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CO$_2$-Rich Xenoliths at Mt. Vulture Volcano (Southern Italy): New Constraints on the Volcano Plumbing System

Gabriele Carnevale[1,2] (ID) | Antonio Caracausi[2,3] (ID) | Massimo Coltorti[4] | Barbara Faccini[4] | Giulia Marras[5] | Michele Paternoster[2,6] | Silvio G. Rotolo[1,2] | Vincenzo Stagno[2,5] | Vittorio Zanon[7] | Filippo Zummo[6]

[1]Dipartimento di Scienze Della Terra e del Mare, Università Degli Studi di Palermo, Palermo, Italy | [2]Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy | [3]Departamento de Geología, Universidad de Salamanca, Salamanca, Spain | [4]Dipartimento di Fisica e Scienze Della Terra, Università di Ferrara, Ferrara, Italy | [5]Dipartimento di Scienze Della Terra, Sapienza Università di Roma, Rome, Italy | [6]Dipartimento di Scienze, Università Della Basilicata, Potenza, Italy | [7]Instituto de Investigação em Vulcanologia e Avaliação de Riscos, Universidade dos Açores, Ponta Delgada, Portugal

Correspondence: Gabriele Carnevale (gabriele.carnevale@unipa.it)

ABSTRACT

This study provides new mineral chemistry data together with micro-thermometric measurements on fluid inclusions hosted in ultramafic xenoliths (lherzolite, wehrlite, and dunite) brought to the surface by the last Mt. Vulture volcano activity (140 ka; southern Italy), and fed by melilitite-carbonatite magmas. Petrographic evidence and mineralogical compositions of Mt. Vulture xenoliths are consistent with an origin in the upper mantle. Fluid inclusions in rock-forming minerals of lherzolite and wehrlite xenoliths are CO$_2$-dominated. The equilibrium temperature calculated by geothermometric estimates ranges from 1039 C ($\pm$36°C) to 1142°C ($\pm$15°C), and entrapment pressures of fluid inclusions with post-trapping re-equilibration correspond to the local crust–mantle boundary (32 km depth), and to a shallow reservoir located at 12–14 km depth. These results contribute to constrain the origin of these xenoliths and the depth of storage of magmas erupted from Mt. Vulture, where carbonatite-like metasomatism and mantle-derived CO$_2$ degassing occur.

1 | Introduction

Mt. Vulture is the easternmost Quaternary volcano in Italy, the only one east of the Apennine chain (Figure S1), and it is located a few tens of km from seismically active areas in the central-southern Apennines (e.g., Chiodini et al. 2004). The origin of this volcanism is related to a vertical slab window inferred beneath the southern Apennines (e.g., D'Orazio et al. 2007; Peccerillo 2017), and the last explosive activity (141 ± 11 ka; Villa and Buettner 2009) was fed by melilitite-carbonatite magmas that brought abundant mantle xenoliths to the surface (e.g., Carnevale et al. 2022; Downes et al. 2002; Jones et al. 2000; Stoppa and Principe 1997).

Carbonatite-like metasomatism of the mantle source has been proposed to explain the genesis of magmas at Mt. Vulture, Etna (e.g., Bragagni et al. 2022; Carnevale et al. 2022), and the Hyblean Plateau (Beccaluva et al. 1998; Marras, Stagno, et al. 2023), with Etna being one of the highest natural CO$_2$ releasers into the atmosphere (e.g., Aiuppa et al. 2019). Mt. Vulture is still degassing mantle-derived CO$_2$ (e.g., Caracausi, Paternoster, and Nuccio 2015) even though its last eruption occurred about 140 ka ago. The mantle xenoliths brought to the surface by diatreme explosive eruptions at Mt. Vulture offer the possibility to investigate the nature of one of the most CO$_2$-rich systems of the Mediterranean region. Considering that mantle-derived xenoliths associated with magmatic events fed by melilitite-carbonatite magmas are rare (e.g.,

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Carnevale et al. 2022; Stoppa and Principe 1997), they are particularly useful because they can store fluids associated with this type of magmatism, and provide important insights into the composition of the upper mantle with the processes that can modify it, and the ascent path of related magmas (e.g., Carnevale et al. 2022; Rosatelli, Wall, and Stoppa 2007; Su, Zhang, Sakyi, et al. 2010). The most straightforward method to obtain information on the fluid composition and the pressure of fluid inclusions trapped in host minerals is micro-thermometry.

