

Manasseite, ferrohombomite 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, ferrohombomite 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. Plain Language Summary Primary solid inclusions of manasseite, ferrohombomite and amesite and biphasic fluid inclusions of H₂O were observed in magnetite and calcite respectively in Sung Valley carbonatite of northeast India. These carbonatite are related to 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 carbonatite have crystallized from. Inclusion data suggests that the parental magma of these carbonatite 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.

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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, ferrohobomite 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, Ferrohobomite; Amesite; Sung Valley, NE India.

Plain Language Summary

Primary solid inclusions of manasseite, ferrohobomite and amesite and biphasic fluid inclusions of H₂O were observed in magnetite and calcite respectively in Sung Valley carbonatite of northeast India. These carbonatites are related to 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 (Keppler, 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 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).

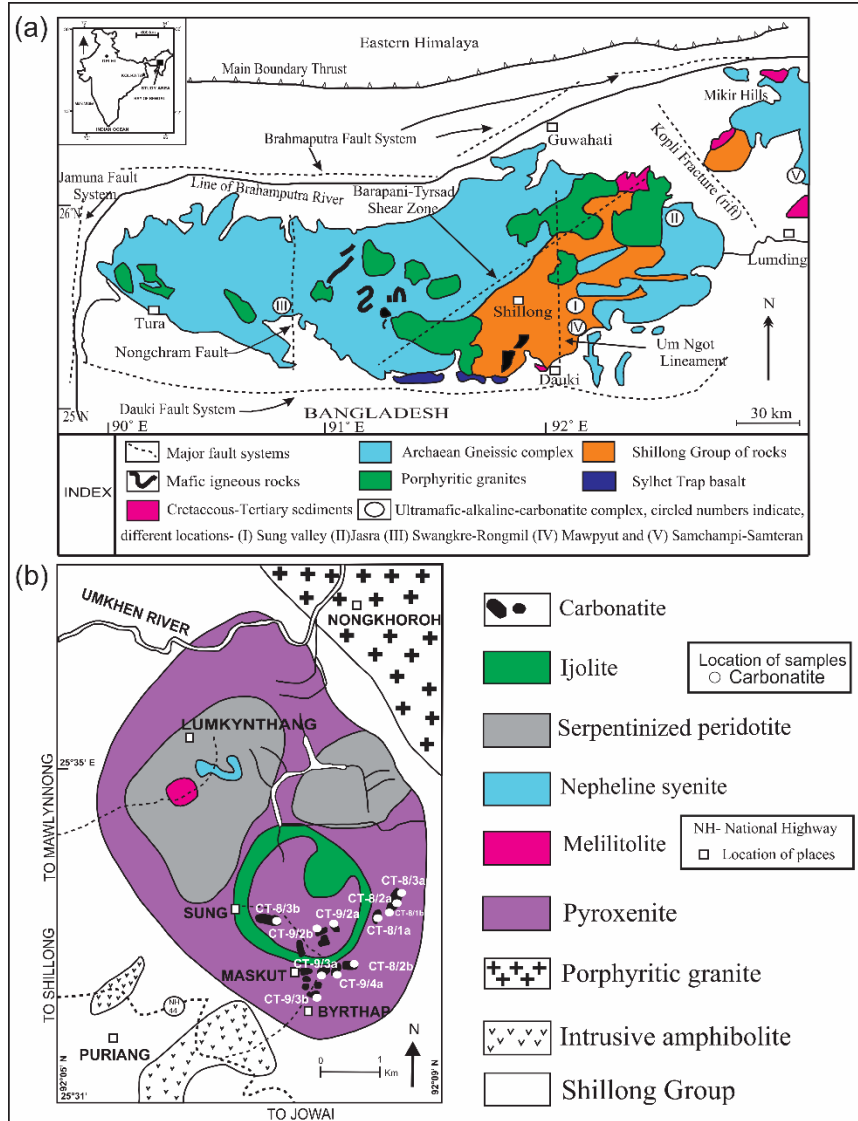


Figure 1. (a) Geological map of the Shillong plateau. (b) Geological map of Sung Valley, Meghalaya, NE India with sample locations. (a, b) Modified after Srivastava & Sinha (2004).

