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Geochemické a izotopové vymezení složení svrchního pláště Českého Masivu

*Geochemical and isotopic constraints on the composition of the upper mantle beneath the
Bohemian Massif*

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Statement of authorship

I, Julie V. Erban Kočergina, declare that this thesis, presented for the Ph.D. degree at Charles University in Prague, is a result of my original research and was written by myself and that all the literary sources were cited properly. Neither this thesis nor its substantial part has been submitted to fulfil requirements for other academic degrees and has not been previously submitted to Charles University in Prague or any other institution.

Prohlášení

Prohlašuji, že jsem závěrečnou práci zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

V Praze, dne 3.09.2024



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RNDr. Julie Erban Kočergina

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List of articles presented in thesis and author's contribution

This dissertation is a compilation of three scientific articles, presented in a cumulative format. Two of the articles have already been published, while one is currently being reviewed for publication.

- I. ERBAN KOCHERGINA, Y.V., ERBAN, V., HORA, J.M., 2022.** Sample preparation and chromatographic separation for Sr, Nd, and Pb isotope analysis in geological, environmental, and archaeological samples. *Journal of Geosciences*, 67 – 3, pp. 273–285

Author's contribution: 90 %

- II. ERBAN KOCHERGINA, Y.V., MAGNA, T., ACKERMAN, L., ŠPAČEK P., XXXX.** Highly siderophile element geochemistry of metasomatized sub-continental lithospheric mantle: Clues from the mantle xenoliths in the western edge of the Bohemian Massif. *Chemical Geology*, under review

Author's contribution: 50 %

- III. KOCHERGINA, Y.V., ACKERMAN, L., ERBAN, V., MATUSIAK-MALEK, M., PUZIEWICZ, J., HALODOVÁ, P., ŠPAČEK, P., TRUBAČ, J., MAGNA, T., 2016.** Rhenium–osmium isotopes in pervasively metasomatized mantle xenoliths from the Bohemian Massif and implications for the reliability of Os model ages. *Chemical Geology* 430, pp. 90–107

Author's contribution: 60 %

This is to confirm the above given partial involvement (in percentage) of RNDr. Julie Erban Kočergina in the fieldwork and sampling, making of the petrographic descriptions, responsibility for the collecting, processing and presentation of chemical data, as well as the determination of the isotopic composition of studied samples.

Dr.sc.nat. Tomáš Magna

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JANOŠEK, V., **ERBAN KOCHERGINA Y.V.**, ANDRONIKOV, A., KUSBACH V., 2022. Decoupling of Mg from Sr–Nd isotopic compositions in Variscan subduction-related plutonic rocks from the Bohemian Massif: implications for mantle enrichment processes and genesis of orogenic ultrapotassic magmatic rocks. *International Journal of Earth Sciences* 111: 1491–1518

NOVAK, M., ANDRONIKOV, A.V., SEBEK, O., KOTKOVA, J., **ERBAN KOCHERGINA, Y.V.**, STEPANOVA, M, STRNAD, L., KRAM, P., FARKAS, J., VESELOVSKY, F., STEDRA, V., CURIK, J., CHRASTNY, V., PRECHOVA, E., HOUSKOVA, M., 2022. Relationship between $\delta^{53}\text{Cr}$ values and progressive weathering of serpentized ultramafic rocks. *Chemical Geology*, 604, 120940

CASAS-GARCÍA, R., RAPPRIICH, V., **KOCHERGINA, Y.V.**, REPSTOCK, A., SCHULZ, B., MAGNA, T., BREITKREUZ, C., 2021. Crustal vs. mantle contributions in the Erzgebirge/Krušné hory: Implications for production of late-Variscan A-type rocks in the Altenberg-Teplice Caldera, Central Europe. *Lithos* 404–405, 106429

HORA, J.M., TABAUD, A-S., JANOŠEK, V., **ERBAN KOCHERGINA, Y.V.**, 2021. Potassic magmas of the Vosges Mts. (NE France) delimit Variscan mantle domains, providing insight into the geodynamics of continental collision. *Lithos*, 402–403, 106304

JANOŠEK, V., HANŽL, P., SVOJTKA, M., HORA, M.H., **ERBAN KOCHERGINA, Y.V.**, GADAS, P., HOLUB, F.V., GERDES, A., VERNER, K., HRDLIČKOVÁ, K., DALY, S., BURIÁNEK, D., 2020. Ultrapotassic magmatism at the hay day of the Variscan Orogeny – the story of the Třebíč Pluton, the largest durbachitic body in the Bohemian Massif. *International Journal of Earth Sciences* 109, 1767–1810

NÁDASKAY, R., **KOCHERGINA, Y.V.**, ČECH, S., ŠVÁBENISKÁ, L., VALEČKA, J., ERBAN, V., HALODOVÁ, P., ČEJKOVÁ, P., 2019. Integrated stratigraphy of an offshore environment

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MYSLIVEČEK, J., RAPPRICH, V., **KOCHERGINA, Y.V.**, MAGNA, T., HALODOVÁ, P., PÉCSKAY, Z., POŇAVIČ, M., 2018. Petrology of weakly differentiated alkaline, high-level intrusive rocks in the Zahořany-Chotiněves Belt near Litoměřice (Czech Republic). *Journal of Geosciences* 63 (4), pp. 317–331

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WALTHER, D., BREITKREUZ, CH., RAPPRICH, V., **KOCHERGINA, Y.V.**, CHLUPÁČOVÁ, M., LAPP, M., STANEK K., MAGNA, T., 2016. The Late Carboniferous Schönfeld–Altenberg Depression on the NW margin of the Bohemian Massif (Germany/Czech Republic): volcanosedimentary and magmatic evolution. *Journal of Geosciences* 61 (4), pp. 371–393

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Goldschmidt 2013: ACKERMAN L., **KOCHERGINA Y.**, ŠPAČEK P. AND MAGNA T. (2013): Highly siderophile element geochemistry of upper mantle xenoliths from NE Bavaria. *Mineralogical Magazine* 77 (5)

Goldschmidt 2013: **KOCHERGINA Y.**, NIEDERMANN S., RAPPRICH V. AND MAGNA T. (2013): Noble gas signature of Tertiary alkaline basalts and xenoliths from central Europe. *Mineralogical Magazine* 77 (5), A1485

Minerály: struktura, vlastnosti, analýza: **KOCHERGINA Y.**, ACKERMAN L., ERBAN V (2013): Re-Os geochemistry of upper mantle xenoliths from the Bohemian Massif. Russian Academy of Science, the Ural branch, Yekaterinburg, Russia

IAVCEI 2013: RAPPRICH V., ERBAN V., MIKOVA J., MAGNA T., **KOCHERGINA Y.**, HALODA J., ACKERMAN L. AND PECSKAY Z. (2013): Mantle domain boundary beneath the Jicin Volcanic Field, Czech Republic: evidence from isotopic composition of primitive alkaline basaltic rocks. International Association of Volcanology and Chemistry of the Earth's Interior (IAVCEI) 2013 assembly, abstract volume. Kagoshima, Japan

Sixth International Orogenic Lherzolite Conference: **KOCHERGINA Y.**, ACKERMAN L., ERBAN V (2014): Rhenium–osmium isotopic composition of mantle xenoliths from the Bohemian Massif. Marrakech, Morocco

Goldschmidt 2014: **KOCHERGINA Y.**, MAGNA T., ACKERMAN L., ERBAN V., RAPPRICH V., MÜNKER C., MARIEN C. (2014): Hf–Os Isotopes in Cenozoic Alkaline Basalts from the Bohemian Massif, Czech Republic

4.seminář odborné skupiny vulkanologie při České Geologické Společnosti: **KOČERGINA J.**, ACKERMAN L., MATUSIAK-MALEK M., PUZIEWICZ J., ERBAN V., TRUBAČ J., MAGNA, T. (2014):

Geochemie a stáří subkontinentální litosféry Českého Masivu pomocí izotopů Re-Os. In Magna T., Rappich V., Radoň M: 4. seminář odborné skupiny vulkanologie při České Geologické Společnosti, s. 12-13. Praha. ISBN 978-80-87487-11-2.

2nd European mantle workshop: **KOCHERGINA Y., ACKERMAN L., ERBAN V., MAGNA T.** (2015): Re–Os and platinum-group elements in massive peridotites from Moldanubian, Bohemian Massif, Czech Republic. In Mateusz Cwiek, Magdalena Matusiak-Malek: Mineralogia. Special Papers, svazek 43. s. 49-50. Wrocław.

Goldschmidt 2015: **KOCHERGINA Y., ACKERMAN L., MAGNA T., KOVASC A:** Re–Os and HSE Distributions in Mohelno–Biskoupky Peridotites, Gföhl Unit, Bohemian Massif. Goldschmidt Abstrakts

8th International Siberian Early Career GeoScientists Conference-2016: **KOCHERGINA, Y.** (2016): Age of mantle beneath the Bohemian Massif: isotopic constraints. In Dr. Nikolay P. Pokhilenko: The 8th International Siberian Early Career GeoScientists Conference: Proceedings of the Conference, s. 92. – IGM SB RAS, IPPG SB RAS, NSU. Novosibirsk, Russia

Otvorený geologický kongres Slovenskej geologickej spoločnosti a České geologické společnosti: **KOCHERGINA, Y.** (2017): Vývoj Re-Os izotopového systému v plášti Českého masivu v kontextu evoluce kůry

17th Meeting of the Central European Tectonic Studies Groups CETEG 2019: **KOCHERGINA Y., NOVÁK M., STRNAD L., ERBAN V.** (2019): Chemical heterogeneity within a single small serpentinite body and its implications for mantle characterization as observed in the Biskoupky serpentinite, Czech Republic.

Abstract

This dissertation consists of three scientific articles, two of which have already been published, and the third is currently undergoing peer review. The complete texts of the publications are appended to this thesis.

This dissertation presents a discussion of the methodology used in the geochemical processing of mantle peridotites and the extraction of information from a limited sample size. In the course of this dissertation, I have acquired proficiency in the methodologies of peridotite sample preparation, acid digestion of the sample, separation of radiogenic Sr–Nd–Pb–Os–Hf isotopes, leaching and determination of total sulfur content in peridotites, separation and determination of siderophile elements, and in-situ determination of elements by laser ablation and electron microprobe. The methodology of sample preparation, separation and measurement of Sr–Nd–Pb isotopes was optimised in the conditions of CGS laboratories. The methodologies were validated by measuring a large number of international isotope standards, and the results were published. This publication forms part of my PhD thesis.

The second part of the dissertation addresses the heterogeneity of the Earth's mantle under the Bohemian Massif. Specific focus was placed on Re–Os isotopes and PGE composition. A total of 14 sites distributed across the Bohemian Massif were selected for the research project. A total of 49 xenoliths were selected for isotopic analysis. A subset of the results from 11 sites was published in Kochergin et al. (2016). The remaining results will be published in the paper by Erban Kochergina et al., which is currently under review.

It was not the intention of this dissertation to resolve all issues of SCLM heterogeneity beneath the Bohemian Massif. However, one of the aims was to contribute to the ongoing discussion on the different types of metasomatism that have influenced its composition. The application of Re–Os isotope analysis and PGE distribution enabled the proposal of subduction in the western

part of the Ohře rift as a factor influencing the composition of the lithospheric mantle to be supported.

The contribution of this work was the calculation of Re–Os model ages for peridotite xenoliths from localities across the Ohře rift. The calculated mantle extraction ages (T_{MA}) range from 0.1 to 2.1 Ga, with several cases of unrealistic "future" ages explained by the presence of metasomatic overprinting. The Re (T_{RD}) compartment ages exhibit a range from 0.1 to 1.6 Ga. However, T_{RD} cannot be directly compared to crustal ages because they represent a minimum age rather than a specific age estimate, also in part due to consideration of total Re removal from the rocks. Accordingly, a modified model age (T_{RDII}) was calculated assuming a non-zero Re content in the pre-metasomatic phase and using a composition representative of the most depleted sample in the suite. The pronounced peak in the calculated T_{RDII} age is between 0.5 and 0.6 Ga, corresponding to the Cadomian orogenic cycle.

Abstrakt

Tato disertační práce sestává ze tří odborných článků, z čehož dva byly již publikovány, třetí je v současné době v recenzním řízení. Plné texty výše uvedených publikací jsou přílohou této práce.

V této disertační práci se zabývám metodikou geochemického zpracování plášťových peridotitů a získáváním informací z omezeného množství vzorku. V rámci této disertační práce jsem se seznámila a osvojila si metodiky přípravy vzorků peridotitu, kyselinového rozkladu vzorku, separace radiogenních izotopů Sr–Nd–Pb–Os–Hf, loužení a stanovení celkového obsahu síry v peridotitech, separace a stanovení siderofilních prvků a in-situ stanovení prvků pomocí laserové ablace a elektronové mikrosondy. Metodika přípravy vzorků, separace a měření izotopů Sr–Nd–Pb byla optimalizována v podmínkách laboratoří ČGS. Tyto metodiky byly ověřeny měřením velkého počtu mezinárodních izotopových standardů, a výsledky byly publikovány. Tato publikace je součástí mé doktorské práce.

Druhá část disertační práce se zabývá heterogenitou zemského pláště pod Českým masivem. Zvláštní pozornost byla věnována izotopům Re–Os a složení PGE. Pro výzkumný projekt bylo vybráno celkem 14 lokalit napříč Českým masivem. Bylo shromážděno 49 xenolitů, které byly považovány za vhodné pro izotopové měření. Podskupina výsledků z 11 lokalit byla publikována v článku Kochergina et al. (2016). Zbývající výsledky budou publikovány v článku Erban Kochergina et al. který je v současné době v recenzním řízení.

Jistě nemohlo být ambicí této disertační práce vyřešit všechny otázky heterogenity SCLM pod Českým masivem, nicméně jedním z cílů bylo přispět k probíhající diskusi o různých typech metasomatismu, které ovlivnily jeho složení. Použití analýzy izotopů Re–Os a distribuce PGE umožnilo podpořit myšlenku subdukce v západní části oherského riftu, která složení litosférického pláště výrazně ovlivnila.

Přínosem práce byl výpočet Re–Os modelového stáří pro peridotitové xenolity z lokalit napříč oherským riftem. Vypočtená stáří extrakce pláště (T_{MA}) se pohybují v rozmezí 0,1 až 2,1 Ga, několik případů nerealistického „budoucího“ stáří je vysvětleno přítomností metasomatického přetisku. Stáří oddělení Re (T_{RD}) vykazují rozmezí od 0,1 do 1,6 Ga. T_{RD} však nelze přímo srovnávat se stářím kůry, protože představuje spíše minimální věkovou hranici než konkrétní odhad stáří, zčásti v důsledku předpokladu nulového obsahu Re v horninách. V souladu s tím bylo vypočteno modifikované modelové stáří (T_{RDII}) za předpokladu nenulového obsahu Re v předmetasomatické fázi a za použití složení odpovídajícího nejvíce ochuzenému vzorku v suitě. Výrazný vrchol ve vypočteném stáří T_{RDII} se pohybuje mezi 0,5 a 0,6 Ga, což odpovídá kadomskému orogennímu cyklu.

