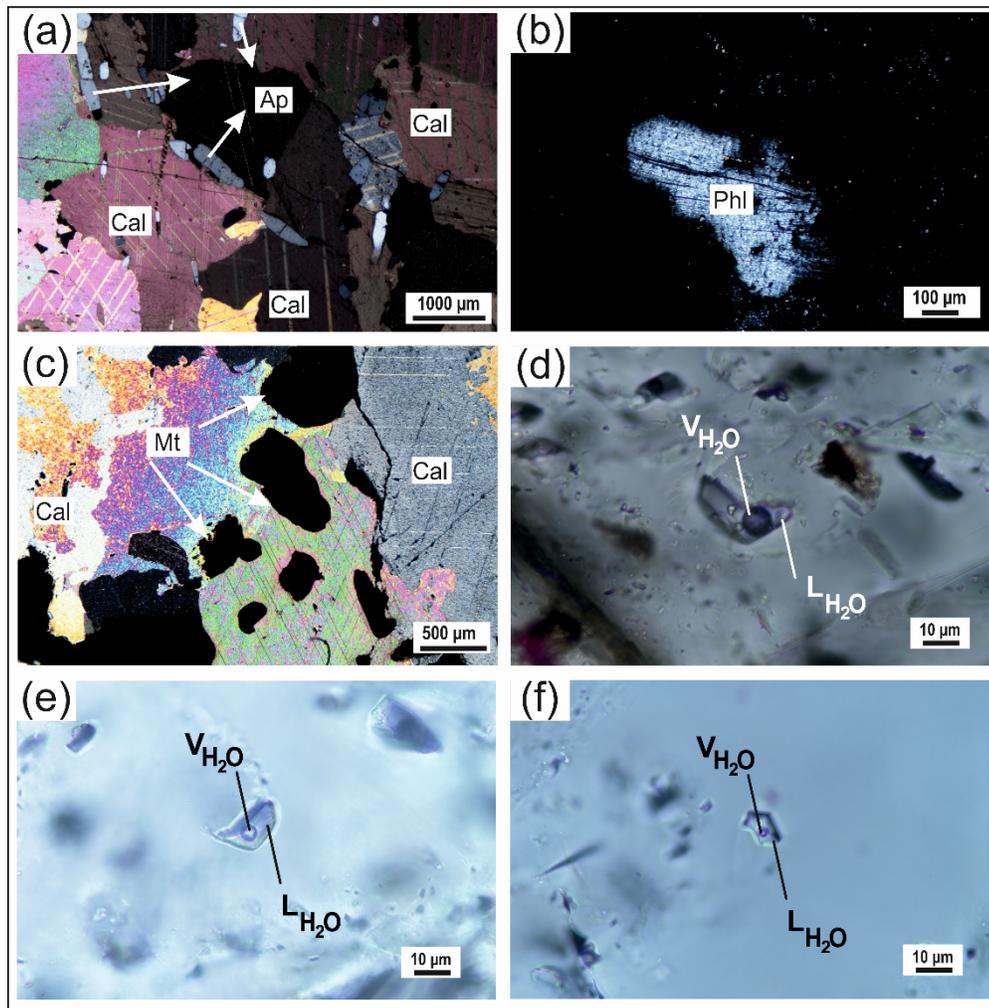
### 1. Micro Raman spectroscopy

Micro Raman spectroscopy was carried out at Wadia Institute of Himalayan Geology (WIHG), Dehradun (India) with the help of a LabRAM HR - Horiba Jovin Yvon Instrument. Argon ion laser with 514.5 nm wavelength and Charged Couple Device (CCD) as detector, were used to obtain Raman spectra. The optimum temperature ( $-70^{\circ}\text{C}$ ) of the CCD was maintained during the analysis. The instrument at WIHG, is also equipped with OLYMPUS® microscope, which was used to set the fluid phases of micron size under the focus of laser. During the analysis 50X and 100X objectives were used. The diameter of laser is between 2 - 4 m and the power settings maintained during the acquisition of Raman spectra are as follows- power  $\sim 4 - 8$  amp and 15 - 40 mW. All the spectra were obtained using the grating 1800 grooves/mm in 100 - 4000  $\text{cm}^{-1}$  spectral region. Synthetic silica standard (characteristic Raman shift at 520.59  $\text{cm}^{-1}$ ) was used during the calibration of the instrument. The spectral resolution of 1 - 2  $\text{cm}^{-1}$  was obtained during the analysis.

## 1. Results

### (a) Petrography

A total of eleven fresh samples were collected and analysed for this study. All these samples were collected from different locations as marked in the geological map (Figure 1b). Petrographical observations suggest that these carbonatite are calcite-carbonatite in nature and almost 80-90% of the contributing carbonates is calcite with some amount of dolomite in some samples (Figure 2a-c). Accessory phosphate mineral is apatite, which shows euhedral to subhedral nature with well-developed form and symmetry to almost rounded shape (Figure 2a). The presence of phlogopite is also observed in these samples (Figure 2b). Magnetite and some ilmenite make up the oxide accessory phases in Sung valley carbonatite (Figure 2c).



**Figure 2.** (a) Photomicrograph showing coarse-grained calcite with subhedral to anhedral apatites in carbonatite sample under cross-polarized light. (b)