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 (Fe_3O_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 ± 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 ± 1.6 , 104.0 ± 1.3 and 101.7 ± 3.6 Ma respectively, while zircons from nepheline-syenite gave an age of 106.8 ± 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 lense, 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°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 μm 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 cm^{-1} spectral region. Synthetic silica standard (characteristic Raman shift at 520.59 cm^{-1}) was used during the calibration of the instrument. The spectral resolution of 1 - 2 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 calciocarbonatite 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).

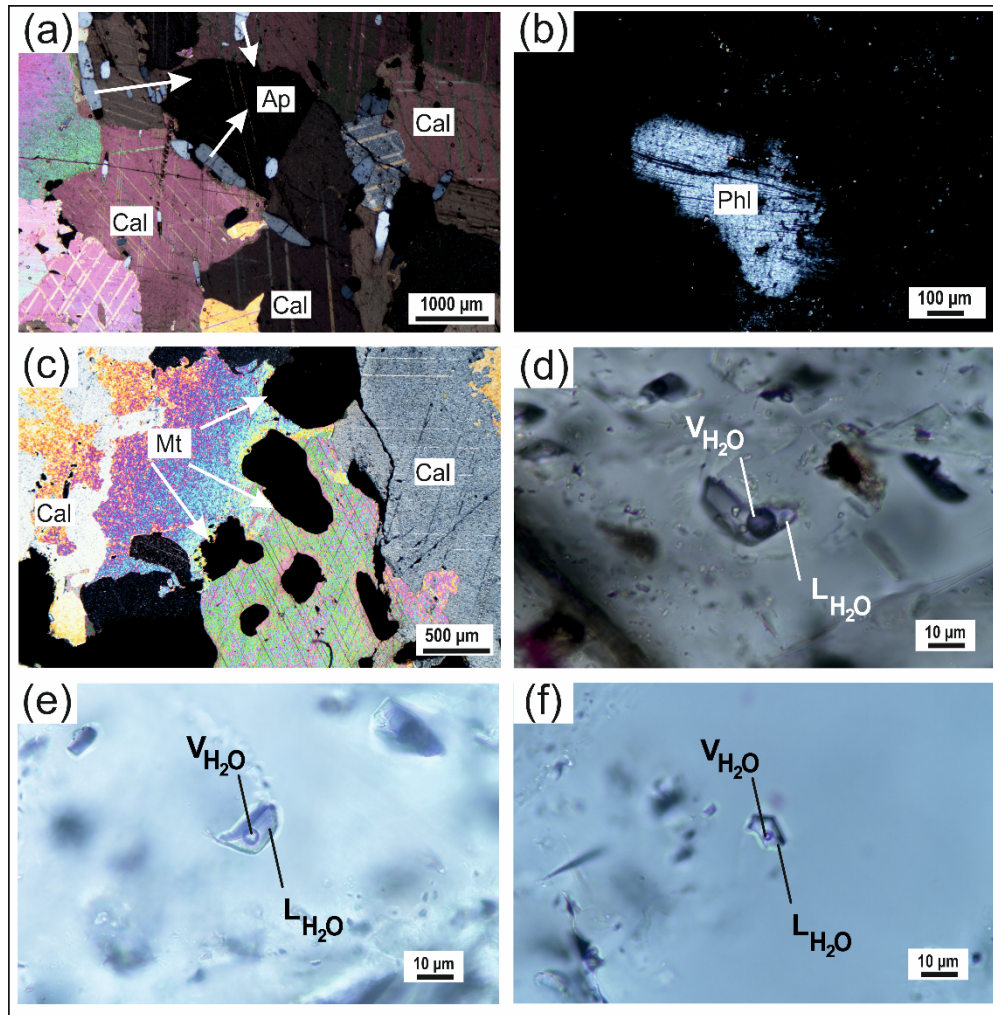


Figure 2. (a) Photomicrograph showing coarse-grained calcite with subhedral to anhedral apatites in carbonatite sample under cross-polarized light. (b)

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 μm 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.

