Characterization of H_2 and hydrocarbons trapped in exhumed metamorphic rocks: origin and fluxes of energy sources in subduction zones

The petrology of hidden deep energy sources

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INTRODUCTION

Methane (CH_4) and molecular hydrogen (H_2) are small volatile compounds with a huge impact on Earth's habitability. These reduced molecules are well known for being key energy sources for microbial life in the deep subsurface, potentially comprising one of Earth's largest biospheres (Whitman et al., 1998; Colman et al., 2017; Magnabosco et al., 2018).

Recent studies suggested that fluid-rock interactions in subduction zones can generate deep metamorphic CH_4- and H_2-rich fluids, offering essential ingredients for sustaining deep microbial life at forearc regions (Mottl et al., 2003; Ohara et al., 2012; Plümper et al., 2017; Vitale Brovarone et al., 2020; Peverelli et al., 2024).

However, the extent to which metamorphic processes can generate deep energy sources at convergent margins and their isotopic fingerprints is largely unconstrained. This scientific gap leads to large uncertainties in other fields of research, such as the study of the redox-state of metamorphic fluids, the production of greenhouse gas, CH_4, and strategic carbon-neutral fuel, H_2, through metamorphic processes.

PETROLOGY AND FLUID INCLUSION ANALYSIS TO UNVEIL UNCONVENTIONAL DEEP ENERGY SOURCES

Petrology is fundamental in order to understand the origin and fluxes of terrestrial volatiles. The investigation of fluid-rock interactions and fluid inclusions (hereafter FIs) preserved in the rock record represents a powerful tool to reconstruct geologic processes and their impact on the evolution of life on our planet.

The aim of this PhD project is to foster our understanding of metamorphic hydrocarbons and H_2, through the petrographic, spectroscopic and isotopic characterisation of FIs trapped in exhumed metamorphic rocks from different geologic settings across the globe. To reach these goals, this PhD project required:

- The selection of a global-scale set of target samples of exhumed ultramafic, metabasic, metasomatic, and metasedimentary rocks, including two field sites for detailed characterisation and more than 17 exhumed metamorphic terranes worldwide, spanning from the Paleoproterozoic to the Eocene.
- The detailed petrographic characterisation of FIs from the micro to the nanoscale, combining optical microscopy, scanning and transmission electron microscopy, micro-Raman spectroscopy and energy dispersive X-ray spectroscopy.
- The development of FIs extraction protocols for the analysis of volatiles abundance and isotopic fingerprints in metamorphic rocks.

DEVELOPMENT OF FLUID INCLUSION EXTRACTION PROTOCOLS FOR $\delta^{13}C_{CH4}$ AND $\delta^{13}C_{CO2}$ CAVITY RING-DOWN SPECTROSCOPY (CRDS) ANALYSIS

Despite being a powerful tool to assess the nature and origin of paleo-geologic fluids, the isotopic characterisation of volatiles extracted from FIs can be hampered by a number of analytical artifacts (Salvi & Williams-Jones, 2003, and references therein) and is commonly based on expensive, and complicated extraction and purification systems, usually not available on the market.

This research project addressed these issues through the development of robust protocols for FIs extraction and $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ analysis through Cavity Ring-Down Spectroscopy (CRDS), a recently developed analytical technique that does not require gas separation and ensures high accuracy while maintaining a compact size and cost compared to conventional systems like Gas Chromatography Isotope Ratio Mass Spectrometry (GC-IRMS).

Blank, isotopic labelling, interlaboratory, and inter-technique comparison experiments highlighted the benefits and drawbacks of two off-line mechanical extraction techniques, namely ball milling and crushing in stainless steel tubes. The protocols developed in this study allowed to replicate previously measured $\delta^{13}C_{CH4}$ values within 1 ‰ (Fig. 1) and could be applied to gas samples with CH_4 and CO_2 concentrations above 10 and 1000 ppm, respectively.

These protocols in combination with petrological FIs characterisation could be exploited on a broad range of geological samples, providing insights into the nature and origin of terrestrial and extraterrestrial volatiles, and could answer extremely relevant scientific questions. For instance, these analytical techniques could be applied in geo-astrobiology to identify evidence of biotic CH_4 and past extraterrestrial life activity, preserved within FIs in Martian rock samples.

However, the results of this study underscore the importance of properly addressing the analytical limitations of mechanical/thermal fluid inclusion extraction techniques, and, in particular, blank CH_4 production, which could be easily misinterpreted as natural biotic CH_4 extracted from the sample.