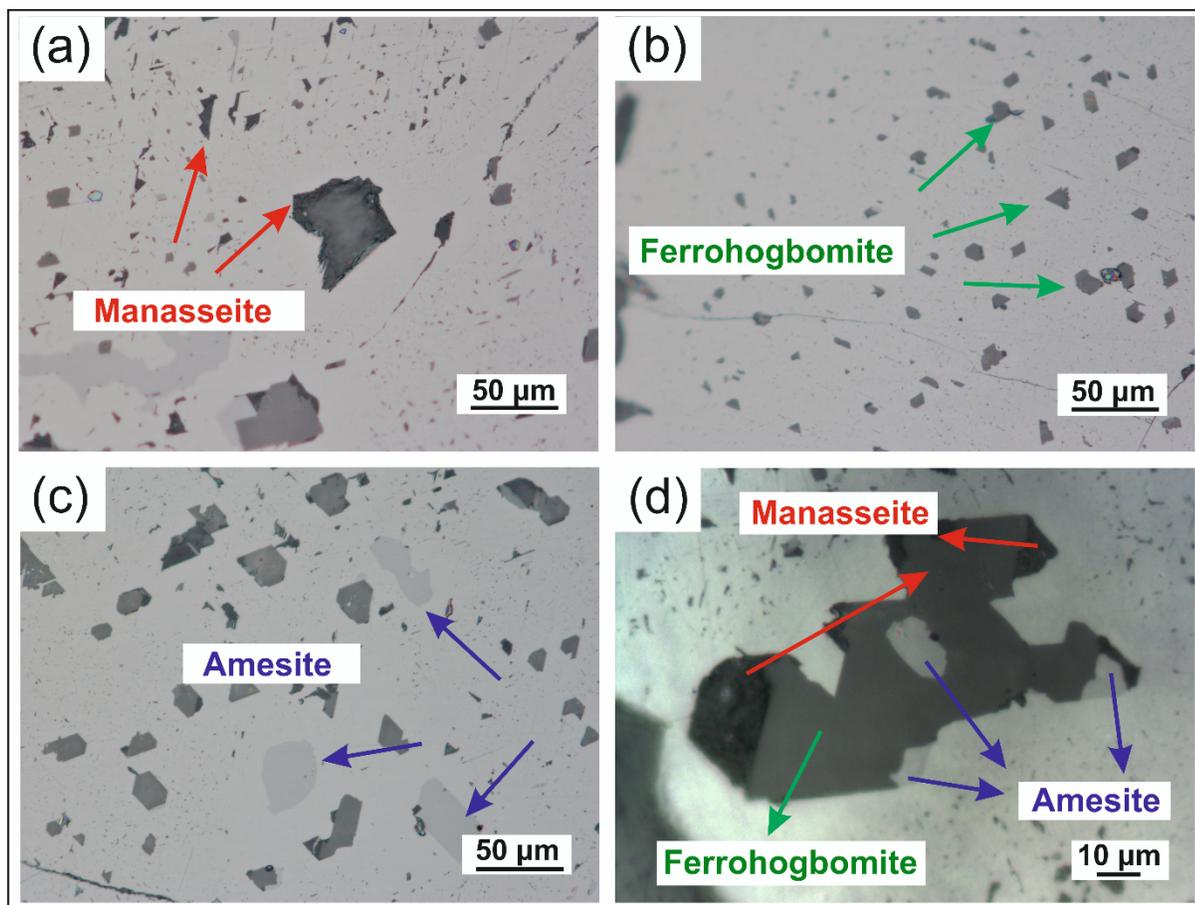
Cross-polarized light photomicrograph of analysed carbonatite samples, showing presence of phlogopite. (c) Photomicrograph showing the presence of accessory magnetite in Sung Valley carbonatite. (d-f) High-resolution photomicrographs of aqueous biphasic primary fluid inclusions hosted by calcite showing the presence of liquid and vapour phases as water. Ap – apatite; Cal – calcite; Mt – magnetite; Phl – phlogopite.

#### 1. Fluid inclusions in calcite

Fluid inclusions study was carried out on the doubly polished wafers of 0.3 to 0.5 mm thickness of these Sung valley carbonatite. Calcite hosts aqueous biphasic fluid inclusions (liquid + vapour) isolated or randomly distributed in the core part of the crystal (Figure 2d-f). The fluid inclusions morphologies range from ellipsoidal to irregular shapes and the size of these fluid inclusions varies between 10 to 30  $\mu\text{m}$  in the longest dimension (Figure 2d-f). An absence of any decrepitation feature suggests that these inclusions have not experienced any re-equilibration. Therefore, these fluid inclusions are primary in nature and trapped during the crystal growth of the calcite (Roedder, 1984) (Figure 2d-f).

#### 1. Mineral inclusions in magnetite

The dominant accessory opaque mineral phase in the Sung valley carbonatite is magnetite, which hosts several mineral inclusions (Figure 3). These inclusions are concentrated in the core of these magnetite crystals. Therefore, these inclusions can be inferred as primary phases, which were trapped during the crystal growth of magnetite (Roedder, 1984). Mineral inclusions in magnetite appear in three different colours under reflected light i.e., black, dark grey and light grey (Figure 3). The dark grey inclusion phases are mostly euhedral, whereas black and light grey phases are subhedral to anhedral respectively (Figure 3). These mineral inclusion phases occur as isolated phases as well as clustered in the core of magnetite.



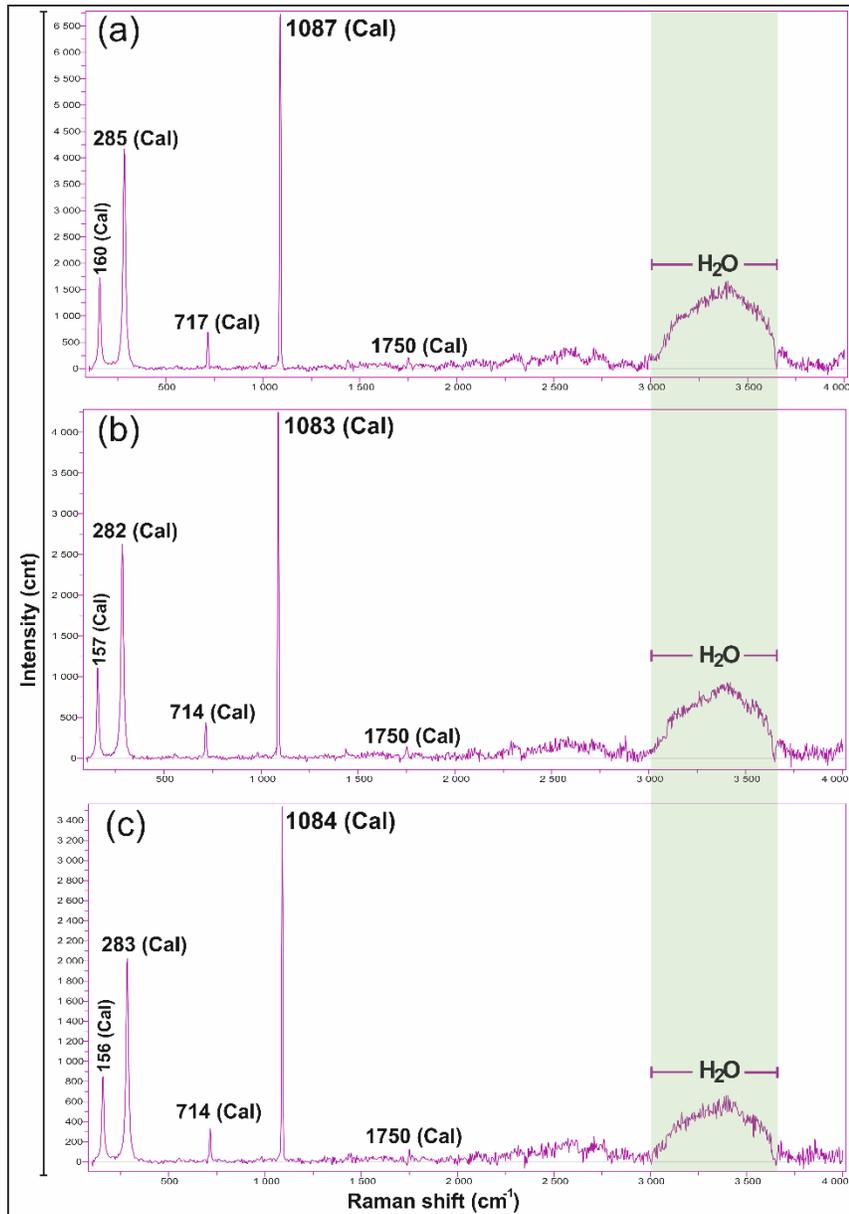
**Figure 3.** (a) Reflected light photomicrograph showing the presence of manasseite inclusions in magnetite. (b) Photomicrograph showing different shapes of inclusions of ferrohobomite in magnetite under reflected light. (c) Reflected light photomicrograph showing the inclusions of amesite in the core of magnetite crystal. (d) Mineral inclusions of manasseite, ferrohobomite and amesite showing textural relationship in closed association.

