Wehrlites from continental mantle monitor the passage and degassing of carbonated melts

S. Aulbach1*, A.-B. Lin2,3, Y. Weiss4, G.M. Yaxley5

Abstract

Continental rifting has been linked to the thinning and destruction of cratonic lithosphere and to the release of enough CO2 to impact the global climate. This fundamental plate tectonic process facilitates the infiltration and mobilisation of small-volume carbonated melts, which may interact with mantle peridotite to form wehrlite through the reaction: enstatite + dolomite (melt) = forsterite + diopside + CO2 (vapour). Application to mantle xenolith suites from various rifts and basins shows that 2.9 to 10.2 kg CO2 are released per 100 kg of wehrlite formed. For the Eastern Rift (Africa), this results in estimated CO2 fluxes of 6.5 ± 4.1 Mt yr−1, similar to estimates of mantle contributions based on surficial CO2 surveys. Thus, wehrlite-bearing xenolith suites can be used to monitor present and past CO2 mobility through the continental lithosphere, ultimately with diffuse degassing to the atmosphere. They may also reveal the CO2 flux in lithospheric provinces where carbonated melts or continent-scale rifts are not observed at the surface.

Introduction

The conversion of tholeiite and harzburgite to an orthopyroxene-poor or -free, clinopyroxene-rich rock classified as wehrlite – a process hereafter referred to as wehrlitisation – requires interaction with silica-undersaturated (ultra)basic melts (e.g., Wallace and Green, 1988; Yaxley et al., 1998). Such melts encompass carbonatites, carbonated silicate melts (e.g., kimberlite) or CO2-bearing silicate melts (e.g., melilitites and nephelineites), which can form by near-solidus melting of peridotite (e.g., Gudfinnsson and Presnall, 2005). Given the strong incompatibility of CO2 in peridotite, low-volume melts are typically carbonated even if the source is not specifically C-rich, as long as the mantle source lies above the depth of redox melting (Hirschmann, 2010). In extensional continental settings, small-volume melts generated in the deep lithospheric or convecting mantle traverse ∼100 to 250 km of subcontinental lithospheric mantle (SCLM) and crust, with which they are initially out of chemical equilibrium, causing extensive reactions to occur (e.g., McKenzie, 1989). Wehrlitisation can result from such reactions and involves the liberation of CO2 vapour (e.g., Wallace and Green, 1988; Yaxley et al., 1998). This, in turn, contributes to diffuse continental degassing, especially in rift settings where lithospheric thinning has occurred (Brune et al., 2017; Foley and Fischer, 2017). It is noticeable that wehrlites are frequently reported in the literature for basalt-borne xenolith suites associated with rifts, faults and basins. These structures are pathways for CO2-rich fluids (Tamburello et al., 2018). However, a link between the release of CO2 to the exosphere during diffuse, non-volcanic degassing and a specific petrological mechanism remains unexplored, and the passage of carbon through the lithosphere is itself poorly documented. Wehrlite-bearing xenolith suites have been entrained in magmas of various ages. Using literature data, we show that wehrlites, as both products and monitors of the passage of CO2-bearing melts, can reveal the otherwise hidden CO2 flux through the shallow SCLM, and its eventual tectonic degassing both in currently and formerly active rifts.

 Depths, Hallmarks and Agents of Wehrlitisation

Published data show that basalt-borne xenolith suites from the spinel facies SCLM (∼40–100 km), mostly associated with off-cratonic lithosphere or cratonic lithosphere in various states of disruption and decratonisation, contain significant proportions of wehrlite (Table S-1). The data compilation encompasses garnet-free xenoliths from various on- and off-cratonic rift systems and basins (Supplementary Information). Indeed, the decarbonation reaction, which causes wehrlitisation, has been experimentally demonstrated to occur at relatively shallow depths corresponding to ∼1.5 to 2.0 GPa (Wallace and Green, 1988, and references therein). This is because the carbonated peridotite solidus features a “ledge” in pressure-temperature space so that on upward movement of carbonatite melts, they must freeze and react to form wehrlites (Wallace and Green, 1988).

