03. Stable and radiogenic isotope geochemistry: development and applications

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Swiss Society of Mineralogy and Petrology (SSMP)

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3.1 Molybdenum isotope evidence for recycling of metasomatized forearc mantle at the Tonga subduction zone


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Molybdenum isotopes have emerged as novel tracers of metal recycling in subduction zones. Open questions remain as to whether or to what extent different subducted lithologies, such as oceanic crust vs. marine sediments, contribute to the Mo isotope signature and hence exert different controls on the terrestrial Mo cycle. To address this, we investigate the Mo isotope signature of the input and output parameters at the Tonga subduction zone factory: basalts and basaltic andesites from the Tonga islands Late, Tofua, Kao and Ata together with pelagic sediments and altered oceanic crust (AOC) samples at DSDP site 595/596 from the subducting Pacific plate. These are accompanied by Mo isotope analyses of exhumed subducted sediments and mafic oceanic crust from the Western Alps and Alpine Corsica, which allow to study the fate of subduction input during prograde metamorphism.

Tonga arc lavas have higher Mo/Ce and extend to higher $\delta^{98/95}$Mo$_{SRM3134}$ compared to the mantle, which covariate with fluid indices, such as Ba/Th and Ce/Pb. This suggests the addition of an isotopically heavy, slab-derived fluid to the Tonga subarc mantle. DSDP site 595/596 samples show that manganese oxide control Mo concentrations (up to 100 ppm) and Mo isotope signature (lower and higher compared to mantle) of pelagic sediments. Pelagic Mn-rich metasediments, covering a wide range of peak metamorphic conditions, display extremely low Mo content and low $\delta^{98/95}$Mo$_{SRM3134}$ (down to $-1.5 \text{‰}$) indicating a loss of isotopically heavy Mo already in the forearc. Also, Mo signatures in mafic eclogites are within the range of AOC, yet extending towards lower $\delta^{98/95}$Mo$_{SRM3134}$, likely due to isotope fractionation during fluid related Mo mobilization and incorporation of light Mo into residual rutile. Our data thus documents prominent loss of isotopically heavy Mo upon early subduction metamorphism. Moreover, when prograde rutile crystallizes, it fixes the largest fraction of Mo in subducting rocks. Consequently, it is very unlikely that slab Mo represents the fluid-mobile Mo source responsible for observed higher Mo/Ce and $\delta^{98/95}$Mo$_{SRM3134}$ in Tonga arc lavas compared to the mantle. We suggest that increasing Mo/Ce along with higher $\delta^{98/95}$Mo$_{SRM3134}$ in Tonga arc lavas is a result of fluid-induced Mo mobilization during the early stages of subduction into the forearc mantle. Subsequent erosion and subduction of this metasomatized forearc mantle into the subarc regions is a plausible alternative recycling process. This is supported by positive covariations of Mo/Ce and $\delta^{98/95}$Mo$_{SRM3134}$ with other fluid mobile elements that are commonly enriched in metasomatized forearc mantle, such as As, Sb and Cs. We propose that this kind of multi-stage recycling of metasomatized forearc mantle is an important process in Mo recycling.
3.2
Titanium isotope heterogeneity in the Earth’s mantle:
a case study of the Horoman peridotite massif

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Titanium isotopes provide a novel tool to trace igneous processes such as magmatic differentiation. The Ti isotope composition of terrestrial rocks varies by up to ~2.1 ‰ in δ⁴⁹Ti (the per mil deviation of ⁴⁹Ti/⁴⁷Ti from the OL-Ti standard) (Deng et al., 2019; Mandl, 2018). Primitive basalts and komatiites define a narrow δ⁴⁹Ti range (e.g. Greber et al., 2017; Millet et al., 2016), suggesting a homogeneous mantle source. While magmatic differentiation significantly fractionates Ti isotopes towards heavy compositions (e.g. Millet et al., 2016), so far, Ti isotope fractionation during partial melting of the mantle is considered to be negligible. In contrast to mantle-derived magmas, peridotites display more variable Ti isotope compositions (Mandl, 2018). To constrain the origin of the observed small-scale mantle heterogeneity, we measured the Ti isotope composition of orogenic peridotites from the Horoman massif (Japan) comprising i) fertile lherzolites, ii) depleted harzburgites and iii) metasomatically overprinted peridotites. In addition, we present Ti isotope data of magmatic derivatives of a metasomatised mantle, i.e. ultrapotassic rocks.