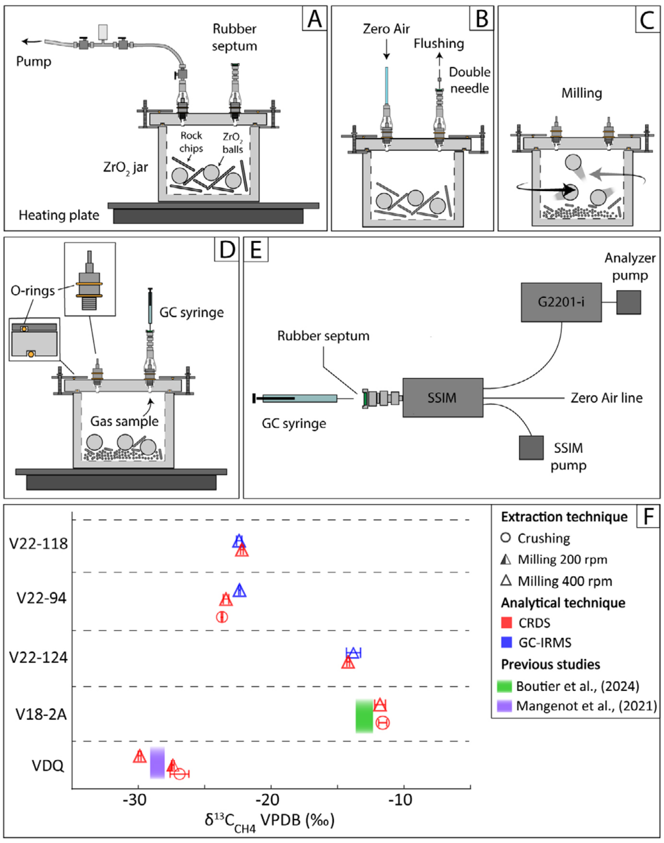

*Figure 1 a-e) Graphical representation of the ball milling extraction protocol steps, including sample loading and jar evacuation **(a)**, flushing and pumping with N_2-O_2 (Zero-Air) **(b)**, milling and fluid inclusion mechanical extraction **(c)**, gas extraction **(d)** and injection in the CRDS analyser with a GC syringe **(e)**. **f)** Results of interlaboratory and inter-technique comparison tests highlighting the reproducibility of the $\delta^{13}C_{CH4}$ VPDB (expressed in ‰) values within 1 ‰.*

CATCH AND RELEASE OF DEEP ENERGY SOURCES

Fluid inclusions within minerals may trap substantial amounts of energy sources, such as CH_4 and H_2, which, upon mechano-chemical release, may generate fluxes large enough to sustain microbial life at hydrothermal systems (McDermott et al., 2015; Klein et al., 2019; Grozeva et al., 2020).

Despite the increasing documentation of CH_4-H_2 FIs in crustal and mantle rocks exhumed from great depths (Vitale Brovarone et al., 2020; Peng et al., 2021; Spranitz et al., 2022; Zhang et al., 2023; Boutier et al., 2024; Peverelli et al., 2024), their evolution, residence time, and impact on volatile fluxes in the deep Earth remain unassessed.

This research project explored a novel approach to the study of deep CH_4-H_2, combining a high-resolution, 0.7 km^2-scale mapping of FIs petrographic-spectroscopic characterisation, and bulk CH_4 concentration and isotope composition measurement from 67 mafic, ultramafic, metasedimentary, and metasomatic rocks from the Belvidere Mountain Complex (BMC), Northern Vermont, USA (Fig. 2).

This allowed reconstructing multiple events of CH_4-H_2 catch and release in/from FIs (Fig. 2), opening a new perspective on the migration and residence time of volatile species and energy sources, such as CH_4, H_2, and NH_3, in deep metamorphic environments.

The FIs trapped in metamorphic/metasomatic rocks of the BMC acted as a sink for deep volatiles, isolating them from active fluid flow for geologic timescales.

The fate of these energy "vessels" – storage and transportation to shallower crustal levels vs. release at depth – was determined by mineralogical transformations and redox reactions throughout their exhumation history towards habitable environments.

The isotopic characterisation of CH_4 extracted from FIs provided a powerful tool to track the origin and reactivity of deep energy sources throughout the BMC tectono-metamorphic history (Fig. 2). This revealed an increasing input of metasediment-derived CH_4 driving pervasive carbonation of the ultramafic-mafic rocks during their exhumation.

THE HIDDEN DIVERSITY OF SERPENTINISATION-DERIVED HYDROCARBONS

The study of CH_4-H_2 FIs trapped in orogenic peridotites represents a powerful tool to understand the potential of different serpentinisation environments to generate energy sources, such as abiotic hydrocarbons and H_2 (Zhang et al., 2021; Boutier et al., 2024).