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There is pervasive evidence for the interaction of SiO$_2$-undersaturated, CO$_2$-bearing melts also with the deep lithosphere, and carbonatitic high-density fluids are observed in diamonds (Fig. 1, Table S-2). Nevertheless, the proportion of wehrlitic garnet both in xenoliths and as inclusions in diamond is minute (≈1 %) compared to the lherzolite or harzburgite paragenesis (Fig. S-1). Thus, wehrlitisation is not an important process in the garnet- and diamond-stable part of the SCLM (>60 and ∼120 km, respectively, depending on geotherm), which typically records lower oxygen fugacities than the shallow SCLM (Supplementary Information). Interaction of carbonated melts with the deep lithosphere leads to graphite/diamond precipitation instead, through a process called redox freezing (Rohrbach and Schmidt, 2011).

Wehrlitisation leads to high clinopyroxene modes at the expense of orthopyroxene relative to other peridotites in the same xenolith suite. Transitional rock types affected by the same process, but at lower melt-rock ratios, also occur, resulting in

![Image of diagrams showing experimental melts and HDFs in diamonds](image-url)

**Figure 1** (a-d) Major element (wt. %) relationships and fractions of liquids ranging from carbonatite to carbonated silicate melt and silica-undersaturated, CO$_2$-(±H$_2$O) bearing silicate melt produced in experiments; high-density fluids (HDFs) in diamonds (Table S-2) shown for comparison. Concentrations of CO$_2$ in the starting mixture are given in parentheses. Differences in liquid composition relate to different starting mixtures, but similarly sloping trends are obtained for the various studies. Trend and separation of carbonatite from carbonated silicate melt in (c) are from Dasgupta et al. (2007). Melt fractions are not reported in all experiments.
clinopyroxene-rich lherzolites and orthopyroxene-poor harzburgites with clinopyroxene/orthopyroxene ratios >1 (e.g., Yaxley and Green, 1996; Lin et al., 2020). Depending on the style of melt interaction (porous flow vs. fractures), olivine-rich, pyroxene-poor to -free dunites may ultimately form (e.g., Shaw et al., 2018). The metasomatic agents inferred for the various wehrlite-bearing xenolith suites range from carbonate to carbonated silicate melts to CO₂-bearing silicate melts (Supplementary Information), which reflect increasing melt volumes and dilution with silicate components (e.g., Gudfinnsson and Presnall, 2005). Based on experimentally produced melts, there is a relationship between melt fraction and CO₂ (% Fig. 1a) and SiO₂ content (% Fig. 1b), producing an inverse correlation between CO₂ and SiO₂ (% Fig. 1c) and between SiO₂ and CaO (% Fig. 1d). The higher melt volumes involved in the generation of SiO₂-rich melts may therefore compensate for their lower CO₂ contents in terms of their ability to convert a given amount of orthopyroxene to clinopyroxene. The link between silica-undersaturated carbonated melts, wehrlites, and decarbonation at low pressure is strengthened by direct observations of CO₂-rich fluid inclusions, carbonates, carbonate-bearing glass veins and melt pockets in wehrlites, with entrapment pressures of 0.8 to 1.7 GPa (e.g., Yaxley et al., 1998; Loges et al., 2019). It is further supported by experimental studies which show that wehrlite forms in equilibrium with carbonated melts (Yaxley and Green, 1996; Gervasoni et al., 2017).

The effects of wehrlitisation on major element contents vary (Fig. 5-2), reflecting the spectrum of SiO₂-undersaturated carbonated melts. In some suites (e.g., Eifel, North Atlantic Craton in Greenland), clinopyroxene in wehrlite is dominated by elevated CaO/Al₂O₃ (Figs. 2a, S-2), in others by elevated FeO (Fig. 2b). The effects on the trace element budget are also heterogeneous (Fig. 5-3), depending not only on the identity of the metasomatic agent and type of melt-rock reaction, but also on lithosphere thickness, as the melt traverses and equilibrates with garnet-bearing peridotite in thick lithospheres (Supplementary Information).