In this work, we present new micro-thermometric data, coupled with mineral chemistry and geothermobarometry of Mt. Vulture xenoliths. We extend our previous study (Carnevale et al. 2022) to different mantle xenoliths (lherzolite, wehrlite, dunite) in order to

further constrain their origin and characterise the behaviour of volatiles (especially CO_2) in the magma storage system. We also discuss the possible future research directions to correlate the mantle wehrlitisation with high CO_2 degassing areas in central-southern Italy.

2 | Results

2.1 | Petrography and Sample Description

Mantle xenoliths were collected from a compact, fine-grained, carbonate-dominated matrix in an ash-tuff deposit (Figure S2). A lherzolite (SLP-xen01), a wehrlite (SLP-xen06), and a dunite (SMC_B-xen01) were selected for this study (Figure 1a–c). They
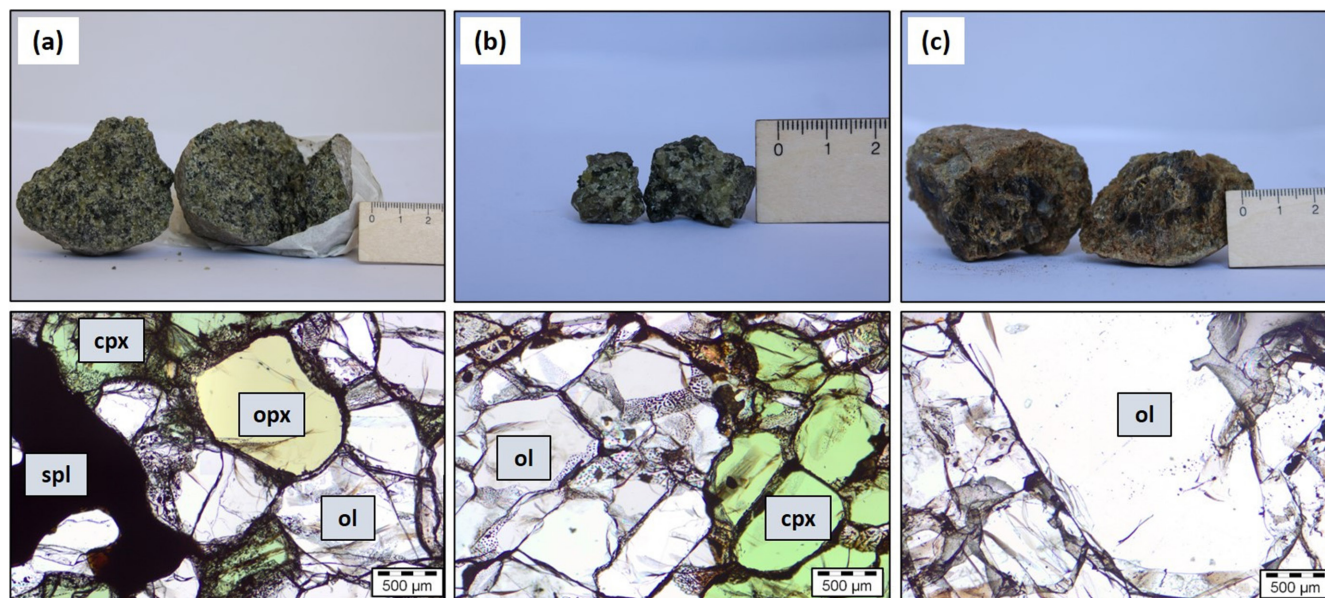

FIGURE 1 | Mantle xenoliths hand specimens and associated plane-polarised light (PPL) photomicrographs of (a) fine-grained lherzolite, (b) medium-grained wehrlite, and (c) coarse-grained dunite, respectively. cpx, clinopyroxene (emerald green Cr-diopside); ol, olivine; opx, orthopyroxene; spl, spinel.
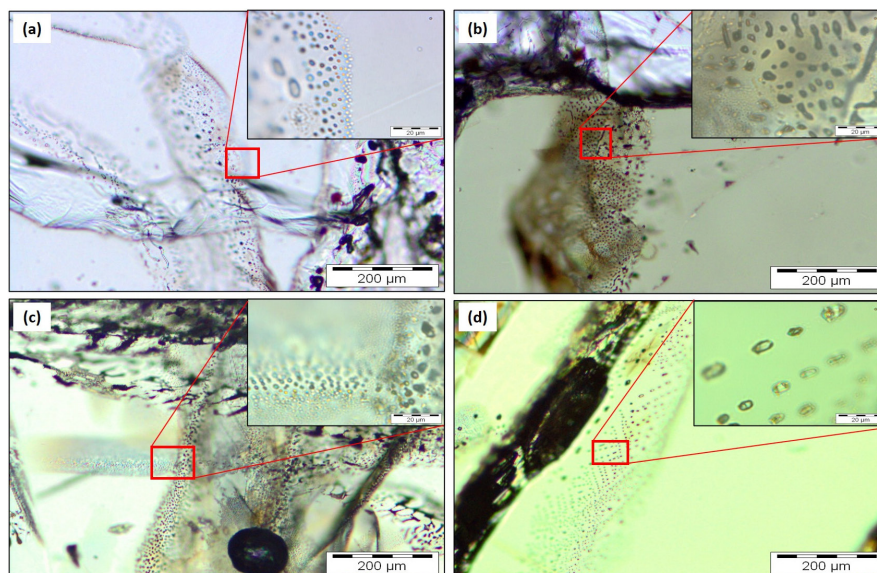

