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

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14   **Abstract.** The North Pamir, part of the western syntax of the India-Asia collision zone, preserves remnants of a

15   poorly understood Paleozoic intra-oceanic subduction zone. To constrain the age of this ancient ocean floor, we

16   analyzed calcite phases in vesicular basalt and basaltic volcanic breccia with U-Pb geochronology using laser-

17   ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS). Dating of radial-fibrous to equant spary

18   calcite yielded three meaningful Visean-Serpukhovian ages. REE + Y data reveal that the basaltic host rock of

19   the calcite and oxidizing seawater are major sources of trace elements during calcite precipitation. U-Pb ages

20   seem to be independent of REE + Y concentrations. Our results demonstrate the potential of calcite dating to

21   constrain the age of ancient ocean floors. We challenge the hypothesis that a continuous early Paleozoic Kunlun

22   Terrane extended from northern Tibet into the North Pamir.

23   **Summary.** Calcite is frequently formed during alteration processes in the basaltic, uppermost layer of juvenile

24   oceanic crust. Weathered oceanic basalts are hard to date with conventional radiometric methods. We show in a

25   case study from the North Pamir, Central Asia, that calcite U-Pb age data—supported by geochemistry and

26   petrological microscopy—has the potential to date sufficiently old oceanic basalts, if the time span between

27   basalt extrusion and latest calcite precipitation (~25 Ma) is considered.

28   **1   Introduction**

29   Constraining the timing of formation of ocean floor basalts is significant to develop models of various tectonic

30   processes given the voluminous occurrence of ocean floor basalts in ophiolites, sections of ocean plate

31   stratigraphy and exhumed subduction complexes, and remnants of island-arcs and oceanic plateaus in ancient

32   convergent margins. However, mafic volcanic rocks, in which zircons are sparse, are challenging to date with

33   radiometric methods. ^{40}Ar/^{39}Ar dating of separated phenocrysts or groundmass is frequently attempted (e.g.,

34   Waagstein et al., 2002; Heath et al., 2018). However, ocean floor alteration (OFA) often disturbs K-Ar isotopic

35   compositions by secondary potassium gain (Staudigel et al., 2013) or loss (Pringle, 2013), making ^{40}Ar/^{39}Ar

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 calcite LA-ICP-MS U-Pb dating of Paleozoic oceanic crust from Central Asia. 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 test tectonic models of the Pamir.

2   Geological background and motivation

The North Pamir magmatic arc formed during subduction of the Paleo-Tethys oceanic lithosphere (e.g., Bazhenov and Burtman, 1982). The arc 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., 2018). 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 represented by a small outcrop of altered ultramafic rocks in the Gez valley (Jiang, 1992). To date, no age data has been presented for those rocks. The green color of the North Pamir arc volcanic rocks implies thorough spilitization, making them unsuitable for $^{40}Ar/^{39}Ar$ 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 age 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

74   purpose, we sampled 4 specimens at 3 different localities in the Chinese Qimgan valley (Figure 1). Samples

75   17NP436a and 17NP436b are from the same locality (sample location at N 39° 18′ 27″, E 74° 51′ 32″) and

76   represent redeposited brecciated mafic volcanic rock with interstitial calcite cement that was formed during an

77   early phase of brecciation (Figure 2a–c). Samples 15NP236 (sample location at N 39° 18′ 18″, E 74° 51′ 30″)

78   and 15NP233 (sample location at N 39° 18′ 16″, E 74° 51′ 47″) are from two localities with amygdaloid-basalt,

79   where 15NP236 was taken from a pillow basalt. We investigated amygdules filled exclusively with calcite

80   (Figure 2e, f)

81   **3   Methods**

82   **3.1   Petrological microscopy, cathodoluminescence microscopy (CL) and X-ray fluorescence**

83   **   microscopy (XFM)**

84   Petrographic thin sections of all samples were studied with conventional light microscopy and

85   cathodoluminescence microscopy (CL). Polished thin sections of all samples were prepared. CL imaging was

86   done using an Olympus BXFM-F microscope equipped with a Lumic hot-cathode electron source and a highly

87   sensitive Olympus XC10 camera at the University of Potsdam. We recognized well preserved primary features

88   (see Sect. 4.1), which were then identified on the rock chips prepared for laser ablation. Detailed sample

89   petrography raises the chances of obtaining robust, meaningful ages, as emphasized recently by Roberts et al.

90   (2021). High resolution reflected light images indicate the position of ablation spots in Appendix A.

91   Additionally, we examined sample 17NP436a with scanning X-ray fluorescence microscopy (XFM). A polished

92   slab cut parallel to the surface examined with LA-ICP-MS was prepared from the same rock chip. XFM maps

93   were collected at the XFM beamline at the Australian Synchrotron (Howard et al., 2020). The incident excitation

94   energy was 18.5 keV. Pixel size and dwell time per pixel are indicated in the figures in Appendix B.