## Modelling CO₂ Loss Via Wehrlitisation

The amount of CO₂ liberated from a volume of wehrlite-bearing peridotite due to interaction with CO₂-bearing, silica-undersaturated melt is estimated based on the decarbonation reaction

\[
\text{4MgSiO}_3 + \text{CaMg(CO}_3)_2 = 2\text{Mg}_2\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 + 2\text{CO}_2
\]

(Eq. 1)

(e.g., Yaxley and Green, 1996). Dolomite is assumed to be dissolved in the metasomatic melt, and wehrlites with high clinopyroxene modes formed from lherzolites and harzburgites with lower clinopyroxene modes (Wallace and Green, 1988; Yaxley et al., 1998). The proportion of a rock mass affected by wehrlitisation is estimated by counting Fe-rich “reaction” dunites and orthopyroxene-poor harzburgites and lherzolites with wehrlites (hereafter “wehrlite-group peridotites”), compared to “other peridotites” comprising harzburgites and lherzolites with clinopyroxene/orthopyroxene ratios <1. Reaction dunites, with low pyroxene modes, form during open-system processes (e.g., Shaw et al., 2018), whereas here an equilibrium process is modelled. Therefore, reaction dunites and olivine-rich harzburgites with high

Figure 2 (a) CaO/Al₂O₃ and (b) FeO content (wt. %) in clinopyroxene from garnet-free xenoliths as a function of modal abundance (%) of clinopyroxene (Table S-1), illustrating varied effects of wehrlitisation. The type of metasomatic agent is inferred on a suite-by-suite basis from the combined FeO and CaO/Al₂O₃ characteristics of clinopyroxene in wehrlite-group peridotites (Fig. 5-2). As an example, for the Tan Lu Fault Belt, wehrlites with clinopyroxene having CaO/Al₂O₃ >6 and FeO <3.5 wt. % are assigned to the carbonatite-metasomatised suite, those with CaO/Al₂O₃ ≤6 and FeO ≥3.5 wt. % to the silicate melt-metasomatised suite, and the remainder to the carbonated silicate melt-metasomatised suite. Filled symbols denote wehrlite-group peridotites, open symbols denote other peridotites. Orthopyroxene-poor, olivine-rich harzburgites and reaction dunites with low clinopyroxene modes likely interacted with silica-undersaturated melt during open-system processes (Shaw et al., 2018).
clinopyroxene/orthopyroxene ratios are not considered in the calculation of the median clinopyroxene abundance or composition in the wehrlite-group peridotites (Table S-3).

The calculations assume closed-system reactions, resulting in minimum estimates for the volume of silica-undersaturated melt passing through the shallow lithosphere (Yaxley et al., 1998). Because Equation 1 is based on diopside, whereas natural clinopyroxenes are not pure diopside, the difference in median clinopyroxene modes between wehrlite-group and other peridotites is weighted by the median diopside component in clinopyroxene (ΔDi). The mass of enstatite required to produce ΔDi is calculated based on the decarbonation reaction, with two moles of CO₂ liberated per mole of diopside formed (Eq. 1). The mass of CO₂ that passed through the shallow lithosphere is estimated by weighting the mass of CO₂ liberated during wehrlitisation by the proportion of wehrlite-group peridotites in each sample suite (Table S-3). The variation of the wehrlite-group proportion in multiple xenolith suites per area is taken as the uncertainty.

The continental lithospheric area affected by wehrlitisation is estimated using area estimates from the literature or information on the total length of associated rifts, such as the Eastern Rift in the East African Rift and the European Cenozoic Rift System (Supplementary Information). Assuming a density of 3350 kg m⁻³ and a conservative 10 km interval of wehrlitisation, the total mass of liberated CO₂ is estimated. Finally, disequilibrium textures indicate that wehrlitisation occurred close in time to entrainment in the host magma, and that no major fluid- or melt-rock interaction has occurred since. Thus, wehrlitisation and CO₂ degassing are taken to be related to periods of active extension, which facilitates the formation and mobility of small-volume melts (Supplementary Information).

