Calcite U-Pb dating of altered ancient oceanic crust in the North Pamir, Central Asia

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Abstract. The North Pamir, part of the western syntax of the India-Asia collision zone, preserves remnants of a poorly understood Paleozoic intra-oceanic subduction zone. To constrain the age of this ancient ocean floor, we analyzed calcite phases in vesicular basalt and basaltic volcanic breccia with U-Pb geochronology using laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS). Dating of radial-fibrous to equant sparly calcite yielded three meaningful Visean-Serpukhovian ages. REE + Y data reveal that the basaltic host rock of the calcite and oxidizing seawater are major sources of trace elements during calcite precipitation. U-Pb ages seem to be independent of REE + Y concentrations. Our results demonstrate the potential of calcite dating to constrain the age of ancient ocean floors. We challenge the hypothesis that a continuous early Paleozoic Kunlun Terrane extended from northern Tibet into the North Pamir.

Summary. Calcite is frequently formed during alteration processes in the basaltic, uppermost layer of juvenile oceanic crust. Weathered oceanic basalts are hard to date with conventional radiometric methods. We show in a case study from the North Pamir, Central Asia, that calcite U-Pb age data—supported by geochemistry and petrological microscopy—has the potential to date sufficiently old oceanic basalts, if the time span between basalt extrusion and latest calcite precipitation (~25 Ma) is considered.

1 Introduction

Constraining the timing of formation of ocean floor basalts is significant to develop models of various tectonic processes given the voluminous occurrence of ocean floor basalts in ophiolites, sections of ocean plate stratigraphy and exhumed subduction complexes, and remnants of island-arcs and oceanic plateaus in ancient convergent margins. However, mafic volcanic rocks, in which zircons are sparse, are challenging to date with radiometric methods. 40Ar/39Ar dating of separated phenocrysts or groundmass is frequently attempted (e.g., Waagstein et al., 2002; Heath et al., 2018). However, ocean floor alteration (OFA) often disturbs K-Ar isotopic compositions by secondary potassium gain (Staudigel et al., 2013) or loss (Pringle, 2013), making 40Ar/39Ar
dating more successful in providing high precision age data for fresh volcanic rocks but problematic if samples
were affected by OFA.

Calcite veins and calcite-filled amygdules are commonly observed in submarine volcanic rocks. Studies show
that calcite formation occurs during OFA by alkalinity-generating reactions, shortly after the eruption of lavas
(e.g. Coogan and Gillis, 2018; Spivack and Staudigel, 1994; Coogan et al., 2016), driven by the infiltrating
seawater and heat extraction from the oceanic crust. Such processes dominantly occur within ~25 Ma after rock
consolidation (Coogan and Gillis, 2018). Therefore, dating the calcite phases in ocean floor volcanic rocks has
the potential to constrain the timing of rock formation.

Calcite LA-ICP-MS U-Pb dating has been applied to a range of geological problems such as dating of
deformation (e.g., Nuriel et al., 2019), diagenesis, and sedimentation (e.g., Godeau et al., 2018), especially since
several international reference materials were established (Roberts et al., 2017; Rasbury et al., 2021). We present
the first study on calcite LA-ICP-MS U-Pb dating of Paleozoic ocean crust. Several types of calcite were dated
from a volcanic sequence in the Carboniferous North Pamir arc (Figure 1, e.g., Bazhenov and Burtman (1982)).
Calcite U-Pb ages are consistent with regional geological data and existing radiometric ages from correlative
volcanic units. With additional petrographic and geochemical data, our work sheds light on the potential of
calcite U-Pb dating on ancient ocean floor volcanics and allows us to place better constraints on tectonic models
of the Pamir.

2 Geological background and motivation

The North Pamir magmatic arc formed during the subduction of the Paleo-Tethys oceanic lithosphere (e.g.,
Bazhenov and Burtman, 1982). It can be traced from the Chinese NE Pamir along strike into the Darvaz
mountain range in the Gorno-Badakhshan province of Tadjikistan and further south into the Badakhshan
province of Afghanistan (Figure 1). Outcrops in the Chinese Oytag and Gez valleys have been correlated with
the South Kunlun Terrane in the north Tibetan West Kunlun by connecting ophiolitic sequences along the
proposed Oytag–Kudi suture (e.g., Mattern et al., 1996). However, existing age dating reveals dissimilarities of
key rock units in this suture in the West Kunlun compared to the North Pamir. The West Kunlun Kudi suture
closed in the Silurian, as interpreted from zircon and monazite LA-ICP-MS U-Pb dating of amphibolite-facies
rock (Zhang et al., 2018a). In contrast, the North Pamir magmatic arc, to which the mafic volcanic rocks and
associated plagiogranites in the Oytag and Gez valleys are assigned, seems to be much younger. It consists of
poorly dated mafic and intermediate volcanics, associated volcaniclastic rocks, and subordinate cherts. A series
of leucogranites and granodiorites, that intruded the arc between 360 and 314 Ma, has been dated recently (Jiang
et al., 2008; Kang et al., 2015; Rembe et al., 2021; Zhang et al., 2006). The Oytag suture itself is a small outcrop
of altered ultramafic rocks in the Gez valley (Jiang, 1992). To date, no age data was presented for those rocks.