The Ti isotope compositions of the Horoman peridotites range from -1.523 ± 0.029 to 0.547 ± 0.015 ‰ (2SD), with a total variation of 2.07 ‰, and include values that are both lighter and heavier than basalts. Heavy Ti isotope compositions are akin to continental crust and likely result from metasomatism of the mantle wedge above the Hidaka subduction zone. In such a scenario, isotopically heavy Ti was inherited from the recycled sediments. In addition, Ti isotope fractionation during mobilisation from the slab may have further contributed to the heavy signature. High δ⁴⁹Ti values (0.114 ± 0.040 to 0.290 ± 0.030 ‰, 2SD) are also found in ultrapotassic rocks, which originate from a mantle source modified by recycled crustal material. Conversely, highly depleted peridotites have extremely light Ti isotope compositions, potentially due to fractionation during high-degree melting of the mantle.

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3.3

A new procedure to investigate in situ Fe isotope compositions in micro-pyrites using Hyperion Radio Frequency source on IMS 1280 HR2.

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Iron isotope compositions of pyrites are considered as a good proxy for past global/local redox conditions and to track microbial activity (Johnson et al., 2020). In situ studies (laser ablation, LA-ICP-MS or secondary ion mass spectrometer, SIMS) of sedimentary pyrites have evidenced inter- and intra-grain Fe isotopic variabilities (e.g. Marin-Carbonne et al., 2014; Whitehouse et al., 2007; Yoshiya et al., 2015). However, the investigation of these micrometer scale variabilities in <20µm pyrites was restricted to the primary beam size. Since 2015, the emergence of a new plasma ion source (Hyperion Radio-Frequency source) enables high spatial resolution measurements by increasing 10 times the beam density compared to the previous 16O Duoplasmatron source (Liu et al., 2018). We developed a new analytical protocol to measure high spatial resolution and high precision Fe isotope compositions applied on micro-pyrites in Archean and Permian-Triassic sediments. This method was calibrated on two SIMS-Cameca 1280HR2 instruments at CRPG-CNRS (France) and at SwissSIMS (Switzerland). A gaussian 3nA primary beam was focused in 3µm, which allows the analysis of micrometric minerals with an analytical precision between 0.25‰ and 0.30‰ (±2σ), similar to the one obtained with the Duoplasmatron for a beam size of 10 to 15 µm. We assessed possible analytical effects induced by either topography or crystal orientation and none of them were identified. This new method opens a robust analytical way for searching micrometer scale Fe isotopic variations in natural samples and for better understanding the oceanic cryptic Fe cycle.

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3.4 First constraints on the role of Hadean components during the formation of Paleoarchean TTGs from India

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Constraints on the chemical evolution of the early Earth are conventionally obtained using geochemical and isotopic compositions of Archean rocks. In the absence of a known rock record beyond ca. 4 Ga, insights into earlier differentiation processes can be obtained either from remnants of Hadean rocks (i.e., detrital zircons and their inclusions) or extinct radionuclides. Using the short-lived $^{146}$Sm-$^{142}$Nd isotope system, signatures for the existence of both chemically enriched and depleted Hadean reservoirs have been identified from mantle-derived rocks in some of the oldest Archean cratons (e.g., Caro et al., 2003; O'Neil et al., 2008). Model ages based on these findings indicate that crust-mantle differentiation started as early as 4.4 Ga (Morino et al., 2017) and proceeded within a tectonic regime that allowed preservation of primordial heterogeneities until at least 2.7 Ga (Debaille et al., 2013). Apart from these insights, little is known about the exact role these primordial reservoirs played during the formation of the Archean continents, which are dominated by the tonalite-trondhjemite-granodiorite (TTG) suite.

In order to better constrain the proportion of reworked Hadean material in the Archean record, rocks from the well-characterized Paleoarchean Bastar and Singhbhum cratons in central and eastern India were investigated using coupled $^{146}$Sm-$^{142}$Nd isotope systematics. A comparison of first results for TTGs from the two terranes reveals no $^{142}$Nd anomalies in Bastar, while the TTGs from Singhbhum define a trend in $\mu^{142}$Nd vs $\varepsilon^{143}$Nd (long-lived) isotope space that extends from the primitive mantle composition up to $\mu^{142}$Nd $\approx +6$ ppm and $\varepsilon^{143}$Nd $= +5$.