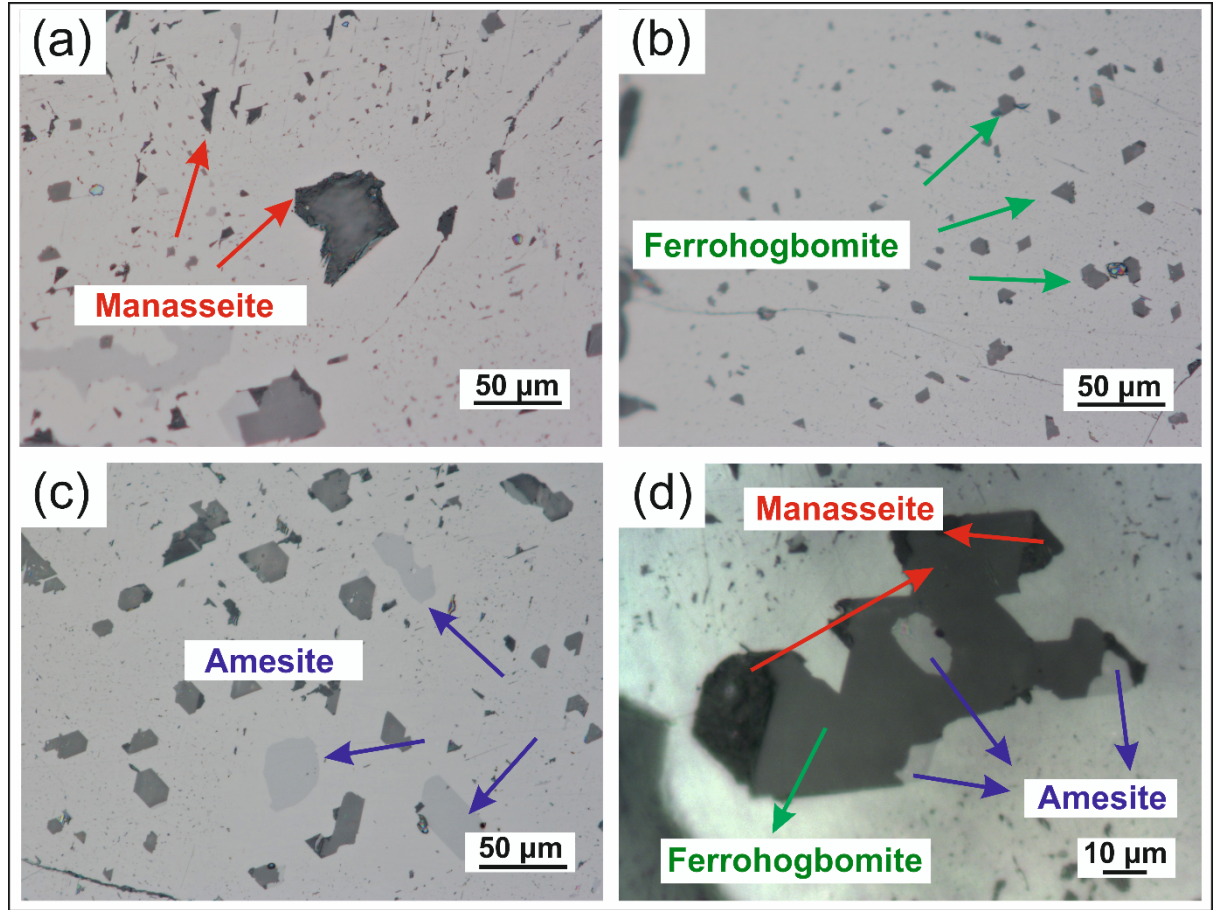


Figure 3. (a) Reflected light photomicrograph showing the presence of manasseite inclusions in magnetite. (b) Photomicrograph showing different shapes of inclusions of ferrohogbomite in magnetite under reflected light. (c) Reflected light photomicrograph showing the inclusions of amesite in the core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

The size of these inclusions varies between 10 to 50 μm (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).