FIGURE 2 | Plane-polarised light (PPL) photomicrographs of textures of fluid inclusions trapped in (a) olivine, (b) orthopyroxene, (c) clinopyroxene in lherzolite, and (d) clinopyroxene in wehrlite from Mt. Vulture.

are rounded, with an average diameter of 4–5 cm (wehrlite and dunite) and a maximum of 10 cm (lherzolite). The lherzolite (Figure 1a) is fine- to medium-grained (0.5–1 mm), the wehrlite (Figure 1b) and dunite (Figure 1c) are medium- to coarse-grained (2–5 mm). The texture is protogranular, except for the dunite which shows a transitional texture between porphyroclastic and tabular equigranular (Mercier and Nicolas 1975). In all xenoliths, minerals are interlocked and randomly oriented, and 120 triple junctions are present. Olivine usually shows undulose extinction and intracrystalline deformation structures, while orthopyroxene and clinopyroxene occur as subhedral/anhedral crystals. Spinel occurs as lobate grains in the lherzolite and wehrlite, while it has subhedral/anhedral shapes in the dunite.

2.2 | Mineral Chemistry

Olivine shows an almost constant chemical composition all across the crystal (e.g., Fo_{89-90}). NiO varies from 0.22 to 0.29 wt% in lherzolite and wehrlite, while it is <0.15 wt% in dunite. Cr_2O_3 content is generally <0.10 wt% (Table S1).

Orthopyroxene is exclusively found in lherzolite. Its composition shows a high proportion of enstatite (En_{86-87}, En = 100* Mg/[Ca + Mg + Fe]) compared to wollastonite (Wo_{2-3}, Wo = 100* Ca/[Ca + Mg + Fe]) and ferrosilite (Fs_{10-11}, Fs = 100* Fe/[Mg + Fe]). It has a limited range of CaO content (1.02–1.20 wt%), high values of Al_2O_3 (5.92–6.27 wt%), and relatively high Cr_2O_3 content (0.48–0.68 wt%) (Table S2).

The composition of clinopyroxene (Wo_{42-44}, En_{49-52}, Fs_{5-7}) (Table S3) is more variable than the coexisting olivine and orthopyroxene. It shows a wider range of Mg# (0.88–0.91) in wehrlite compared to the almost constant Mg# (0.88) of the lherzolite (Mg# = [Mg/Mg + Fe^{2+}]). Similarly, CaO (19.49–20.37 wt%) and Cr_2O_3 (0.89–1.53 wt%) contents in wehrlite show higher values and a wider range if compared with CaO (18.56–18.86 wt%) and Cr_2O_3 (0.77–0.85 wt%) contents in the lherzolite. The analytical

TABLE 1 | Micro-thermometric data of lherzolite and wehrlite xenoliths.

Sample	Mineral analysed	N measures	Th_L (°C)	ρ (g/cm³)	ρ (g/cm³)$_{corrected}$
SLP-xen01 (lherzolite)	Olivine (3)	127	Th_L − 26.8–29.9	0.60–1.06	0.62–1.11
	Orthopyroxene (2)	85	Th_L − 25.6–29.9	0.60–1.05	0.62–1.10
	Clinopyroxene (2)	131	Th_L − 25.5–30.0	0.60–1.05	0.62–1.10
SLP-xen06 (wehrlite)	Olivine (4)	127	Th_L − 16.2–29.1	0.63–1.01	0.65–1.06
	Clinopyroxene (6)	184	Th_L − 20.1–26.8	0.68–1.03	0.71–1.08