However, deciphering the serpentinisation and

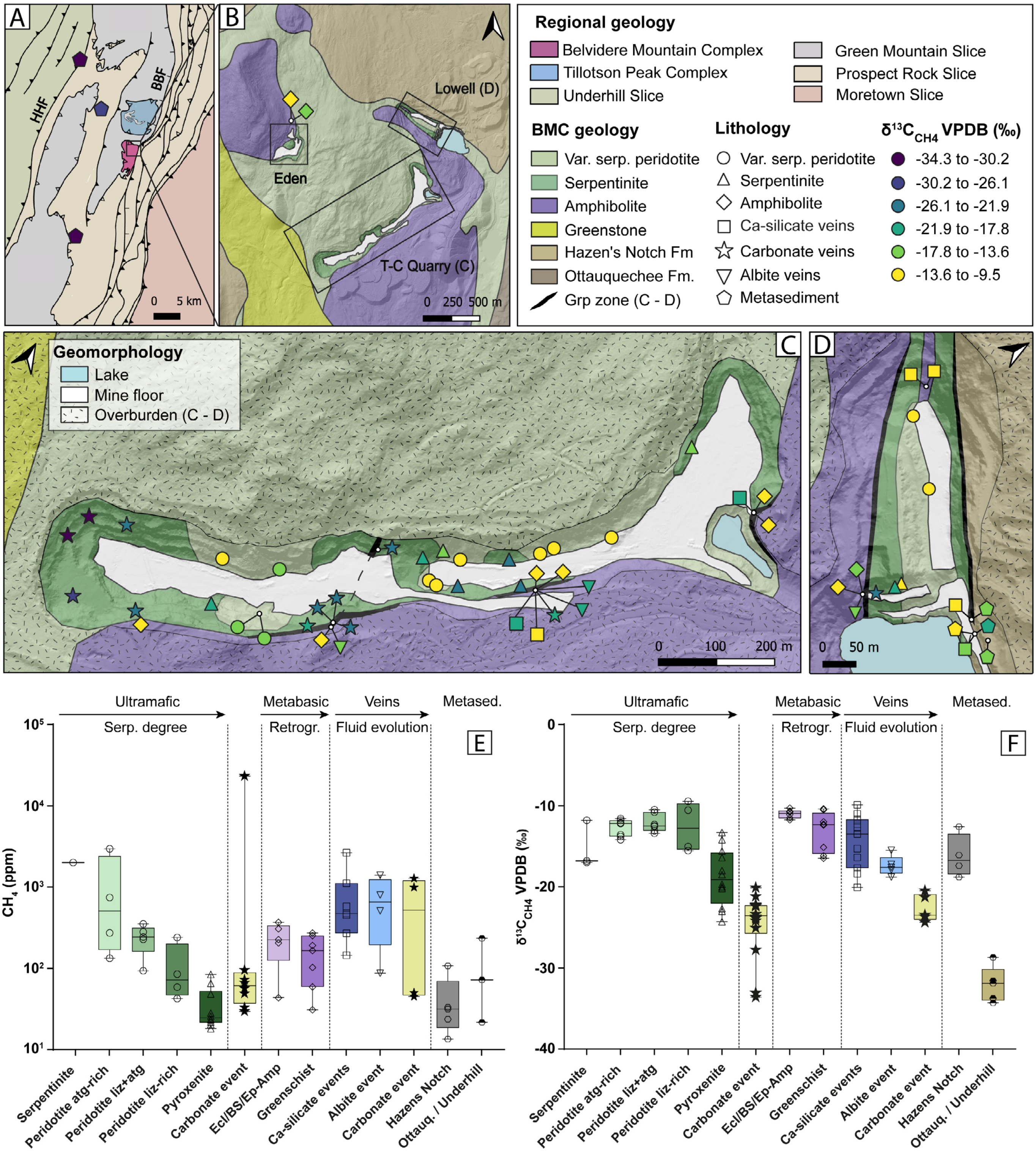

Figure 2 a-d) *Mapping of CH_4 distribution and isotopic fingerprints in the BMC area. Geological maps are modified after Gale (2007), Ratcliffe et al. (2011), and Honsberger (2023). Symbols represent samples analyzed for bulk fluid inclusion isotope analysis. The symbol shape indicates the type of lithology. Symbol colors refer to the bulk $\delta^{13}C_{CH4}$ value (see the legend for color scale).* ***e)*** *Boxplots of bulk CH_4 concentrations expressed in ppm (logarithmic scale) measured on gas samples extracted from different rock types, highlighting a correlation between the CH_4 content and the serpentinisation degree of ultramafic and retrogression and metabasic host rocks and mineralogical transformation of FIs-hosting minerals.* ***f)*** *Boxplots of bulk $\delta^{13}C_{CH4}$ expressed in permill relative to the VPDB measured on gas samples extracted from different rock types depicting multiple CH_4 generation/migration events characterised by distinct isotopic fingerprints. Abbreviations: Atg = Antigorite. BBF = Burgess Brach Fault Zone; BMC = Belvidere Mountain Complex; Liz = Lizardite. GMS = Green Mountain Slice; Grp = Graphite; HHF = Honey Hollow Fault Zone; Metased. = Metasediment. MTS = Moretown Slice; Ottauq. = Ottauquechee. PRS = Prospect Rock Slice; Retrogr. = Retrogression. Serp = Serpentinisation. TPC = Tillotson Peak Complex; UHS = Underhill Slice; Var. serp. = Variably serpentinised.*

energy source generation history of exhumed ophiolites can be extremely challenging. Subducted mantle lithosphere can preserve evidence of multi-stage fluid-rock interaction, from the subseafloor down to the serpentine-out reaction in subduction zones (Debret et al., 2013; Padrón-Navarta et al., 2013; Scambelluri et al., 2014; Vitale Brovarone et al., 2020; Ressico et al., 2024), leading to the entrapment of multiple fluid inclusion populations and CH_4-H_2 generation events (Zhang et al., 2021).