The green color of the North Pamir arc volcanic rocks, however, implies thorough spilitization, making them
unsuitable for \(^{40}\text{Ar}^{39}\text{Ar}\) dating. We propose that abundant calcite associated with spilitic basalts are a product of
OFA, and that calcite ages can serve as a constraint on the formation of ocean floor. Specifically, they provide
the possibility of directly dating OFA as a proxy for the emplacement of mafic volcanic rocks.

We conducted calcite dating based on detailed petrographic and geochemical observations in order to provide
age constraints on the North Pamir arc volcanic rocks and test its correlation with the West Kunlun. For that
purpose, we sampled 4 specimens at 3 different localities in the Chinese Qimgan valley (Figure 1). Samples 17NP436a and 17NP436b are from the same locality (sample location at N 39° 18’ 27”, E 74° 51’ 32”) and represent redeposited brecciated mafic volcanic rock with interstitial calcite cement that was formed during an early phase of brecciation (Figure 2a–c). Samples 15NP236 (sample location at N 39° 18’ 18”, E 74° 51’ 30”) and 15NP233 (sample location at N 39° 18’ 16”, E 74° 51’ 47”) are from two localities with amygdaloid-basalt, where 15NP236 was taken from a pillow basalt. We investigated amygdules filled exclusively with calcite (Figure 2e, f).

3 Methods

3.1 Petrological microscopy, cathodoluminescence microscopy (CL) and X-ray fluorescence microscopy (XFM)

Petrographic thin sections of all samples were studied with conventional light microscopy and cathodoluminescence microscopy (CL). Polished thin sections of all samples were prepared. CL imaging was done using an Olympus BXFM-F microscope equipped with a Lumic hot-cathode electron source and a highly sensitive Olympus XC10 camera at the University of Potsdam. We recognized well preserved primary features (see Sect. 4.1), which were then identified on the rock chips prepared for laser ablation. Detailed sample petrography raises the chances for robust, meaningful ages, as emphasized recently by Roberts et al. (2021). High resolution reflected light images indicate the position of ablation spots in Appendix A.

Additionally, we examined sample 17NP436a with scanning X-ray fluorescence microscopy (XFM). A polished slab parallel to the surface examined with LA-ICP-MS was prepared from the same rock chip. XFM maps were collected at the XFM beamline at the Australian Synchrotron (Howard et al., 2020). The incident excitation energy was 18.5 keV. Pixel size and dwell time per pixel are indicated in the figures in Appendix B.

3.2 Laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS)

Rock samples were processed at the School of Earth and Environmental Sciences, The University of Queensland. Samples 15NP233 and 15NP236 were cut and mounted to round mounts with one-inch diameters (Figure 2e, f), for samples 17NP436a and 17NP436b we used polished rock chips (Figure 2b, c). Samples mounts were polished with standard polishing procedures and finished with a 0.25 micrometer diamond suspension.

LA-ICP-MS U-Pb dating and geochemical analysis was performed at The University of Queensland following methods in Su et al. (2020) and Yang et al. (2021). Laser ablation was achieved using an ASI RESOlution 193 ArF nm excimer laser system. Following evacuation of air, He carrier gas was introduced into the laser cell at a flow rate of 0.35 l/min. 0.005 l/min of N₂ gas was also introduced to the laser cell to enhance the measurement sensitivity. The gas mixture was then introduced into the plasma torch of a Thermo iCAP RQ quadruple ICP-MS with 1.06 l/min Ar nebulizer gas. No reaction gas was employed. The laser was run with a 100 µm diameter round spot at 10 Hz, with a measured instrument laser-fluence (laser pulse energy per unit area) of 2.5 J/cm². For U-Pb dating, each spot had 8 s of background, 20 s of data acquisition, and 15 s of wash out. For trace elemental analysis, each spot had 6 s of background, 25 s of data acquisition, and 10 s of wash out. Prior to data
acquisition, ICP-MS signals were optimized during tuning. For our session, ~950 kcps of $^{238}$U counts and ~0.22 of $^{206}$Pb/$^{208}$U were achieved for measuring NIST612 glass using line scans of 3 µm/s, 10 Hz, 50 µm round laser pit, and 3 J/cm$^2$.

U-Pb isotopes for geochronology ($^{206}$Pb, $^{207}$Pb, $^{208}$Pb, $^{232}$Th, and $^{238}$U) were measured with the following dwell times, $^{206}$Pb (0.025 s), $^{207}$Pb (0.055 s), $^{208}$Pb (0.005), $^{232}$Th (0.005 s), and $^{238}$U (0.02 s). Both glass standard NIST614 and matrix-matched calcite standards were measured, bracketing unknown spots. NIST614 glass was used for correction of $^{207}$Pb/$^{206}$Pb fractionation and instrument drift in the $^{238}$U/$^{206}$Pb ratio (Woodhead and Hergt, 2001). Raw data were processed using Iolite software v3.64 (Paton et al., 2011). After the initial correction, a matrix-matched calcite reference material of known age was used for further correction of matrix-related mass bias impacting the measured $^{238}$U/$^{206}$Pb ratios, following the approach described elsewhere, as summarized in Yang et al. (2021). We used a cross-calibrated in-house calcite reference material AHX-1D and PTKD-2 and an international reference material WC-1 (Roberts et al., 2017) in our laser ablation session. The accuracy of unknown spots is checked by measuring WC-1 and PTKD-2 as monitoring standards. For WC-1 we obtained an age of 251 ± 1 Ma (2σ), consistent with the recommended age of 254.4 ± 6.4 Ma (Roberts et al., 2017). The in-house PTKD-2 standard gave an age of 154 ± 3 (2σ), consistent with our recommended age of 153.7 ± 1.7 Ma (2σ), calibrated by isotope dilution. Therefore, we note that the accuracy for our measurements can be calculated as 1.5 % for WC-1 and 0.3 % for PTKD-2. Uncertainty propagation was done according to the principles defined by Horstwood et al. (2016). We present two age uncertainties as ±α/β (2σ), where α is without propagated systematic uncertainties, and β is with propagated systematic uncertainties. We propagated our analytical errors (typically <5% (2σ)) on $^{238}$U/$^{206}$Pb ratios by incorporating $^{238}$U decay constant error, long-term variance of the reference materials $^{238}$U/$^{206}$Pb ratios in the lab, and the analytical error of the monitor standard. This resulted in a total propagated systematic uncertainty of 4.6% (2σ) into the analytical error.