Note: In brackets are the number of analysed minerals; Th_L, homogenisation temperature to liquid phase; ρ, density.
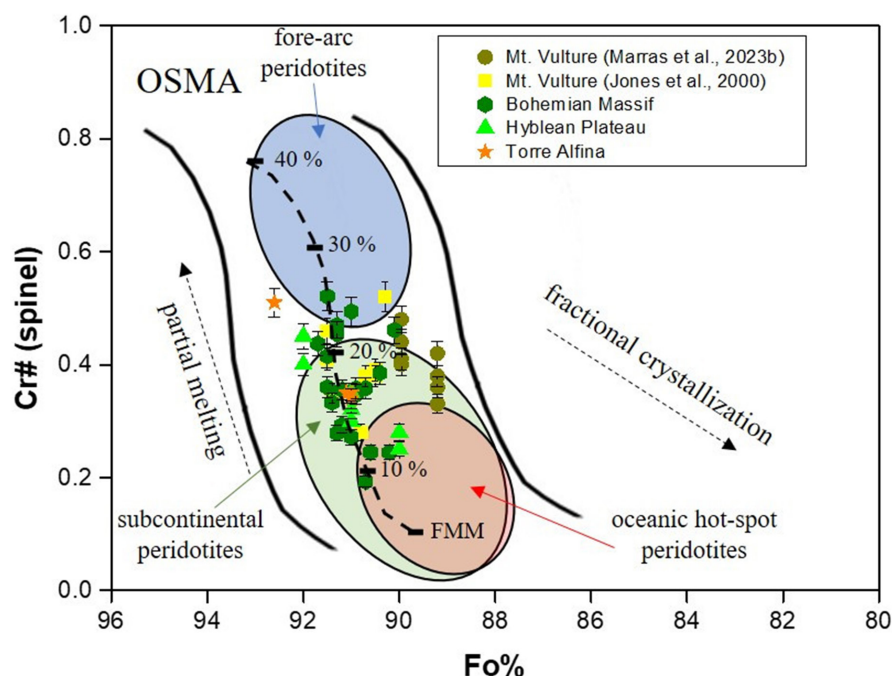

FIGURE 3 | Olivine-Spinel Mantle Array (OSMA) diagram showing the composition of olivine-spinel pairs of mantle xenoliths from Mt. Vulture (Jones et al. 2000; Marras, Carnevale, et al. 2023). Olivine-spinel pairs of mantle xenoliths from different areas are: Hyblean Plateau (Correale et al. 2012; Perinelli et al. 2008; Scribano et al. 2009), Bohemian Massif (Hackerman et al. 2013), Torre Alfina (Conticelli and Peccerillo 1990). OSMA, melting trend (% of melt in peridotite), and the field of oceanic hot-spot peridotite field are from Arai (1994), while compositional fields of fore-arc and subcontinental peridotites are from Ahmed et al. (2016). Cr# = [Cr/(Cr + Al)]. FMM, fertile MORB mantle.

dataset is reported in Data S1, and details of the analytical methods are provided in Text S1.

2.3 | Petrography and Micro-Thermometry of Fluid Inclusions

FIs (Figure 2a–d) are generally rounded (2–10 μm in diameter) with re-equilibration features, such as (i) the presence of dark halos (Bodnar 2003), and (ii) stretched shapes (Figure 2d). No primary FIs were found, and clinopyroxene is the main host for secondary FIs (i.e., trapped after the crystal growth), as evidenced by the presence of abundant trails in sealed fractures. The scarce presence and small size (<1 μm) of FIs in dunite xenoliths prevented the micro-thermometric analyses. Further details on the analytical methods and textural distributions of FIs can be found in Text S1.

In all studied xenoliths, FIs are characterised by melting temperatures (Tm) ranging between −56.5°C and −57.0°C (±0.1°C), with variable homogenisation temperatures from the vapour to the liquid phase (Th_L). In olivines from lherzolite and wehrlite, Th_L varies from −26.8°C to 29.9°C and from −16.2°C to 29.1°C, respectively, corresponding to density ranges (ρ) of 0.62–1.11 and 0.65–1.06 g/cm^3. In orthopyroxene Th_L varies from −25.6°C to 29.9°C (ρ = 0.62–1.10 g/cm^3). In clinopyroxene from lherzolite, Th_L varies from −25.5°C to 30.0°C (ρ = 0.62–1.10 g/cm^3), while from wehrlite varies from −20.1°C to 26.8°C (ρ = 0.71–1.08 g/cm^3). Details of the micro-thermometric data are given in Table 1. The full dataset is reported in Data S1.

