

The Earth's interior redox state investigated through mantle xenoliths and mineral inclusions in diamonds: implications for large-scale magmatic events

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INTRODUCTION

The Earth's interior oxygenation (i.e., its redox state, f_{O_2}) is an important topic in mantle petrology and geochemistry due to its primary role in many processes occurring at depth, such as diamond formation, metasomatism, and partial (redox) melting. Variations in the oxygenation of the Earth's interior through time have been proposed to play a crucial role in the genesis and composition of mantle-derived primitive melts (Stagno & Fei, 2020), with consequent mobilization of C-O-H-S volatile elements in the form of CO_2 , H_2O , and SO_2 fluids. This, in turn, has affected the deep volatile cycle and chemistry of gases released during volcanic activity, which had a significant impact on the development of the terrestrial atmosphere and, importantly, the growth of life (Kasting & Catling, 2003; Scaillet & Gaillard, 2011). In addition, ascending oxidized fluids can also carry trace elements (e.g., Sc, V, Hg) with implications for their impact on the surface environments over time. The temporal evolution of the redox state is recorded by mantle-derived rocks through redox-sensitive minerals like spinel and garnet in xenoliths (peridotites and eclogites) or trapped in diamonds (Frost & McCammon, 2008). These minerals buffer the local f_{O_2} through the oxidation/reduction of Fe they host in the crystal structure. Terrestrial atmosphere and mantle seem to have experienced a simultaneous increase of O_2 through time (Stagno & Fei, 2020), linked by the onset of several geodynamical processes. For instance, the Great Oxidation Event (GOE) (2.5–2.0 Ga), and the Neoproterozoic Oxygenation Event (NOE) (1.0–0.8 Ga) coincided with the plate tectonics initiation, the continents formation and a large production of magmas (from komatiites to arc magmas and kimberlite blooms; Stagno & Fei, 2020 and reference therein). Oxidized CO_2 -rich melts that likely formed when an influx of oxygen from recycled material or upwelling of oxidized primordial material from the lower mantle interact with graphite or diamond (Frost et al., 2004; Wu et al., 2022) erupted between 250 and 50 Ma ago. During this period, large igneous provinces (LIPs) emplaced.

Large Igneous Provinces (LIPs)

The LIPs are characterized by terrestrial or submarine volcanism comprising enormous volumes of emitted lavas that emplaced within short time accompanied by wide-scale outgassing of CO_2 and SO_2 (Ernst & Bell, 2010; Black & Gibson, 2019) with a dramatic impact on the climate and environment. In fact, a temporal linkage exists between LIP events and the occurrence of the "big five" mass extinction and oceanic anoxic events (OAEs) of the Phanerozoic. Perturbations of C and S cycles triggered by large-scale volcanic eruptions (Jones et al., 2016) can be recorded in the coeval sediments worldwide distributed (Jenkyns, 2010) along with anomalous concentrations of mantle-derived trace elements like Hg (Yin et al., 2021), largely used as a LIP geochemical proxy in the sedimentary record (Grasby et al., 2019).

Aims of the thesis

The general objective of this thesis was to provide a link between the redox evolution of the Earth's mantle and the onset of large magmatic events. To have a comprehensive understanding of how Earth's interior f_{O_2} can affect the speciation and extraction of volatiles, I investigated the redox state of natural mantle rocks like spinel-peridotites (Marras et al., 2023a, b), Archean eclogites (Marras et al., 2024) and E-type diamonds, representative of different geological setting like continental lithospheric mantle and ancient subducted oceanic crust. The results allowed modeling the speciation of volatiles like CO_2 and SO_2 with respect to C and S and posing it as the cause of LIPs events. At this aim, the possible volcanic contribution was searched on sedimentary boundaries such as the Bonarelli level (~94 Ma), the diagenesis of which is synchronous to the large-scale volcanic activity of Caribbean, High Arctic and Madagascar LIPs.