Trace elemental analysis was conducted in the same ablation areas as the U-Pb spots but without overlapping with U-Pb spots. Prior to data acquisition, ICP-MS signals were optimized during tuning while the oxide production rate was controlled to be as low as possible. Our session was run when Th/Th ratio was <0.002 for measuring NIST612 glass using line scans of 3 µm/s, 10 Hz, 50 µm round laser pit, and 3 J/cm$^2$. $^{43}$Ca was measured as an internal standard. Data reduction was conducted using the Iolite software v3.64 (Paton et al., 2011) with the Trace Element data reduction scheme. All reported concentrations were after international standardization using Ca (Ca = 40.1 %).

4 Results

4.1 Petrography and calcite occurrences

In the Chinese Qimgan valley, basaltic to andesitic volcanic rocks contain large amounts of calcite in amygdules, in between single lava pillows, and volcanic breccia layers (Figure 2 and Appendix A). Two samples, 15NP233 and 15NP236, are altered amygdaloid-basalts with published geochemistry (Supplementary Table 1, Rembe et al., 2021). Samples 17NP436a and 17NP436b are from a volcanic breccia, rich in calcite cement fragments and calcite-overgrown, angular volcanic rock fragments. The samples were collected from 3 localities, whereby 17NP436a and 17NP436b are from the same locality.
Amygdules in samples 15NP233 and -236 show one generation of spary or botryoidal calcite with typical sweeping extinction under cross-polarized light (Figure 3a, b). Sample 15NP233 has vesicles up to 5 mm in diameter filled exclusively with calcite. Sample 15NP236 has much smaller vesicles, around 1 mm in diameter, filled with either calcite or zeolite. Both samples show high “Loss on Ignition” (LOI) values and anomalous major element values for whole rock geochemistry, accounting for high secondary, volatile rich mineral content (Supplementary Table 1). No fractures or veins cut across amygdules in these samples.

In samples 17NP436a and b, fracture and pore space in basaltic rock fragments shows multiple calcite generations (Figure 3c, d). Most calcite formed prior to deposition of the breccia. Specifically, isolated cement fragments are fully embedded in a fine-grained matrix (e.g., in sample 17NP436b). They may have formed in fractures of a volcanic edifice and were redeposited after its collapse. In some cases, calcite cement is still attached to the basaltic clasts and a series of 4 consecutive mineralization phases can be recognized (numbered 1 to 4 in Figure 3d, schematically depicted in Figure 3e-g). Some of the volcanic rock fragments show an early, hydrothermal clay layer (Figure 3c and phase 1 in Figure 3d). The rock fragments—or if present, the clay coatings—are overgrown by a first generation of radial-fibrous calcite. Larger voids are filled with late, equant calcite (phase 2 and 3 in Figure 3d). The early, medium to coarse spary calcite cements (2 and 3 in Figure 3d) and the matrix are crosscut by fine-spary calcite filled fissures (4 in Figure 3d) The fissures are distinguishable from the spary calcite in transmitted and reflected light and were avoided during ablation.

Cathodoluminescence microscopy imaging reveals fibrous botryoidal textures of the vesicle filling calcite of samples 15NP233 and 15NP236. They usually show no luminescence or a zonation of dull-yellowish and non-luminescent fringes (Figure 4a,b). Bright yellow luminescence irregularly occurs along the rims of the vesicles. Secondary fractures, crosscutting the vesicular fabric were not observed. We prepared slides from the rock chips analyzed with LA-ICP-MS of samples 17NP436a and 17NP436b (Figure 4c-f). The basalt breccia samples 17NP436a and 17NP436b show non-luminescent to dull yellow luminescent spary calcite. Bright yellow luminescence was observed along hairline subzones, which are interpreted as grain boundaries. The largely non-luminescent spary calcite fragments stand out against the yellow luminescent altered volcaniclastic matrix. Matrix and spary calcite fragments are intersected by bright-yellow, late-stage calcite (phase 4 in Figure 3d) filled fractures (e.g., Figure 4c). They are well visible in transmitted and reflected light and were avoided during ablation.