3 | Discussion

The lack of plagioclase and garnet, and the presence of spinel as Al-bearing mineral phase in lherzolite, speculate that
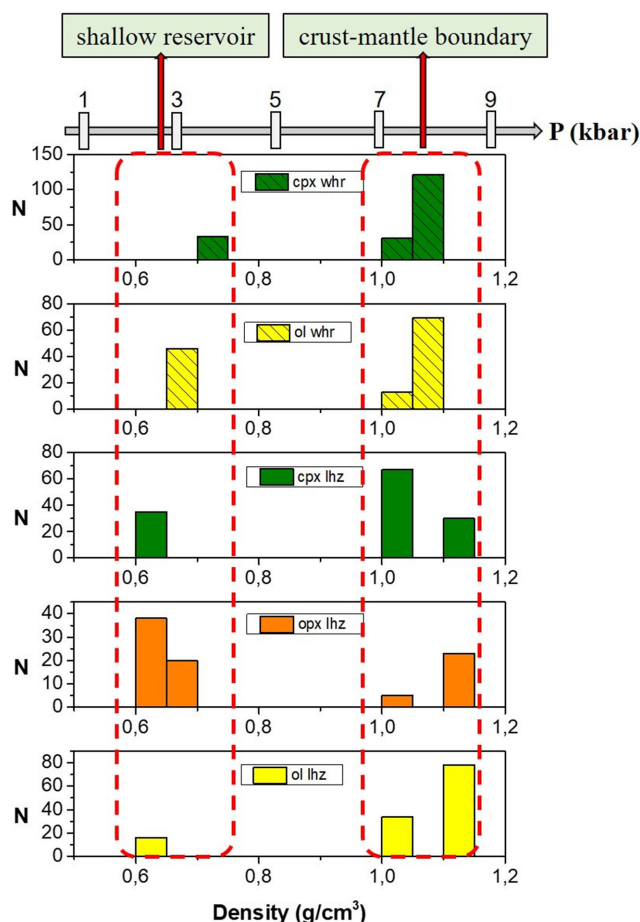

FIGURE 5 | Frequency distribution of densities of fluid inclusions hosted by olivine, orthopyroxene and clinopyroxene in lherzolite (lhz) and wehrlite (whr) xenoliths from Mt. Vulture. N, number of measurements.
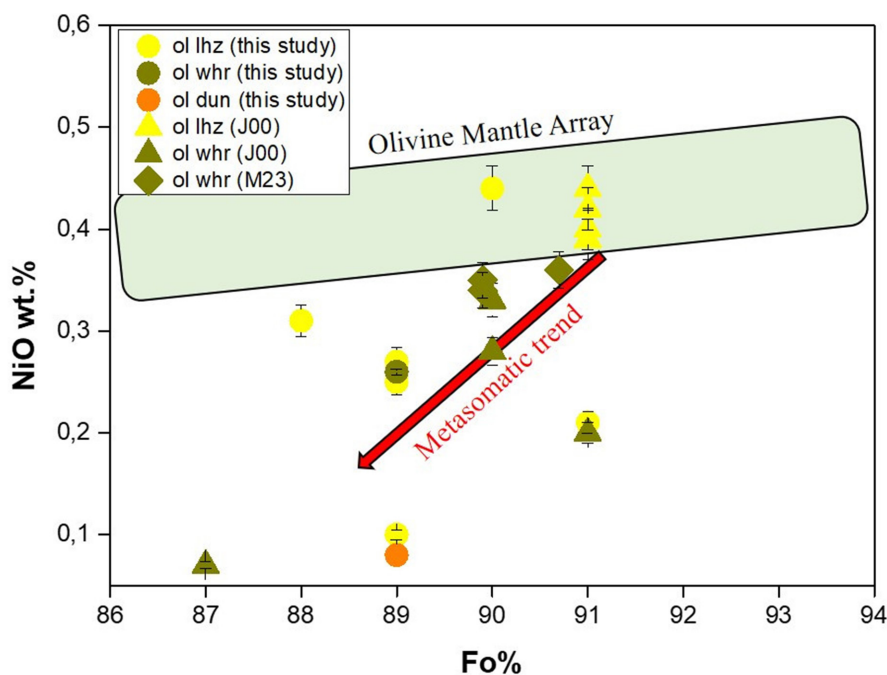

FIGURE 4 | Fo% verses NiO wt% in olivine from Mt. Vulture mantle xenoliths. Values from Jones et al. (2000, J00) and from Marras, Stagno, et al. (2023, M23) are also depicted for comparison. Olivine-mantle array (mantle peridotite area) is according to Takahashi (1986). The red arrow indicates a possible metasomatic trend. dun, dunite; lhz, lherzolite; whr, wehrlite.

xenoliths equilibrated at pressures between 8–9 and 15–20 kbar (Borghini, Fumagalli, and Rampone 2010; Su, Zhang, Asamoah, et al. 2010).