RESULTS AND DISCUSSIONS

Hyblean mantle xenoliths (Sicily): a record of extensive oxidizing events involving S and C-species

Direct evidence of volatile mobilization at depth comes from fluid inclusions in silicate minerals like olivine, where the retained noble gases (He, Ar, Ne) can give information about their source. In this work, a suite of eight mantle spinel-peridotite xenoliths from the Valle Guffari (Hyblean Plateau, Sicily) was investigated to better understand the Hyblean mantle metasomatism and its redox evolution (Marras et al., 2023b).

Chemical and textural analysis were conducted by EMPA and SEM; $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in spinel was measured by both in situ synchrotron (beamline ID8, ESRF, Grenoble) and conventional ^{57}Fe Mössbauer spectroscopy (Sapienza University, Rome). Inclusions in olivine were studied by micro-Raman (Milano-Bicocca University, Milano), whereas OH bands were mapped by regular grids across olivine crystals (including inclusion trail regions) through micro-FTIR (beamline SISSI, Elettra, Trieste). Finally, noble gases isotopes (He, Ar, Ne) were analyzed from unaltered olivine grains by mass spectrometry (INGV, Palermo).

The calculated equilibration pressure (P) and temperature (T) of 0.9-1.2 GPa and 950-1050°C, respectively, along with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.27 and 0.31 measured in spinel, make Hyblean samples more oxidized than other peridotitic suites worldwide distributed from both cratonic and abyssal settings, with $\log f_{\text{O}_2}$ (with respect to

fayalite-magnetite-quartz buffer; FMQ) ranging between 0.28 and 1.27 (Fig. 1). Based on the $\log f_{\text{O}_2}$ vs $\text{Cr}^{\#}_{\text{spinel}}$ relationship proposed by Ballhaus et al. (1991), the samples fall in the lightly metasomatized xenoliths field, similarly to the metasomatized Vitim off-craton peridotites. At these redox conditions, coexisting C-O-H fluids (Fig. 1) consist of CO_2 and H_2O . The occurrence of microveins of silicate glass are taken as evidence of interaction with metasomatic fluids/melts. In addition, the fluid inclusions consist of Mg-Ca carbonates \pm sulfide \pm sulfur \pm CO_2 for the most reduced sample and Mg-Ca carbonates \pm Na-rich sulfates \pm CO_2 for the most oxidized sample (Fig. 1). This suggests that Na-bearing carbonatitic to carbonate-silicate melts are possible metasomatic agents. The chemical heterogeneity from the core to the rim observed in spinels (in particular, in terms of Cr_2O_3 vs Al_2O_3) and the high $\log f_{\text{O}_2}$ recorded with respect to the ambient lithospheric mantle (-2 to 0 ΔFMQ ; Fig. 1) are further evidence of a significant oxidation event that could have happened all at once or at several steps, controlled by the melt/rock ratio. The noble gases, along with the oxidized redox conditions, the geochemical evidence of interaction with Na- CO_2 -rich melts, the chemical composition of the analyzed inclusions (C-S-Na-rich), and the previous isotopic evidence of a sedimentary/organic C component in Hyblean peridotitic mantle (Correale et al., 2015), suggest the contribution of a slab-derived component. In conclusion, the lithospheric mantle beneath the Hyblean Plateau can be taken as an example of the role that metasomatic subduction-related CO_2 -rich silicate-bearing melts play in the oxidation of the lithospheric mantle and the mobilization of volatile elements.

First Fe^{3+} determination in spinel inclusions of olivine from a Mt. Vulture wehrlite

To date, the knowledge of redox conditions of spinel- and garnet-bearing peridotites is limited to Iherzolite and harzburgite, where the application of the available oxy-thermobarometers requires the coexistence of spinel (or garnet), olivine and orthopyroxene. However, there are no available models to determine the f_{O_2} of wehrlites, orthopyroxene-poor or clinopyroxene-rich mantle rocks formed due to the interaction of a former Iherzolite/harzburgite with metasomatic CO_2 -bearing silicate melts (Aulbach et al., 2020). This study (Marras et al., 2023a) was conceptualized with the goal of retrieving the f_{O_2} of the mantle beneath Mt. Vulture volcano (Italy) through the study of a wehrlitic lapillus emitted during the last eruption (~140 kyr ago), containing olivines with multiple tiny (< 40 μm) inclusions of spinel (Fig. 2a).