In order to better understand calcite phases, we further study 17NP436a with high-resolution synchrotron X-ray fluorescence mapping (Howard et al., 2020), following methods described in Vanghi et al. (2019). Sr maps show elevated concentration for the phase 2 and 3 calcite and much lower content in fissure filling calcite phase 4, suggesting different geochemical regimes (Appendix B).

4.2 LA-ICP-MS U-Pb Dating

Four samples from three field sites were prepared for analysis. We obtained data from 839 single spots from 18 laser ablation areas (Appendix A), 3–6 ablation areas per sample (Figure 5, Figure 6), data table in Supplementary Table 2. For age calculation we used the IsoplottR program (Vermeech, 2018) version 3.5 running in R version 3.6.0. Ages are calculated for individual ablation areas by linear regression in a Tera
Wasserburg plot. From the 839 single spot ablation data only 16 had to be omitted due to U content below detection limit.

4.2.1 17NP436a

Six ablation areas were targeted in basalt breccia sample 17NP436a (Figure 5a-f). They are placed on isolated coarse-sparitic, equant calcite cement fragments (areas A, C, D, E) and coarse-sparitic radial-fibrous to equant calcite cement still connected to their basaltic substratum (areas B, F). Propagated errors are generally small (~5%) and MSWD values are low to moderate. Area A is an isolated fragment of coarse-sparty cement (Figure 4c) and yielded a lower intercept age of 331 ± 2/15 Ma (MSWD = 1.7) calculated from 119 single spot data points. Eighty-two ablation spots yielded a lower intercept age of 324 ± 4/16 Ma (MSWD = 2.3) for Area B. Sixty-four ablation spots gave a lower intercept age of 308 ± 7/16 Ma (MSWD = 2.5) for Area C. Area D gave a similar lower intercept age of 307 ± 6/15 Ma (MSWD = 4.2, n = 40). Area E gave a rather low age of 298 ± 10/17 Ma with an elevated MSWD of 4.7, defined by 37 ablation spots. Sixty-one ablation spots on area F (Figure 4f) defined a lower intercept age of 304 ± 7/16 Ma (MSWD = 3.5).

4.2.2 17NP436b

In basalt breccia sample 17NP436b, 4 ablation areas were targeted (Figure 5g-j). They are placed on isolated coarse-sparitic, equant calcite cement fragments. Propagated errors are generally small (~5%) and MSWD values are low to moderate. Area A (Figure 4d) yielded a lower intercept age of 339 ± 6/17 Ma (MSWD = 1) defined by 38 ablation spots. Area B yielded a lower intercept age of 322 ± 3/15 Ma (MSWD = 4.8) defined by 47 ablation spots. Twenty-nine laser spots on area C (Figure 4e) yielded a lower intercept age of 328 ± 4/16 Ma (MSWD = 1.7). Twenty-three ablation spots gave a lower intercept age of 316 ± 9/17 Ma (MSWD = 2.4).

4.2.3 15NP236

Five ablation areas were targeted in vesicular basalt sample 15NP236 (Figure 6a-e). Each ablation area represents one calcite filled vesicle. Due to the small vesicles, only few spots were placed per area. Propagated errors are moderate to large (6-36%) and MSWD values are low to moderate. Area A yielded a lower intercept age of 351 ± 29/33 Ma (MSWD = 2.2) defined by 14 single ablation spots. Fifteen ablation spots on area B gave a lower intercept age of 306 ± 64/65 Ma with a low MSWD of 1.4. Ten spots on area C gave an age of 350 ± 15/22 Ma (MSWD = 2.2). Area D yielded a very young age of 206 ± 73/73 Ma (MSWD = 0.84) defined by 10 ablation spots. A similarly young age of 272 ± 57/58 Ma (MSWD = 4.3) was defined by 18 laser spots for area E.

4.2.4 15NP233

Three ablation areas were placed on calcite in three filled vesicles in sample 15NP233 (Figure 6f-h). Propagated errors are small (~5%) and MSWD values are moderate. Area A gave an age of 324 ± 4/16 Ma (MSWD = 2.4) defined by 60 ablation spots. Ninety-nine ablation spots on area B yielded a similar age of 327 ± 5/16 Ma (MSWD = 2.5). Fifty-eight ablation spots on area C gave a slightly higher age of 337 ± 7/17 Ma (MSWD = 9.8).
4.3 LA-ICP-MS Geochemistry

For each laser ablation area, we measured Ca, Mn, Sr, Zr, Ba and REE + Y geochemical data (a total of 380 single spot analyses) using LA-ICP-MS (data in Supplementary Table 3). Calcite REE patterns normalized to chondrite (Boynton, 1984) are mostly flat to slightly “U” shaped (Appendix C). REE content of the vesicle-hosted calcite is higher (61 ppm mean total REE content in sample 15NP233, 59 ppm in sample 15NP236) compared to the breccia calcite cement (8 ppm in 17NP436a and 12 ppm in 17NP436b). LREE are enriched over MREE (LaN/SmN) and negatively correlate with enriched MREE over HREE values (DyN/YbN) in all samples. The vesicle filling calcite shows both positive and negative Ce/Ce* values between 0.75 and 1.41, the breccia calcite cement shows negative values between 0.18 and 0.92. Negative Ce anomalies are usually associated with oxidizing conditions producing Ce4+ instead of Ce3+ (e.g., Alibo and Nozaki, 1999). We observe positive to slightly negative Gd anomalies (GdGd* = GdN/sqrt(EuN×TbN); Figure 7a). Positive Yb/HoN anomalies are common (Figure 7b). Negative Ce/Ce* and Eu/Eu* anomalies together with higher Gd/Gd* and Yb/HoN in the calcite cement of the volcanic breccia are interpreted to reflect a stronger influence of infiltrating seawater (Ce/Ce* = CeN/sqrt(LaN×PrN); Eu/Eu* = EuN/sqrt(SmN×TbN)).