Xenoliths show no poikilitic or cumulitic textures, and olivines show the presence of intracrystalline deformation structures. On the Cr# of spinel verses Fo% of olivine diagram (Figure 3), the studied xenoliths plot in a restricted range within the Olivine-Spinel Mantle Array (OSMA) (Marras, Carnevale, et al. 2023). The NiO content in olivines is lower than typical mantle values, although it shows similar compositional ranges with respect to literature data from both Mt. Vulture and Hyblean mantle xenoliths (Figure 4) (e.g., Jones et al. 2000; Scribano et al. 2009). Interestingly, high-Fo and low-NiO olivines have been described in subduction-related rocks that required partial melting of a carbonated mantle source (Ammannati et al. 2016; Elburg et al. 2006). The presence of low-NiO olivines may reflect the interaction between the peridotite and a carbonate-rich metasomatic agent, where olivine and clinopyroxene grow at the expense of orthopyroxene. This process, known as wehrlitisation, is based on the reaction: enstatite + dolomite (melt) = forsterite + diopside + CO_2 (vapour) (e.g., Yaxley and Green 1996). Similarly, the

TiO_2 in clinopyroxenes from Mt. Vulture xenoliths is similar to the content reported in carbonatite-metasomatised mantle xenoliths from different geodynamic settings (e.g., Gorring and Kay 2000). Although the absence of the cumulate textures and the chemistry of minerals (e.g., high Mg#) can be consistent with an origin from a metasomatised mantle, we cannot exclude a derivation of the xenoliths from the crust–mantle boundary, where wehrlite layers are interbedded with olivine and clinopyroxene cumulates (e.g., Kovács, Zajacz, and Szabó 2004).

The histograms of the densities of FIs (Figure 5) show a polymodal distributions, and the range of Tm in lherzolite and wehrlite (–56.5°C to −57.0°C ± 0.1°C) suggests that FIs consist of almost pure CO_2. The highest corrected densities of FIs in all minerals from lherzolite and wehrlite are in the range of 1.10–1.11 g/cm^3, corresponding to minimum fluid entrapment pressure of 8.5–9.0 kbar (≈27–28 km). The low-density peaks are at 0.6–0.7 g/cm^3, corresponding to minimum fluid pressure between 2.0 and 4.0 kbar (≈6–12 km). These latter are generally associated with late-stage fractures near the crystal rims (Figure S3), whereas the high density FIs are uniformly distributed throughout the crystal (Figure S4).
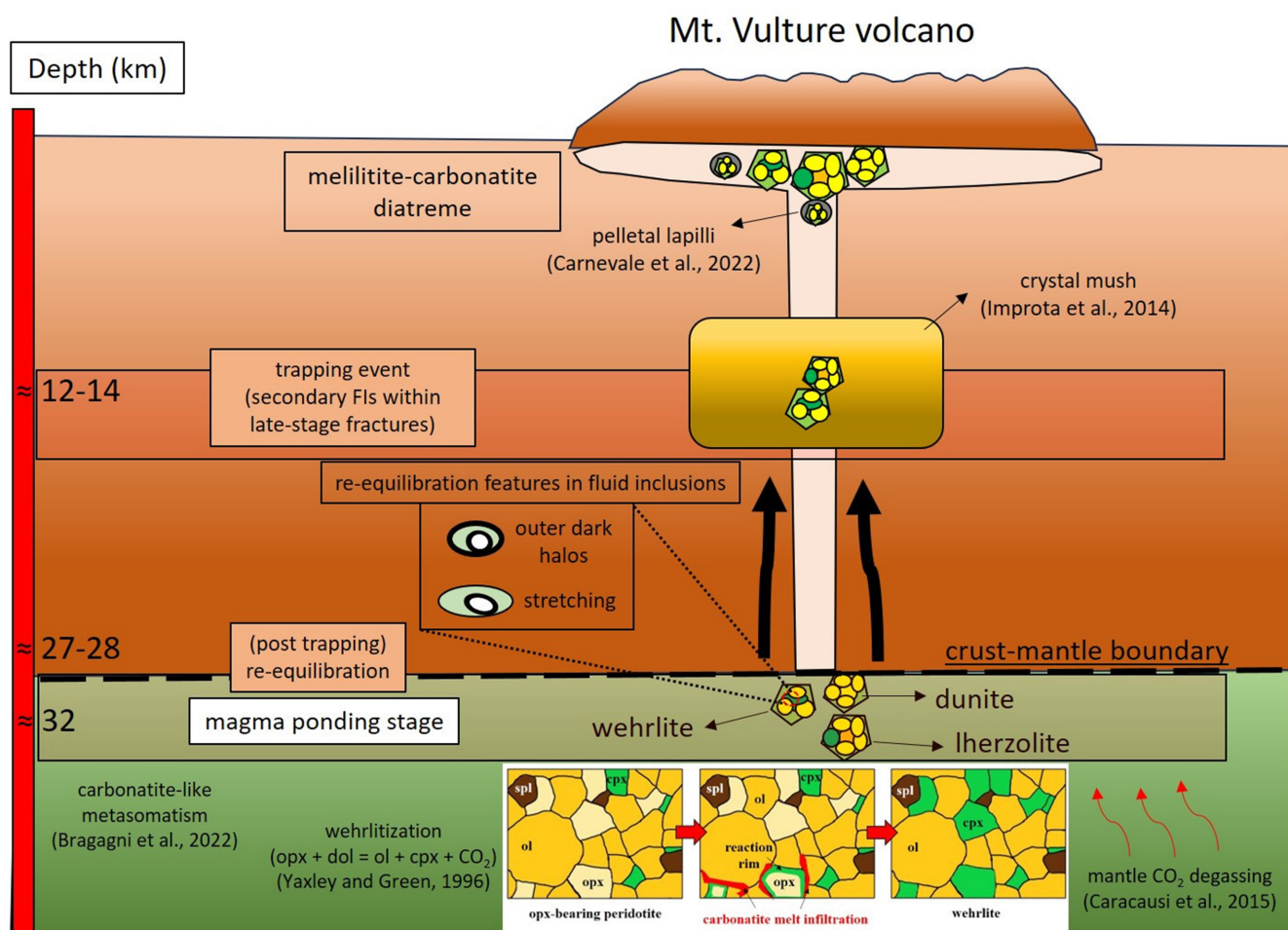