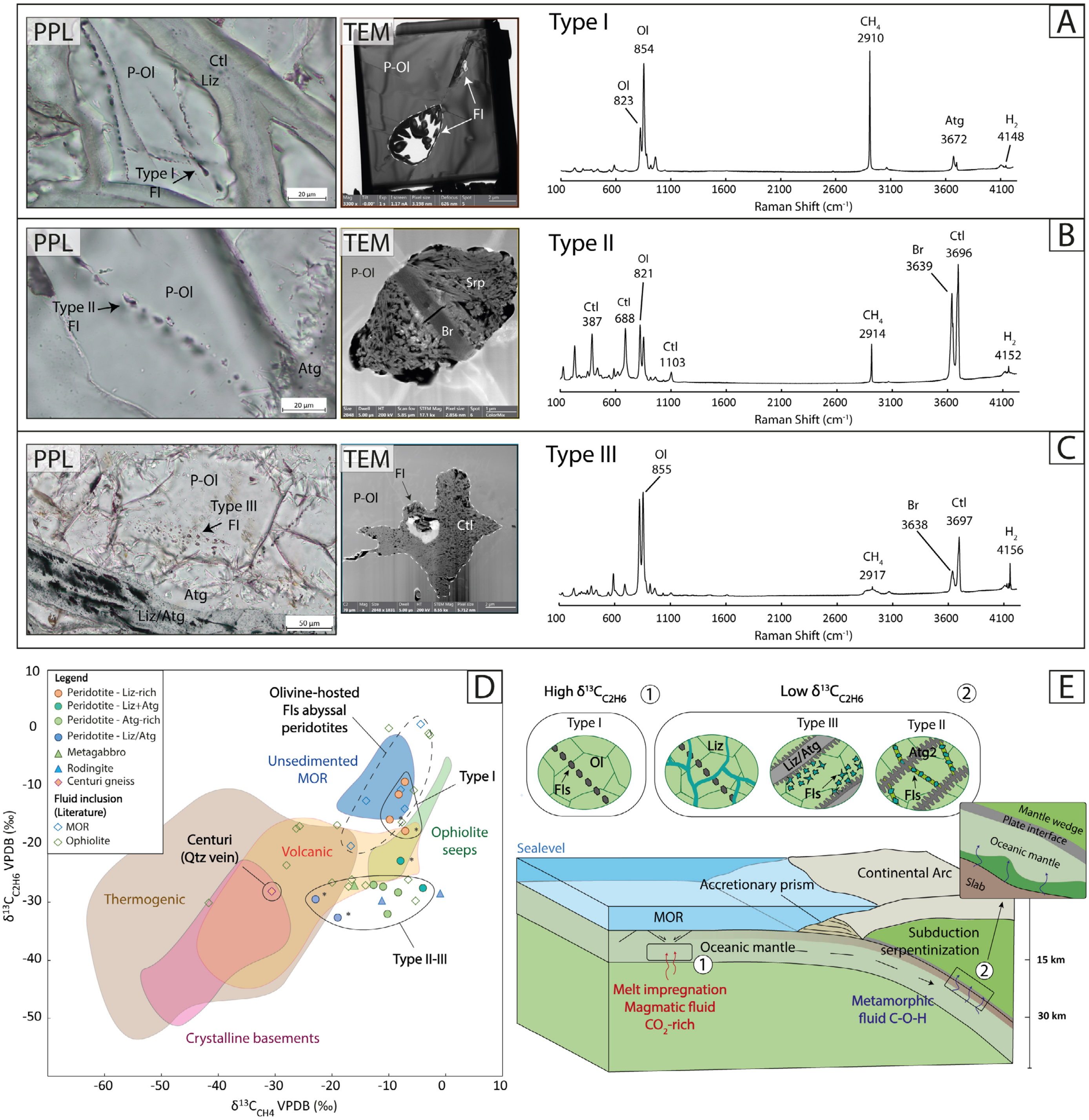

Figure 3 a-c) *The three main populations of multiphase olivine-hosted fluid inclusions (Type I, II, and III) trapped in the Monte Maggiore orogenic peridotite imaged at the optical microscope under plane polarised light (PPL) and through transmission electron microscopy (TEM), and representative micro-Raman spectra highlighting changes in the composition of trapped solid phases and CH_4-H_2 gas mixtures.* ***d)*** *$\delta^{13}C_{CH_4}$ vs. $\delta^{13}C_{C_2H_6}$ diagram of mechanically extracted FIs in the Monte Maggiore massif, highlighting a clear difference between Type I FIs and Type II-III FIs populations. The diagram also displays FIs literature data of C_1 and C_2 alkanes (symbols) and terrestrial surface and submarine emissions (coloured regions). Asterisks highlight samples with low C_2H_6 concentrations.* ***e)*** *Reconstructed model of the fluid-rock interaction history experienced by the Monte Maggiore peridotite, associated microstructures, and events of hydrocarbon-H_2 genesis from a mid-ocean-ridge setting (1) to the Alpine subduction (2). Abbreviations: Atg = antigorite; Br = brucite; Ctl =chrysotile; FI = fluid inclusion; Liz = lizardite; MOR = mid-ocean-ridge; P-Ol = primary olivine; Qtz = quartz.*

The micro- and nanoscale FIs petrographic-spectroscopic study and CH_4-C_2H_6 isotope analysis on 42 samples of ultramafic rocks, meta-gabbros, and rodingite from the Monte Maggiore orogenic peridotite, Northern Corsica, demonstrates that subducted and exhumed oceanic lithosphere can retain a diverse record of energy sources.