The size of these inclusions varies between 10 to 50  $\mu\text{m}$  (Figure 3). The magnetite hosted mineral inclusions were also found closely associated with each other (Figure 3d). However, no significant pattern of replacement was observed among these phases. This suggests that these inclusions are cogenetic in nature, which were trapped during magnetite crystal growth. The inclusions in magnetite are interpreted as trapped phases from the parental magma of Sung valley carbonatite from which these minerals have crystallized ‘in situ’.

### 1. Raman spectroscopy of inclusions

To determine the phase composition of the mineral and fluid inclusions, micro

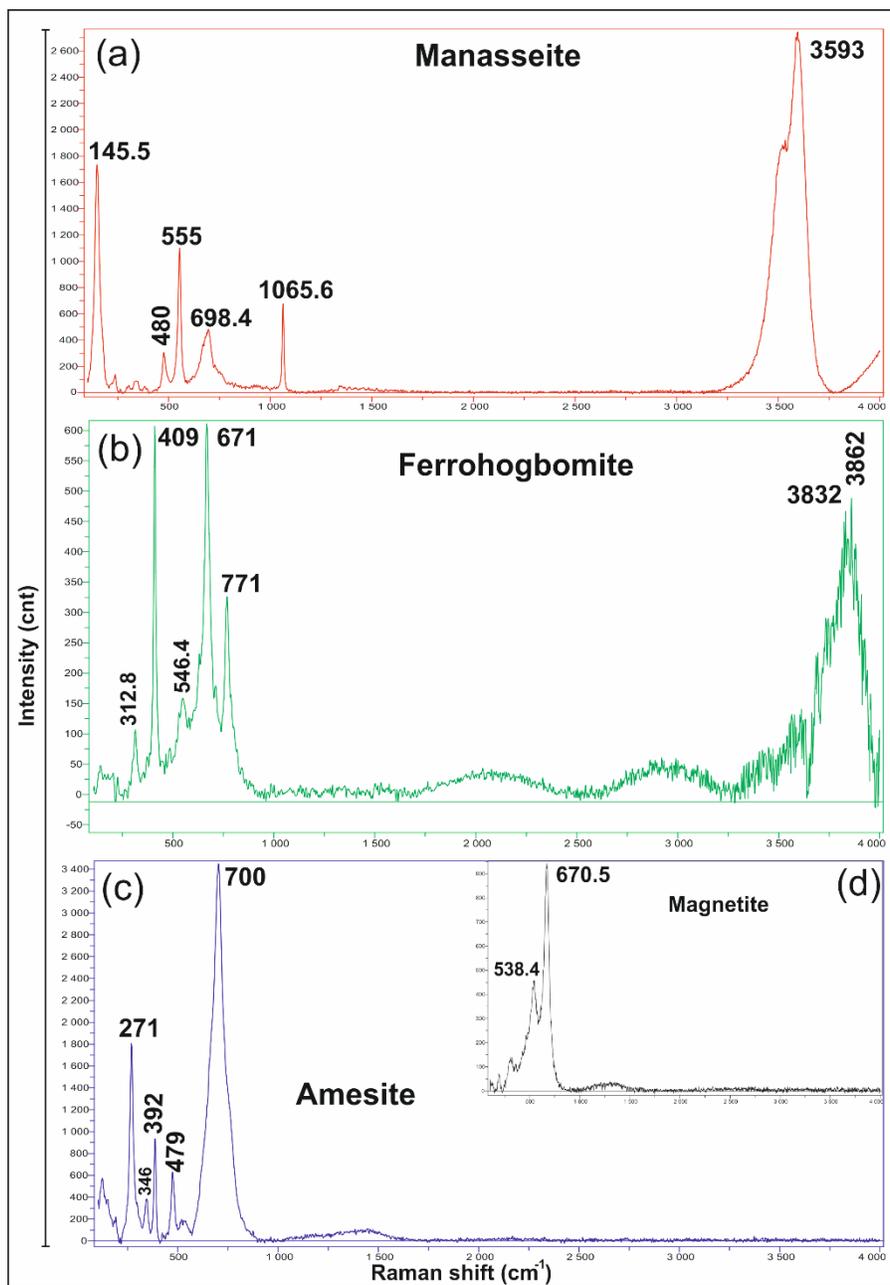
Raman spectroscopy was employed. The calcite hosted biphasic fluid inclusions (liquid and vapour) were identified as water (Figure 4).



**Figure 4.** (a-c) Raman spectra of aqueous biphasic fluid inclusions and host calcite showing symmetric hump of water at  $\sim 3000\text{--}3600\text{ cm}^{-1}$  and characteristic vibrations of calcite.

Raman spectrum of host calcite shows vs stretching bands at  $\sim 1085 \text{ cm}^{-1}$  and s bands at  $\sim 284 \text{ cm}^{-1}$  with some mw bands at  $\sim 711 \text{ cm}^{-1}$  and w bands at  $1750 \text{ cm}^{-1}$  (Chukanov & Vigasina, 2020). Raman spectrum of aqueous biphasic fluid inclusions (liquid + vapour) shows characteristic symmetrical hump of the water at  $\sim 3000\text{-}3600 \text{ cm}^{-1}$  (Frezzotti et al., 2012). Raman spectrum of these fluid inclusions also suggests that the water contained in these fluid inclusions is a low-salinity ( $<1 \text{ NaCl wt. \%}$ ) liquid water (Frezzotti et al., 2012) (Figure 4).