Here, for the first time, in-situ synchrotron Mössbauer spectroscopy (ESRF, Grenoble; Fig. 2b) was used to determine the Fe oxidation state of spinel inclusions in olivine (Fig. 2a), exploiting the high spatial resolution of the

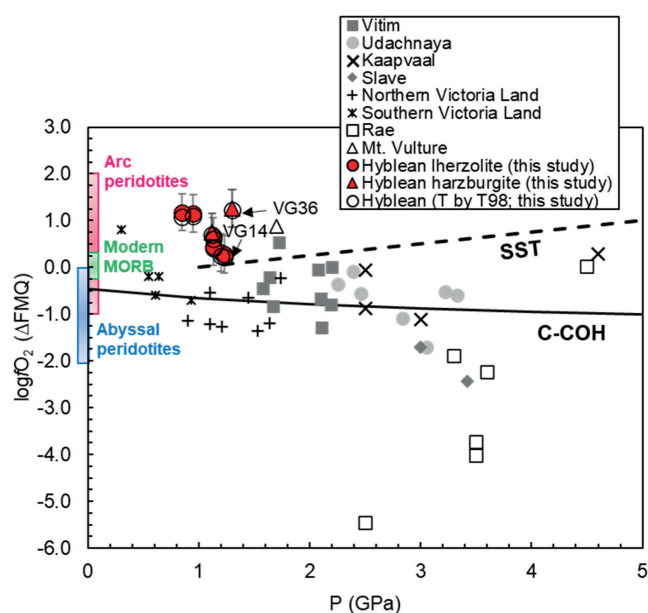


Figure 1 $\log f_{\text{O}_2}$ (ΔFMQ) plotted as a function of equilibrium P for Hyblean peridotites and literature samples (see references in Marras et al. 2023b). Reference values for MORB, abyssal and arc peridotites (Frost and McCammon 2008) are shown. The buffer C-COH (graphite/C-O-H fluids equilibrium; Ulmer and Luth 1991) is reported along with the sulfide-to-sulfate transition line (SST) from Chowdhury and Dasgupta (2020). Samples VG14 and VG36, the most reduced and the most oxidized samples, respectively, are indicated by arrows.

technique (area of $15 \times 6 \mu\text{m}^2$). Moreover, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ measurements of both spinel and host olivine were combined with chemical and spectroscopic analysis (micro-FTIR).

The determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for olivine range between 0.03–0.05 and for the entrapped spinels between 0.40–0.45. These ratios are higher than those reported in the literature for mantle spinel-bearing harzburgites/lherzolites. The calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ partitioning coefficient between olivine and spinel ranges between 0.06 and 0.13. The mantle origin of the trapped spinel inclusions was constrained by the absence of core-to-rim chemical variation, the absence of $\text{Mg}\#_{\text{spinel}}$ versus $\text{Fo}_{\text{olivine}}$ positive correlation related to liquidus minerals, and the consistency between the composition of the spinel inclusions and host olivine and those reported for orthopyroxene-bearing wehrlitic xenoliths from the same area.

Given the above evidence, it is proposed that the calculated f_{O_2} (0.8–1.0 ΔFMQ ; Fig. 1) likely records the interaction between a pristine spinel-bearing lherzolite and a CO_2 -rich metasomatic agent before spinels were trapped in olivines at mantle depths. Importantly, this investigation opens to the possibility of retrieving information about the f_{O_2} of mantle peridotites, even without spinel crystals in the rock matrix, by analyzing the $\text{Fe}^{3+}/\Sigma\text{Fe}$ and chemical composition of spinel inclusions in olivine, which allows reconstructions of the volatile speciation in the mantle.