5 Discussion

5.1 Calcite age data and its significance

In newly formed submarine volcanic rocks, calcite formation marks the phase of alkalinity-generating reactions. Alkalinity describes the acid neutralizing capacity by formation of alkali and alkaline earth metal ion species during rock weathering (e.g., Spivack and Staudigel, 1994). This is crucial for interpreting OFA calcite U-Pb ages, implying that these ages should be no older than the “true” rock formation age. High temperature hydrothermal alteration is also a common phenomenon for submarine volcanic environments. This is, in contrast, restricted to discrete zones, such as veins, shear zones, and hydrothermal upflow zones (Harlov and Austrheim, 2013; Honnorez, 2003). It changes the mineral composition of the volcanic host rock completely, such that primary igneous textures are obliterated (e.g. epidosites, Honnorez, 2003). Such rock types must be avoided as they are unlikely to produce ages related to OFA. By dating isolated calcite, far from hydrothermal upflow zones, we determine the age range of OFA occurring shortly after rock consolidation. This gives a first order minimum age estimate for ocean floor formation, if not the actual age of formation. This must not be mistaken with the radiometric ages of the volcanic rock itself (e.g., ages of zircon U-Pb dating).

We observed one botryoidal to sparry calcite phase in the vesicular basalts (Figure 3a, Figure 4a, b). Four stages of mineralization were observed in the basaltic breccia: (1) hydrothermal clay, (2) radial-fibrous calcite, (3) coarse equant-sparry calcite and (4) fissure filling calcite crosscutting the entire fabric (Figure 3b-g). The presence of radial-fibrous and sparry, equant calcite crystals is typical of continuous calcite precipitation in a porous substratum (Gonzalez and Carapente, 1992). In a first phase, radial-fibrous calcite grows along the wall of the voids and successively reduces the porosity of the substratum, thereby hindering fluid flow. This reduces the calcite precipitation rate and the amount of nucleation, leading to larger, equant calcite crystals in the center of the voids. This model can be adopted for a first calcite phase (2 and 3 in Figure 3d). As the radial-fibrous and the equant calcite growth reflects one process, both calcite phases were chosen for ablation. The phase 4 fine-sparitic
filled fissures are interpreted to reflect a later tectonic event, expressed by differential stress, pressure solution and reprecipitation of calcite in open joints (Figure 3g).

To explore the geologic significance of our age data, we first applied a very conservative filter closely examining ages with MSWD < 2 and 2σ-error < 10%, as their isotope ratios are most likely measured from single homogenous domains (e.g., Lan et al. (2022)). Subsequently, we also discuss all ages for a full view on the age spectrum.

Our samples show generally a low variability in ablation area ages and initial lead values (Figure 5 and Figure 6). 2σ-errors with propagated systematic uncertainties are typically around 5%, only vesicular basalt sample 15NP236 shows high 2σ-errors. However, multi-stage calcite formation and possible subsequent alteration lead to MSWD values above two and elevated age errors. Primary calcite was eventually affected by alteration and crystallization of calcite with deviant chemistry even within microscopically identified seemingly homogenous phases (e.g. phase 2 and 3 in Figure 3d). This is made visible by CL imaging of yellow-luminescent subzones penetrating non-luminescent phase 2 and 3 calcite zones in Figure 4f. However, ablation spots placed on ablation areas 17NP436a_A, 17NP436b_A and 17NP436b_C largely fall on what we interpret as phase 2 and 3, radial-fibrous to equant calcite, characterized by non-luminescence (Figure 4c-e). The lower intercept ages are 331 ± 2/15 Ma (17NP436a_A), 339 ± 6/17 Ma (17NP436b_A) and 328 ± 4/16 Ma (17NP436b_C), which consistently constraints the volcanic breccia to the Visean-Serpukhovian boundary. All ablation areas of basalt breccia samples 17NP436a and 17NP436b and vesicular basalt sample 15NP233 overlap within propagated 2σ-errors. Their scatter reflects either the mixed ages of multiple calcite formation events during the late Mississippian to Pennsylvanian which cannot be resolved, or minor isotope disturbance (by heating and/or fluid flow) during a much younger event. Vesicular basalt sample 15NP236 yielded less defined regressions, thus high age errors, caused by the small spread of the limited number of ablation spots. However, two ablation areas 15NP236_B and 15NP236_D gave MSWD values of 1.4 and 0.84 respectively, while yielding much different lower intercept ages. 15NP326_B gave an age of 306 ± 64/65 Ma, which overlaps with the ages of 15NP326_A (351 ± 29/33 Ma, MSWD = 2.2) and 15NP326_C (350 ± 15/22 Ma, MSWD = 2.2). 15NP236_D gave an age of 206 ± 73/73 Ma, which is apparently younger. This leads us to conclude, that Carboniferous primary ages were affected by young events causing isotope disturbance and shift of the apparent, yet mixed ages towards younger values. This might be true to a limited degree for all samples with MSWD > 2.