Raman spectrum of host magnetite shows its vs vibrations at  $670.5 \text{ cm}^{-1}$  and s vibrations at  $538.4 \text{ cm}^{-1}$  (Fig 5d). Black coloured mineral inclusions hosted by magnetite were identified as manasseite (Figure 5a), which is now renamed as hydrotalcite-2H ( $\text{Mg}_6\text{Al}_2(\text{OH})_{16}[\text{CO}_3]\cdot 4\text{H}_2\text{O}$ ) (Mills et al., 2012; Frost et al., 2014).



**Figure 5.** (a-c) Raman spectra of manasseite, ferrohogbomite and amesite. Inset (d) Raman spectrum of host magnetite.

Manasseite is a layered double hydroxide (LDC) from hydrotalcite supergroup. It shows its characteristic Raman bands at  $1065.6\text{ cm}^{-1}$  assigned to symmet-

ric stretching modes (Frost et al., 2014; Chukanov & Vidasina, 2020; RRUFF database- ID: R060527.2) (Figure 5a). Strong vibrations are assigned to Raman bands at  $145.5\text{ cm}^{-1}$  and  $555\text{ cm}^{-1}$ , whereas weak vibrations are assigned at  $480\text{ cm}^{-1}$  and  $698.4\text{ cm}^{-1}$  (Chukanov & Vidasina, 2020). Characteristic hydroxyl group (-OH) vibrations were also detected at  $3593\text{ cm}^{-1}$  (Chukanov & Vidasina, 2020) (Figure 5a). Dark grey coloured mineral inclusions in magnetite were identified as ferrogobomite  $(\text{Mg,Al})_6\text{Al}_{14}(\text{Ti,Fe})_2\text{O}_{30}(\text{OH})_2$ , showing its main vibrations at  $671, 409, 771, 546.4$  and  $312.8\text{ cm}^{-1}$  along with the characteristic -OH vibrations at around  $3832$  and  $3862\text{ cm}^{-1}$  (Orozbaev et al., 2011; Chukanov & Vidasina, 2020; RRUFF database-RRUFF ID: R070156) (Figure 5b). Raman spectroscopy of these light grey coloured mineral inclusions hosted by magnetite shows that these are amesite  $(\text{Mg}_2\text{Al}(\text{AlSiO}_5)(\text{OH})_4)$ , a member of serpentine group (Figure 5c). Raman spectra of amesite show strong vibrations of Raman bands at  $700$  and  $392\text{ cm}^{-1}$  and characteristic bands at  $479, 346,$  and  $271\text{ cm}^{-1}$  (Andreani et al., 2013; Chukanov & Vidasina, 2020) (Figure 5c). However, the Raman spectra of amesite do not show -OH vibrations (Figure 5c), which could be absent in some hydrous minerals if -OH is substituted by fluorine (F) (Robert et al., 1993). Raman spectra were recorded repeatedly for these solid inclusions and similar results were obtained. Additional Raman spectra of these phases are available in supplementary data (Figure S1).

## 1. Discussion

### (a) Petrogenesis of Sung Valley carbonatite

Petrogenetic evolution of Sung Valley carbonatite have been explained in detail by earlier workers using the mineralogical, geochemical and isotopic proxies (Veena et al., 1998; Srivastava & Sinha, 2004; Srivastava et al., 2005; Basu & Murty, 2006; Melluso et al., 2010; Srivastava et al., 2019). Based on Pb, Sr and Nd isotopic systematics, Veena et al. (1998) suggested that Sung Valley carbonatite has derived from a metasomatised source of EM2-HIMU signature. Stable isotope systematics of C suggest that these carbonatite contain recycled crustal carbon (Ray et al., 1999; Basu & Murty, 2006; Srivastava et al., 2005; Choudhary et al., 2020). Basu & Murty (2015) measured nitrogen and argon concentrations and isotopic ratios in Sung Valley carbonatite and they concluded that these carbonatite show primary as well as the recycled nitrogen and argon concentrations.

Mantle peridotite gets metasomatised to carbonated peridotite through interaction of Mg-rich carbonate melts derived from partial melting of subducted oceanic crust (Li et al., 2017). Continuation of this reaction between Mg-rich carbonate melts/ magnesiocarbonatite magma and mantle peridotite generates primary calciocarbonatite (similar to carbonatite of the present study) at lower pressures (Dalton & Wood, 1993). Experimental studies carried out by several workers suggest that primary carbonatitic melts may generate at depths  $>70\text{ km}$  by direct melting of carbonated peridotite at  $\sim 2\text{--}3.5\text{ GPa}$  pressure (Wyllie & Huang, 1976; Wallace & Green, 1988; Eggler, 1978, 1989; Wyllie, 1989; Ryabachikove et al., 1989; Thibault et al., 1992; Dalton & Wood, 1993;

Sweeney, 1994; Dalton & Presnall, 1998; Lee & Wyllie, 1998; Wyllie & Lee, 1998). Geochemical evidences further suggest that carbonatitic magma can be formed from very low degree of partial melting (<5 %) of carbonated peridotite (Wyllie & Huang, 1975; Nelson et al., 1988; Dalton & Presnall, 1998; Harmer et al., 1998; Harmer, 1999; LeRoex et al., 2003; Gudfinnsson & Presnall, 2005; Dasgupta et al., 2007; Bell & Simonetti, 2010). Sung Valley carbonatite are purely calciocarbonatite (Figure 2), which formed from a very low degree of partial melting (~0.1 %) of carbonated peridotite (Srivastava & Sinha, 2004; Srivastava et al., 2005). The calciocarbonatite are the first phase to precipitate from primary hydrous carbonatitic melt generated from low degree partial melting of carbonated peridotite and this calciocarbonatitic phase is followed by calcite-dolomite-carbonatite (Lee et al., 2000). Since the composition of Sung Valley carbonatite is also calciocarbonatitic (Figure 2) it can be argued, that the parental magma to these carbonatite was derived as first melt from quite a low degree of partial melting (~0.1 %) of carbonated peridotite at lower pressures (> 2.5 GPa) (Srivastava & Sinha, 2004; Srivastava et al., 2005) in the subcontinental lithospheric mantle (Dalton & Wood, 1993).