List of abbreviations

BM – Bohemian Massif

BABI – Basaltic Achondrite Best Initial

BSE – Bulk Silicate Earth = the Primary Uniform Reservoir = Crust + Mantle = Primitive Mantle. Silicate portion of the Earth after the core separation, before the crust-mantle differentiation.

SCLM – SubContinental Lithospheric Mantle represents a rigid, non-convective chemical, thermal and mechanical boundary layer insulating the continental crust (Mohorovičić discontinuity) and the convective asthenosphere mantle

MORB – Mid-Ocean Ridge Basalts. Products of partial melting of mantle peridotite (Iherzolite). Primary MORB liquid can only be produced by melting of peridotites at pressures over 15 kb, deeper than 40 km or 80 km for normal (N)-MORBs.

N-MORB – Normal-MORB, upper, depleted mantle

E-MORB – Enriched-MORB, deeper enriched source

T-MORB – Transitional-MORB, mixing of N- and E- magmas during ascent and/or in shallow chambers.

CC – continental crust

OIB – Oceanic Island Basalts, type of basalt that erupted within the oceans, mainly in intraplate settings. OIB are commonly olivine-bearing lavas with subalkalic (tholeiitic) and alkalic compositions.

DM – Depleted Mantle = N-MORB source

PUM – Primitive Upper Mantle. The PUM composition is derived here from the major-element and rare-earth-element (REE) contents of mantle Iherzolites.

CHUR – chondritic uniform reservoir

FOZO – Focal Zone is the isotopic composition of the lower mantle: $^{87}\text{Sr}/^{86}\text{Sr} = 0.7025$, $\epsilon\text{Nd} = +9$, $^{206}\text{Pb}/^{204}\text{Pb} = 19.5$

HIMU – high- μ , $\mu = ^{238}\text{U}/^{204}\text{Pb}$, enriched in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, depleted in $^{87}\text{Sr}/^{86}\text{Sr}$. The origin: (i) recycled oceanic crust, (b) metasomatically enriched oceanic lithosphere

EM1 – Enriched Mantle 1 - slightly more radiogenic in $^{87}\text{Sr}/^{86}\text{Sr}$, no Pb enrichment, very low $^{143}\text{Nd}/^{144}\text{Nd}$, high Th/U and low (U, Th)/Pb ratios. The origin: (i) recycling of delaminated subcontinental lithosphere, (ii) recycling of subducted ancient pelagic sediment.

EM2 – Enriched Mantle 2 – more radiogenic in $^{87}\text{Sr}/^{86}\text{Sr}$ and radiogenic Pb. Origin: (i) recycling oceanic crust and small amount of subducted sediment, (b) recycling of melt-impregnated oceanic lithosphere.

ECRIS – European Cenozoic Rift System, 1100 km long rift system. It is a continuous system that includes the Spanish Valencia Trough, the French Massif Central, Black Forest and Vosges, Hegau, Urach, Rhenish Massif, Vogelsberg and the Bohemian Massif.

Incompatible elements (K, Rb, Cs, Ta, Nb, U, Th, Y, Hf, Zr, LREEs). Elements not accepted in mantle minerals. These elements concentrated in the crust with $D^{s/l} \ll 1$.

Compatible elements (Ni, Cr, Co, V, Sc) concentrate in the mantle, those with $D^{s/l} \geq 1$.

REE – Rare Earth Elements, lanthanides.

LILE – Large Ion Lithophile Elements. These elements have ionic radii too large to be accommodated in crystal structure of typical mantle phases.

HFSE – High Field-Strength Elements: Hf, Zr, Ti, Nb, and Ta. These elements have a high charge-to-radius ratio, which generates an intense electronic field around each ion, and makes it unstable in an ionic silicate crystal.

HSE – Highly siderophile elements: Re, Os, Ir, Ru, Rh, Pt, Pd, and Au (Re, Au+PGE). The $D^{\text{metal/silicate}}$ values $\geq 10\,000$.

MSE – Moderately siderophile elements: Ga, P, W, Co, Ag, Ni, Sb, As, Ge, Mo. The $D^{\text{metal/silicate}}$ values range from ~ 3 to 10000.

SSE – Slightly siderophile elements: Mn, V, Mo, W, Fe. The $D^{\text{metal/silicate}}$ values ≤ 1 .

PGE – Platinum group elements: Os, Ir, Ru, Rh, Pt, and Pd

I-PGE – Os, Ir, Ru

P-PGE – Pt, Pd, Rh

Byr – billion years, used to show the time interval

Ga – Billion years, used to refer a time point in geological history

Ma – Million years, used to refer a time point in geological history

ppm – parts per million

ppb – parts per billion

ID – isotope dilution

Preface

The dissertation thesis is organized in a cumulative format. This Ph.D. thesis consists of three Chapters and an appendix with three scientific articles, of which two have been published and one is currently under review.

The initial chapter is dedicated to the problem of radiogenic isotopes and describes the basic principles of the behaviour of radiogenic isotopes.

The following part of the study addresses the composition of the lithospheric mantle beneath the Bohemian Massif. The radiogenic isotopes Sr–Nd and Os are of greatest interest. Consequently, this section describes the oxidation state of the mantle beneath the Bohemian massif, which confirms the great influence of metasomatism on its composition.

In Part III of the dissertation, I provide in detail the principle of sample preparation, separation and measurement of Re and Os isotopes. A similar detailed description did not appear in any of my publications, and thus I have chosen to present this methodology in a separate chapter.

The initial journal article in the appendix focuses on the methodology for the preparation of specimens for the analysis of radiogenic isotopes, specifically strontium (Sr), neodymium (Nd) and lead (Pb). The second and third journal articles are focused on the isotopic composition of Re–Os in peridotite xenoliths from the BM. The second publication is focused on Re–Os isotope systematics and PGE composition of mantle xenoliths from the westernmost part of the Ohře (Eger) Rift in NE Bavaria. The most significant outcome of this chapter is evidence of subduction and mantle contamination by subducted sediments. The third publication is focused on Re–Os isotope compositions of mantle xenoliths from the entire Bohemian Massif, including localities from Germany, the Czech Republic and Poland. The most significant achievement of this chapter is a comparison of the Re–Os model ages of the studied peridotite xenoliths with

the Nd model ages of the crustal units from the Bohemian Massif. The most significant outcomes of the thesis are finally highlighted in the conclusions.

CHAPTER 1: Introduction

Radiogenic isotopes as geochemical tracers

The field of mantle geochemistry aims to elucidate the nature, history and evolution of the Earth's mantle through the study of the chemical and isotopic composition of both mantle samples and the melts derived from it.

Isotope geochemistry plays an important role in geological research. Radiogenic isotopes can be used as tracers in analytical geochemistry. The radiogenic isotopic studies of igneous rocks focus mainly on isotopes of incompatible, lithophile (Sr, Nd, Hf, Pb) and siderophile (Os) trace elements. Radiogenic isotope ratios, expressed as $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, and $^{187}\text{Os}/^{188}\text{Os}$ have been accumulated for a range of magmatic systems.

Strontium isotopes

Strontium is an alkaline earth metal with a similar ionic radius to that of calcium, resulting in a common substitution of Sr^{2+} for Ca^{2+} in minerals (Ca-feldspars, calcite, dolomite, apatite) as well as in plant and animal tissues. It is almost omnipresent in nature, often in readily measurable amounts. Strontium has four stable isotopes: ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . While the proportions of the ^{84}Sr , ^{86}Sr and ^{88}Sr are almost fixed in nature, the ^{87}Sr content is highly variable as it is a daughter product of the radioactive ^{87}Rb decay. The Sr isotopic composition is commonly expressed as $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. As a rule of thumb, it has never been observed to be lower than 0.69897 (basaltic achondrite best initial - BABI, (Hans et al., 2013)). Values between ~ 0.702 and ~ 0.707 are typical of mantle and mantle-derived rocks (such as serpentinites or basalts), marine sediments reach $^{87}\text{Sr}/^{86}\text{Sr}$ ratios broadly from 0.707 to 0.709, modern seawater has $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7092 (Peucker-Ehrenbrink and Fiske, 2019), rainwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is normally around 0.710 (Erban Kochergina et al., 2021; Pearce et al., 2015), likely reflecting the

influence of seawater salts carried by atmospheric circulation. The most diverse $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are obtained for felsic rocks (e.g., granites) which range from 0.702 up to 1, or even higher. The signature of clastic sediments depends on its source, but it is usually confined between 0.705 and 0.750 (Faure and Mensing, 2004).

Rubidium is an alkali metal with a similar ionic radius to that of potassium. Rb^+ substitutes for K^+ in minerals like K-feldspar and micas. Rubidium has two naturally occurring isotopes, stable ^{85}Rb and radioactive ^{87}Rb . The rubidium half-life is 48.8 Gyr (Steiger and Jager, 1977). Due to the long half-life of the $^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$ decay the ^{87}Sr radiogenic ingrowth is very slow although, in favourable situations such as high Rb/Sr elemental ratios, radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be generated in a geologically short time.

The use of Sr as an isotopic tracer is based on a fact that different natural reservoirs can have contrasting $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic fingerprints. This is generally inherited from magmatic rocks as an ultimate source of Sr in nature. The Sr isotopic signature of the rock is a result of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ during rock formation and time-integrated ingrowth of the radiogenic ^{87}Sr since then. However, the latter process is the more effective the higher is the Rb content in the mineral. This leads to contrasting $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic fingerprints of individual minerals even within one rock massive. The diverse water–rock interaction properties of these rock-forming minerals (congruent and incongruent dissolution, ion exchange etc.) are thus governing the isotopic composition of the potential leachate.

Since bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ can be affected by secondary processes, obtaining the primary Sr isotopic ratios in mantle rocks relies on either removing secondary phases or obtaining pure mineral separates of the primary ones. In practice this means picking minerals to avoid secondary phlogopitic mica or acid washing those separates to remove any remaining secondary carbonates.

Mantle peridotite xenoliths mostly contain pyroxenes and garnets that have LREE-depleted compositions and low Rb/Sr ratio relative to PUM (Pearson et al., 2014). The Rb-Sr method has largely been used for dating igneous rocks. If the initial ratio $^{87}\text{Sr}/^{86}\text{Sr}$ is known or can be estimated, then t can be determined, provided that it can be assumed that the system has been closed with respect to Rb and Sr mobility from time t until the present:

$$t = \frac{1}{\lambda} \ln \left\{ 1 + \frac{^{86}\text{Sr}}{^{87}\text{Rb}} \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right) \text{P} - \left(\frac{^{86}\text{Sr}}{^{87}\text{Sr}} \right) \text{I} \right] \right\},$$

where present-day Sr isotope ratio (P) is measured by mass spectrometry, and the atomic $^{87}\text{Rb}/^{86}\text{Sr}$ ratio is calculated from Rb/Sr weight ratio. Common analytical practise involves analyses of representative bulk samples and individual mineral fractions following decomposition and isolation of Rb and Sr. Nonetheless, modern instrumental developments appear to provide less time-consuming in-situ approach, yielding ages with comparable uncertainty to that obtained by conventional methods.

Neodymium isotopes

Samarium and neodymium are rare earth elements. Neodymium has seven natural isotopes: ^{142}Nd (27.153 %), ^{143}Nd (12.173 %), ^{144}Nd (23.798 %), ^{145}Nd (8.293 %), ^{146}Nd (17.189 %), ^{148}Nd (5.756 %), and ^{150}Nd (5.638 %) (Meija et al., 2016). Samarium has seven naturally occurring isotopes: ^{144}Sm (3.1 %), ^{147}Sm (15.0 %), ^{148}Sm (11.2 %), ^{149}Sm (13.8 %), ^{150}Sm (7.4 %), ^{152}Sm (26.8 %), and ^{154}Sm (22.0 %), where ^{147}Sm , ^{148}Sm and ^{149}Sm are all radioactive with long half-lives (about 10^{16} yr) and for geological meaning these isotopes can be considered stable.

Unlike Rb and Sr, Sm and Nd display highly comparable chemical properties, and large ranges of Sm/Nd ratio in whole rock systems are rare (Dickin, 2005). Due to its slightly lower ionic radius, Sm is generally more compatible than Nd in the Earth's mantle. The fractionation of Sm

from Nd during melting and crystallisation processes alters the Sm/Nd ratios in minerals, which, over time, will result in a change in the relative abundance of ^{143}Nd and ^{142}Nd . The Sm–Nd system is completely immune to disturbance during erosion and sedimentation.

$^{143}\text{Nd}/^{144}\text{Nd}$ as well as $^{176}\text{Hf}/^{177}\text{Hf}$ are plotted in epsilon (ϵ) notation. The ϵ -notation is defined as follows:

$$\epsilon\text{Nd sample} = \left[\frac{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_{\text{sample}}}{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_{\text{CHUR}}} - 1 \right] \times 10^4,$$

where CHUR stands for “chondritic uniform reservoir”. The $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ of CHUR are 0.512638 and 0.1967, respectively (Dickin, 2005). The ϵNd allows to determine whether the mantle source of the samples had long-term enrichment ($\epsilon^{143}\text{Nd} < 0$) or depletion ($\epsilon^{143}\text{Nd} > 0$) of a light rare earth-enriched component (typical for melts).

Lead isotopes

Lead has four stable isotopes ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , where only ^{204}Pb is non-radiogenic. The other lead stable isotopes are the final decay products of three decay chains from uranium and thorium, and U–Pb dating was employed to yield the first high-precision age of the Earth (Patterson, 1956). Lead isotopes are an effective tool in studies of mantle and crustal evolution. Using the different isotopes in conjunction makes it possible to identify the nature of differentiation events and place constraints on their timing (Dickin, 2005). A series of arrays to the right of the geochron on the Pb–Pb ‘isochron’ diagram was first found by several scientists who studied ocean-island basalts (e.g., Gast et al., 1964; Tatsumoto, 1966, 1978; Sun et al., 1975). The slopes of OIB arrays correspond to apparent ages between 1 and 2.5 Gyr. This can be interpreted in three different ways: (i) as a product of a two-component mixing process, (ii) as a result of mantle differentiation events, (iii) as a result of the continuous evolution of reservoirs with changing μ values ($\mu = ^{238}\text{U}/^{204}\text{Pb}$).