Calcite ages are consistent with published radiometric ages of correlative rock units in the North Pamir arc, including two hornblende 40Ar/39Ar ages of ~350 Ma from a meta-andesite, zircon U-Pb ages of ~329 Ma from felsic to intermediate volcanics in Altyn Darya valley (Schwab et al., 2004), and zircon U-Pb ages of ~360 to 314 Ma from island arc granites (Ji et al., 2018; Rembe et al., 2021) (Figure 8). All these ages are interpreted by the aforementioned authors to be primary magmatic ages and reflect the age of emplacement of those units.

5.2 Calcite REE + Y geochemistry

Whole rock geochemical data of altered basalt has a flat Cl-normalized REE pattern (Boynton, 1984), implying an intra-oceanic arc origin (Jiang et al., 2008; Rembe et al., 2021). We suggest a possible control of the basalt geochemistry on calcite REE patterns; any process altering this signal would significantly change the calcite REE pattern (Debruyne et al., 2016).
REE partition coefficients between aqueous solution and precipitating calcite have been studied by experiments (e.g., Perry and Gysi, 2018; Voigt et al., 2017), suggesting that variable physicochemical conditions could lead to strongly differing integration of rare earth elements into the calcite lattice. We show that calcite cements of samples 17NP436a and b are distinguishable from vesicle fillings in samples 15NP233 and -236 (Figure 7a, b).

Calcite must be the major REE + Y sink as our samples do not show any intergrowing, co-precipitated mineral phase. The dominance of calcite hints at precipitation from CO₂-rich seawater derived hydrothermal fluids under low temperature conditions (Talbi and Honnorez, 2003; Honnorez, 2003). This happened in the upper few 100 meters of the oceanic crust. We assume a low mineralization temperature. Under this condition, Eu is trivalent and negative Eu/Eu* is directly inherited from the fluid reservoir (Debruyne et al., 2016). Pronounced negative Ce/Ce* values are a typical inherited signal of oxidizing seawater (e.g., Alibo and Nozaki, 1999); in correlation with increasing Y/Yb values, they trace back to oxidative sorption by Fe-Mn O(OH) species (Debruyne et al., 2016). Positive Gd/Gd* values may be interpreted as a seawater signal (e.g., Baar et al., 1985). However, markedly positive Gd anomalies together with positive Y/Yb values are less commonly reported. Similar features were observed for high salinity waters of the Jordan graben lakes (e.g., Möller et al., 2007). Because ocean floor aquifer porosities are highly heterogeneous (e.g., Fisher and Becker, 2000), the higher porosity of volcanic breccias 17NP436a and 17NP436b may have promoted seawater infiltration, leading to lower REE concentrations and more pronounced Ce/Ce*, Eu/Eu*, Gd/Gd* and Y/Yb anomalies compared to amygdaloidal basalt samples. We note, that Gd anomalies strongly correlate with REE concentration. Although, LA-ICP-MS data acquisition was done according to international standards, we cannot completely exclude the possibility of polyatomic interference of the measured ¹⁵⁷Gd isotope with ¹⁴¹Pr²⁶O* (May and Wiedmeyer, 1998).

5.3 Implications on tectonic models of the Pamir

The results from petrological thin section examination, showing primary calcite fabrics, together with LA-ICP-MS trace element geochemistry, which reflect sea water infiltration, typical for OFA, are major arguments for preserved, primary U-Pb isotope ratios. Our studies constrain the arc volcanic rocks in the NE Pamir to Middle-Upper Mississippian (Visean-Serpukhovian) (Figure 8), significantly younger than correlative lithologies in the West Kunlun, which are dated to the Cambrian (e.g. Yixieke dacite, Xiao et al. (2005), Kudi ophiolite, Wang et al. (2021)). The results carry significant implications for the interpretation of Mesozoic and Cenozoic geodynamic evolution of the Tibet-Pamir orogen. Since the pioneering works of Bertman et al. (1963), Bertman and Molnar (1993), Pan (1994), Mattern et al. (1996), Xiao et al. (2002) and references therein, the Kudi-Oytag suture, or the “Paleozoic suture”, has been hypothesized to be a single, once continuous, E-W-striking feature that was bent towards the north by Cenozoic indentation of the Pamir into a postulated Tarim-Tajik block.

Recent publications outline an early Paleozoic history of the West Kunlun arc magmatism (Figure 9a). The southward subduction of the Proto-Tethys started in the Terreneuvian, dated by the 531 Ma Nanpingxueshan pluton in the Tianshuihai Group (Yin et al., 2020). As a consequence of the development of the Yixieke volcanic arc (Xiao et al., 2005) and the Yierba arc, the South Kunlun was intruded by the Yierba adakitic diorite at ca. 513 Ma (Yin et al., 2020). In response to slab roll-back, the Kudi ophiolite formed in a back-arc position between 513–516 Ma (Wang et al., 2021). The Proto-Tethys closed in the Silurian between 431–420 Ma (Wang et al., 2020) with exhumation of metamorphic units starting from ca. 440 Ma, as dated by monazite U-Pb from the Saitula Group (Zhang et al., 2018a). Closure of the Proto-Tethys was followed by the intrusion of A-type
post-orogenic granites, dated as 420–405 Ma by zircon U-Pb in the North Kudi granite (Yuan et al., 2002; Liu et al., 2014).