### 1. An ultra-hydrous parental magma of Sung Valley carbonatite

Carbonatitic magmas are generally believed to contain a significant amount of H<sub>2</sub>O and these magmas also work as major carrier of CO<sub>2</sub> and H<sub>2</sub>O in Earth's mantle (Gittins, 1989; Ray & Ramesh, 2006). Recent studies on natrocarbonatite at Oldoinyo Lengai (Tanzania) also suggest that these carbonatite are sourced from hydrous carbonatitic magma (de Moor et al., 2013). Aqueous biphasic fluid inclusions hosted by calcite in Sung Valley carbonatite also indicate an H<sub>2</sub>O saturated parental carbonatitic magma for the studied carbonatite (Figure 2). Choudhary et al. (2020) also detected polyphase and biphasic fluid inclusions of CO<sub>2</sub>-H<sub>2</sub>O hosted by apatite in Sung Valley carbonatite. However, the composition of fluid inclusions hosted by calcites in Sung Valley carbonatite in the present study is strictly restricted to H<sub>2</sub>O (Figure 4). Our study is the first to report the presence of such hydrous minerals (manasseite, ferrohogbomite and amesite) as inclusions in resistant mineral such as magnetite from calciocarbonatite (Figure 5). These mineral inclusions in magnetite (Figure 3) represent the nature of parental carbonatite magma more accurately than any of the bulk rock geochemical proxies, as grain scale heterogeneity and primary inclusions cannot be taken into account in bulk rock geochemical analysis. Occurrence of only hydrous minerals as inclusions in magnetite along with fluid inclusions of H<sub>2</sub>O in calcite in these carbonatite (Figure 4 & 5) strongly points toward an ultra-hydrous nature of the parental magma. This ultra-hydrous nature may have been acquired during partial melting of possibly a phlogopite and amphibole bearing carbonated peridotite. Crystallization of such hydrous minerals in carbonated peridotite can be facilitated during metasomatism. We opine that such hydration of the parental magma to these carbonatite could have resulted through the exhaustion of hydrous minerals (such as phlogopite and amphibole in their stability zone) during partial melting of the source in wet solidus region, as carbonatitic magmas are derived through very low degree of partial melting

(~0.1 %) of carbonated peridotite at pressure  $> 2.5$  GPa (Srivastava et al., 2005; Sokol et al., 2013). Under such conditions, exhaustion of hydrous minerals during low degree of partial melting can significantly contribute towards abundance of dissolved water in such magmas (Jones et al., 2013). The incorporation of water in carbonatitic magmas can significantly modify their structure (Foustoukos & Mysen, 2015) and likely cause an enhancement in their intake of incompatible trace elements and metasomatic efficiency (Yaxley et al., 1991; Hammouda & Keshav, 2015). Abundance of incompatible trace elements in Sung Valley carbonatite is also documented (Srivastava et al., 2005; Choudhary et al., 2020), which also points towards the ultra-hydrous nature of the parental carbonatitic magma of these carbonatite.

It may be noted that manasseite, amesite and ferrohobomite can also form through alteration of primary minerals (Andreani et al 2013; Zhitova et al., 2018; Chukanov & Vidasina, 2020). Hence, there is a possibility that the mineral phases are a result of hydrothermal alteration. However, stable isotopes (C & O) analyses of these carbonatite clearly suggested that these carbonatite are not affected by any secondary hydrothermal alteration (Choudhary et al., 2020). Additionally, this alternative method of formation of these minerals in magnetites by lower-temperature alteration is not consistent with preservation of these phases as inclusions in high-temperature magnetites in the present case (Figure 5). Furthermore, absence of manasseite (hydrocarbonate) as essential or accessory phases in these carbonatite (Figure 2) also suggests that this mineral phase is primary magmatic in nature and has not derived from any alteration process. Moreover, ferrohobomite can only be formed from the replacement of ilmenite in the presence of extra oxygen (Hejny et al., 2002) and not magnetite, but in the present case, all the inclusions of ferrohobomite are restricted to the host magnetite (Figure 3). Furthermore, all the hydrous mineral inclusions are concentrated in the core of the studied magnetites (Figure 5). Hence these mineral inclusions are primary in nature and are not product of any alteration process. On the basis of solid inclusions in magnetite and fluid inclusion in calcite (Figure 2d-f) reported in this study, we argue that the parental magma to Sung Valley carbonatite, derived from wet solidus melting of carbonated peridotite, was ultra-hydrous in nature and thus provides some direct evidence for an unplumbed more hydrous carbonatite melts on a global scale. It can also be opined that such ultra-hydrous nature with an abundance of dissolved water can significantly reduce the viscosity of carbonatitic magma.

## 1. Conclusions

Based on this study, the following conclusions can be made:

- The Sung Valley carbonatite have derived from a parental magma generated by low degree partial melting of phlogopite and amphibole bearing carbonated peridotite.
- Biphasic fluid inclusions of  $H_2O$  hosted by calcite and solid minerals inclusions of manasseite, ferrohobomite and amesite hosted by magnetite

suggest that the parental magma was ultra-hydrous in nature.

- Such hydrous nature (with dissolved water) of these carbonatitic magmas can significantly lower the viscosity of these magmas.

#### **Data Availability Statement**

All data reported in this manuscript are listed in Supporting Information S1 and can be found on .....

#### **Declaration of Competing Interest**

We declare that we have no known competing/ financial interests that could influence the work reported in this paper.

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#### **References**

- Acharya, S. K., Mitra, N. D., & Nandy, D. R., (1986). Regional geology and tectonic setting of northeast India and adjoining region, in *Geology of Nagaland ophiolite: Memoirs of the Geological Survey of India*, 119, 6-12.
- Andreani, M., Daniel, I., & Pollet-Villard, M., (2013). Aluminum speeds up the hydrothermal alteration of olivine. *American Mineralogist*, 98(10), 1738-1744.
- Basu, S., & Murty, S. V. S., (2006). Noble gases in carbonatite of Sung Valley and Ambadongar: implications for trapped components. *Chemical Geology*, 234 (3-4), 236-250.
- Basu, S., & Murty, S. V. S., (2015). Nitrogen and argon in Sung Valley and Ambadongar carbonatite complexes: Evidence of incomplete homogenization of mantle and recycled components. *Journal of Asian Earth Science*, 107, 53-61.
- Bell, K., & Simonetti, A., (2010). Source of parental melts to carbonatite-critical isotopic constraints. *Mineralogy and Petrology*, 98(1), 77-89.
- Brooker, R. A., & Kjarsgaard, B. A., (2011). Silicate-carbonate liquid immiscibility and phase relations in the system  $\text{SiO}_2\text{-Na}_2\text{O-Al}_2\text{O}_3\text{-CaO-CO}_2$  at 0.1–2.5 GPa with applications to carbonatite genesis. *Journal of Petrology*, 52(7-8), 1281-1305.
- Choudhary, S., Sen, K., & Kumar, S., (2021). Pyroxenite hosted chalcopyrites from Sung valley, Meghalaya, NE India: Implications for formation of both high- and low-temperature sulphides in plume derived magma. *Geological Society, London, Special Publications*, 518.