Despite the near-synchronous formation of the Paleoarchean TTG crust in the two cratons, between ca. 3.5 to 3.3 Ga, these results demonstrate that their protoliths sampled distinct reservoirs, which may be indicative of Archean mantle heterogeneity. The observed $\mu^{142}$Nd vs $\varepsilon^{143}$Nd correlation among Singhbhum TTGs can be explained by a two-stage model in which a reservoir first differentiated from a primitive mantle at 4.2 $\pm$0.1 Ga and evolved until differentiation of the granitoids. Alternatively, the Nd isotopic signatures may have been inherited from a pre-existing mafic/ultramafic crust extracted from a Hadean depleted reservoir. Consistent with this observation, Eo- to Paleoarchean enclaves of mafic and ultramafic composition from the Singhbhum craton yield clearly resolved positive anomalies ($\mu^{142}$Nd up to ca. $+6 \pm 3$ ppm). Both scenarios thus require an additional crust-mantle differentiation event, postdating the one that produced the $^{142}$Nd anomalies identified so far in studies of Eoarchean terranes by 200-300 Myr (Morino et al., 2017).

REFERENCES
3.5

Trace elements and Sr isotopes in hydrothermal vein epidote from the Albula area

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Hydrothermal veins can be used to investigate the hydration of the granitic continental crust. A common vein-filling mineral is epidote \([\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) - \text{Ca}_2\text{Al}_2\text{Fe}^{2+}_3\text{Si}_3\text{O}_{12}(\text{OH})]\), whose complex crystalline structure incorporates large amounts of a wide range of trace elements from the mineralizing fluid. While Rb concentrations are negligible in epidote, contents of the highly fluid-mobile Sr can reach a few wt%, allowing for the measurement of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios. In combination with trace elements and U-Pb data, Sr isotopes can be used to determine the origin and pathways of the vein-forming fluid.

Epidote-bearing hydrothermal veins are widespread in the Albula area (eastern Swiss Alps). We distinguish epidote-bearing veins based on their host rock: 1) V1: veins related to the greenschist-facies Eo-alpine metamorphism hosted by gneissic meta-granodiorite and 2) V2: veins hosted by cataclastic meta-granodiorite. In both cases, the host rock – deformed to different extents – is the Albula Granite, a Variscan to post-Variscan granodiorite that intruded the basement of the Err nappe of the Lower Austroalpine domain at the present-day Albula Pass. A third type of epidote-bearing veins (V3) crosscuts the Triassic meta-sediments in the area.

We report LA-ICP-MS data of trace elements measured in epidote of all vein types recognized at Albula Pass. TIMS data of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios are presented for epidote of V1 veins. All vein types consist of epidote ± quartz. Epidote in V1 veins is also locally associated with minor (< 1 %) chlorite and albite. Trace element data confirm the petrographic distinction into V1, V2 and V3 epidote-bearing veins, as highlighted by the respective data clusters in diagrams comparing light elements (B and Li), fluid-mobile (Sr and Pb) and immobile ones (Y and REE), and transition metals (Cr and V). This might be related to different sources of V1, V2 and V3 vein-forming fluids, and also reflect successive fluid pulses. REE patterns of all samples are clearly different than the LREE-enriched patterns typical of granitic rocks and of the REE-rich member of the epidote group (allanite). This suggests a source outside the Albula Granite for the epidote-forming fluids of all vein types.