Mineral inclusions in E-type diamonds from Siberian craton: witnesses of redox heterogeneities and eclogite as robust redox buffers

Subduction is the main carrier of oxidized material into the deep mantle and has a key role in changing the mantle redox state and controlling the volatiles (re)cycle (C, O, H, S, N, B) through time (Frost & McCammon, 2008; Stagno et al., 2019). Most kimberlite-borne mantle eclogites have been proven to be the product of metamorphic transformations that the oceanic crust (i.e., the protolith) undergoes during subduction into the subcontinental lithospheric mantle (Eskola, 1914; Ringwood, 1975). The study of eclogite xenoliths and more rare samples

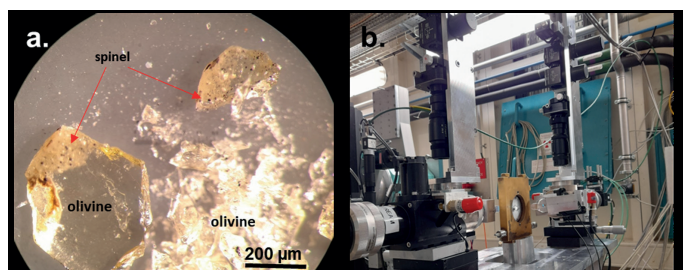


Figure 2 a) Mt. Vulture olivine grains with tiny ($< 40 \mu\text{m}$) spinel inclusions (black dots). b) Internal view of beamline ID18 of ESRF where in-situ synchrotron Mössbauer spectroscopy analyses were performed.

represented by mineral inclusions in eclogitic diamonds (E-type) allows reconstructing the ancient protolith nature and its redox evolution. Most eclogite xenoliths fall in the P - T field where diamond is thermodynamically stable and likely equilibrated with C-O-H fluids/melts. However, the primary redox state of these rocks could be masked by the interaction with circulating (metasomatic) oxidized fluids, which likely acted themselves as growth media for diamonds to form (Luth & Stachel, 2014). In this study, we investigated a suite of diamonds with E-type inclusions from the Siberian craton (Russia) to track the chemical and redox evolution of the subducted oceanic protolith, providing a model of diamond formations and the effect of metasomatism on the redox conditions of eclogites through time.

The coexisting garnet and clinopyroxene inclusions (Fig. 3), both exposed (after polishing) and trapped, have sizes ranging from 20 to $100 \mu\text{m}$. The garnet and clinopyroxene hand-picked from the host eclogite of one diamond were also analyzed. The major elements and vanadium were measured by electron microprobe analyses on the exposed inclusions, while the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of both exposed and encapsulated inclusions was measured by in-situ Synchrotron Mössbauer spectroscopy (ESRF, Grenoble; Fig. 2b). Finally, the micro-Raman spectroscopy was employed to investigate additional tiny inclusions still trapped.

The compositions of garnet and clinopyroxene inclusions overlap with those for Udachnaya eclogitic xenoliths (e.g., Mikhailenko et al., 2020). Equilibrium T - P are 870 – $1170 (\pm 60)^\circ\text{C}$ and 4.3 – $6.9 (\pm 0.4)$ GPa and are supported by Raman elastic geobarometry applied on a coesite inclusion observed in one of the studied diamonds. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet inclusions (0.02 to 0.07) and in clinopyroxene (0.11 to 0.20) is consistent with that measured on the eclogite host rock.