The nanostructure, mineral assemblages, and CH_4-H_2 gas mixtures preserved within olivine-hosted multiphase FIs highlighted different generations of olivine-hosted multiphase FIs characterised by distinct CH_4-C_2H_6 isotopic patterns (Fig. 3).

The $\delta^{13}C$-enriched C_2H_6 component points to the preservation of abiotic hydrocarbons formed in a mid-ocean-ridge setting, while the $\delta^{13}C$-depleted C_2H_6 component is related to multiple high-pressure serpentinisation events in the Alpine subduction zone. These results highlight possible differences in the hydrocarbon sources occurring in different geo-dynamic settings, or relevant changes in the C_1-C_2 carbon isotope fractionation during abiotic polymerisation reactions.

This study underlines the potential of CH_4-C_2H_6 isotope analysis combined with micro to nanoscale FIs characterisation to distinguish between different hydrocarbon sources and geodynamic settings of deep energy production, which could be otherwise hindered by long-lived and complex fluid-rock interaction histories.

The complex CH_4-C_2H_6 isotopic patterns preserved in the Monte Maggiore FIs underscore our limited understanding of abiotic low-molecular-weight hydrocarbons generation through fluid-rock interactions, which could provide valuable tools in the identification of biotic vs. abiotic hydrocarbons on Earth, and in extraterrestrial environments.