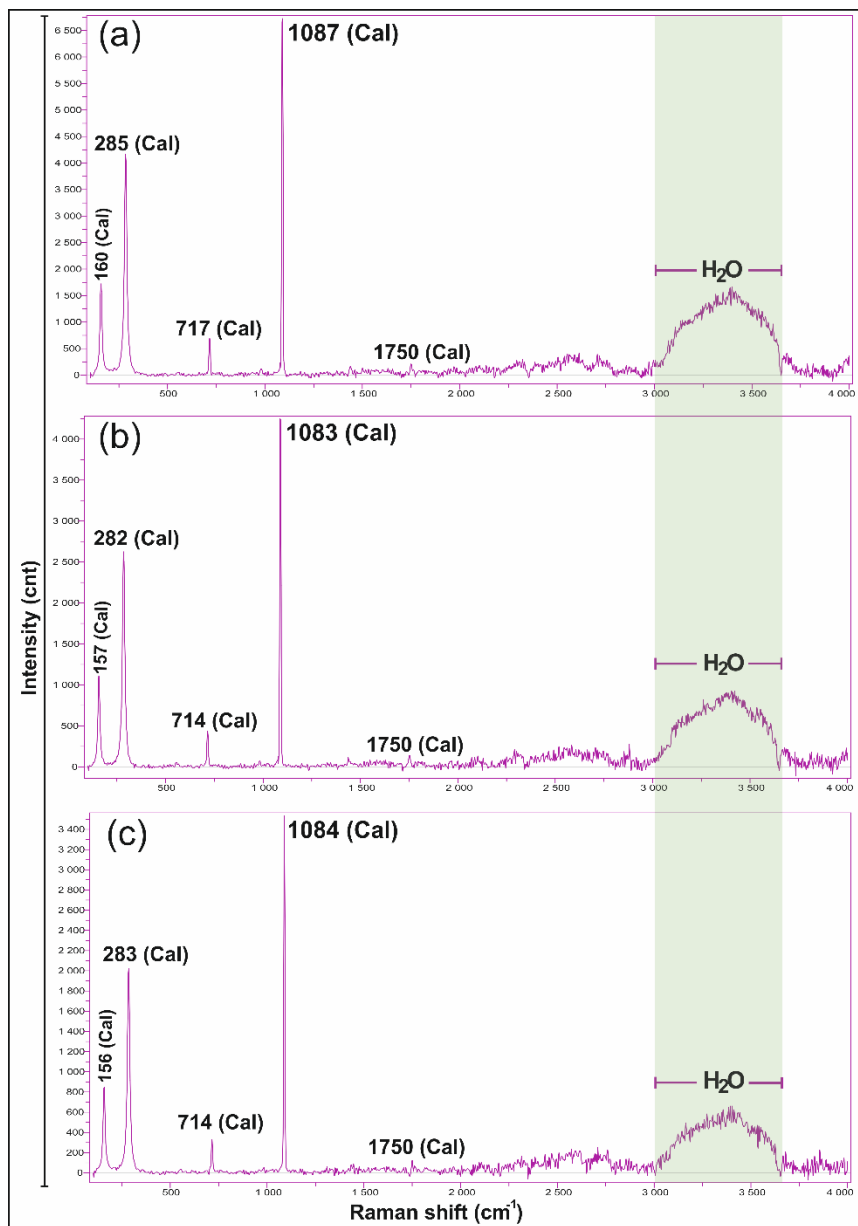


Figure 4. (a-c) Raman spectra of aqueous biphasic fluid inclusions and host calcite showing symmetric hump of water at $\sim 3000\text{--}3600\text{ cm}^{-1}$ and characteristic vibrations of calcite.

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 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 cm^{-1} and s vibrations at 538.4 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).