FIGURE 6 | Simplified cross section of the Mt. Vulture magma storage system with post-trapping re-equilibration event at the crust–mantle boundary and a trapping event at shallower depth. A graphical sketch of the wehrlitisation process is also shown, where the infiltration of the metasomatic agent into the orthopyroxene-bearing peridotite leads to the formation of the wehrlite as a metasomatic product.

Magma ascent might halt at chemical and physical disconti-
nuities (Menand 2011) as the crust–mantle boundary (e.g.,
Zanon and Frezzotti 2013; Zanon et al. 2020; Zanon, Silva,
and Goulart 2023), and this has consequences on FIs densities.
Indeed, the ΔP (Pentrapment—Pponding) generated might be
so high to induce re-equilibration of the density of FIs, and re-
equilibration of FIs is faster than chemical re-equilibration of
the silicate mineral system of the xenoliths (e.g., Andersen and
Neumann 2001). This makes micro-thermometry suitable to
highlight the whole magma path during its ascent. Thus, the
FIs trapped in lherzolite and wehrlite xenoliths could register
a magma ponding at the local crust–mantle boundary (32 km
depth, Kelemework et al. 2021), and likely reflect a temporary
residence of the magma at a shallow level (12–14 km depth)
(Figure 6), as corroborated by previous studies (Carnevale
et al. 2022; Improta, De Gori, and Chiarabba 2014).

Re-equilibration pressures were calculated at the inferred equi-
librium temperature of 1039°C (±36°C), obtained for the lherzo-
lite using the equation of Nimis and Grütter (2010). Equilibrium
temperatures calculated with different geothermometers

(Wells 1977; Bertrand and Mercier 1985; Brey and Köhler 1990)
are within the range of 1053°C–1142°C (Data S1). Figure 7 shows
the pressure–temperature ranges of Mt. Vulture xenoliths along
the carbonate-bearing lherzolite solidus in the CMAS-CO_2 sys-
tem (Hammouda and Keshav 2015). In mantle domains beneath
both Mt. Vulture and Hyblean area, carbonatite melts play an
important role in metasomatic processes (Marras, Stagno, et
al. 2023; Marras, Carnevale, et al. 2023), and mantle CO_2 out-
gassing is still ongoing at Mt. Vulture (Caracausi, Paternoster,
and Nuccio 2015). Particularly, wehrlitisation of mantle xeno-
liths as a consequence of carbonatite metasomatism has been
described at Mt. Vulture (Carnevale et al. 2022), and recent stud-
ies show how the decarbonation reactions can be used to esti-
mate the associated CO_2 loss (e.g., Aulbach et al. 2020). Thus,
the wehrlitisation process could potentially be used to assess the
role of carbonatite metasomatism and its effect on CO_2 degas-
sing in central-southern Italy.