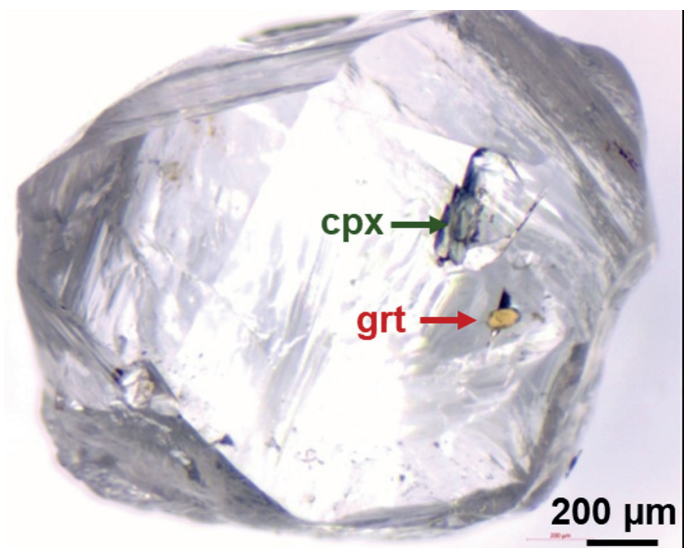


Figure 3 Eclogitic diamond from Siberian craton (this study) with coexisting clinopyroxene and garnet inclusions.

The bulk rock composition was reconstructed to constrain the nature of the subducted protolith for the eclogitic inclusions. Oxides like TiO_2 , Al_2O_3 , CaO and MgO (in wt.%) are typical of protoliths like peridotite-derived melts. The f_{O_2} of the convecting mantle source (i.e., f_{O_2} of the protolith) can be retrieved through the V vs MgO relationship, according to a recent study by Aulbach and Stachel (2022). In fact, we observed that V concentration acts as a robust proxy to retrieve the redox conditions of the protolith since it is not shifted by metasomatic processes occurring during eclogite residence in the cratonic mantle. The f_{O_2} of the eclogitic inclusions (i.e., the metamorphic minerals), calculated by Fe^{3+} -based oxy-thermobarometry, suggests that diamond formed from chemically diverse CO_2 - H_2O -bearing fluid/melt (with the contribution of CH_4). In conclusion, our data indicate that eclogites can buffer the f_{O_2} over aeons with a minor effect of metasomatism preserving, therefore, the conditions for diamond formation.

Evidence of a highly oxidized Archean subducted slab from V. Grib eclogites (NW Russia)

The f_{O_2} of eclogitic rocks is linked to the redox evolution of the oceanic protolith during subduction and residence in the lithospheric mantle. This allows modeling the speciation of volatile elements and the stability of diamond or graphite versus carbonate. Previous studies have shown that the f_{O_2} of natural eclogites varies significantly, ranging from -6 to -0.1 log units (ΔFMQ), related to the low Fe^{3+} content of garnets in eclogites, generally lower than 10%. Moreover, reconstructions of magmatic f_{O_2} (i.e., protolith redox conditions) from geochemical analyses of ancient unaltered eclogites and E-type diamonds (see above paragraph) suggest that Archean

mantle source conditions were reducing (Aulbach & Stagno, 2016).

Marras et al. (2024) investigated C-free mantle eclogites dated at 2.84 Ga from the V. Grib kimberlite pipe (Arkhangelsk Diamondiferous Province), one of the main diamond extraction sites in Russia. The Fe oxidation state of coexisting garnet and clinopyroxene was investigated by conventional Mössbauer spectroscopy (Bayerisches Geoinstitut, Bayreuth).

The equilibrium P and T for the V. Grib eclogites were found to be mostly within the diamond stability field, ranging from 3.0 to 5.2 GPa and 720 to 1050°C, respectively. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ of garnet from five samples (between 0.03 and 0.20) exceeded the typical range reported for eclogitic garnets and correlated positively with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of clinopyroxene (0.18 and 0.38; Fig. 4). Consistently with what proposed for the Siberian eclogitic diamonds (see above paragraph), a major role of metasomatism for the oxidized conditions recorded by the V. Grib eclogites is excluded. Instead, we propose that the high f_{O_2} and bulk-rock $\text{Fe}^{3+}/\Sigma\text{Fe}$ were inherited by an oxidized magmatic protolith that implies the presence of an oxidized mantle source. In contrast to the reduced redox conditions recorded by Archean eclogitic xenoliths distributed worldwide, the V. Grib eclogites are the most oxidized eclogite rocks, and this might have contributed to the mobilization of C in the form of CO_2 , explaining the unusual C-free feature of these rocks.