TOWARDS A GLOBAL INVENTORY OF METAMORPHIC HYDROCARBONS

For the first time, petrographic-spectroscopic analysis of FIs from several exhumed metamorphic terranes across the globe revealed the widespread presence

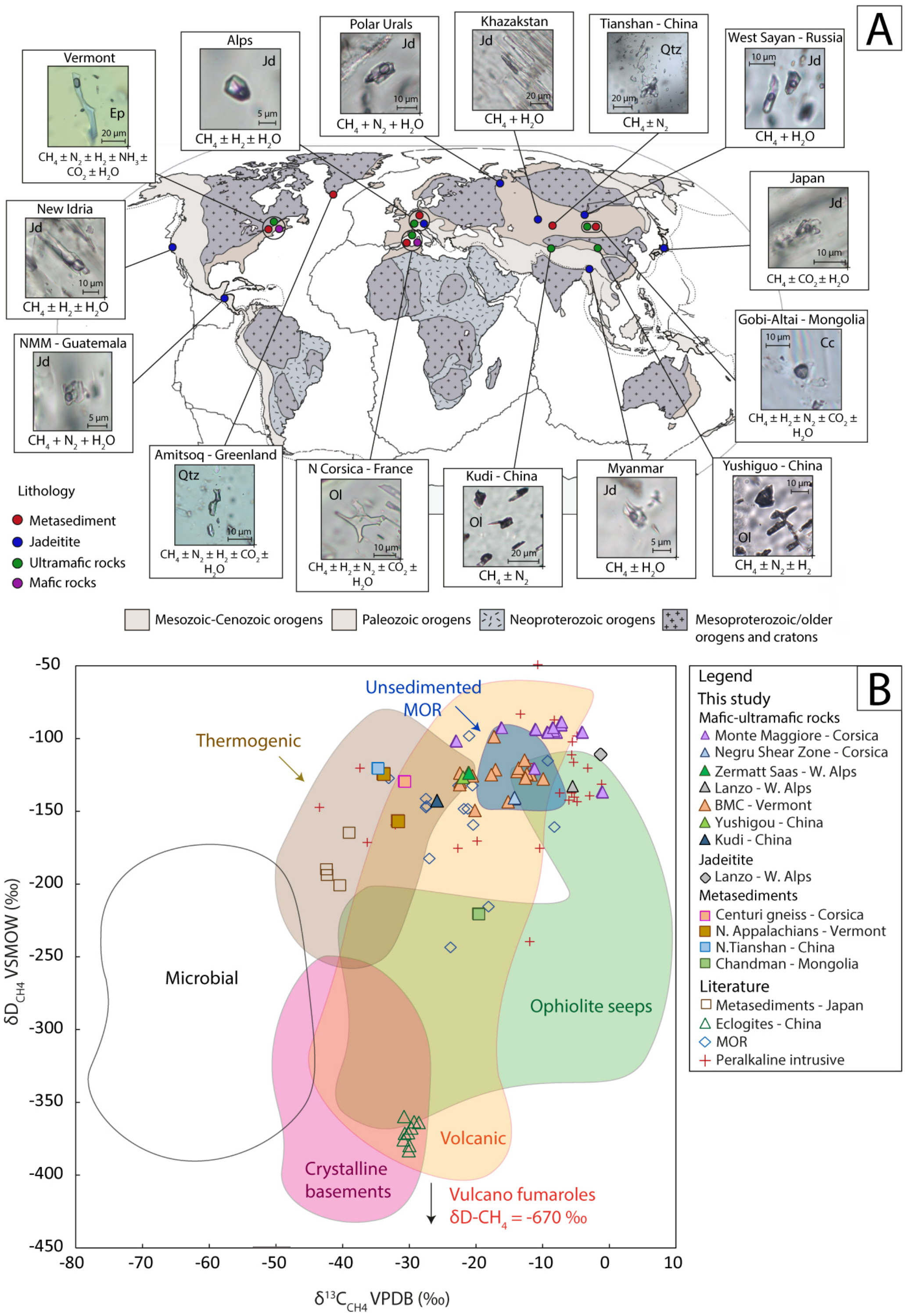

Figure 4 a) *Worldwide distribution of energy sources, i.e., CH_4, H_2, and NH_3, in metasediments (red circle), jadeitites (blue circle), ultramafic (green circle), and mafic (purple circle) rocks from exhumed metamorphic terranes, and orogens from, the Mesoproterozoic to the Cenozoic. Each locality investigated in this study is associated with a photomicrograph of representative fluid inclusions, and the list of fluid species identified through micro-Raman spectroscopy. The base map is after Tsujimori and Harlow (2012).* ***b)*** *The $\delta^{13}C_{CH4}$ vs. δD_{CH4} diagram, expressed in ‰ relative to the VPDB and VSMOW, respectively. The color-filled symbols show the isotopic composition of the CH_4 extracted FIs from this study, including variably metamorphosed and metasomatised mafic-ultramafic rocks (triangles), a jadeitite sample (rhomb), and metasediments (squares). Data from the literature are represented by empty symbols. The coloured regions represent the CH_4 isotopic composition from terrestrial surface and submarine emissions from the literature.*