The low \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios of 0.713086-0.713835 (± 0.003-0.005 ‰) suggest that the V1 fluid was not in equilibrium with the Rb-rich abundant feldspars and rare micas of the host granodiorite. The initial \(^{207}\text{Pb}/^{206}\text{Pb}\) ratio of 0.8334 ± 0.0043 obtained from U-Pb dating indicates no enrichment of the V1 fluid in uranogenic Pb. Sr and Pb isotopic data from V1 epidote therefore support the hypothesis that the presented trace element and isotopic signatures were acquired by the V1 fluid outside the host Albula Granite from a Rb- and U-poor but Sr- and Pb-rich lithology, such as carbonatic or marly sediments.
3.6
New isotope constraints on the Mg oceanic budget point to cryptic modern dolomite formation

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The oceanic magnesium budget is important to our understanding of Earth’s carbon cycle, because similar processes control both (e.g., weathering, volcanism, and carbonate precipitation). However, dolomite sedimentation and low-temperature hydrothermal circulation remain enigmatic oceanic Mg sinks. In recent years, magnesium isotopes ($^{26}$Mg) have provided new constraints on the Mg cycle, but the lack of data for the low-temperature hydrothermal isotope fractionation has hindered this approach. Here we present new $^{26}$Mg data for low-temperature hydrothermal fluids, demonstrating preferential $^{26}$Mg incorporation into the oceanic crust, on average by $\varepsilon_{\text{solid-fluid}} \approx 1.6\%$. These new data, along with the constant seawater $^{26}$Mg over the past ~20 Myr, require a significant dolomitic sink (estimated to be 1.5–2.9 Tmol yr$^{-1}$; 40–60% of the oceanic Mg outputs). This estimate argues strongly against the conventional view that dolomite formation has been negligible in the Neogene and points to the existence of significant hidden dolomite formation.

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3.7 Mo isotope fractionation induced by magma differentiation along the Kos Plateau Tuff (Aegean arc)

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Differentiation of primitive basaltic magmas is a fundamental process contributing to the production of intermediate to silica-rich magmas. Changing pressure, temperature, and $f_O^2$ conditions induce fractional crystallization of hydrous magmas on their pathway through the crust. As a consequence thereof magmatic cumulates derived from aggregation of exsolved mineral phases (e.g., amphiboles) segregate while the melt evolves along the liquid line of descent (LLD). Associated changes in bulk chemistry, bonding environments and shifts in coordination state cause mass-dependant isotope fractionation.

Modern arc crust formation records source contamination (e.g., slab derived fluids), as well as secondary mixing and assimilation processes that may blur geochemical fingerprints of the source magmas. Heavy stable isotopes are increasingly applied to investigate and distinguish between fluid dominated (source contamination) versus fractional crystallization dominated processes of the derivative magmas. Molybdenum isotopes have recently been explored to trace both, variable source components and magmatic isotope fractionation, in order to better constrain calc-alkaline magma genesis and element recycling in subduction zones.

We will present an extended Mo isotopic dataset on bulk rock samples and mineral separates of the magmatic differentiation suite of the Kos plateau Tuff along the Aegean volcanic arc. Our detailed dataset sheds light on key players that fractionate Mo isotopes as a consequence of magma differentiation prior to eruption and offers new insight into reported discrepancies between heavy and light $\delta^{100/95}$Mo$_{NIST}$ reservoir formation of emerging modern arc crust.
3.8 Rapid, continuous scans of radiocarbon archives by laser ablation


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While Accelerator Mass Spectrometry (AMS) enables rapid and high-precision measurements of radiocarbon (\(^{14}\)C) in carbonate archives (e.g. speleothems, corals), the conventional sampling techniques require labor-intensive and time-consuming sample preparation. Using laser ablation (LA) to liberate CO\(_2\)/CO directly from solid samples reduces not only the preparation time significantly, but allows data acquisition along a continuous path.

The LA-AMS setup installed in 2013 at ETH Zurich (Welte, et al. 2016) has recently been improved in order to achieve higher signal intensities and consequently higher measurement precision as well as simpler instrumental maintenance. By redesigning the sample cell and reducing the optical path length of the laser, the fluence on the sample could be increased from previously 1-2 J cm\(^{-2}\) to now 8-23 J cm\(^{-2}\), leading to more efficient generation of gaseous carbon from CaCO\(_3\). The laser spot size was reduced from 110 \(\mu\)m x 680 \(\mu\)m to 75 \(\mu\)m x 140 \(\mu\)m, improving the overall spatial resolution of the setup. The background level of the method has been determined to have a F\(^{14}\)C of 0.009 ± 0.002 and reaches a precision of less than 1% for modern samples.

The capabilities of this world-wide unique system will be presented by means of several carbonate samples including stalagmites and corals. The suitability of the technique for other matrices, such as wood and oxalates will be discussed and first results of a novel data-evaluation scheme including the use of suitable smoothing filters will be presented.