The present-day μ value of upper mantle is 6 or less (White et al., 1993, White, 2013), whereas the best estimates for Bulk Silicate Earth are around 8. The depleted mantle has lower μ than bulk Earth, as confirmed by the calculations of White (White et al., 1993, White, 2013), who suppose Pb not to be derived from some primitive mantle reservoir, but instead it can easily be supplied by mantle plumes, which clearly penetrate the upper mantle.

Lutetium–Hafnium isotopes

The Lu–Hf isotope system has obvious similarities with Sm–Nd isotope system: all elements are lithophile and refractory with high condensation temperatures. They behave incompatibly during melting and are concentrated in the melt over the residual solid (Vervoort, 2014). Lutetium is the heaviest and the least abundant of the REE, and has a 3+ valence. Lutetium has two isotopes: stable ^{175}Lu (97.4%) and radioactive ^{176}Lu (2.6%), which decays to ^{176}Hf by beta decay. Hafnium is a high-field-strength element (HFSE) and has six naturally occurring isotopes: radiogenic ^{176}Hf (5.26 %) and stable ^{174}Hf (0.16 %), ^{177}Hf (18.60 %), ^{178}Hf (27.28 %), ^{179}Hf (13.62 %), ^{180}Hf (35.06 %). The Lu–Hf method is used to determine absolute ages (“isochron” method), and also is utilized for dating of metamorphism. The short half-life of ^{176}Lu is $3.719 \pm 0.007 \times 10^{10}$ y, (Hayakawa et al., 2023).

$^{176}\text{Hf}/^{177}\text{Hf}$ is plotted in epsilon (ϵ) notation,

$$\epsilon\text{Hf sample} = \left[\frac{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_{\text{sample}}}{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_{\text{CHUR}}} - 1 \right] \times 10^4$$

Rhenium–Osmium isotopes

During the last two decades the Os isotope mantle geochemistry began to play an important role in research. Unlike Rb–Sr, Sm–Nd, or Lu–Hf isotopic systems, Re–Os systematics are different because of osmium compatibility during partial melting while rhenium behaves

incompatibly (Brenan, 2008). Therefore, the Re–Os isotopic system could be used as a geochronometer for mantle peridotites (Luguet and Pearson, 2019).

Osmium has seven stable isotopes: ^{184}Os (0.02 %), ^{186}Os (1.59 %), ^{187}Os (1.96 %), ^{188}Os (13.24 %), ^{189}Os (16.15 %), ^{190}Os (26.2 %), and ^{192}Os (40.78 %). Rhenium has one stable ^{185}Re (37.4%), and one radiogenic ^{187}Re (62.6%) with long half-life ($4.23 \pm 0.13 \times 10^{10}$ y).

Osmium is a member of the platinum group elements (PGE) and highly siderophile elements (HSE), along with Re. These elements are primarily sequestered into the core or metal during planetary differentiation, with subordinate amounts in the mantle and crust (Shirey and Walker, 1998). The distribution coefficients of PGE between metals and silicates are greater than 10 000 (Roy-Barman et al., 1998; Jones and Drake, 1986). Rhenium and Os chalcophile nature is manifested in distribution coefficients between sulfide and silicate melts, with orders of magnitude variation from 10 to 1000 for Re (Roy-Barman et al., 1998; Jones and Drake, 1986) and 3.0×10^4 to 4.8×10^4 for Os (Crocket et al, 1992; Roy-Barman et al., 1998). During mantle differentiation, Os behaves as a compatible element that is retained in mantle residues, while Re behaves in a relatively incompatible manner and is partially removed from the mantle source. As a result, crustal materials are generally highly depleted in Os and relatively enriched in Re. This large fractionation of parent and daughter material during mantle melting and the subsequent radiogenic addition of ^{187}Os results in greatly variable $^{187}\text{Os}/^{188}\text{Os}$ ratios in various geological reservoirs.

Before 1994 all studies reported Os composition in terms of $^{187}\text{Os}/^{186}\text{Os}$ ratios, because of the modern chondritic and mantle $^{187}\text{Os}/^{186}\text{Os} \sim 1$ (Walker, 2016). Many laboratories measured $^{187}\text{Os}/^{188}\text{Os}$ then converting to $^{187}\text{Os}/^{186}\text{Os}$ by multiplying the measured ratio by 0.12. However, Walker et al. (1994) analysed Pt-rich samples from Norilsk (Russia), and concluded that the enrichment of ^{186}Os is the result of the decay of ^{190}Pt . Since then, the $^{187}\text{Os}/^{186}\text{Os}$ ratio has been discontinued and laboratories have gradually switched to using the $^{187}\text{Os}/^{188}\text{Os}$ ratio.

The increased variability of $^{187}\text{Os}/^{188}\text{Os}$ in different rocks underlines the great interest in Os isotope analyses. This is particularly apparent when data for the primitive upper mantle ($^{187}\text{Os}/^{188}\text{Os} \sim 0.1296$; e.g., Meisel et al., 2001) are compared with mid-ocean ridge and arc basalts ($^{187}\text{Os}/^{188}\text{Os}$ up to ~ 1.5 ; e.g., Alves et al., 2002; Brandon et al., 1999; Chen et al., 2019), continental basalts ($^{187}\text{Os}/^{188}\text{Os}$ broadly between 0.134 and 0.446; e.g., (Huang et al., 2017; McBride et al., 2001) and upper continental crust (Peucker-Ehrenbrink et al., 2012). Additional Os isotope variability is introduced in destructive margins, young oceanic subducted sediments ($^{187}\text{Os}/^{188}\text{Os}$ between 0.68 and 0.92; e.g., (Mullen et al., 2015) and highly radiogenic oceanic crust ($^{187}\text{Os}/^{188}\text{Os}$ up to 25 in eclogites (Becker, 2000), up to 27 in eclogitic sulfide inclusions in Kimberly diamonds (Richardson et al., 2001).

The Re–Os system can effectively date mantle-depletion and mantle-enrichment events. Osmium model ages can be used to date sub-continental lithospheric mantle. The T_{MA} age shows the time of a sample separation from the mantle with the assumption of its closed system behaviour (e.g., Shirey and Walker, 1998). The T_{RD} model age represents the minimum age for a Re depletion event. It assumes a two-stage evolution of the sample Re budget including total Re removal by partial melting and its possible later influx from host lava. In Kochergina et al., (2016), we discuss the use of Re–Os for the dating of mantle processes and we also suggest a way to calculate a modified T_{RDII} model age, assuming a non-zero Re content during the pre-metasomatic stage and using a composition of the most depleted sample in our suite (Kochergina et al., 2016).

Highly siderophile elements

Among many elemental and isotope tracers, the group of highly siderophile elements (HSE: Re, Au, Os, Ir, Ru, Rh, Pt, Pd) has gained considerable attention given their strong partitioning into metal, stark concentration contrasts in the pristine mantle and derivative melts versus

chemically evolved lithologies (Day et al., 2016; Becker and Dale, 2015; Lorand and Luguet, 2016; Luguet and Reisberg, 2016).

At low pressures, the HSE have a strong affinity for Fe-metal and sulfides versus coexisting silicates or oxides (Day et al., 2016), with partition coefficients estimated at $>10^4$. From the HSE group, Re shows a partial affinity for silicate phases (Brenan, 2008). The HSE behave to some extent differently during melting: iridium-PGE (I-PGE: Os, Ir, Ru) have melting temperatures > 2000 °C and, together with Re, concentrate in the metal phase whilst platinum-PGE (P-PGE: Pt, Pd, Rh) have melting temperature < 2000 °C and typically concentrate in the residual liquid (Goldstein et al., 2009). The crystallization of mafic and ultramafic magmas appears to leave the I-PGE in magmatic cumulates whereas the P-PGE and Re concentrate in the differentiated products (Brenan et al., 2016).

The metasomatic modification of lithospheric mantle, caused mainly by the interaction with ascending fluids and melts, has also been investigated for HSE and Re–Os isotope systematics (e.g., (Ackerman et al., 2009b; Kochergina et al., 2016; Luguet and Reisberg, 2016). Luguet and Reisberg 2016 systematically described the effects of metasomatic agents on HSE behaviour of non-cratonic peridotites: 1) Percolation of S-undersaturated silicate melts resulting in a decrease of HSE and S, the ^{187}Os signatures could be modified toward more radiogenic values; 2) percolation of S-saturated silicate melts is typified by Pd moderately enrichments compared to Pt, leading to the primitive upper mantle (PUM)-like HSE patterns and non-radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signatures; 3) percolation of C–O–S fluid/vapors lead to an increase in Os and Pd, in contrast to Ir and Pt and radiogenic $^{187}\text{Os}/^{188}\text{Os}$; 4) syn- and/or post-eruption alteration is manifested in sub-chondritic $\text{Os}_\text{N}/\text{Ir}_\text{N}$ ratios, due to volatilization or remobilization of Os (Fig. 1).

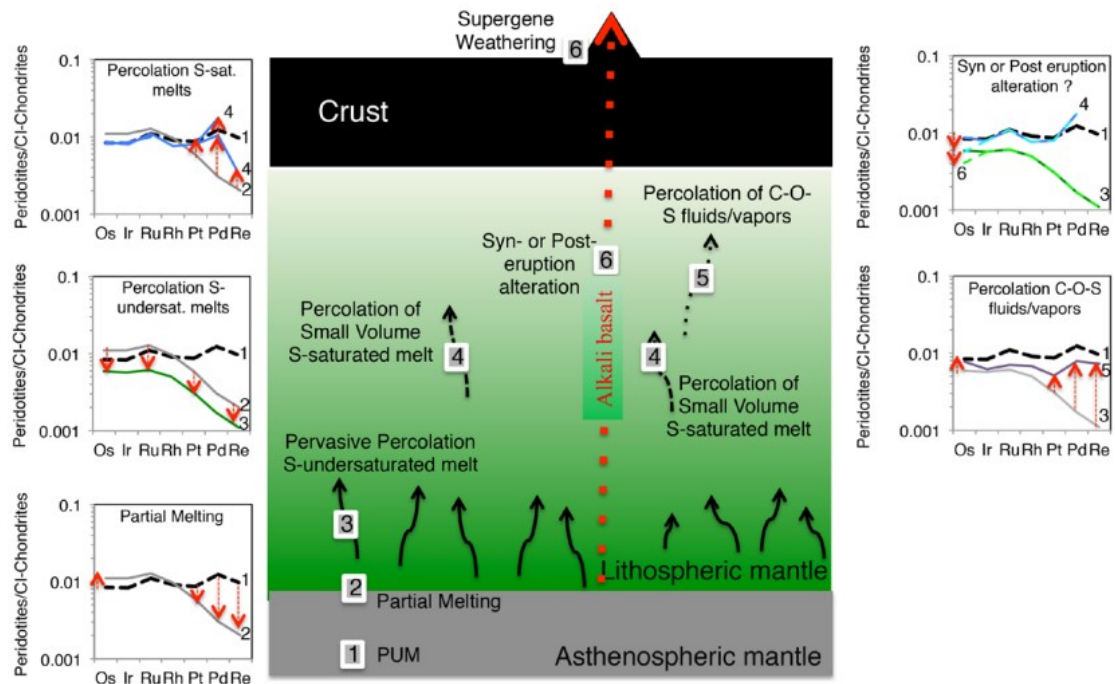


Figure 1. Schematic petrological history of non-cratonic peridotite xenoliths and its effects on HSE signatures, adopted from Lugué and Reisberg (2016). Sample normalized by Orgueil CI-chondrite (Fisher-Godde et al. 2010).

CHAPTER 2: Geochemical and isotopic constraints on the composition of the upper mantle beneath the Bohemian Massif

Variscan basement of the Bohemian Massif

The Bohemian Massif is a tectonic unit consolidated during the Variscan (Hercynian) orogeny (McCann, 2008). It formed between the Upper Devonian and Lower Carboniferous (ca. 380–280 Ma) as a result of closure of the Rheic ocean and collision between Laurussia (Laurentia+Baltica+Avalonia) and Gondwana supercontinents (Franke, 2000, Kroner and Romer, 2013). The entire Variscan orogeny extends from northernmost Africa through Spain, southern England, France, and Germany to the Czech Republic and Poland as its eastern promontory. In fact, it is a continuation of the Ouachita–Alleghanian orogeny in North America and is also often correlated with Devonian–Carboniferous part of the Altai orogeny. The Bohemian Massif is the largest preserved remnant of the Variscan basement in Europe. Boundary of the Bohemian Massif generally traces the geographic outline of the Czech Republic, although it overlaps to adjacent parts of Poland, Germany and Austria. The entire Variscan belt is traditionally subdivided into several major units with distinctively different lithology, metamorphism and tectonic styles (Schulmann et al., 2009, 2014). These can be distinguished also within the Bohemian Massif (Fig. 2):

- Saxothuringian Unit to the north, either Neoproterozoic Peri-Gondwanan crust (Kroner et al., 2007) or microcontinent assemblage (Franke, 2000) with Paleozoic cover corresponding to the continental crust of the Armorican plate (Schulmann et al. 2009);
- Moldanubian Unit to the south, high- to medium-grade metamorphosed domain intruded by Carboniferous granitic plutons, altogether forming the high-grade core of the orogeny (Schulmann et al. 2009);
- Brunia Neo-Proterozoic basement with Paleozoic cover;

- Teplá–Barrandian Unit between Saxothuringian and Moldanubian, consisting of Neoproterozoic basement and its Early Palaeozoic cover. It is interpreted as an independent crustal block (the Bohemia Terrane of South Armorica *sensu*) (Franke, 2000; Schulmann et al., 2009).