- Choudhary, S., Sen, K., Kumar, S., Rana, S., & Ghosh, S., (2020). Forsterite reprecipitation and carbon dioxide entrapment in the lithospheric mantle during its interaction with carbonatitic melt: a case study from the Sung Valley ultramafic–alkaline–carbonatite complex, Meghalaya, NE India. *Geological Magazine*, 158(3), 475-486.
- Chukanov, N. V., & Viggiani, M. F., (2020). Vibrational (Infrared and Raman) spectra of minerals and related compounds (721-739). *Cham: Springer*.
- Church, A. A., & Jones, A. P., (1995). Silicate–carbonate immiscibility at Oldoinyo Lengai. *Journal of Petrology*, 36(4), 869-889.
- Dalton, J. A., & Presnall, D. C., (1998). The continuum of primary kimberlitic melt composition in equilibrium with lherzolite: data from the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CO<sub>2</sub> system. *Journal of Petrology*, 39, 1953–1964.
- Dalton, J. A., & Wood, B. J., (1993). The compositions of primary carbonate melts and their evolution through wallrock reaction in the mantle. *Earth and Planetary Science Letters*, 119(4), 511-525.
- Dasgupta, R., (2013). Ingassing, storage, and outgassing of terrestrial carbon through geologic time. *Reviews in Mineralogy and Geochemistry*, 75(1), 183-229.
- Dasgupta, R., (2018). Volatile-bearing partial melts beneath oceans and continents—Where, how much, and of what compositions? *American Journal of Science*, 318(1), 141-165.
- Dasgupta, R., & Hirschmann, M. M., (2006). Melting in the Earth’s deep upper mantle caused by carbon dioxide. *Nature*, 440, 659-662.
- Dasgupta, R., & Hirschmann, M. M., (2007). Effect of variable carbonate concentration on the solidus of mantle peridotite. *American Mineralogist*, 92, 370-379.
- Dasgupta, R., Hirschmann, M. M., & Smith, N. D., (2007). Partial melting experiments of peridotite+ CO<sub>2</sub> at 3 GPa and genesis of alkalic ocean island basalts. *Journal of Petrology*, 48(11), 2093-2124.
- Dawson, J. B., (1998). Peralkaline nephelinite–natrocarbonatite relationships at Oldoinyo Lengai, Tanzania. *Journal of Petrology*, 39, 2077–2094.
- de Moor, J. M., Fischer, T. P., King, P. L., Botcharnikov, R. E., Hervig, R. L., Hilton, D. R., Barry, P. H., Mangasini, F., & Ramirez, C., (2013). Volatile-rich silicate melts from Oldoinyo Lengai volcano (Tanzania): Implications for carbonatite genesis and eruptive behaviour. *Earth and Planetary Science Letters*, 361, 379-390.
- Desikachar, S. V., (1974). A review of the tectonic and geologic history of eastern India in terms of plate tectonics theory. *Journal of the Geological Society of India*, 15, 137-149.

- Eggler, D. H., (1978). The effect of CO<sub>2</sub> upon partial melting of peridotite in the system Na<sub>2</sub>O–CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub>–CO<sub>2</sub> to 35 kb, with an analysis of melting in a peridotite–H<sub>2</sub>O–CO<sub>2</sub> system. *American Journal of Science*, 278, 305– 343.
- Eggler, D. H., (1989). Carbonatite, primary melts, and mantle dynamics. In: Bell, K. (Ed.), *Carbonatite—Genesis and Evolution*. Unwin Hyman, London. 561– 579.
- Evans, P., (1964). The tectonic framework of Assam: *Journal of the Geological Society of India*, 5, 80-96.
- Foustoukos, D. I., & Mysen, B. O., (2015). The structure of water-saturated carbonate melts. *American Mineralogist*, 100(1), 35-46.
- Frezzotti, M. L., Tecce, F., & Casagli, A., (2012). Raman spectroscopy for fluid inclusion analysis. *Journal of Geochemical Exploration*, 112, 1-20.
- Frost, R. L., Scholz, R., & López, A., Theiss, F. L., (2014). Vibrational spectroscopic study of the natural layered double hydroxide manasseite now defined as hydrotalcite-2H–Mg<sub>6</sub>Al<sub>2</sub> (OH)16[CO<sub>3</sub>] 4H<sub>2</sub>O. *Spectrochimica Acta Part A: Molecular and Biomolecular*, 118, 187-191.
- Gittins, J., (1989). The origin and evolution of carbonatite magmas. In: Bell, K. (Ed.), *Carbonatite: Genesis and Evolution*. Unwin Hyman Inc., Winchester, Massachusetts, 580–600.
- Gittins, J., & Jago, B. C., (1998). Differentiation of natrocarbonatite magma at Oldoinyo Lengai volcano, Tanzania. *Mineralogical Magazine*, 62(6), 759-768.
- Green, D. H. & Wallace, M. E., (1988). Mantle metasomatism by ephemeral carbonatite melts. *Nature*, 336(6198), 459-462.
- Gudfinnsson, G. H., & Presnall, D. C., (2005). Continuous gradations among primary carbonatitic, kimberlitic, melilititic, basaltic, picritic, and komatiitic melts in equilibrium with garnet lherzolite at 3–8 GPa. *Journal of Petrology*, 46(8), 1645-1659.
- Gupta, R. P., & Sen, A. K., (1988). Imprints of the Ninety-East Ridge in the Shillong Plateau, Indian Shield: *Tectonophysics*. 154 (3-4), 335-341.
- Halama, R., Vennemann, T., Siebel, W., & Markl, G., (2005). The Grønnedal-Ika carbonatite–syenite complex, South Greenland: carbonatite formation by liquid immiscibility. *Journal of Petrology*, 46(1), 191-217.
- Hammouda, T., & Keshav, S., (2015). Melting in the mantle in the presence of carbon: Review of experiments and discussion on the origin of carbonatite. *Chemical Geology*, 418, 171-188.
- Hammouda, T., & Laporte, D., (2000). Ultrafast mantle impregnation by carbonatite melts. *Geology*, 28(3), 283-285.