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Variations of Fe isotope compositions of ophiolite-derived rocks within the Variscan allochthonous domain

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The Variscan belt results from the Devonian to Carboniferous collision of Laurussia (formed of Laurentia, Baltica and Avalonia) and Gondwana. The Variscan belt in Western and Central Europe is divided into different domains: (1) the Saxothuringian Zone (external domain; Gondwana zones with Cadomian imprint), (2) the Teplá-Barrandian Zone and Moldanubian Zone (internal domain; Allochthon), and (3) the Brunia-Moravo-Silesian Zone, localised at the margin of Baltica during the early Palaeozoic (e.g. Franke et al., 2017). The Allochthonous domain is mainly composed of superposed nappes derived from peri-Gondwana regions.

Devonian ophiolite-derived rocks form a discontinuous structure within the Allochthonous domain and can be followed from the Sudetes to the Iberic Peninsula. The basic and ultrabasic magmatic precursors were emplaced along the northern Gondwana margin during the Cambro-Ordovician rifting associated with the opening of the Rheic Ocean (von Raumer et al., 2015). Different models explain the Cambro-ordovician ophiolite-derived rocks as the remnants of: 1) a narrow ocean between Gondwana and Armorica ("Galicia-South Brittany-Moldanubian" or "Medio-European" ocean; e.g. Matte, 2001); 2) an intra-continental back-arc basin related to a late-Cambrian active margin setting along the northern margin of Gondwana (von Raumer et al., 2015); or 3) the oriental branch of the Rheic ocean (Stephan et al., 2019).

This study compares the Fe isotope compositions of various Variscan localities, in order to investigate 1) if Fe isotopes can allow determining common magmatic signatures between the ultrabasic and basic rocks from various localities of the Allochthonous domain, and 2) if and how Fe isotopes have fractionated in basic rocks during the pre-Variscan Cambro-Ordovician magmatism, and during the Variscan subduction and collision.

Fe isotopes were analysed in a series of Alpine eclogites (Aiguilles Rouges Massif; Adula nappe: San Bernardino and Trescolmen) derived from a Variscan protolith. The first set of data shows MORB-like δ⁵⁶Fe values of +0.06 to +0.18‰ for most eclogites. Besides, two eclogite samples from the Adula nappe have δ⁵⁶Fe values of +0.20 and +0.32‰, that are heavier than MORB and typical for OIB (see El Korh et al., 2017 and references therein for a review).

These results are comparable to the data obtained for the high-pressure metabasites of the Ile de Groix (Armorican Massif; +0.16 to +0.33‰; El Korh et al., 2017) and for the low-pressure Limousin ophiolite-derived rocks (French Massif Central; +0.03 to +0.18‰; El Korh et al., submitted). By contrast, lighter δ⁵⁶Fe were measured in eclogites from the Münchberg Massif (Saxothuringian zone, Bohemian Massif Germany) (−0.068 to +0.014‰; Pohlner et al., 2019).

The heterogeneous iron isotope signatures within the Moldanubian zone and Bohemian Massif suggest: 1) different magmatic events along the northern margin of Gondwana during the Cambro-Ordovician rifting; 2) different tectonic settings and/or mantle sources for the magmatic emplacement of the basic and ultrabasic protoliths; and/or 3) different metamorphic overprints during the Varican and Alpine orogenies.

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Mid-temperature (350 – 550°C) thermochronology using the apatite U-Pb method

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Thermochronological measurements have been frequently used since the 1960’s to provide a quantitative understanding of many geological processes, such as the exhumation of the crust, and the cooling histories and preservation potential of mineralised deposits. All thermochronological methods are founded on the assumption that temperature is the dominant process that drives the open system behaviour of isotopes, which is exploited via the mathematics of diffusion to generate plausible time(t)-Temperature(T) solutions. The 40Ar/39Ar method was reported as a potential mid-temperature thermochronometer by Lovera et al. (1989), although numerous studies (e.g. Villa and Hanchar, 2013; Popov et al., 2020) have invalidated the initial assumptions, and have shown that Ar loss is dominantly a function of the fluid interaction history. Alternatively, analyses using the U-Pb system in accessory phases (apatite, titanite, rutile; e.g. Paul et al., 2018, 2019) suggest these have the potential to yield accurate and continuous t-T paths, and thus that the dominant process that drove Pb-loss was thermally driven diffusion, in some cases.