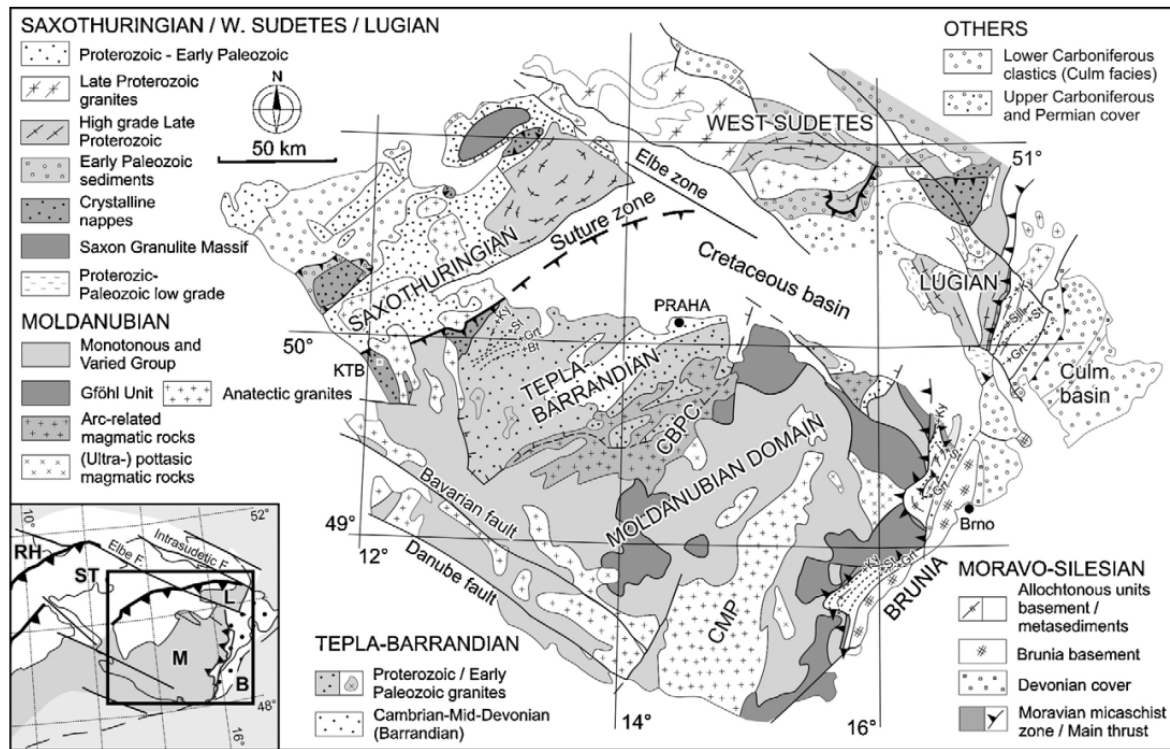


Figure 2. Simplified geological map of the Bohemian Massif, adopted from Schulmann et al., 2009. CBPC: Central Bohemian Plutonic Complex; CMP: Central Moldanubian Pluton. The lower left insert shows the Bohemian Massif's position in the European Variscides frame. RH: Rhenohercynian zone; ST: Saxothuringian Zone; M: Moldanubian Zone; B: Brunia Continent; L: Lugian domain.

The Variscan orogenic process in the Bohemian Massif was largely controlled by two-sided subduction of Cambro–Ordovician Saxothuringian oceanic lithosphere and Moravo–Silesian Cadomian crust below the Moldanubian towards southeast and northwest, respectively. The subduction appears to have operated since at least 400 Ma and is indicated by synchronous eclogitization of the Saxothuringian crust and its exhumation along the suture (Schulmann et

al., 2009, 2014). Low- to medium-grade metamorphic rocks prevail in the Saxothuringian, whereas high-grade rocks are characteristic for the Moldanubian. Mantle metasomatism likely took place at ~ 340 Ma, during the final Variscan collision (Schaltegger et al., 1996, 1999). Dostal et al., (2020) compared the compiled Nd isotopic data and the T_{DM} ages of the mantle-derived rocks from the whole Bohemian Massif (Fig. 3). They described that the Late Paleozoic mantle-derived rocks have radiogenic $\epsilon Nd_{(t)}$ values of old depleted mantle model ages. In contrast, Late Proterozoic-Early Paleozoic within-plate mafic igneous rocks show positive $\epsilon Nd_{(t)}$ and younger Nd model ages (Fig.3). This suggests that the entire Bohemian Massif had a cogent history during Variscan orogeny, and the modification of the SCLM is probably due to contamination of a mantle source by fluids and silicic melts from subducted sediments (Ackerman et al., 2009a; Erban Kochergina et al. *under review*; Dostal et al., 2019a; 2019b; Krmičková et al., 2020; Soder and Romer, 2018).

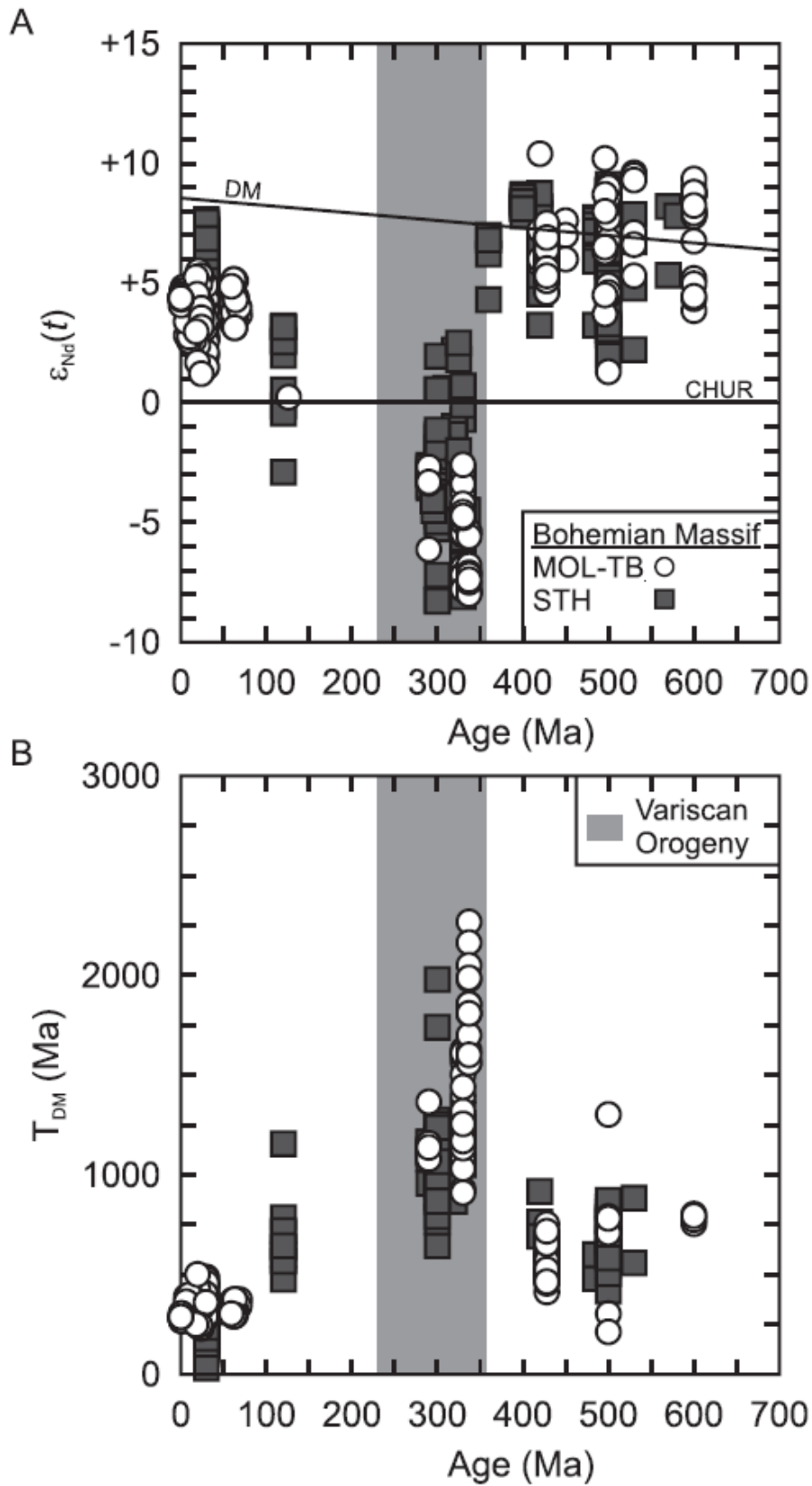


Figure 3. Epsilon Nd and Nd model ages calculated for mantle-related rocks from the Bohemian Massif. Figure adopted from Dostal et al., 2020

Peridotites of the Bohemian Massif

Orogenic peridotites and peridotite xenoliths provide a wealth of knowledge about geochemical processes operating in the mantle. The composition of the mantle directly affects the composition of mafic rocks. The occurrence of massive peridotites in the BM is associated with its pre-Variscan and Variscan history, and the occurrence of mantle xenoliths is associated with the Cenozoic period.

The crystalline basement contains various serpentinised relicts of pre-Variscan mantle tectonically incorporated into high-temperature–high-pressure crustal rocks. (e.g. McCann, 2008; Downes, 2001). Further, mantle rocks are represented by abundant xenoliths hosted by Cenozoic intra-plate primitive lavas (Ackerman et al., 2013b; Fediuk, 1994, Kochergina et al., 2016; Matusiak-Małek et al., 2010, 2014; Medaris et al., 1990, 2005a, 2015a; Puziewicz 2011, 2015; Ulrych and Pivec, 1997; Ulrych et al., 2004, 2011).

Peridotites of the Saxothuringian Unit of the Bohemian Massif

The Mariánské Lázně complex

The Mariánské Lázně Complex (MLC) is a southeast dipping eclogite-bearing allochthonous body displaying some meta-ophiolite features. It represents a vestige of the Early Paleozoic Saxothuringian ocean (Matte et al., 1990) with MORB oceanic crust formed in the Early Cambrian that was subducted and eclogitized in the Mid-Devonian (Collet et al., 2018; Medaris et al., 2011). It is located along a major tectonic boundary between Saxothuringian and Teplá–Barrandian Units (Fig. 2). Its metamorphism was the result of a short-lived episode of subduction and exhumation during Late Devonian (Frasnian-Famennian) time (Mlčoch and Konopásek, 2010).

The MLC is composed of predominant metabasic rocks with subordinate amounts of extensively serpentinized peridotites. The harzburgitic protoliths were largely recrystallized to

a medium-temperature assemblage of forsterite+enstatite tremolite+chlorite prior to serpentinization (Medaris et al, 2011).

The Sm–Nd age of eclogite facies metamorphism in the MLC was determined at 367 ± 4 and 377 ± 7 Ma (Beard et al., 1995). Using the U–Pb method in zircons from migmatized amphibolites the exhumation of the mafic rocks was dated at the age of ~ 360 Ma (Timmermann et al., 2004). The synthesis of available age data for various MLC segments (Collett et al. 2018) indicates a complex polyphase evolution of the entire area, with ages ranging from ~ 500 to ~ 350 Ma.

The T-7 borehole

One of the best studied mantle samples from the Saxothuringian part of the Bohemian Massif are samples from 450 meters T-7 borehole, located in northern Bohemia, ~ 20 km southeast of the Erzgebirge near the village Staré. The T-7 peridotite consists of interlayered garnet lherzolite, harzburgite, and phlogopite-garnet pyroxenite (Medaris et al., 2015b). Peridotite provides evidence for partial melting, cryptic metasomatism, and modal metasomatism (Medaris et al., 2015b). Metasomatised samples contain phlogopite; they are depleted in HFSE, enriched in LREE, and show highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}\sim 0.7090$. Altogether it signifies a subduction component in the metasomatising melt. Medaris et al. (2015b) suggest that metasomatism occurred at high temperatures and pressures ($1030\text{--}1150^\circ\text{C}$ and $36.1\text{--}48.0$ bar) in the garnet stability field, and was probably associated with Variscan subduction and amalgamation of the BM.

Peridotites of the Moldanubian Unit of the Bohemian Massif

The occurrence of spinel and garnet peridotites accompanied by garnet pyroxenites and eclogites in the Moldanubian is predominantly limited to the Gföhl Unit representing the uppermost tectonic unit in the Moldanubian Zone of the Bohemian Massif. It consists of HT–

HP felsic rocks (mostly gneisses and granulites) with estimated P–T conditions of 900–1000°C and 15–18 kbar (Faryad, 2009; Kusbach et al., 2015; Medaris et al., 2005), but it also hosts abundant bodies of peridotites, pyroxenites and eclogites having different sources, history and P–T–t paths (Ackerman et al., 2009a; Kusbach et al., 2015; Medaris et al., 1990, 2005, 2006; Racek et al., 2006, 2008). Based on major and trace elements composition, P–T conditions and cooling rates, three types of peridotites were identified by Medaris et al. (2005):

- Type I (the Mohelno type peridotite: peridotites from Mohelno, Biskoupky, and Lom pod Libínem): Mg–Cr spinel or garnet peridotites devoid of garnet pyroxenite or eclogite layers have depleted major element and REE compositions, yield P–T estimates (1100–1400°C) that lie in a low P/T (15–30 kbar) regime, and experienced very rapid cooling. They most likely represent the suboceanic mantle lithosphere. Spinel peridotites from Mohelno and Biskoupky could have been stable up to pressures of 21–22 kbar, and their equilibration temperature at ~1100 °C is less than that of garnet peridotites at ~ 1300 °C (Medaris et al., 2005).

- Type II (the Horní Bory type peridotite: peridotites from Bory and Sklenné): Mg–Cr to Fe–Ti spinel-garnet peridotites associated with abundant garnet pyroxenite layers with relatively high Fe contents. Their petrogenesis is closely related to subduction melt/rock reactions (Ackerman et al., 2009a). Samples lie in the low to medium P/T regions (from 20 to 50 kbar, 800 to 1200 °C) (Medaris et al., 2005).

- Type III (the Nové Dvory type peridotite: peridotites Nové Dvory, Hamry): Mg–Cr garnet peridotites with lenses/layers of eclogite and garnet pyroxenite show variable LREE depletion to enrichment, yield P–T estimates (from 30 to 60 kbar 800 to 1300 °C) in a medium P/T regime, and cooled more slowly than Type I. This type of peridotite is most likely derived from subcontinental lithosphere.

Uranium–Pb zircon dating of the Gföhl orthogneisses and granulites shows an age range of 500–390 Ma for magmatic protolith of the Gföhl unit (Friedl et al., 2004; Schulmann et al., 2005). The age of high-grade metamorphism is Carboniferous, the age of peak metamorphic conditions ranging from ~350 to 340 Ma (U–Pb) (Friedl et al., 2004; Kroner et al., 2007; Schulmann et al., 2005), the cooling ages range from ~330 to 325 Ma (Ar–Ar) (Dallmeyer et al., 1992; Fritz et al., 1996).

The Sm–Nd ages for garnet peridotites, pyroxenites and eclogites from the Gföhl Unit yield a wide range from ~377 to 324 Ma with generally large errors (Beard et al., 1992; Becker, 1997; Brueckner et al., 1991; Medaris et al., 1995). The Re depletion model ages (T_{RD}) of the Gföhl Unit peridotites range from 0.5 to 1.1 Ga (Ackerman et al., 2009a; Kochergina et al., 2015; Medaris et al., 2012), corresponding to other peridotite localities from the Bohemian Massif (Ackerman et al., 2009a; Medaris et al., 2015b), but are resolvedly younger than peridotites from lower Austria (0.1–2.1 Ga) in the southern Bohemian Massif (Becker et al., 2001).