of life essential ingredients, *i.e.*, CH_4, C_2H_6, NH_3, and H_2, in FIs trapped in a wide variety of lithologies (Fig. 4a,b), including a vast collection of jadeitites from Guatemala, USA, Russia, Alps, and Japan spanning the entire Phanerozoic (results published in Peverelli et al., 2024); metasediments, including Cambrian dolomitic marbles from the Chandman massif (Mongolia), Carboniferous graphitic schists from Western Tianshan, and Paleoproterozoic graphitic schists from Amitsoq (Southern Greenland); ultramafic rocks, including Alpine de-serpentinisation veins from the Zermatt Saas Fee unit, in the Western Alps, and metasomatic diopside veins from the Negru Shear Zone, in Alpine Corsica (results published in Dobe et al., 2025).

The petrology and isotope analysis of fluid inclusions trapped in exhumed metamorphic rocks allowed to open a new window into the distribution, nature, and isotopic fingerprints of deeply sourced metamorphic CH_4 from the Paleoproterozoic to the Eocene, and from various geodynamic contexts. Figure 4b provides a first insight into the preliminary global distribution of metamorphic CH_4 isotopic signatures, combining the results obtained throughout this PhD project, with other fluid inclusion isotope studies from different localities and lithologies (Suzuki et al., 2017; Zhang et al., 2023).

Developing a global dataset of metamorphic CH_4 distribution, isotopic fingerprints, and abundance in rocks could provide answers to fundamental scientific questions such as the extent to which metamorphic processes influenced the climate and habitability of our planet in the past and at present.

Exploring the petrology and geochemistry of deep unconventional energy sources preserved in the rock record could change dramatically our understanding of the link between plate tectonics and life emergence and evolution on Earth.

REFERENCES

Boutier, A., Martinez, I., Sissmann, O., Agostini, S., Daniel, I., Van Baalen, M., Mana, S., Vitale Brovarone, A. (2024) - Complexity of graphite formation in response to metamorphic methane generation and transformation in an orogenic ultramafic body. Geochim. Cosmochim. Ac., 364, 166-183.

Colman, D.R., Poudel, S., Stamps, B.W., Boyd, E.S., Spear, J.R. (2017) - The deep, hot biosphere: Twenty-five years of retrospection. P. Natl. Acad. Sci. USA, 114, 6895–6903.

Debret, B., Nicollet, C., Andreani, M., Schwartz, S., Godard, M. (2013) - Three steps of serpentinization in an eclogitized oceanic serpentinization front (Lanzo Massif – Western Alps). J. Metamorph. Geol., 31, 165–186.

Dobe, R., Giuntoli, F., Olivieri, O.S., Siron, G., Viola, G., Menegon, L., Vitale Brovarone, A. (2025) - Tracking molecular hydrogen migration along a subduction shear zone. Geol. Soc. Am. Bull.

Gale, M.H. (2007) - Bedrock Geologic Map of the Hazens Notch and Portions of the Eden and Lowell Quadrangles, Vermont.

Grozeva, N.G., Klein, F., Seewald, J.S., Sylva, S.P. (2020) - Chemical and isotopic analyses of hydrocarbon-bearing fluid inclusions in olivine-rich rocks. Philos. T. R. Soc. A, 378, 20180431.

Honsberger, I.W. (2023) - Newly recognized blueschist-facies metamorphism (glaucophane-omphacite-garnet), Belvidere Mountain Complex, northern Appalachians. Geosphere, 19, 645–653.

Klein, F., Grozeva, N.G., Seewald, J.S. (2019) - Abiotic methane synthesis and serpentinization in olivine-hosted fluid inclusions. P. Natl. Acad. Sci., 116, 17666–17672.

Magnabosco, C., Lin, L.-H., Dong, H., Bomberg, M., Ghiorse, W., Stan-Lotter, H., Pedersen, K., Kieft, T.L., van Heerden, E., Onstott, T.C. (2018) - The biomass and biodiversity of the continental subsurface. Nature Geosci., 11, 707–717.

McDermott, J.M., Seewald, J.S., German, C.R., Sylva, S.P. (2015) - Pathways for abiotic organic synthesis at submarine hydrothermal fields. P. Natl. Acad. Sci., 112, 7668–7672.

Mottl, M.J., Komor, S.C., Fryer, P., Moyer, C.L. (2003) - Deep-slab fluids fuel extremophilic Archaea on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195. Geochem. Geophys. Geosyst., 4.

Ohara, Y., Reagan, M.K., Fujikura, K., Watanabe, H., Michibayashi, K., Ishii, T., Stern, R.J., Pujana, I., Martinez, F., Girard, G., Ribeiro, J., Brounce, M., Komori, N., Kino, M. (2012) - A serpentinite-hosted ecosystem in the Southern Mariana Forearc. P. Natl. Acad. Sci., 109, 2831–2835.