This scenario is similar to the oxidized peridotite source proposed to explain the origin of picrites from the Emeishan LIP (Wu et al., 2022), which had significant implications for the release of large amounts of CO_2 to the atmosphere and, in turn, with the end-Capitanian mass extinction (~262 Ma ago).

A mineralogical, geochemical and isotopic study of the Bonarelli level (Gubbio, Italy)

Sedimentary rocks record paleo-environmental events that might have occurred at local and global scales. Among these, large volcanic eruptions throughout the Earth's history have driven sudden changes in the chemical composition of the terrestrial atmosphere and caused mass extinction. LIPs are known to be coeval to the Phanerozoic largest mass extinctions and the OAEs, characterized by strong perturbations of carbon and sulfur cycles. The identification of these global-scale events in the sedimentary record is made possible by using key geochemical signatures such as high organic matter content (up to 30%) and positive excursions in the $\delta^{13}\text{C}$ curve (Jenkyns, 2010). The Bonarelli level, a ~0.9-m thick layer made up of organic-rich shales, cropping out at the Valle della Contessa section in Gubbio (Italy; Fig. 5) within the pelagic limestones of the Scaglia Bianca For-

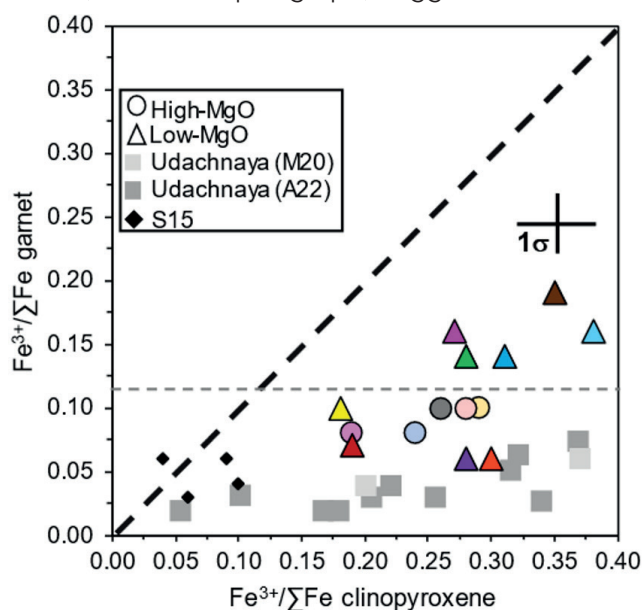


Figure 4 The $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet and clinopyroxene from this study compared with values for natural eclogites from Udachnaya and synthetic samples (see Marras et al., 2024 for the references). The dashed grey line is the maximum $\text{Fe}^{3+}/\Sigma\text{Fe}$ reported in the literature for eclogitic garnets.

mation, is considered a stratigraphic marker of the OAE2 (Cenomanian-Turonian, ~94 Ma). This event was likely triggered by submarine volcanism of the High Arctic and Caribbean LIPs or subaerial volcanism of Madagascar LIP (Grasby et al., 2019 and references therein). Despite the extensive lithological, biostratigraphic, and carbon isotopic studies conducted on the selected section, a comprehensive investigation of the LIP signature in this locality is still needed and could benefit from the use of Hg concentration as a geochemical marker, combined with Hg, C, S and Sr isotopes.

In this study, X-ray diffraction, petrographic and geochemical (Total Organic Carbon, Hg concentration, trace elements, Hg, S and Sr isotopes) analyses on various samples collected from the Bonarelli level along with rocks samples from the Scaglia Bianca Formation were performed to explore the link between OAEs and LIP volcanism.