Results and Discussion

In the xenolith suites considered, 6–15% clinopyroxene was added due to wehrlitisation (Table S-3), corresponding to ΔDi of 3.5 to 12% and requiring conversion of 6.4 to 22 kg of enstatite (Table 1). Weighted by the proportion of wehrlite-group peridotites in the spinel facies rock column, this amounts to 0.2 ± 0.1 kg (Hoggar Swell) to 2.4 ± 1.5 kg (Eastern Rift) CO₂ per 100 kg of wehrlitised peridotite (Table 1). The continental area affected by wehrlitisation ranges from 110 × 10⁶ km² (European Cenozoic Rift System) to 4500 × 10⁶ km² (Tan Lu Fault Belt). Taking the proportion (and its variability gauged as 1σ) of wehrlite-group peridotites entrained with basalts in each area as representative, this yields total masses of released CO₂ from 24 (±15) × 10⁶ Gt to 2100 (±1700) × 10⁶ Gt. For estimated timespans of activity from 10 to 40 Myr, this amounts to CO₂ fluxes of 1.4 ± 0.1 Mt yr⁻¹ (Pannonian Basin) to 70 ± 58 Mt yr⁻¹ (Tan Lu Fault Belt (Table 1). These estimates indicate significant mantle contributions to the total tectonic and volcanic CO₂ flux at the time of active rifting. For comparison, for conservative flux densities, 40 Mt CO₂ yr⁻¹ is estimated for combined present-day active rifts (Brune et al., 2017). Further, amplitudes >80 Mt CO₂ yr⁻¹ are estimated for the “Mesozoic CO₂ high”, which was associated with a total rift length of 50,000 km (Brune et al., 2017). This suggests that the Tan Lu Fault Belt, which was most active in the Early Cretaceous, was a major contributor to the contemporaneous greenhouse climate. For the Eastern Rift, we obtain ~6.5 ± 4.1 Mt CO₂ yr⁻¹ compared to 6–18 Mt CO₂ yr⁻¹ attributed to magmatic intrusions into the crust based on surficial CO₂ flux measurements (Hunt et al., 2017). The similar order of magnitude for estimated mantle contributions to CO₂ degassing in the Eastern Rift suggests that wehrlites are well suited to monitor the present and past passage of CO₂ through the shallow lithosphere, which ultimately degassed to the atmosphere. All CO₂ mass estimates are minima because open-system processes (e.g., dunitisation) cannot be quantified using our method. Further, a proportion of clinopyroxene in hederolites, which were attributed to “other peridotites”, may have resulted from wehrlitisation instead. It is also possible that the affected lithospheric depth interval is >10 km (e.g., in the North Atlantic Craton in Greenland it is 20 km; Supplementary Information). Moreover, the width of the affected lithosphere adjacent to rifts may be broader than assumed here.

Modern degassing of mantle-derived CO₂-rich fluids and gases is correlated to active fault systems and extensional tectonic regimes (Brune et al., 2017; Tamburello et al., 2018). A link

![Table 1](https://example.com/table1.png)

<table>
<thead>
<tr>
<th>Locality</th>
<th>Agenta</th>
<th>Area/durationb</th>
<th>ΔDi²</th>
<th>Enstatitec</th>
<th>Dolomitec</th>
<th>Perid CO₂ (1σ)</th>
<th>CO₂ flux (1σ)g</th>
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<tr>
<td>Unit</td>
<td>1000 km²/Myr</td>
<td>%</td>
<td>kg</td>
<td>kg</td>
<td>kg</td>
<td>Mt yr⁻¹</td>
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<td>20</td>
<td>9.3</td>
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<td>6.5 (4.1)</td>
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<td>7.1</td>
<td>13</td>
<td>6.1</td>
<td>0.6 (0.4)</td>
<td>4.1 (2.4)</td>
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<tr>
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<td>7.1</td>
<td>0.3 (0.3)</td>
<td>16 (13)</td>
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<tr>
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<td>22</td>
<td>10.2</td>
<td>0.3 (0.2)</td>
<td>13 (11)</td>
<td></td>
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<td>18</td>
<td>8.0</td>
<td>0.8 (0.7)</td>
<td>41 (34)</td>
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</tr>
<tr>
<td>TLFB combined</td>
<td>4500/30</td>
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<td>14.2</td>
<td>70 (58)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Middle Atlas</td>
<td>400/40</td>
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<td>20</td>
<td>9.4</td>
<td>1.5 (0.4)</td>
<td>5.1 (1.2)</td>
<td></td>
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<tr>
<td>Hhoggar Swell</td>
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<td>6.4</td>
<td>2.9</td>
<td>0.2 (0.1)</td>
<td>1.5 (0.8)</td>
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<tr>
<td>WEVF</td>
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<td>19</td>
<td>8.8</td>
<td>1.9 (1.2)</td>
<td>1.7 (1.1)</td>
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</tr>
<tr>
<td>Pannonian basin</td>
<td>133/20</td>
<td>8.7</td>
<td>16</td>
<td>7.4</td>
<td>0.6 (0.1)</td>
<td>1.4 (0.1)</td>
<td></td>
</tr>
</tbody>
</table>