4 | Conclusions

The main results of this study can be summarised as follows:

- The mineral assemblage and the mineral chemistry of Mt.
  Vulture xenoliths are consistent with an origin close to
  the crust–mantle boundary, and reflect a reaction with a
  carbonate-rich metasomatic agent;

- Geothermometers constrain the equilibrium temperatures
  between 1039°C (±36°C) and 1142°C (±15°C), while the
  minimum pressure corresponds to the lower stability limit
  of spinel peridotite at 8–9 kbar;

- The first FIs trapping event recorded a magma ponding at the
  local crust–mantle boundary (32 km depth) with post-trapping
  re-equilibration processes. The second trapping event oc-
  curred at a shallower depth (12–14 km) and corresponds to a
  former crystal mush (Improta, De Gori, and Chiarabba 2014).

Thus, this study further provides new details on the Mt.
Vulture plumbing system constraining its roots directly to the
crust–mantle boundary, and represents an example of how a
carbonate-rich metasomatic agent can influence the paragene-
sis and mineral chemistry of mantle xenoliths, according to pre-
vious data (Carnevale et al. 2022; Caracausi et al. 2009, 2013;
Jones et al. 2000).

For future research, as the correlation between CO_2 mantle de-
gassing and seismicity is recognised (e.g., Chiodini et al. 2004,
2020; Buttitta et al. 2023), detailed studies on mantle xenoliths
could be useful to assess the role of the wehrlitisation processes
in those areas with high mantle CO_2 degassing such as in
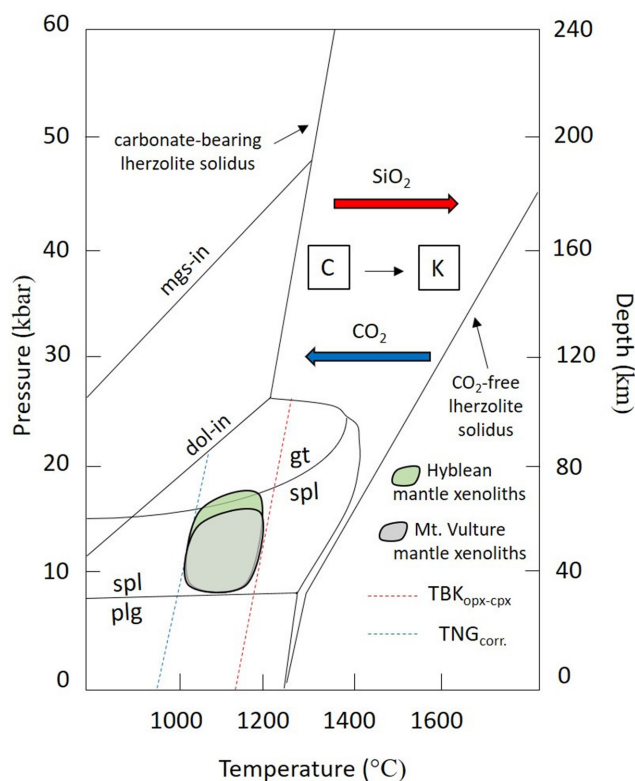central-southern Italy.

FIGURE 7 | Mt. Vulture mantle xenoliths in the pressure–temperature
region of interest along the carbonatite (C)-kimberlite (K) transition from
the carbonate-bearing to the CO_2-free lherzolite solidus in the system
CMAS-CO_2 (Hammouda and Keshav 2015). Lower and upper temperature-
lines from the applied geothermometers are shown ($TNG_{corr.}$ = Nimis and
Grütter 2010; $TBK_{opx–cpx}$ = Brey and Köhler 1990) with the plagioclase-out
boundary at 8–9 kbar and the spinel-garnet phase transition boundary
at 15–20 kbar (Borghini, Fumagalli, and Rampone 2010; Su, Zhang,
Asamoah, et al. 2010). Hyblean mantle xenoliths are also shown for
comparison (Correale et al. 2012; Perinelli et al. 2008; Scribano et al. 2009).
The slightly wider field of Hyblean xenoliths is due to the presence of some
kelyphitic garnet-websterites (Scribano 2009).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

All data are presented within the article and the supplementary material.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.