Post-Variscan evolution and Cenozoic volcanism

Variscan consolidation of the Bohemian Massif was followed by several episodes of sedimentation and volcanism. Permo–Carboniferous post-orogenic extension led to the development of a series of sedimentary basins comprising also coal beds and voluminous volcanism of predominantly basaltic composition. Another period of intense sedimentation appeared during the Cretaceous depositing extensive marine strata mainly in the Northern Bohemia (Nadaskay et al., 2019). Tertiary sedimentation accompanied tectonic reactivation of the Bohemian Massif, in response to the plate collision of Europe and Africa associated with the Alpine Orogeny. This led to formation of present-day relief, opening of extensional basins within the Ohře Rift in the Northwest and also voluminous effusive basaltic to phonolitic volcanism (Lustrino and Wilson, 2007).

Post-Variscan volcanism within the Bohemian Massif is a part of the European Cenozoic Rift System (ECRIS) (Lustrino and Wilson, 2007), reaching from Spain to Poland. H. Stille stressed the fact that volcanism roughly follows the Variscan blocks (Fig.4; (Stille, 1964). First (and rare) signs of volcanism are documented already from the Upper Cretaceous, long before the onset of the extension regime. Cenozoic volcanic rocks in the Bohemian Massif form an arc-shaped belt which extends over 500 km from its western to its easternmost parts. The Ohře Rift (180 km long and ≤ 30 km wide) is the locus of the largest preserved amounts of volcanic rocks in the belt. The Ohře rift zone is a part of the ECRIS (Prodehl et al., 1995), which traverses the lithosphere of central and western Europe from the Mediterranean to the North Sea, over a distance of 1100 km. It is a continuous system that includes the Spanish Valencia Trough, the French Massif Central, Black Forest and Vosges, Hegau, Urach, Rhenish Massif, Vogelsberg and the Bohemian Massif (Lustrino and Wilson 2007; Ulrych and Pivec 1997). The Ohře Rift continues to the NE beyond the Elbe Fault Zone to the Sudetic Marginal Fault (SW Poland) where the Ohře Rift is marked by numerous isolated lava outcrops, which form the so-called Lubansko–Frýdlant volcanic "complex" (Puziewicz et al., 2015). The eastern segment contains mainly isolated volcanic edifices within the Labe–Odra fault system, whereas two large volcanic complexes are situated in the west: České Středohoří Volcanic Complex and Doupovské Hory Volcanic Complex.

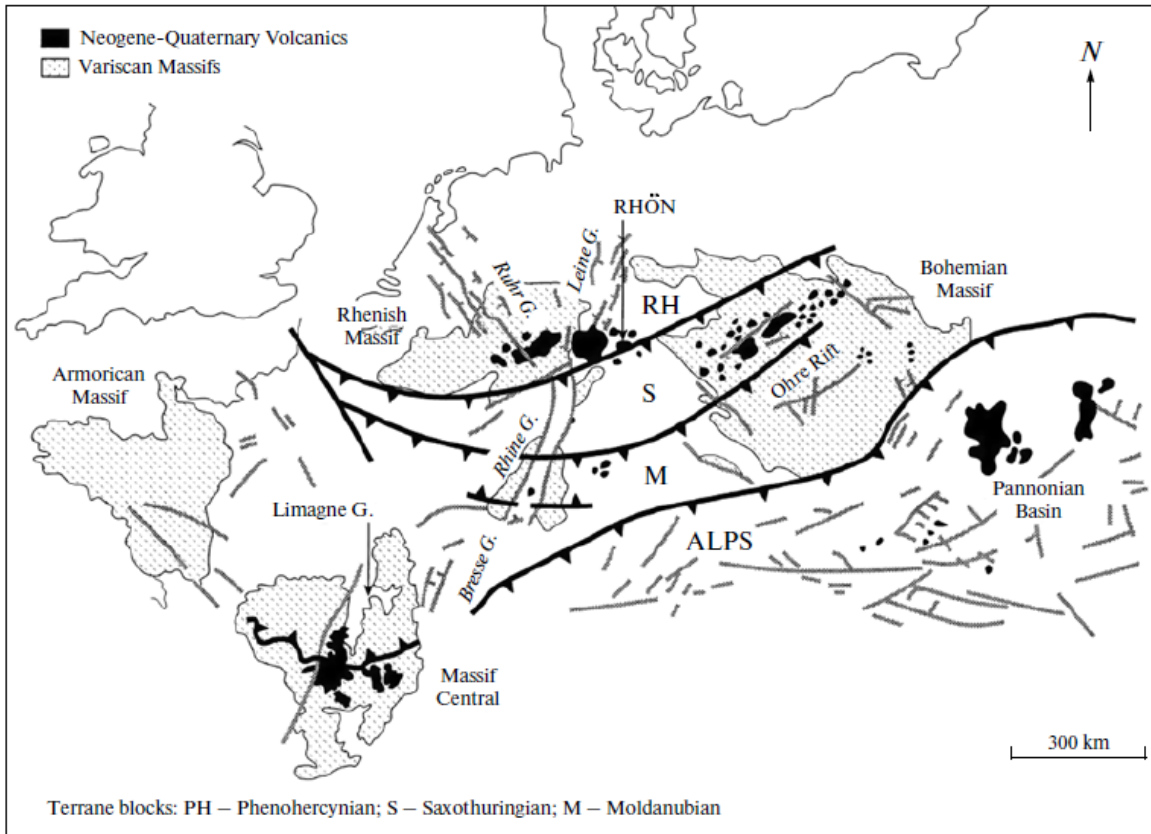


Figure 4. The of the Cenozoic basalt fields in Europe, adopted from Wilson and Downes (1991).

The thickness of the lithosphere beneath the Ohře Rift is approximately 80 km in the west and 120 km in the east (Babuška and Plomerová, 2006, 2010, 2013). Quaternary volcanism is evident in the western part of the Ohře Rift (the Vogtland and western Bohemia area) and seismic studies show that the local uplift of the Mohorovicic discontinuity beneath this area indicates a seismic discontinuity at a depth of ~50 to ~60 km (Geissler et al. 2007). The Mohorovicic discontinuity beneath Lower Silesia and Upper Lusatia is located at depths of 30–35 km (e.g; Grad et al., 2008; Majdanski et al., 2006; Puziewicz et al., 2015).

Based on ages, geochemical and mineralogical characteristics of volcanic rocks and paleo stress conditions, Ulrych et al., (2011) have defined three distinct periods of volcanic activity:

1. Pre-rift period (Late Cretaceous to Mid Eocene, 79–49 Ma), compressional stress field;
2. Syn-rift period (Mid Eocene to Mid Miocene, 42–16 Ma), tensional stress field;
3. Late-rift period (16–0.26 Ma)
 - 3.1 Mid to Late Miocene episode (16–6 Ma), compressional stress field,
 - 3.2 Late Miocene to Early Pleistocene episode (6–0.9 Ma), tensional stress field,
 - 3.3 Early to Late Pleistocene episode (0.9–0.26 Ma), compressional stress field.

Regarding the volume and number of individual volcanic bodies, the second, syn-rift period, is by far the most important. Geochemically, the Cenozoic volcanism has a typical intraplate alkaline character with prevailing basanites, tephrites and foidites followed by differentiated lavas up to phonolites and trachytes, intrusive equivalents of all these rocks and rare exotic lavas such as melilitites or polzenites.

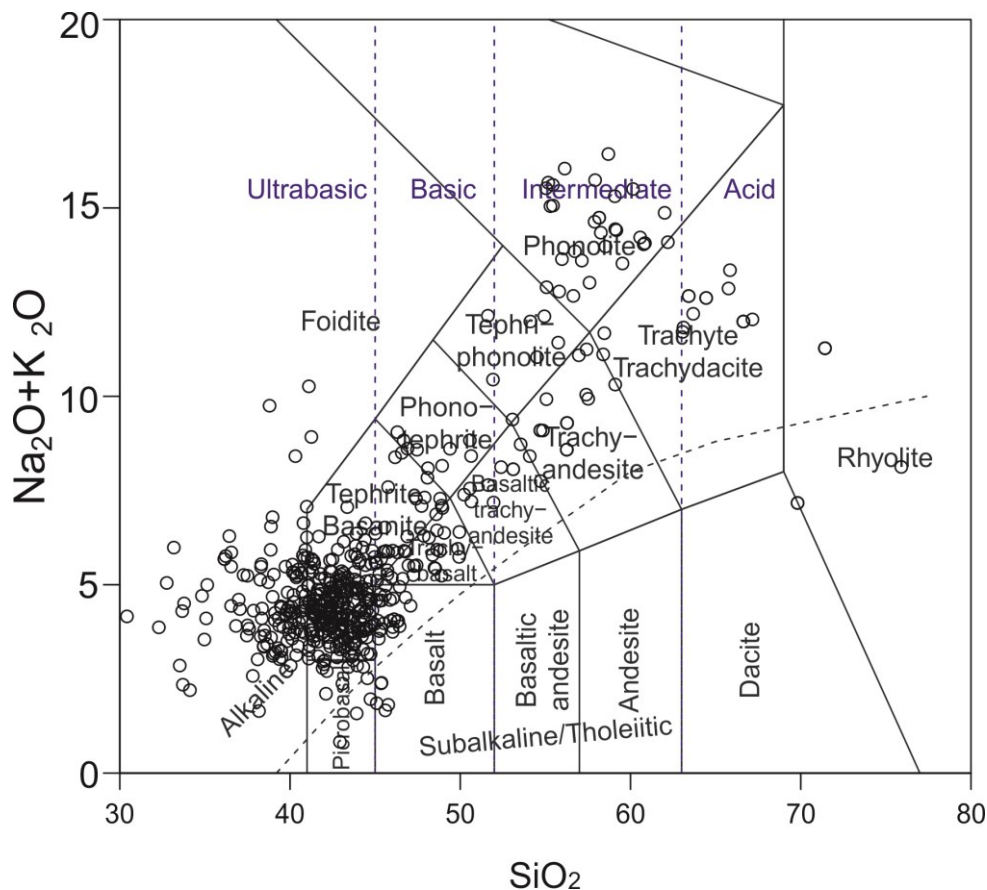


Figure 5. Total alkali vs. silica diagram (*TAS*; *Le Bas et al., 1986*) from the Bohemian Massif, data from *Lustrino and Wilson, 2007*

Many primitive lava flows contain abundant mantle xenoliths, *Ulrych and Adamovič (2004)* list further 106 individual volcanoes containing macroscopic ultramafic xenoliths. By far the most prominent and best-studied locality is the *Kozákov* volcano (*Ackerman et al., 2007*; *Christensen et al., 2001*; *Medaris et al. 2015a*). All studied xenolith suites record chemical depletion of mantle by partial melting and subsequent metasomatism by basaltic and/or alkaline silicate melts (*Ackerman et al., 2007, 2015a*; *Geissler et al., 2007*; *Matusiak-Małek et al., 2010, 2013, 2014*; *Puziewicz et al., 2011, 2015*; *Špaček et al., 2013*). Garnet peridotite xenoliths have never been found in basalts of the Bohemian Massif; however, *Špaček et al. (2013)* described rare mantle xenoliths from *Zinst* basanite lava flow (Upper Palatinate, Bavaria, Germany) containing zoned mineral clusters of fine-grained symplectites representing former garnet and its reaction products during melt–rock reactions and transport of the xenoliths to surface. *Ackerman et al. (2013)* re-examined these xenoliths and described the presence of the carbonatite metasomatism overprint, which is the subject of much debate. Based on petrographic characteristics, major and trace element compositions, as well as Sr–Nd isotopic data on monzodiorite–essexite–sodalite syenite suites and the associated dike swarms of the *Roztoky* Intrusive Complex (České středohoří), *Skála et al., (2014)* suggested variable crustal contributions and/or a heterogeneous mantle source, with indices of carbonatite-like influence although no such rocks have been reported there. Later, *Rapprich et al. (2017)* published the first unequivocal evidence of the presence of carbonatites in the Bohemian Massif. The silicified carbonatite sample was found in the *R2* drill hole (*Roztoky nad Labem, Roztoky* Intrusive Complex) at the depth of 152.9–154.8 m. The stable C–O isotopic composition ($\delta^{18}\text{O} = 7.43 \text{ ‰}$, $\delta^{13}\text{C} = -2.46 \text{ ‰}$) of this sample is clearly distinct from surrounding sedimentary rocks of the Bohemian Cretaceous Basin, which probably sourced carbonates from older

subduction events. The $^{87}\text{Sr}/^{86}\text{Sr}_{30} \sim 0.7062$ and $\epsilon\text{Nd}_{30} = -10.8$ points to an enriched mantle reservoir without known counterparts among alkaline silicate rocks from the Ohře Rift. The authors assume that this is a lithospheric mantle modified during the Variscan subduction. The Sr–Nd isotopes may indicate a continuum of enriched radiogenic isotope systematics in worldwide carbonatite occurrences.

Sr-Nd-Pb isotopic composition of mantle beneath the Bohemian Massif

Most studies of the isotopic composition of the upper mantle beneath the Bohemian Massif are based on the study of the isotopic composition of extrusive volcanic rocks (Ackerman et al., 2015b; Dostal et al., 2019 a, b, 2000; Haase and Renno, 2008; Krmíčková et al., 2020; Ulrych et al., 2011). Most of the data available in the literature come from the study of massive peridotites, while a handful of data has been collected on peridotite xenoliths. There are several reasons for this: (i) mantle xenoliths often are very small in size; (ii) peridotites usually contain small amounts of Nd, Sr and Pb, which complicates the process of separation and measurement of their isotope compositions; (iii) most isotope analyses are performed on clinopyroxene separates, so it is critically important to clarify whether the clinopyroxene is primary or secondary (metasomatism) in origin.

Much more research has been done on mantle-derived rocks (Dostal et al., 2019 a,b, 2000; Haase and Renno, 2008; Holub et al., 2003, 2012; Krmíčková et al., 2020; Ulrych et al., 2011). Deriving the isotopic composition from the composition of basalt also has several pitfalls: (1) mantle heterogeneity is smaller than the scale of the melting regions in the shallow mantle; (2) basalts are isotopically less extreme and less variable than their mantle source (Stracke, 2021).

Very often research on mantle and mantle-derived rocks focuses only on Nd isotopes because of the high probability that secondary low-temperature processes have strongly altered the

original Sr isotopic composition. Massive peridotites from the Moldanubian unit are the most thoroughly studied in the Bohemian Massif (Fig. 6, 7), and their study is connected with the exploration of the subduction of the lithospheric plates and ultrapotassic plutonic rocks. Massive peridotites and pyroxenites from this dataset show various Nd isotope compositions, and ϵNd_{337} varies from -6 to $+10$ (Fig. 6).