Padrón-Navarta, J.A., Sánchez-Vizcaíno, V.L., Hermann, J., Connolly, J.A.D., Garrido, C.J., Gómez-Pugnaire, M.T., Marchesi, C. (2013) - Tschermak's substitution in antigorite and consequences for phase relations and water liberation in high-grade serpentinites. Lithos, 178, 186–196.

Peng, W., Zhang, L., Tumiati, S., Vitale Brovarone, A., Hu, H., Cai, Y., Shen, T. (2021) - Abiotic methane generation through reduction of serpentinite-hosted dolomite: Implications for carbon mobility in subduction zones. Geochim. Cosmochim. Ac., 311, 119–140.

Peverelli, V., Olivieri, O.S., Tsujimori, T., Giovannelli, D., Shi, G., Cannaò, E., Piccoli, F., Vitale Brovarone, A. (2024) - Cold-subduction biogeodynamics boost deep energy delivery to the forearc. Geochim. Cosmochim. Ac., 138, 195-207.

Plümper, O., King, H.E., Geisler, T., Liu, Y., Pabst, S., Savov, I.P., Rost, D., Zack, T. (2017) - Subduction zone forearc serpentinites as incubators for deep microbial life. P. Natl. Acad. Sci., 114, 4324–4329.

Ratcliffe, N.M., Stanley, R.S., Gale, M.H., Thompson, P.J., Walsh, G.J., With contributions by Hatch Jr., N.L., Rankin, D.W., Doolan, B.L., Kim, J., Mehrtens, C.J., Aleinikoff, J.N., McHone, J.G., Cartography by Masonic, L.M. (2011) - Bedrock geologic map of Vermont (Report No. 3184), Scientific Investigations Map. Reston, VA.

Ressico, F., Cannaò, E., Olivieri, O.S., Pastore, Z., Peverelli, V., Malaspina, N., Vitale Brovarone, A. (2024) - Behaviour of fluid-mobile elements across a high-pressure serpentinization front (Monte Maggiore unit, Alpine Corsica). Chem. Geol., 662, 122228.

Salvi, S. & Williams-Jones, A. (2003) - Bulk analysis of volatiles in fluid inclusions. In: "Fluid Inclusions: Analysis and Interpretation", I. Samson, A. Anderson, D. Marshall, eds. Mineralogical Association of Canada.

Scambelluri, M., Pettke, T., Rampone, E., Godard, M., Reusser, E. (2014) - Petrology and Trace Element Budgets of High-pressure Peridotites Indicate Subduction Dehydration of Serpentinized Mantle (Cima di Gagnone, Central Alps, Switzerland). J. Petrol., 55, 459–498.

Spránitz, T., Padrón-Navarta, J.A., Szabo, C., Szabó, Á., Berkesi, M. (2022) - Abiotic passive nitrogen and methane enrichment during exhumation of subducted rocks: Primary multiphase fluid inclusions in high-pressure rocks from the Cabo Ortegal Complex, NW Spain. J. Metamorph. Geol., 40, 1291-1319.

Suzuki, N., Saito, H., Hoshino, T. (2017) - Hydrogen gas of organic origin in shales and metapelites. Int. J. Coal Geol., 173.

Tsujimori, T. & Harlow, G. (2012) - Petrogenetic relationships between jadeitite and associated high-pressure and low-temperature metamorphic rocks in worldwide jadeitite localities: A review. Eur. J. Mineral., 24, 371-390.

Vitale Brovarone, A., Sverjensky, D.A., Piccoli, F., Ressico, F., Giovannelli, D., Daniel, I. (2020) - Subduction hides high-pressure sources of energy that may feed the deep subsurface biosphere. Nat. Commun., 11, 3880.

Whitman, W.B., Coleman, D.C., Wiebe, W.J. (1998) - Prokaryotes: the unseen majority. P. Natl. Acad. Sci., 95, 6578–6583.

Zhang, L., Wang, Q., Ding, X., Li, W.-C. (2021) - Diverse serpentinization and associated abiotic methanogenesis within multiple types of olivine-hosted fluid inclusions in orogenic peridotite from northern Tibet. Geochim. Cosmochim. Ac., 296, 1–17.

Zhang, L., Zhang, L., Tang, M., Wang, X., Tao, R., Xu, C., Bader, T. (2023) - Massive abiotic methane production in eclogite during cold subduction. Natl. Sci. Rev., 10, nwac207.