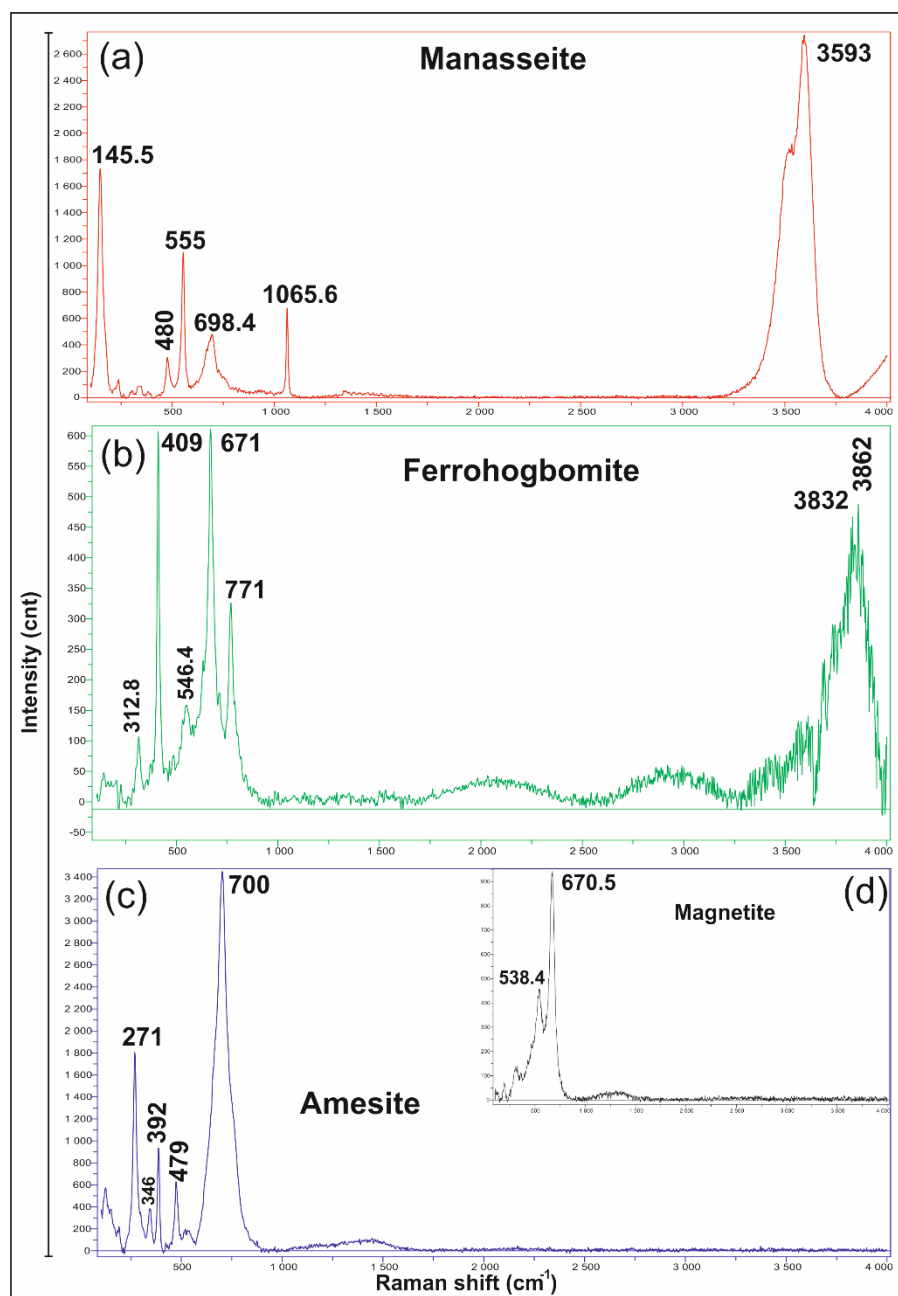


Figure 5. (a-c) Raman spectra of manasseite, ferrohogbomite and amesite. Inset (d) Raman spectrum of host magnetite.

Manasseite is a layered double hydroxide (LDC) from hydrotalcite supergroup. It shows its characteristic Raman bands at 1065.6 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 cm^{-1} and 555 cm^{-1} , whereas weak vibrations are assigned at 480 cm^{-1} and 698.4 cm^{-1} (Chukanov & Vidasina, 2020). Characteristic hydroxyl group (-OH) vibrations were also detected at 3593 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 cm^{-1} along with the characteristic -OH vibrations at around 3832 and 3862 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 cm^{-1} and characteristic bands at $479, 346,$ and 271 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; Ryabachikova 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 ($\sim 0.1\%$) of carbonated peridotite (Srivastava & Sinha, 2004; Srivastava et al., 2005). The calicocarbonatite are the first phase to precipitate from primary hydrous carbonatitic melt generated from low degree partial melting of carbonated peridotite and this calicocarbonatitic 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 ($\sim 0.1\%$) 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_2O and these magmas also work as major carrier of CO_2 and H_2O 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_2O saturated parental carbonatitic magma for the studied carbonatite (Figure 2). Choudhary et al. (2020) also detected polyphase and biphasic fluid inclusions of CO_2 - H_2O 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_2O (Figure 4). Our study is the first to report the presence of such hydrous minerals (manasseite, ferrogobomite 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_2O in calcite in these carbonatite (Figure 4 & 5) strongly points toward a 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 & Vigasina, 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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[Earth and Space Science]