TLFB Tan Lu Fault Belt, WEVF West Eifel Volcanic Field

aType of metasomatic agent involved in wehrlitisation: 1 carbonatite (40–48 wt. % CO₂), 2 carbonated silicate melt (10–30 wt. % CO₂), 3 silica-undersaturated silicate melt (1–5 wt. % CO₂)

bEstimated area affected by wehrlitisation and duration of metasomatism/degassing

cDifference between median clinopyroxene abundances in wehrlite-group (reaction dunites not counted) and other peridotite xenoliths, weighted by median diopside component (Table S-3)

dMass of enstatite (per 100 kg of peridotite converted to wehrlite) required for conversion to mass of diopside corresponding to ΔDi

eMass of dolomite in the liquid (per 100 kg of peridotite converted to wehrlite) corresponding to 1/4 of the moles of enstatite as per the decarbonation reaction: 4 MgSiO₃ + CaMgSi₂O₆ = 2 MgSO₄ + CaMgSi₃O₇ + 2 CO₂

fMass of CO₂ liberated from 100 kg wehrlite-bearing peridotite using proportion of wehrlite-group peridotites and its variability in Table S-3

gMegatonnes CO₂ degassed per year for the estimated area and duration (comment b)
between wehrlitisation and extensional settings is also evident in all cases studied here. Tamburello et al. (2018) find that current degassing is more prevalent in central Western Europe and the western United States than in cratonic areas. This probably reflects that extension leads to lithosphere thinning, as occurred in the Wyoming Craton and in eastern North China Craton, which hosts part of the Tan Lu Fault Belt. In these settings, oxidised melts collect carbon previously stored in the SCLM (Foley and Fischer, 2017), followed by decarbonation as the melts encounter the solidus ledge of carbonated peridote (Wallace and Green, 1988). In this case, not only the lithosphere associated with rifts and faults that are recognisable at the surface should be regarded as potential sites of wehrlitisation and CO$_2$ release, but also lithosphere affected by unsuccessful rifting and thinning, such as the North Atlantic Craton in Greenland, as well as cratonic regions recognised as partially or wholly decribated (Aulbach, 2019).

Moreover, deep lithosphere loss causes lithospheric heating and decompression, as evidenced by microstructural and compositional evidence for garnet breakdown (Supplementary Information). This might not only exude diamondiferous lithosphere to the shallower mantle where it is oxidised, but also causes crustal metamorphism, which is an important contributor to atmospheric CO$_2$ (Kerrick, 2001).

**Conclusions and Outlook**

Wehrlites typically constitute ~20% of mantle xenolith suites in extensional settings, where continental lithospheres are thinned, facilitating the generation and percolation of small-volume carbonated melts along rifts, faults or in basins. The decarbonation reaction can be applied to wehrlites to estimate the minimum amount of CO$_2$ that passed through the shallow (~60–100 km) lithosphere. Based on wehrlite-bearing xenolith suites, we calculate CO$_2$ liberation of 24 ± 15 thousand to 2.1 ± 1.7 million Gt CO$_2$, with estimated CO$_2$ fluxes of 1.4 ± 0.1 Mt yr$^{-1}$ to 70 ± 58 Mt yr$^{-1}$. Ultimate diffuse degassing of this CO$_2$ is expected to significantly affect climate. Importantly, wehrlitisation may occur wherever continental lithosphere is reactivated, also in lithospheric provinces where prominent rifts are absent and carbonated melts have not been emplaced at the surface. One such example is the basaltic volcanic province of southeastern Australia, where not only the link between wehrlitisation and carbonate melts have not been established at the surface. One such example is the basaltic volcanic province of southeastern Australia, where not only the link between wehrlitisation and carbonate melts have not been established at the surface. One such example is the basaltic volcanic province of southeastern Australia, where not only the link between wehrlitisation and carbonate melts have not been established at the surface. One such example is the basaltic volcanic province of southeastern Australia, where not only the link between wehrlitisation and carbonate melts have not been established at the surface. One such example is the basaltic volcanic province of southeastern Australia, where not only the link between wehrlitisation and carbonate melts have not been established at the surface.

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**Additional Information**

Supplementary Information accompanies this letter at [http://www.geochemicalperspectivesletters.org/article2031](http://www.geochemicalperspectivesletters.org/article2031). © 2020 The Authors. This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at [http://www.geochemicalperspectivesletters.org/copyright-and-permissions](http://www.geochemicalperspectivesletters.org/copyright-and-permissions).

**References**