However, corresponding early Paleozoic geologic events or rock records in the North Pamir have not been reported. Instead, previous works on mafic to intermediate volcanic rocks and granitoids of the North Pamir show major subduction related arc magmatic activity in the mid to late Carboniferous (Rembe et al., 2021; Jiang et al., 2008; Ji et al., 2018; Kang et al., 2015; Ruzhentsev et al., 1977). Carboniferous arc magmatic rocks found in the Waqia (Tang et al., 2020) and East Mazar (Li et al., 2006) tectonic slivers, reflect the closure of a remnant ocean basin, whereas major arc magmatic activity was focused on the North Pamir arc further to the west (Figure 9b). Stratigraphic relations and hiatus point to a soft collision and obduction of that North Pamir arc in the early Permian (Rembe et al., 2021). No broad Paleozoic magmatic activity younger than Lower Devonian is known in the West Kunlun. The Carboniferous North Pamir arc granitoids intrude largely into poorly dated mafic volcanic rocks. Our calcite U-Pb ages agree with the only known ages of this volcanic unit from Schwab et al. (2004) (Figure 8). They corroborate the dissimilarity of the West Kunlun and North Pamir arc volcanic rocks, and therefore argue against the existence of a continuous Paleozoic suture extending from the Pamir to the West Kunlun.

Recent studies on the Gissar and Kyzylkum segment of the South Tien Shan (STS) of Uzbekistan (Figure 1), West of the North Pamir document the presence of early Carboniferous metamorphism and constrain the volcanic age of meta-basalts from the northern Kyrgyz segment by zircon U-Pb dating to 320–300 Ma (Konopelko et al., 2019 and references therein). This is coeval with arc magmatic activity along the North Pamir arc. Konopelko et al. (2019) propose an archipelago model for the late Paleozoic suture zones in the STS, characterized by high-T metamorphism, rapid exhumation, and multiple subduction zones. This archipelago might have been connected to the Paleo-Tethys realm. We argue for a North Pamir arc continuing from the northeastern Pamir into the Tajik northwestern Pamir and the Gissar segment of the South Tien Shan.

### 6 Conclusion

Calcite phases in Paleozoic ocean floor volcanic rocks were studied with LA-ICP-MS. From four samples we investigated a total of 18 laser ablation areas. Three ablation areas yielded high quality lower intercept ages, 331 ± 15 Ma (17NP436a_A), 339 ± 17 Ma (17NP436b_A) and 328 ± 16 Ma (17NP436b_C), each with MSWD < 2 and propagated 2α-error < 10%, which we interpret representing timing of individual geologic events. The majority of the remaining ablation area ages from volcanic breccia samples 17NP436a and 17NP436b as well as vesicular basalt sample 15NP233 overlap with this age within propagated 2α-errors. They show slightly elevated MSWDs, implying that they are mixed ages. Sample 15NP236 has the most complex age results, possibly caused by more severe disturbance of the isotope ratios by younger events. Ages of samples 17NP436a, 17NP436b and 15NP233 agree with existing radiometric ages of correlative volcanic units in the North Pamir, demonstrating that calcite formed during ocean floor volcanism, due to coeval or subsequent ocean floor alteration, provides a valuable age constraint to the timing of volcanism. We note that these calcite ages do not directly date the formation of these volcanic rock but provide minimal age constraints within a timespan of about 25 Ma of ocean floor alteration.

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Age data must be evaluated in the light of detailed petrographic analysis, including petrographic microscopy and cathodoluminescence microscopy, as well as geochemistry of the investigated calcite. Geochemical data supports our hypothesis of an ocean floor alteration related origin of the investigated calcite. However, we underline that interpretation of REE content in calcite is not straight forward, since the trace element uptake by calcite is dependent on a multitude of factors.

The presence of Middle to Upper Mississippian ocean floor in the North Pamir argues against models invoking a continuous, early Paleozoic Kunlun belt, stretching from the West Kunlun far into the North Pamir. They support the presence of a mid to late Carboniferous volcanic arc system, tying the North Pamir more to comparative units in the Tien Shan.

7 Appendices

Appendix A: Reflected light images, Fig.A1–A4
Appendix B: X-ray fluorescence microscopy (XFM) maps, Fig. B1–6
Appendix C: REE data of each ablation area, Fig.C1

8 Code and data availability

Whole rock geochemistry data used from literature (Rembe et al. (2021), S1) as well as LA-ICP-MS isotope data (S2) and geochemistry (S3) will be uploaded to UQ eSpace (https://espace.library.uq.edu.au/), run by the University of Queensland, upon acceptance.

9 Author contribution

JR, RZ, ERS, and JK conceptualized the project. Fieldwork was carried out by JR, ERS, JK, and CJ. Methodological concept preparation, Laboratory work and data interpretation was done by RZ, JR, JXZ, YF, and DLH. JR prepared a first draft of the manuscript and all authors contributed to the review and editing procedure.

10 Competing interests

All authors declare that they do not have any conflict of interest.