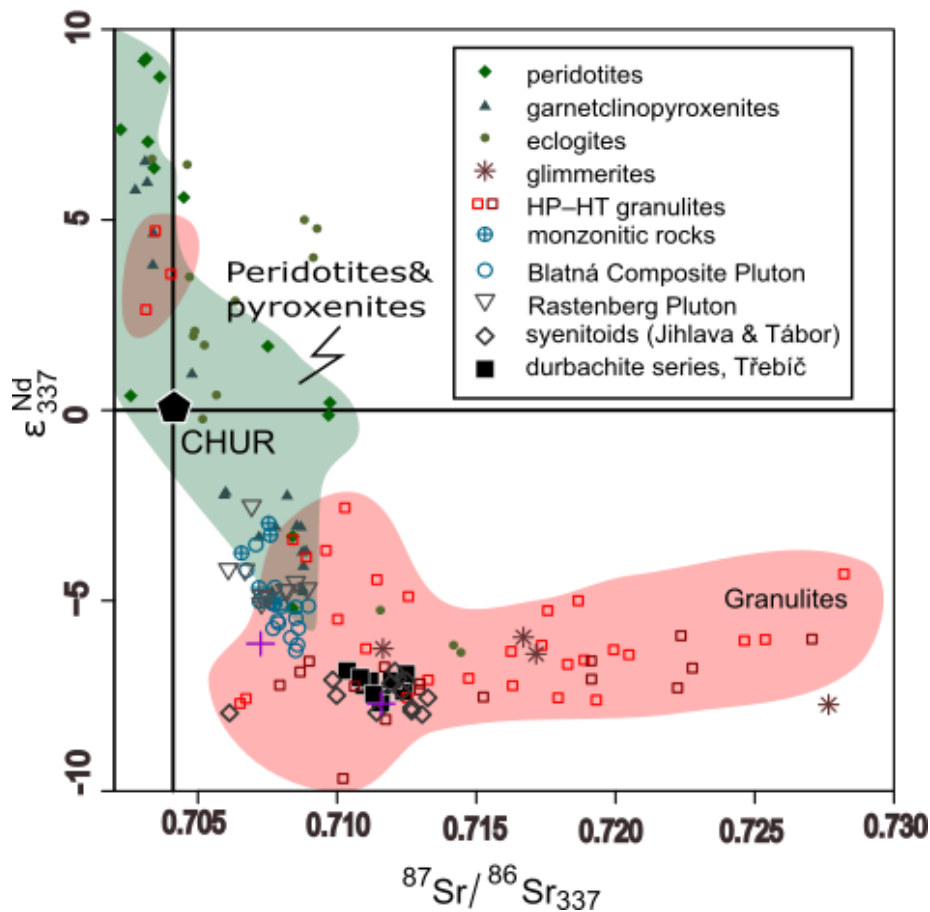


Figure 6. Modified from figure 12 c of Janoušek et al., (2020). Binary plot of $^{87}\text{Sr}/^{86}\text{Sr}_{337}$ vs. ϵNd_{337} showing the analyses from the Třebíč Pluton (Janoušek et al., 2020), Moldanubian Grt/Spl peridotites, Grt pyroxenites and eclogites (whole-rocks and Cpx: Brueckner et al. 1991; Beard et al. 1992; Becker 1996a, b; Medaris Jr. Et al. 1995, 2009; Ackerman et al. 2009; Kusbach et al. 2015), glimmerites (Becker et al. 1999), Moldanubian HP–HT granulites (Valbracht et al. 1994; Vellmer 1992; Becker 1997; Janoušek et al. 2004 and unpublished data; Kusbach et al. 2015), Blatná Composite Pluton of the CBPC (including monzonitic rocks—

Janoušek et al. 2010 and unpublished data, all recalculated to 346 Ma), Rastenberg Pluton (Gerdes et al. 2000) as well as Tábor and Jihlava syenitoids (Janoušek et al. 2019).

Figure 7 shows the Sr–Nd isotopic composition of upper mantle beneath the Bohemian Massif. Massif peridotites represent Variscan mantle, and rare peridotite xenolith data represent post-Variscan Cenozoic mantle composition. Moldanubian and Saxothuringian massive peridotites show a broad scale Sr–Nd isotope composition (Fig 7), where ϵ_{Nd_t} vary from -10 to $+11$. In contrast, samples of peridotite xenoliths have higher ϵ_{Nd_t} values ($+2$ to $+9$), similar to those in Cenozoic volcanic rocks ($+5$ to $+7$) (Dostal et al, 2019a).

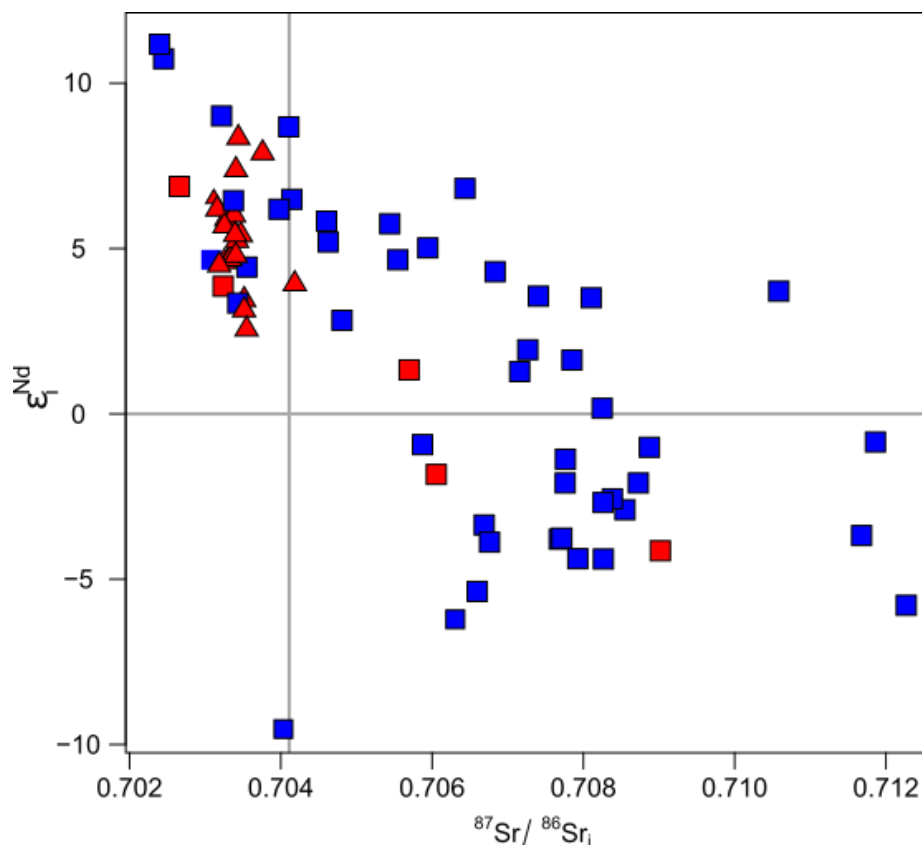


Figure 7. Sr–Nd isotopic composition of peridotites from the BM. Red symbols denote samples from Saxothuringian Unit, blue symbols denote samples from Moldanubian Unit. Peridotite xenoliths data (triangles) are from Ackerman et al., 2007, 2013, Blusztajn and Shimizu, 1994, Matusiak-Malek et al., 2014. Massif peridotites data (squares) are from Ackerman et al., 2009a, 2020, Beard et al., 1992, Kusbach et al., 2015, Medaris et al., 1995, 2009, 2013, 2015a, Svojtka

et al., 2016, Erban Kochergina unpublished data. Epsilon Nd and initial isotopic ratios are calculazted to the sample's closer ages.

Re-Os isotopic composition of peridotites from the Bohemian Massif

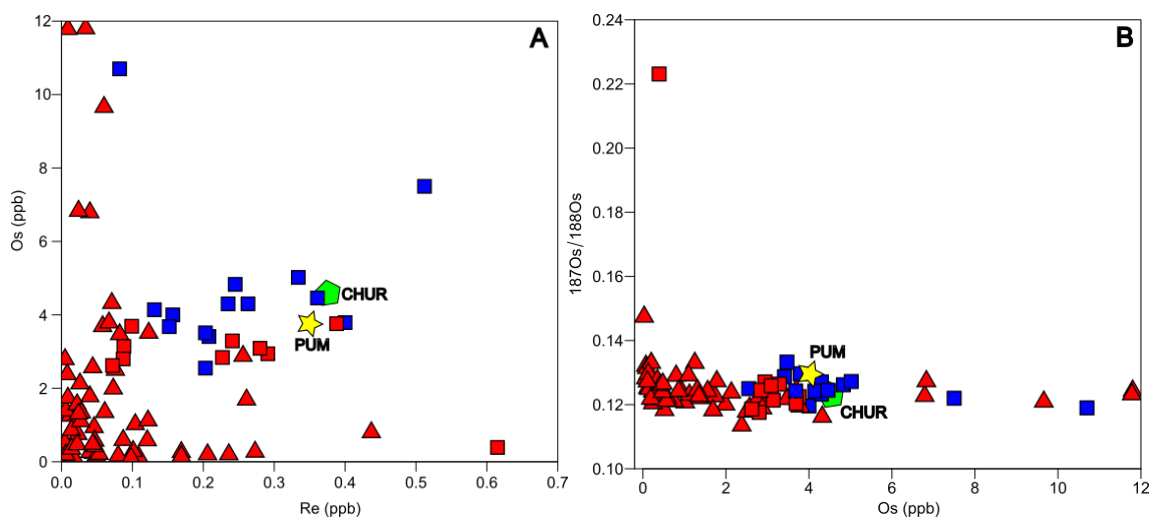
The analysis of HSE concentrations and Os isotope compositions is technically challenging, but the number of papers on Re–Os in mantle and mantle-derived rock samples of the Bohemian Massif has increased in the last decade. In Table 1 we list publications related to Re–Os isotopic composition of mantle rocks from the Bohemian Massif Massif.

Table 1. Reference list of Re–Os data from the Bohemian Massif.

Publication	Samples	Data
<i>Peridotite xenoliths</i>		
Ackerman, L., Walker, R. J., Puchtel, I. S., Pitcher, L., Jelínek, E., Strnad, L. (2009) Effects of melt percolation on highly siderophile elements and Os isotopes in subcontinental lithospheric mantle: a study of the upper mantle profile beneath Central Europe, <i>Geochimica et Cosmochimica Acta</i> , 73, 2400-2414.	Spinel peridotites	HSE, bulk-rock $^{187}\text{Os}/^{188}\text{Os}$
Kochergina, Y.V., Ackerman, L., Erban, V., Matusiak-Malek, M., Puziewicz, J., Halodová, P., Špaček, P., Trubač, J., Magna T. (2016) Rhenium-osmium isotopes in pervasively metasomatized mantle xenoliths from the Bohemian Massif and implications for the reliability of Os model ages, <i>Chemical Geology</i> , 430, 90-107.	spinel peridotites	Re-, Os-abundances, bulk-rock $^{187}\text{Os}/^{188}\text{Os}$
<i>Massive peridotites and pyroxenites</i>		

<p>Ackerman, L., Kotková, J., Čopjaková, R., Sláma, J., Trubač, J., Dillingerová, V. (2020) Petrogenesis and Lu-Hf dating of (ultra)mafic rocks from the Kutná Hora Crystalline Complex: implications for the Devonian evolution of the Bohemian Massif, <i>Journal of Petrology</i>, 61, 8, ega075</p>	<p>eclogites, pyroxenites, peridotites</p>	<p>Re-, Os- abundances, bulk-rock $^{187}\text{Os}/^{188}\text{Os}$</p>
<p>Ackerman, L., Haluzová, E., Bizimis, M., Sláma, J., Svojtka, M., Hirajima, T., Erban, V. (2016) Re-Os and Lu-Hf isotopic constraints on the formation and age of mantle pyroxenites from the Bohemian Massif, <i>Lithos</i>, 256-257, 197-210.</p>	<p>spinel and garnet pyroxenites</p>	<p>bulk-rock $^{187}\text{Os}/^{188}\text{Os}$</p>
<p>Medaris, L. G., Ackerman, L., Jelínek, E., Magna, T. (2015) Depletion and Cryptic Metasomatism of Central European Lithospheric Mantle: Evidence from Elemental and Li Isotope Compositions of Spinel Peridotite Xenoliths, Kozákov Volcano, Czech Republic, <i>International Journal of Earth Sciences</i>, 104, 1925-1956.</p>	<p>garnet peridotites</p>	<p>Re-, Os- abundances, bulk-rock $^{187}\text{Os}/^{188}\text{Os}$</p>
<p>Ackerman, L., Pitcher, L., Strnad, L., Puchtel, I. S., Jelínek, E., Walker, R. J. (2013) Highly siderophile element (HSE) geochemistry of peridotites and pyroxenites from Horní Bory: implications for HSE behaviour in subduction-related upper mantle, <i>Geochimica et Cosmochimica Acta</i>, 100, 158-175.</p>	<p>Peridotites, pyroxenites</p>	<p>HSE, bulk- rock $^{187}\text{Os}/^{188}\text{Os}$, sulphide petrography</p>

Becker, H., Carlson, R.W., Shirey, S.B. (2004). Slab-derived osmium and isotopic disequilibrium in garnet pyroxenites from a Paleozoic convergent plate margin (lower Austria). <i>Chemical Geology</i> 208, 141–156	peridotites	HSE, bulk-rock $^{187}\text{Os}/^{188}\text{Os}$
Becker, H., Shirey, S.B., Carlson, R.W. (2001). Effects of melt percolation on the Re–Os systematics of peridotites from a Paleozoic convergent plate margin. <i>Earth and Planetary Science Letters</i> 188, 107–121.	peridotites	Re-, Os-abundances and bulk-rock $^{187}\text{Os}/^{188}\text{Os}$
<i>Lamproites</i>		
Krmíček, L., Ackerman, L., Hrubý, J., Kynický, J. (2020) The highly siderophile elements and Re-Os isotope geochemistry of Variscan lamproites from the Bohemian Massif: implications for regionally dependent metasomatism of orogenic mantle, <i>Chemical Geology</i> , 532, 119290.	lamproites	HSE, bulk-rock $^{187}\text{Os}/^{188}\text{Os}$