- Harmer, R. E., (1999). The petrogenetic association of carbonatite and alkaline magmatism: constraints from the Spitskop Complex, South Africa. *J. Petrol.*, 40(4), 525-548.
- Harmer, R. E., & Gittins, J., (1998). The case for primary, mantle-derived carbonatite magma. *Journal of Petrology*, 39(11-12), 1895-1903.
- Harmer, R.E., Lee, C. A., & Eglinton, B. M., (1998). A deep mantle source for carbonatite magmatism: evidence from the nephelinites and carbonatite of the Buhera district, SE Zimbabwe. *Earth and Planetary Science Letters*, 158(3-4), 131-142.
- Hejny, C., Gnos, E., Grobety, B., & Armbruster, T., (2002). Crystal chemistry of the polysome ferrohögbohmite-2 N 2 S, a long-known but newly defined mineral species. *European Journal of Mineralogy*, 14(5), 957-967.
- Jones, A. P., Genge, M., & Carmody, L., (2013). Carbonate melts and carbonatite. *Reviews in Mineralogy and Geochemistry*, 75(1), 289-322.
- Kelemen, P. B., Manning, C. E., (2015). Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Sciences*, 112(30), E3997-E4006.
- Kent, R. W., Pringle, M. S., Müller, R. D., Saunders, A. W., & Ghose, N. C., (2002).  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  geochronology of the Rajmahal basalts, India, and their relationship to the Kerguelen Plateau. *Journal of Petrology*, 43, 1141-1153.
- Kent, R. W., Saunders, A. D., Kempton, P. D., & Ghose, N. C., (1997). Rajmahal basalts, eastern India: mantle source and melt distribution at a volcanic rifted margin. In: Mahoney JJ, Coffin MF (eds) Large igneous provinces – *Continental, Oceanic and Planetary Flood Volcanism, Geophys. Monogr. Ser.*, 100, 145-182.
- Keppler, H., (2003). Water solubility in carbonatite melts. *American Mineralogist*, 88(11-12), 1822-1824.
- Krishnamurthy, P., (1985). Petrology of the carbonatite and associated rocks of Sung Valley, Jaintia hills district, Meghalaya, India. *Journal of Geological Society of India*, 1-78, 26(6), 361-379.
- Kumar, D., Mamallan, R., & Diwedy, K. K., (1996). Carbonatite magmatism in northeast India. *Journal of Southeast Asian Earth Sciences*, 13, 145-158.
- Le Roex, A. P., Bell, D. R., & Davis, P., (2003). Petrogenesis of group I kimberlites from Kimberley, South Africa: evidence from bulk-rock geochemistry. *Journal of Petrology*, 44(12), 2261-2286.
- Lee, W. J., Fanelli, M. F., Cava, N., & Wyllie, P. J., (2000). Calcicarbonatite and magnesiocarbonatite rocks and magmas represented in the system  $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$  at 0.2 GPa. *Mineralogy and Petrology*, 68(4), 225-256.

- Lee, W. J., & Wyllie, P. J., (1997). Liquid Immiscibility in the Join  $\text{NaAlSiO}_4$ - $\text{NaAlSi}_3\text{O}_8$ - $\text{CaCO}_3$  at 1 GPa: Implications for Crustal Carbonatite. *Journal of Petrology*, 38(9), 1113-1135.
- Lee, W. J. & Wyllie, P. J., (1998). Processes of crustal carbonatite formation by liquid immiscibility and differentiation, elucidated by model systems. *Journal of Petrology*, 39(11-12), 2005-2013.
- Li, S. G., Yang, W., Ke, S., Meng, X., Tian, H., Xu, L., He, Y., Huang, J., Wang, X. C., Xia, Q., & Sun, W., (2017). Deep carbon cycles constrained by a large-scale mantle Mg isotope anomaly in eastern China. *National Science Review*, 4(1), 111-120.
- Melluso, L., Srivastava, R. K., Guarino, V., Zanetti, A., & Sinha, A. K., (2010). Mineral compositions and petrogenetic evolution of the ultramafic-alkaline-carbonatitic complex of Sung Valley, northeastern India. *Canadian Mineralogist*, 48(1), 205-229.
- Mills, S. J., Christy, A. G., Génin, J. M., Kameda, T., & Colombo, F., (2012). Nomenclature of the hydrotalcite supergroup: natural layered double hydroxides. *Mineralogical Magazine*, 76(5), 1289-1336.
- Nandy, D. R., (1980). Tectonic pattern in northeastern India: *Indian Journal of Earth Sciences*, 7, 103-107.
- Nelson, D. R., Chivas, A. R., Chappell, B. W., & McCulloch, M. T., (1988). Geochemical and isotopic systematics in carbonatite and implications for the evolution of ocean-island sources. *Geochimica et Cosmochimica Acta*, 52, 1-17.
- Novella, D., (2014). The interaction between silicate minerals and COH bearing melts in the Earth's mantle (Doctoral dissertation).
- Orozbaev, R. T., Yoshida, K., Bakirov, A. B., Hirajima, T., Takasu, A., Sakiev, K. S., & Tagiri, M., (2011). Preiswerkite and högbomite within garnets of Aktyuz eclogite, Northern Tien Shan, Kyrgyzstan. *Journal of Mineralogical and Petrological Sciences*, 106(6), 320-325.
- Poli, S., (2015). Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids. *Nature Geoscience*, 8(8), 633-636.
- Ray, J. S., & Pande, K., (2001).  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  age of carbonatite-alkaline magmatism in Sung valley, Meghalaya, India. *Journal of Earth System Science*, 110(3), 185-190.
- Ray, J. S., & Ramesh, R., (2006). Stable carbon and oxygen isotopic compositions of Indian carbonatite. *International Geology Review*, 48(1), 17-45.
- Ray, J. S., Ramesh, R., & Pande, K., (1999). Carbon isotopes in Kerguelen plume-derived carbonatite: evidence for recycled inorganic carbon. *Earth and Planetary Science Letters*, 170(3), 205-214.