11 Acknowledgement

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Figure 1: Overview map of the North Pamir and surroundings. The yellow star marks the position of the Qimgan valley, as noted. The meaning of the other star symbols is explained in Figure 8. Map drawn after Konopelko et al. (2019), Li et al. (2020), and Henan Institute of Geological Survey (2014).
Figure 2: Sample photographs of hand specimen of sample 17NP436a (a) and polished rock block used for LA-ICP-MS measurements of sample 17NP436a (b) and 17NP436b (c). Field photograph of well-preserved amygdaloidal pillow-basalts in Oytag valley near Qimgan valley (d), with white arrows pointing at calcite filled vesicles (arrow a) and massive interstitial calcite (arrow b). Polished rock specimen 15NP236 (e) and 15NP233 (f) of similar rocks, were used for LA-ICP-MS.
Figure 3: Typical calcite filled vesicles of sample 15NP236 (a), in this case with spary calcite and zeolite mineralization. The white arrow marks preserved perlitic structures. Botryoidal calcite was found in both amygdaloid-basalt samples, the example in (b) is from 15NP233. Figure 3c shows a thin section photograph of sample 17NP436a. White arrows indicate radial fibrous calcite (a), dark styloliths (b), calcite filled fissures (c). Figure 3a, b, c under crossed polarized light. Figure 3d shows a schematic sketch of microphotograph Figure 3c, delineating a sequence of 4 events: (1) formation of hydrothermal clay, (2) precipitation of fibrous-radial calcite along the walls of brecciated volcanic rock fragments, (3) late-stage equant calcite formation, (4) pressure solution and formation of styloliths (dark lines) and reprecipitation of dissolved calcite in fissures (green). Areas 2 and 3 are targets for laser ablation. In figures (e)-(f) a schematic sequence of events leading to the formation of the basaltic breccias is sketched. (e) Fracturing of the basaltic rock and formation of clay (1) and calcite cement phases (2) and (3), (f) disarticulation and sedimentation of debris containing isolated calcite cement fragments. (g) late stage pressure solution and fissure formation of phase (4). Red arrows schematically mark stress regime.
Figure 4: Microphotographs under plain light (a) and Cathodoluminescence (b) of an exemplary vesicle of sample 15NP236 show primary botryoidal structure of the calcite. Primary calcite seems non-luminescent to dull-luminescent. Cathodoluminescence images of ablation areas 17NP436a_A (c), 17NP436b_A (d) and 17NP436b_C (e) show relatively homogenous non-luminescent calcite cement fragments with a small portion of bright yellow veins. The calcite cement fragments are embedded in a dull-yellow luminescent volcaniclastic matrix. All three samples yielded high quality calcite U-Pb ages (MSWD < 2). Ablation area 17NP436a_F (f), which has a high portion of bright yellow calcite, yielded a less precise age (MSWD = 3.5). Ablation spots for geochemistry and U-Pb dating are marked with grey circles.
Figure 5: Tera-Wasserburg plots of ablation area ages on basalt breccia samples 17NP436a and 17NP436b. All errors are given as 2σ.
Figure 6: Tera-Wasserburg plots of ablation area ages on vesicular basalt samples 15NP236 and 15NP233. All errors are given as 2σ.
Figure 7: (a) Mixing trend between high total REE—negative Gd/Gd* and low total REE—positive Gd/Gd* composition. (b) Higher Y/Ho values correlate with low total REE. Y and Ho normalized against chondrite values of Anders and Grevesse (1989). (e, f) +15NP233, -236, o -17NP436A, -B; color-code see Appendix A.
Figure 8: (a) Map of the northeastern Pamir with location of radiometric ages for the North Pamir arc volcanic rocks, shown in (c). (b) Detailed field locations of samples in the Qinggan valley (map after Henan Institute of Geological Survey (2014)). There is a sedimentary hiatus between the Middle Pennsylvanian and the Guadalupian (Rembe et al., 2021). (c) Overview of selected literature data and newly obtained data for OFA of the North Pamir Carboniferous arc.
Figure 9: (a) Paleogeographic situation in the mid-Cambrian: The roll-back of the Proto-Tethys slab caused the formation of the Kudi ophiolite, exposed in the Buziwan valley (Wang et al., 2021). (b) Paleogeographic situation in the late Mississippian: The North Pamir arc formed along an intra-oceanic subduction zone (Jiang et al., 2008) forming the Oytag segment in its eastern branch. Subduction related Waqia granite (Tang et al., 2020) and East Mazar granite (Li et al., 2006), both today part of tectonic slivers, suggest the presence of a remnant oceanic basin between Tianshuihai and South Kunlun Terrane accretionary complex, as suggested by (Zhang et al., 2018b). Small photographs show pillow basalts in the Kudi section (in a) and Oytag near Qimgan (in b). SKT-South Kunlun Terrane, TSHT-Tianshuihai Terrane, NPA-North Pamir volcanic arc, NKT-North Kunlun Terrane.
Appendix A: Reflected light images of all investigated samples with marked ablation areas. Letter, attached to the yellow boxes, appended to the sample name, labels the ablation areas. Colors of label boxes are consistent with colors of in-text figures.
Appendix B: XFM Map
Appendix C: Overview REE data per ablation area
### Appendino 1: Whole rock geochemistry from Rembe et al., 2021

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*Supplementary Table 1: Whole rock geochemistry*
**Supplementary Table 2: LA-ICP-MS age data.**

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