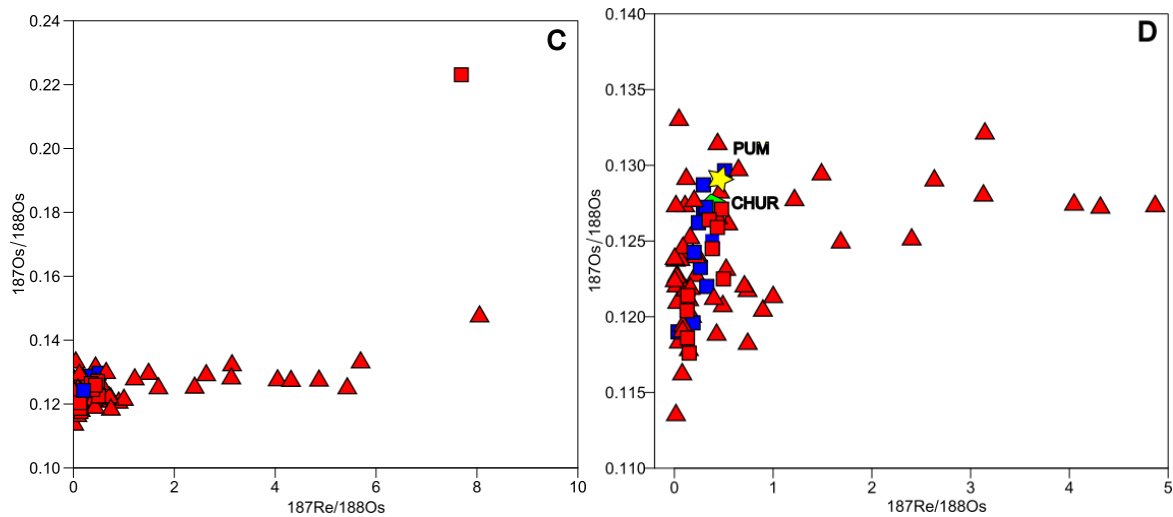


Figure 8. *Re-Os composition of mantle samples from the Bohemian Massif. Red symbols denote samples from Saxothuringian Unit, blue symbols denote samples from Moldanubian Unit. Triangles denote peridotite xenolites, squares- massive peridotites/pyroxenites. Moldanubian massif peridotites/pyroxenites from Ackerman et al., (2009a), Erban Kočergina unpublished data, Medaris et al. (2009), Saxothuringian massif peridotites from Medaris et al. 2015, Saxothuringian peridotite xenoliths from Ackerman et al., (2009b), Kochergina et al., (2016), Erban Kochergina et al. (under review). PUM - primitive upper mantle (Re, Os — Becker et al., 2006; $^{187}\text{Re}/^{188}\text{Os}$, $^{187}\text{Os}/^{188}\text{Os}$ — Meisel et al., 2001; CHUR - chondritic uniform reservoir (Fisher-Godde et al. 2010).*

Most peridotite xenoliths have low Re concentration, which can be interpreted as a result of high degrees of partial melting of the SCLM beneath the BM. Radiogenic $^{187}\text{Os}/^{188}\text{Os}$ composition of the peridotite xenoliths as well as the high $^{187}\text{Re}/^{188}\text{Os}$ ratio be caused by host-basalt contamination (Kochergina et al., 2016) or contamination by eclogites/subducted sediments (Erban Kochergina et al., under review).

Oxidation state of the mantle beneath the Bohemian Massif

The SCLM can be chemically modified by (i) partial melting and (ii) metasomatic interactions caused by infiltrating fluids or melts. The presence of newly formed minerals such as apatite, phlogopite, amphibole or secondary clinopyroxene is referred to as “modal” metasomatism. Geochemical overprinting of pre-existing mineral phases, expressed by changes in trace element and/or isotope composition rather than by formation of new phase is referred as “cryptic” metasomatism.

One of the parameters that metasomatism can change is the oxidation state of lithospheric mantle. The peridotite oxygen fugacity (fO_2) can be calculated from the olivine and spinel compositions, using the formulation of (Ballhaus et al., 1991). The oxidation state of the mantle is important for the elements sensitive to the system's redox condition (e.g., Fe, C, S, U, Re, Ir). The global mean for non-cratonic peridotites equals $\Delta FMQ -0.68$; (Foley, 2011), where $\Delta FMQ = \log fO_2(\text{sample}) - \log fO_2(\text{fayalite-magnetite-quartz})$. The average for the metasomatically overprinted peridotites worldwide is $\Delta FMQ +0.38$, 0.86 log units higher than for the unaffected peridotites ($\Delta FMQ -0.48$) (Foley, 2011).

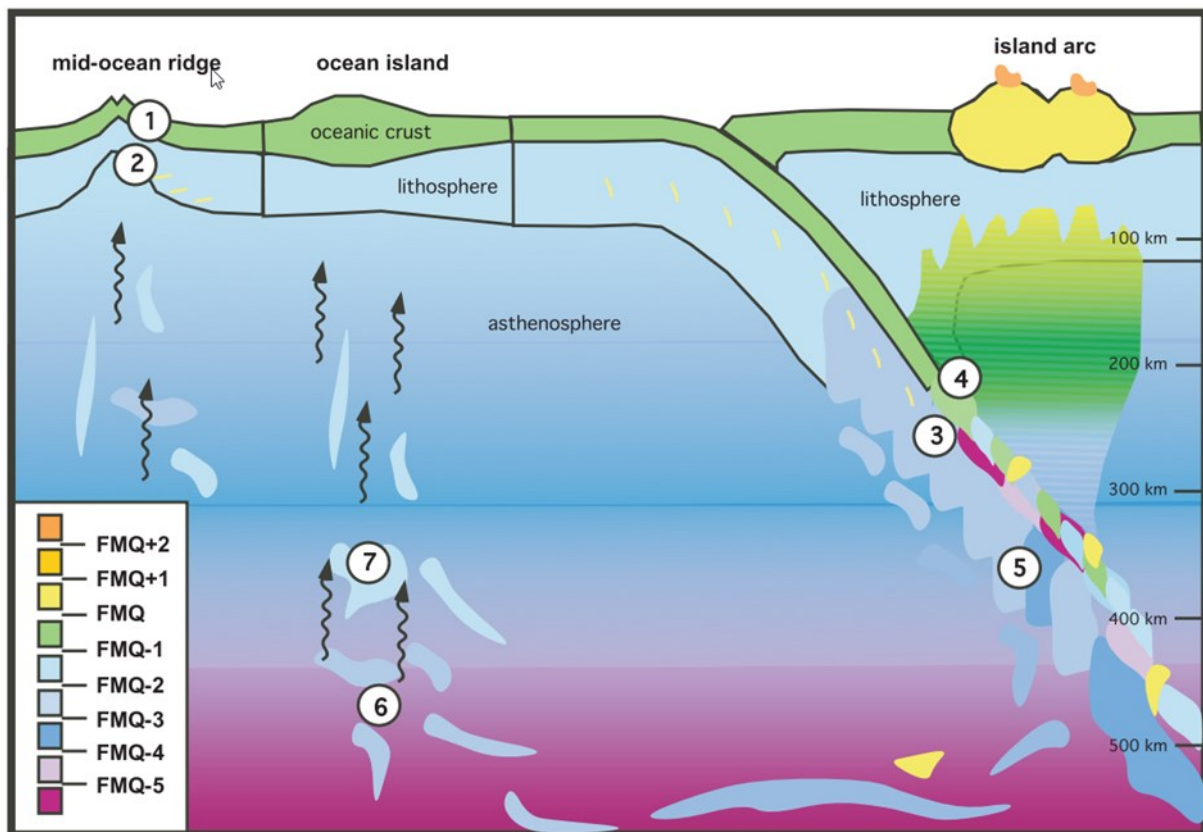


Figure 9. Adopted from Foley (2011). Schematic illustration showing the formation, alteration and subduction of oceanic crust and lithosphere relevant to the fixation of redox conditions and later redox melting. (1) MORB oxidation state is approximately FMQ -1. Hydrothermal alteration results in serpentine and magnetite formation. (2) The lower lithosphere is slightly more reduced than basalts at the surface. It is impregnated by more water-rich, low-degree melts that form pyroxenite veins. (3) Part of the water is released during subduction. Carbonates introduced at the surface may remain in the solid residue (yellow blocks). (4) Subducted sedimentary material provides Na and K that may help to depress the solidus temperature at a later stage. (5) The subducted lithosphere at depths of 150–350 km contains rocks with a mixture of redox states, but is generally more oxidized than the surrounding mantle. Redox melting is probably rare in the subduction zone environment because of the low thermal gradients. (6) Recycled blocks in the mantle at 250–400 km, derived either by peeling off from the lower oceanic lithosphere or from deep recycling of ocean crust, are mostly at fO_2

2–3 log units above the ambient mantle peridotite in the region of hydrous redox melting. Generally not oxidized enough for widespread carbonate redox melting. Water release by oxidation of methane in the lower blocks leads to melting by hydrous redox melting at higher levels (7). Many ‘plumes’ may be upward movement of small-degree melts and fluids that cause major melting beneath the lithosphere under ocean islands. They are also a contributor to basaltic melts at mid-ocean ridges. Redox melting may be concentrated in pyroxenitic material in the recycled blocks.

The positive ΔfO_2 is more typical for subduction-related peridotites, as was described by (Cao et al., 2011) in Chinese North Qilian eclogites with ΔFMQ from 0 to 2.5. Seawater-altered samples have negative ΔfO_2 with ΔFMQ -2 to ~ 0 , (Deschamps et al., 2013). Samples from the Kozákov volcano from the Bohemian Massif show lower ΔfO_2 with ΔFMQ from -0.04 to 0.65 (Ackerman et al., 2007). The elevated ΔFMQ of peridotites from NE Bavaria relative to the global average for non-cratonic peridotites (ΔFMQ -0.68 ; (Foley, 2011) could be a result of metasomatism due to subduction and/or eclogite contamination. The ΔfO_2 of samples from NE Bavaria is comparable to the oxidation state of spinel peridotites (Group A) across Massif Central, France (Uenver-Thiele et al., 2017, 2014). The negative ΔfO_2 of samples from the Bohemian Massif from this suite suggests possible seawater alteration (Fig. 10).

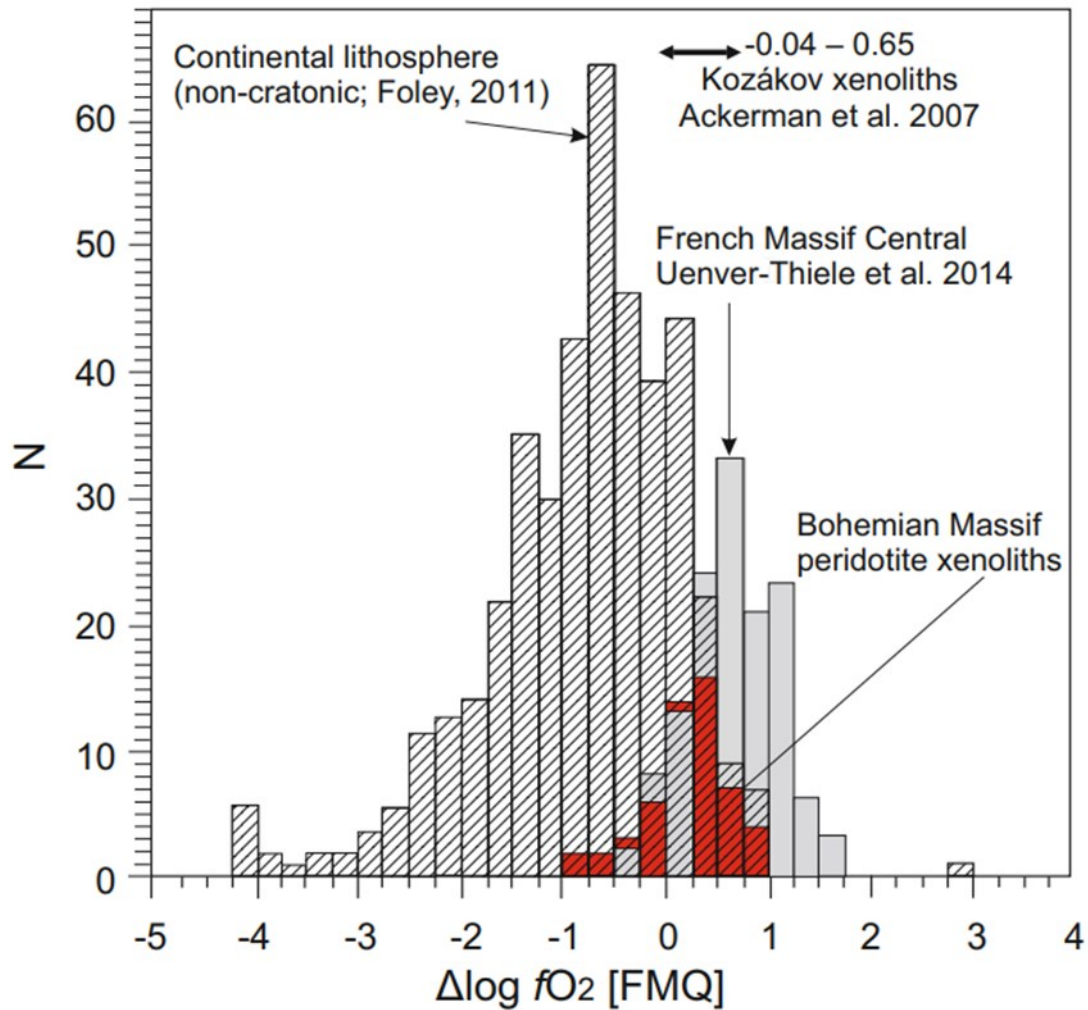


Figure 10. Histograms illustrating the ranges in $\Delta \log fO_2$ for (a) a global compilation of non-cratonic lithospheric mantle—hashed line (Foley, 2011); (b) Massif Central peridotite xenoliths—grey colour; (c) Bohemian massif peridotite xenoliths from Kozákov (Ackerman et al., 2007) and NE Bavaria (unpublished data).

Non-traditional isotopes

The advancements in instrumental methods allow to extend research to study the behaviour of non-traditional isotopes (e.g., Li, Mg, Cr, Fe, Zn, Ca and many others) also in the lithospheric mantle. Therefore, there is an ever-increasing number of publications trying to constrain the

processes taking place in the mantle using non-traditional isotopes and/or combining the results of traditional and non-traditional isotope systems. Surveys of mantle composition indirectly by using derivative melts of mantle (e.g., lamprophyres, lamproites) are becoming increasingly common.

For example, Janoušek et al., (2022) described a decoupling of mantle-compatible Mg and mantle incompatible Sr–Nd isotope systems in Variscan subduction-related plutonic rocks from the Bohemian Massif. Majority of Mg-rich studied samples show similar Mg isotopic composition as local orogenic peridotites ($\delta^{26}\text{Mg}$ from -0.53‰ to -0.33‰), close to the global mantle average (-0.25‰). (Janoušek et al 2022). Authors concluded that $\delta^{26}\text{Mg}$ of the progressively metasomatized harzburgitic mantle is mostly buffered by the mantle end-member. On the other hand, Sr–Nd–Pb are swamped by the crustally derived contribution.