The results show that Bonarelli level mineral fraction is mainly composed of quartz, phyllosilicates, sulfates (barite and jarosite) associated with sulfides. Sharp anomalies of Hg were observed and correlated positively with chalcophile elements such as Cu, Ni and Fe and with the amount of sulfate/sulfide. Due to the affinity of Hg with the organic matter (Grasby et al., 2019), the Hg concentration was normalized to TOC (Hg/TOC). However, the collected samples show that the Hg signal is still preserved. The results from this study indicate that the Valle della Contessa section records an extra input of Hg released into the environment around 94 Ma ago. Integrating these data with Hg, S and Sr isotopic analyses, we observe a (deep) magmatic contribution for Hg that correlates with a slight positive shift of the sedimentary $\delta^{34}\text{S}$ isotopic signature toward mantle values, plus a continental origin for Sr related to huge weathering. In conclusion, we interpret our results as evidence of the LIP emplacement and large-scale CO_2 , SO_2 and Hg release.

FINAL REMARKS AND FUTURE PERSPECTIVES

The results of this multidisciplinary investigation have revealed novel information about the mechanism of mantle oxidation, the heterogeneous redox conditions of the upper mantle over time and space, as well as the crucial role of redox-driven processes in mobilizing volatiles, which have implications for sedimentary and biological processes on the Earth's surface. Furthermore, this study has raised new questions, some of which have been preliminarily addressed. Given the evidence of a mantle origin for the Hg released in the frame of LIPs, preliminary (and in progress) in situ synchrotron high-pressure and -temperature stability and liquid structure experiments were conducted on the sulfide Hg end-member, i.e., cinnabar (HgS), to understand the mechanism of Hg

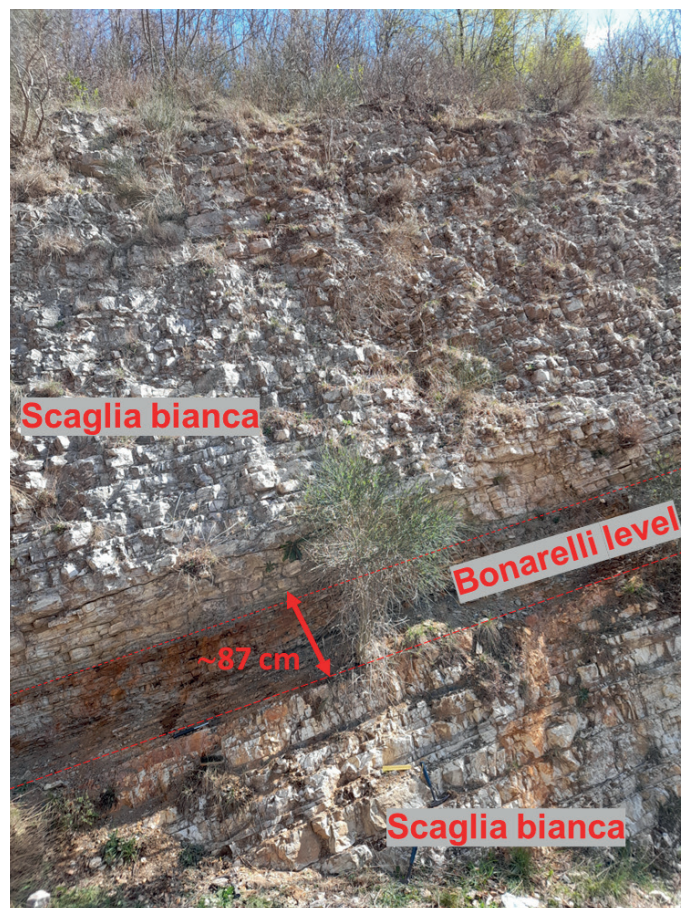


Figure 5 Stratigraphic section object of this study located in Valle della Contessa (Gubbio, Italy), where the black-shale Bonarelli level (dark; ~87 cm thick) outcrops with the micritic limestone Scaglia Bianca (grey).

mobilization from the mantle source. These experiments laid the groundwork for future solubility experiments of Hg in oxidized LIP-related melts, which are crucial for modelling the deep Hg cycle from the mantle to the atmosphere during large magmatic events.

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