- Ray, J. S., Trivedi, J. R., & Dayal, A. M., (2000). Strontium isotope systematics of Amba Dongar and Sung Valley carbonatite-alkaline complexes, India: evidence for liquid immiscibility, crustal contamination and long-lived Rb/Sr enriched mantle sources. *Journal of Asian Earth Sciences*, 18, 585–94.
- Ritter, X., Sanchez-Valle, C., Sator, N., Desmaele, E., Guignot, N., King, A., Kupaenko, I., Berndt, J., & Guillot, B., (2020). Density of hydrous carbonate melts under pressure, compressibility of volatiles and implications for carbonate melt mobility in the upper mantle. *Earth and Planetary Science Letters*, 533, 116043.
- Robert, J. L., Beny, J. M., & Della Ventura, G., (1993). Crystal-chemical control of the OH-F distribution between trioctahedral and dioctahedral sites. *European Journal of Mineralogy*, 7-1s.
- Roedder, E., (1984). Volume 12: fluid inclusions. *Mineralogical Society of America*, 12.
- Ryabachikove, I. D., Brey, G., Kogarko, L. N., & Bulatov, V. K., (1989). Partial melting of carbonated peridotite at 50 kbar. *Geokhimiya*, 1, 3–9.
- Sarma, K. P., & Dey, T., (1996). Re-look on Shillong Plateau. *Bulletin of Pure and Applied Sciences*, 15F(2), 51–54.
- Schettino, E., & Poli, S., (2020). Hydrous carbonatitic liquids drive CO<sub>2</sub> recycling from subducted marls and limestones. *Carbon in Earth's Interior*, 209-221.
- Sengupta, P. R., & Agarwal, N. K., (1998). The tectonic segments of Northeastern India and associated gold mineralisation. *Journal of the Geological Society of India*, 1-78, 52(5), 549-556.
- Sifre, D., & Gaillard, F., (2012). April. Electrical conductivity measurements on hydrous carbonate melts at mantle pressure. In EGU General Assembly Conference Abstracts (p. 10869).
- Sokol, A. G., Kupriyanov, I. N., & Palyanov, Y. N., (2013). Partitioning of H<sub>2</sub>O between olivine and carbonate-silicate melts at 6.3 GPa and 1400 C: Implications for kimberlite formation. *Earth and Planetary Science Letters*, 383, 58-67.
- Sokol, A. G., Kupriyanov, I. N., Palyanov, Y. N., Kruk, A. N., & Sobolev, N. V., (2013). Melting experiments on the Udachnaya kimberlite at 6.3–7.5 GPa: Implications for the role of H<sub>2</sub>O in magma generation and formation of hydrous olivine. *Geochimica et Cosmochimica Acta*, 101, 133-155.
- Srivastava, R. K., Guarino, V., Wu, F. Y., Melluso, L., & Sinha, A. K., (2019). Evidence of sub-continental lithospheric mantle sources and open-system crystallization processes from in-situ U–Pb ages and Nd–Sr–Hf isotope geochemistry of the Cretaceous ultramafic-alkaline-(carbonatite) intrusions from the Shillong Plateau, north-eastern India. *Lithos*, 330, 108-119.

- Srivastava, R. K., Heaman, L. M., Sinha, A. K., & Shihua, S., (2005). Emplacement age and isotope geochemistry of Sung Valley alkaline-carbonatite complex, Shillong Plateau, northeastern India: implications for primary carbonate melt and genesis of the associated silicate rocks. *Lithos*, 81(1-4), 33-54.
- Srivastava, R. K., & Sinha, A.K., (2004). Early Cretaceous Sung Valley ultramafic-alkaline-carbonatite complex, Shillong Plateau, Northeastern India: petrological and genetic significance. *Mineralogy and Petrology*, 80(3-4), 241-263.
- Storey, M., Kent, R. W., Saunders, A. D., Hergt, J., Salters, V. J. M., Whitechurch, H., Sevigny, J. H., Thirlwall, M. F., Leat, P., Ghose, N. C., & Gifford, M., (1992). Lower Cretaceous volcanic rocks on continental margins and their relationship to the Kerguelen Plateau. *Proceedings of the Ocean Drilling Program Scientific Results*. 120, 33–53.
- Sweeney, R. J., (1994). Carbonatite melt compositions in the Earth's mantle. *Earth and Planetary Science Letters*, 128(3-4), 259-270.
- Thibault, Y., Edger, A. D., & Lloyd, F. E., (1992). Experimental investigation of melts from a carbonated phlogopite lherzolite: implications for metasomatism in the continental lithosphere. *American Mineralogist*, 77, 784– 794.
- Veena, K., Pandey, B. K., Krishnamurthy, P., & Gupta, J. N., (1998). Pb, Sr and Nd isotopic systematics of the carbonatite of Sung Valley, Meghalaya, Northeast India: implications for contemporary plume-related mantle source characteristics. *Journal of Petrology*, 39, 1875–84.
- Viladkar, S. G., Schleicher, H., & Pawaskar, P., (1994). Mineralogy and geochemistry of the Sung Valley carbonatite complex, Shillong, Meghalaya, India. *Neues Jahrbuch für Mineralogie*, MhH11, 499–517.
- Wallace, M. E., & Green, D. H., (1988). An experimental determination of primary carbonatite magma composition. *Nature*, 335(6188), 343-346.
- Wyllie, P. J., (1989). Origin of carbonatite: evidence from phase equilibrium studies. In: Bell, K. (Ed.), *Carbonatite—Genesis and Evolution*. Unwin Hyman, London, 500– 545.
- Wyllie, P. J., & Boettcher, A. L., (1969). Liquidus phase relationships in the system CaO-CO<sub>2</sub>-H<sub>2</sub>O to 40 kilobars pressure with petrological applications. *American Journal of Science*, 267, 489-508.
- Wyllie, P. J., & Huang, W. L., (1975). Peridotite, kimberlite, and carbonatite explained in the system CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub>. *Geology*, 3(11), 621-624.
- Wyllie, P. J., & Huang, W. L., (1976). Carbonation and melting reactions in the system CaO-MgO-SiO<sub>2</sub>-CO<sub>2</sub> at mantle pressures with geophysical and petrological applications. *Contributions to Mineralogy and Petrology*, 54, 79–107.

- Wyllie, P. J., & Huang, W. L., (1976). Carbonation and melting reactions in the system CaO–MgO–SiO<sub>2</sub>–CO<sub>2</sub> at mantle pressures with geophysical and petrological applications. *Contributions to Mineralogy and Petrology*, 54, 79–107.
- Wyllie, P. J., Lee, & W. -J., (1998). Model system controls on conditions for formation of magnesiocarbonatite and calciocarbonatite magmas from the mantle. *Journal of Petrology*, 39, 1885–1893.
- Yaxley, G. M., Crawford, A. J., & Green, D. H., (1991). Evidence for carbonatite metasomatism in spinel peridotite xenoliths from western Victoria, Australia. *Earth and Planetary Science Letters*, 107(2), 305-317.
- Ying, J., Zhou, X., & Zhang, H., (2004). Geochemical and isotopic investigation of the Laiwu–Zibo carbonatite from western Shandong Province, China, and implications for their petrogenesis and enriched mantle source. *Lithos*, 75(3-4), 413-426.
- Zhitova, E. S., Krivovichev, S. V., Yakovenchuk, V. N., Ivanyuk, G. Y., Pakhomovsky, Y. A., & Mikhailova, J. A., (2018). Crystal chemistry of natural layered double hydroxides: 4. Crystal structures and evolution of structural complexity of quintinite polytypes from the Kovdor alkaline-ultrabasic massif, Kola peninsula, Russia. *Mineralogical Magazine*, 82(2), 329-346.