Novák et al., (2022) focused on stable Cr isotope systematics in three mantle-derived domains of Central European Variscides: the serpentized peridotite body at Biskoupky, two serpentized peridotite bodies at the Kutná Hora Complex, and serpentinite from the Mariánské Lázně Complex. The authors concluded that mantle-derived rocks show homogeneous $\delta^{26}\text{Cr} \sim -0.12\text{‰}$, identical to the currently accepted mantle value. Weathering and serpentization appear to affect the Cr isotopic composition by shifting $\delta^{26}\text{Cr}$ toward heavier values, up to $+0.14\text{‰}$.

Lithium isotopes have proven to be a good tool for identifying subduction, fluid-assisted interactions and mantle contamination by sedimentary rocks (Ackerman et al., 2013). Several studies have already been published on the investigation of extremely variable potassic melts (lamprophyric to lamproitic), the result of partial melting of the orogenic mantle beneath the Bohemian Massif (Abdelfadil et al., 2014; Krmíček et al., 2020a, 2020b, 2016). The Li isotopic and elemental composition of lamprophyres largely overlap with the $\delta^7\text{Li}$ of sedimentary and metamorphic rocks representing Gondwana Upper Crust. Krmicek et al., (2020b) suggest that

this is the type of crustal material that had been subducted to metasomatize the upper mantle beneath the Bohemian Massif. Positive (up to +5.1‰) $\delta^7\text{Li}$ of lamproites from Saxo-Thuringian and Moldanubian Zones indicate that their source may have been modified by subducted oceanic lithosphere.

Chapter 3: Sample preparation, chromatographic separation and measurements of Os isotopic ratios and HSE concentrations in mantle peridotites

The whole-rock HSE concentrations and Os isotopes could be determined by isotope dilution (ID) of approximately 1–2 g of sample powder. Under oxidative conditions, Os forms OsO_4 gas, which can permeate plastics and Teflon. The Carius tube digestion method is the most suitable for Os analyses. Samples are digested in sealed Carius tubes using 4 ml concentrated HCl and 5 ml concentrated HNO_3 at $\sim 260^\circ\text{C}$ for 48 – 72 h (Shirey and Walker, 1995). The original design of the thick-walled glass tubes for sample digestion was described by Carius in 1865. Shirey and Walker (1995) suggest using borosilicate glass Carius tubes with a 20 cm long body with 1.3 cm inner diameter (i.d.) and 1.9 cm outer diameter (o.d.). These tubes have a 5 cm long sample introduction neck with 0.6 cm i.d. and 0.9 cm o.d. tubing (Fig. 11-A). During the sample loading, the lower half of the tube is immersed in ice (Fig. 11-B), where all reagents including spikes (enriched isotopes) are chilled upon addition to the tube. Chilling of the tube (i) helps to reduce the vapour pressure of the reagents and makes the sealing more reliable, and (ii) slows down the Re and Os loss from the tube due to the oxidation during loading. The Carius tubes are sealed using an oxygen-propane torch and placed in a steel jacket with a threaded cap (Fig. 11-C, D). When the samples are at a room temperature, Carius tubes in the jackets could be slowly heated in the oven. After the decomposition tubes are removed from the jackets and left in the ice, to prevent gas leakage during opening and eliminate Os loss. After opening, the ampoules are immediately transferred to a clean laboratory, followed by separation of Os and other HSE. The sample digestion is crucial for the HSE analyses, described in detail by Shirey and Walker (1995).

Osmium is extracted from the *aqua regia* solution into CCl_4 (Fig. 11-E) and then back-extracted into HBr (Fig. 11-F) (Cohen and Waters, 1996). The separation process is as follows. After

complete opening of the Carius tubes, the *aqua regia* with the decomposed material is poured into 15 ml centrifuge tubes and subsequent centrifugation. Centrifugation helps to separate the *aqua regia* with elements of interest from the undecomposed silicate matrix. After that *aqua regia* is poured into 50 ml centrifuge tubes with 2 ml of CCl_4 . After shaking and centrifugation we could observe 2 phases in 50 ml centrifuge tubes: the CCl_4 containing Os at the bottom, and *aqua regia* containing Re, Pd, Pt, Ir, and Rh above it. Subsequently, CCl_4 is extracted very carefully to pre-prepared 15 ml Teflon beakers containing 4 ml concentrated ultra-pure HBr (44 – 49%, Romil). To remove all Os from the matrix we repeat the process of mixing the sample with 2 ml of CCl_4 , shaking and centrifugation three times. Then 15 ml Teflon beakers with HBr and CCl_4 are placed on the hot plate for 12 hours where reaction occurs at a temperature of 70°C to reduce Os to HBr. The final Os fraction is purified by micro-distillation following Birck et al., (1997) (Fig. 11-G). One drop of ultra-pure HBr (0.02 ml of 8.8 N) is pipetted into the tip of a conical vial. The dried (after HBr) residue of nearly-pure Os is dissolved in one drop of 8 % m/v CrO_3 in H_2SO_4 (12N). This mixture is placed on the cap of the conical vial. The vial is then placed over the cap and sealed tightly in the upside-down position, wrapped completely in aluminium foil except for a hole at the conical end of the vial, and placed on a hot plate for at least three hours at 80°C . In this arrangement, the Os oxidizes at the expense of Cr, volatilizes and subsequently re-dissolves in the cooler HBr in the conical vial tip. The whole process leads to a complete separation of Os from Re.

Iridium, Ru, Pt, Pd and Re are separated by anion exchange chromatography using 1.6 ml of BioRad AG1-X8 resin (mesh 100–200), (Fig. 11-H). Separation is performed using PP 12 ml columns (Biorad), i.e. the same as used for Sr and REE fraction precleaning. After purification (combination of 10 M HCl, 14 M HNO_3 and MQ water) and equilibration of the columns with 1 M HCl, the Re fraction is captured using 12 ml of 6M HNO_3 .



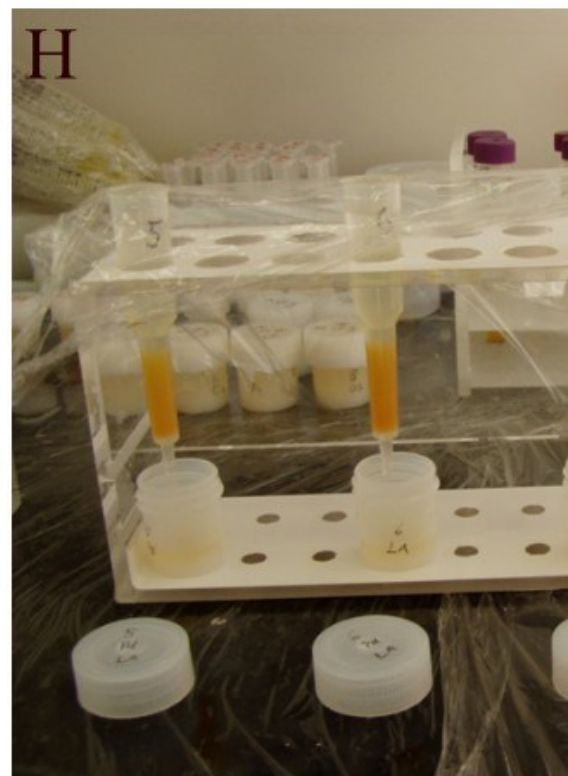
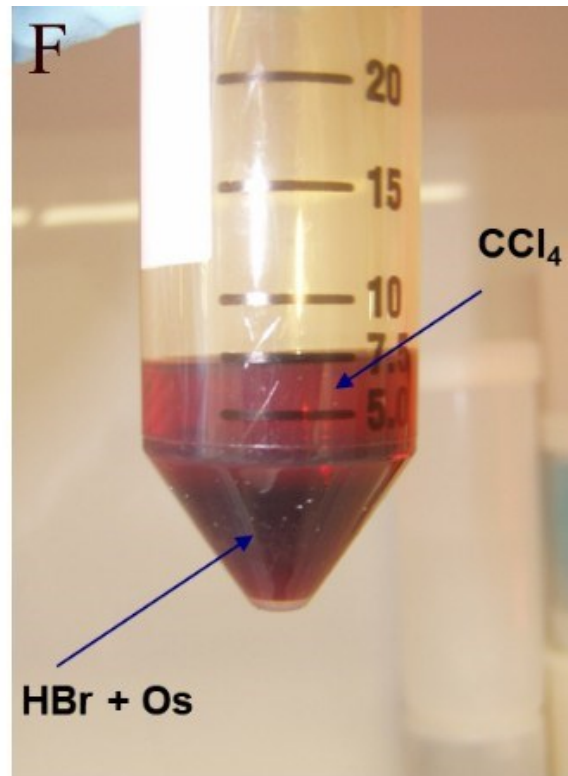
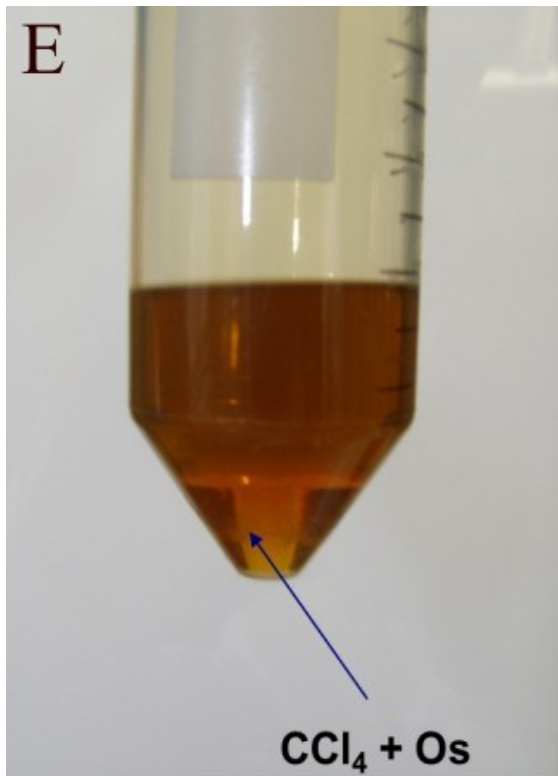


Figure 11. Re – Os separation method. A-Carius tubes used for digestion, B- chilled samples with spike and aqua regia in ice before sealing, C- the sample should be shaken vigorously after sealing to mix the acid, sample and spike for better digestion, D- Carius tubes wrapped

in Al foil and steel jacket, used for sample protection, E- 50 ml centrifuge tube with 2 ml of CCl_4 on the bottom and aqua regia on the top after centrifugation, F- HBr with Os on the bottom and HCl_4 on the top of the 50 ml centrifuge tube after centrifugation, G- micro distillation process in Savillex Teflon vial with conical interior, Os fixed in the drop of HBr at the tip of a cone. Photos were provided by Jakub Trubač.

Conclusions

Modern geochemical techniques offer significant potential for investigating the structure and processes occurring within the Earth's mantle. It is becoming increasingly necessary to analyse samples of a smaller size or those containing low concentrations of the elements under study. In the publication by Erban Kochergina et al. (2022), I present improved methods for sample digestion for isotope analysis. The particularity of these digestion methods addresses issues that can arise with varying sample matrices, ensuring complete dissolution of the sample before column chromatography. Pre-separation using cation-exchange columns is effective in addressing the challenge of dealing with samples with considerable volume, such as peridotite and serpentinite samples with relatively low Nd concentrations. The methods presented here have been validated using a large variety of isotopic standards.

Peridotite xenoliths brought to the surface by basaltic lavas attest to a variety of mantle processes, including partial melting, melt percolation or refertilization. The whole rock Re–Os concentrations and Os isotopic compositions were determined for 49 xenoliths collected from 14 localities across the northern BM (Erban Kochergina, under review; Kochergina et al., 2016). Xenoliths from the BM are characterized by a relatively small size (up to 10 cm). The majority of the studied xenoliths, with the exception of those from the western edge of the BM, display an absence of primary sulphides. In the publication Erban Kochergina et al., (under review), I focused on the study of xenoliths that were characterised by high sulfide content. It was determined that some samples contained not only secondary sulfides but also primary sulfides. In contrast with our initial expectations, the samples in question exhibit a markedly low sulfur content. Peridotites from Zinst and Teichelberg show lower S abundances (17–65 ppm) than those from Hirschentanz (76–149 ppm), in all cases well below the S abundance of the Earth's primitive upper mantle (PUM) estimated at 250 ± 50 ppm (Lorand, 1990) and only marginally overlapping the S content of the depleted mantle at 119 ppm (Salters and Stracke,

2004). The elevated sulfure concentration is found to be correlated with the presence of secondary metasomatic sulfides.

Most samples were affected by variable extent of metasomatic overprint, which is frequently accompanied by low Os concentrations. The majority of samples demonstrated Os concentrations below 1 ppb. Rhenium concentrations in the whole suite are below the primitive mantle value. A subset of samples shows evidence for Re addition from host basaltic rocks, consistent with the presence of abundant melt pockets with secondary sulphides.

The $^{187}\text{Os}/^{188}\text{Os}$ ratios range from 0.1135 to 0.1474 and cannot be directly related to individual mantle domains, implying the inability of more recent tectonic events to reset the original Os isotopic systematics. Several samples showed high radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios. Unlike the samples from Krzeniow (Poland) with elevated $^{187}\text{Os}/^{188}\text{Os}$ and high $^{187}\text{Re}/^{188}\text{Os}$ (up to 5.69), where we assume contamination by basalt, the samples from the western edge of the BM represent mantle contaminated by eclogite or sediment during subduction. For these samples, we have ruled out possible contamination by the surrounding basalt because its isotopic composition (0.1330–0.1370) is lower than that of the studied peridotites (0.1314–0.1474).

The calculated mantle extraction ages (T_{MA}) range from ~0.1 to 2.1 Ga, whereas future ages obtained for nine samples indicate metasomatic overprints.

The assumption of $\text{Re}/\text{Os} = 0$ for calculating T_{RD} may under-estimate the true Re/Os of the sample prior to a metasomatic event. We therefore performed a second-step calculation of T_{RDII} by considering the most depleted sample of the suite (13BR3) to be representative of the composition of the regional depleted mantle. It follows that the T_{RDII} ages of samples from this study (<0.1–2.0 Ga) may represent a more realistic estimate of the age of mantle melting than T_{RD} (<0.1–1.6 Ga). The main maximum in the T_{RDII} histogram (~0.45–0.6 Ga) corresponds to Cadomian basement of the Saxothuringian Unit. There is no significant evidence that a major

mantle depletion episode took place during Variscan orogeny or later phases of the Bohemian Massif evolution.

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APPENDIX

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