We present U-Pb bulk grain (ID-TIMS) and intra grain (LA-MC-ICP-MS) U-Pb data from apatites to evaluate the accuracy of thermal history solutions obtained from U and Pb isotopic data. Apatites have been extracted from Triassic, peraluminous leucosomes from the Andes of Ecuador and Colombia, where the geological history since 260 Ma has been tightly constrained (Spikings et al., 2015). Thermal history (t-T) solutions are obtained by inverting the U-Pb dates and grain sizes using the Pb-in-apatite diffusion parameters of Cherniak at al. (1991). The accuracy of the t-T solutions is assessed by comparison with the already well-established tectonic history of the Northern Andes. Inversion of bulk (ID-TIMS) U-Pb dates of single apatites with a range of grain sizes yields sensible t-T solutions in some cases, confirming the utility of U-Pb thermochronology (Cochrane et al., 2014; Paul et al., 2018). However, a majority of ID-TIMS dates yield scattered plots when compared to grain size, which is not predicted by volume diffusion with a constant set of diffusion parameters and a homogeneous parent isotope distribution (Paul et al., 2019). We investigate the cause of scatter by examining the effects of U zonation, compositional variation, metatamically and petrological boundary conditions. Element mapping using LA-ICPMS reveals a highly heterogeneous distribution of U, and the mode of zonation can be highly varied within a single leucosome (e.g. oscillatory, core enriched and rim enriched). Inversion of in-situ U-Pb dates acquired along core-rim transects yields accurate t-T solutions when U zonation is accounted for. We conclude that U zonation has a significant influence on bulk apatite U-Pb dates when the rocks reside for a significant amount of time in the Apatite Pb Partial Retention Zone (APbPRZ; Paul et al., 2019). Additional analyses of numerous igneous apatites suggest that U zonation is ubiquitous, and thus ID-TIMS dates are generally not amenable for accurate thermochronology, and an in-situ method is required. A majority of apatites also have zoned concentrations of Mn, Fe and REE, although their influence on the activation energy for Pb diffusion appears to be minor. Mn may be an exception, and preliminary data suggests that apatites with ~3000ppm Mn may have activation energies that are ~5% higher than Mn concentrations of ~500ppm. Metamictization appears to have no influence on Pb diffusion in apatite, presumably due to the high temperatures (350 – 350°C) of the Apatite Pb Partial Retention Zone. We created a MATLAB script to examine the influence of mineral boundary conditions by modelling the ingrowth and volume diffusion of Pb isotopes in apatite inclusions (nullifying the assumption of Dodson, 1973). Results show that Pb-in-apatite closure temperatures can be 100°C higher for partition coefficients of 1 compared to 0.3. These results indicate the importance of understanding the influence of the crystal petrological environment when constructing t-T solutions. Finally, we have applied computational inversion to synthetic apatite U-Pb dates obtained from common, natural thermal history paths, to assess the impact of accuracy of common Pb corrections on the accuracy of thermal history solutions.

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P 3.3

Constraints on the Double Spike method: Comparison of different calibration methods based on theoretical calculations and experimental Ti-Isotope analysis.

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For high-precision isotope analysis of elements with four or more stable isotopes, the double spike technique is the method of choice to accurately correct for mass fractionation induced by sample preparation and analyzes. It is therefore crucial to investigate the potential, accuracy and limitations of this powerful tool in Isotope Geochemistry. In order to produce accurate results this method strongly depends on the quality of the Double spike calibration. In this study we compare different established calibration methods that use the direct measurements of the double spike composition (e.g. Millet & Dauphas, 2014; Nanne et al., 2017) or its substitution by a unit vector (Rudge et al., 2009) for the Ti isotope system. Furthermore, we investigate the potential use of several Ti standards with artificially fractionated isotope compositions via ion exchange chromatography as a calibration tool. With theoretical predictions based on a mathematica skript and complementary experimental data obtained by multicolonlector inductively coupled plasma mass spectrometry (MC-ICP-MS) analysis of Ti-Isotopes, we will examine which of the three methods yields the best results for the double spike calibration.

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