Supporting Information for

[Manasseite, ferrohogbomite and amesite in Sung Valley carbonatites: Implications for unplumbed ultra-hydrous nature of parental carbonatite magma]

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Contents of this file

Figures S1

Introduction

[Additional Raman spectra of manasseite, ferrohogbomite and amesite (Figure S1)]

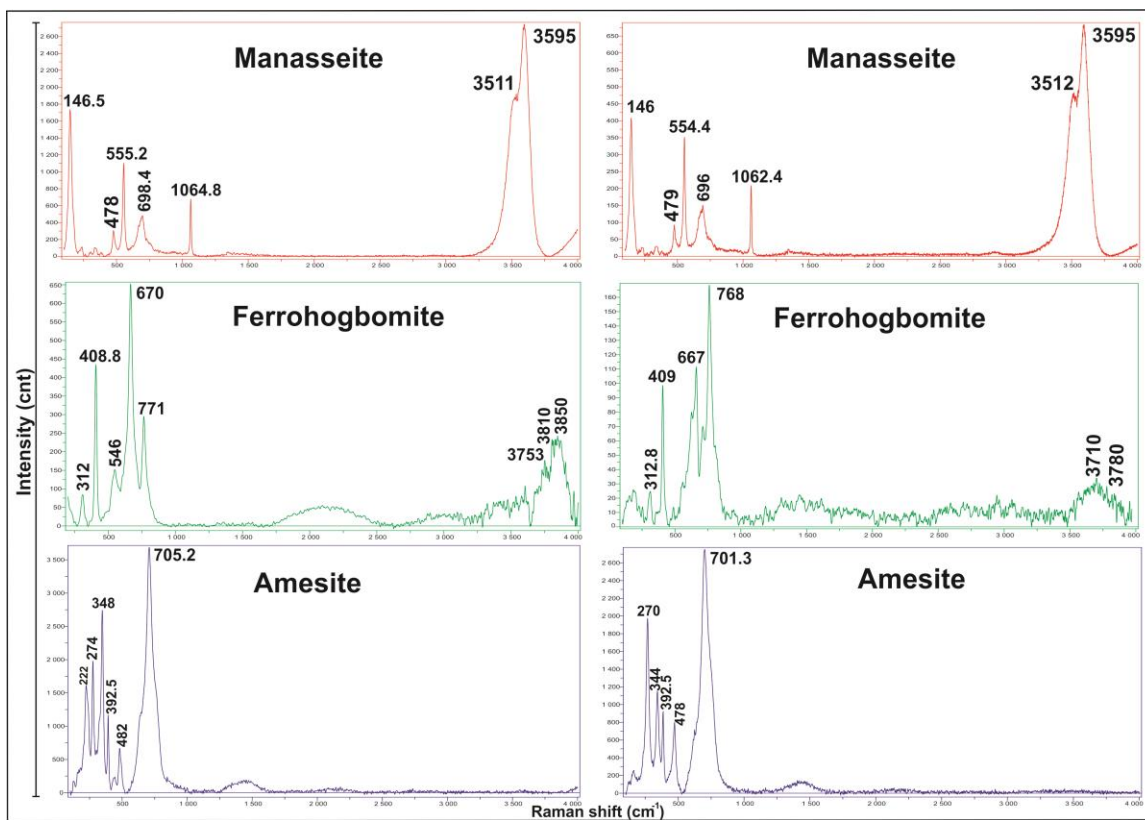


Figure S1. Supporting Information Figure S1. Additional Raman spectra of manasseite, ferrohogbomite and amesite obtained with repeated analyses.