95   **3.2   Laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS)**

96   Rock samples were processed at the School of Earth and Environmental Sciences, The University of

97   Queensland. Samples 15NP233 and 15NP236 were cut and mounted on one-inch diameter round mounts (Figure

98   2e, f); for samples 17NP436a and 17NP436b, we used polished rock chips (Figure 2b, c). Sample mounts were

99   polished using standard polishing procedures and finished with a 0.25 micrometer diamond suspension.

100   LA-ICP-MS U-Pb dating and geochemical analysis was performed at the Radiogenic Isotope Facility of the

101   Centre for Geoanalytical Mass Spectrometry, The University of Queensland following methods in Su et al.

102   (2020) and Yang et al. (2021). Laser ablation was achieved using an ASI RESOlution 193 ArF nm excimer laser

103   system. Following evacuation of air, He carrier gas was introduced into the laser cell at a flow rate of 0.35 l/min.

104   0.005 l/min of N_2 gas was also introduced to the laser cell to enhance the measurement sensitivity. The gas

105   mixture was then introduced into the plasma torch of a Thermo iCAP RQ quadruple ICP-MS with 1.06 l/min Ar

106   nebulizer gas. No reaction gas was employed. The laser was run with a 100 µm diameter round spot at 10 Hz,

107   with a measured instrument laser-fluence (laser pulse energy per unit area) of 2.5 J/cm^2. For U-Pb dating, each

108   spot had 8 s of background, 20 s of data acquisition, and 15 s of wash out. For trace elemental analysis, each spot

109   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/^{238}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 s), ^{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 cross-calibrated in-house calcite reference materials 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 (2 σ), 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 the 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. The ThO/Th ratio during our session was <0.002 for 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, whereas 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

147 diameter filled exclusively with calcite. Sample 15NP236 has much smaller vesicles, around 1 mm in diameter,

148 filled with either calcite or zeolite. Both samples show high "Loss on Ignition" (LOI) values and anomalous

149 major element values for whole rock geochemistry, accounting for high secondary, volatile rich mineral content

150 (Supplementary Table 1). No fractures or veins cut across amygdules in these samples.

151 In samples 17NP436a and b, fracture and pore space in basaltic rock fragments shows multiple calcite

152 generations (Figure 3c, d). Most calcite formed prior to deposition of the breccia. Specifically, isolated cement

153 fragments are fully embedded in a fine-grained matrix (e.g., in sample 17NP436b). They may have formed in

154 fractures of a volcanic edifice and were redeposited after its collapse. In some cases, calcite cement is still

155 attached to the basaltic clasts and a series of 4 consecutive mineralization phases can be recognized (numbered 1

156 to 4 in Figure 3d, schematically depicted in Figure 3e-g). Some of the volcanic rock fragments show an early,

157 hydrothermal clay layer (Figure 3c and phase 1 in Figure 3d). The rock fragments—or if present, the clay

158 coatings—are overgrown by a first generation of radial-fibrous calcite. Larger voids are filled with late, equant

159 calcite (phase 2 and 3 in Figure 3d). The early, medium to coarse spary calcite cements (2 and 3 in Figure 3d)

160 and the matrix are crosscut by fine-sparitic calcite filled fissures (4 in Figure 3d) The fissures are distinguishable

161 from the spary calcite in transmitted and reflected light and were avoided during ablation.

162 Cathodoluminescence microscopy imaging reveals fibrous botryoidal textures of the vesicle-filling calcite of

163 samples 15NP233 and 15NP236. They usually show no luminescence or a zonation of dull-yellowish and non-

164 luminescent fringes (Figure 4a,b). Bright yellow luminescence irregularly occurs along the rims of the vesicles.

165 Secondary fractures crosscutting the vesicular fabric were not observed. We prepared slides from the rock chips

166 analyzed with LA-ICP-MS of samples 17NP436a and 17NP436b (Figure 4c-f). The basalt breccia samples

167 17NP436a and 17NP436b show non-luminescent to dull yellow luminescent spary calcite. Bright yellow

168 luminescence was observed along hairline subzones, which are interpreted as grain boundaries. The largely non-

169 luminescent spary calcite fragments stand out against the yellow luminescent altered volcaniclastic matrix.

170 Matrix and spary calcite fragments are intersected by bright-yellow, late-stage calcite (phase 4 in Figure 3d)

171 filled fractures (e.g., Figure 4c). They are clearly visible in transmitted and reflected light and were avoided

172 during ablation.

173 In order to better understand calcite phases, we further study 17NP436a with high-resolution synchrotron X-ray

174 fluorescence mapping (Howard et al., 2020), following methods described in Vanghi et al. (2019). Sr maps show

175 elevated concentration for the phase 2 and 3 calcite and much lower content in fissure filling calcite phase 4,

176 suggesting different geochemical regimes (Appendix B).

177 **4.2   LA-ICP-MS U-Pb Dating**

178 Four samples from three field sites were prepared for analysis. We obtained data from 839 single spots from 18

179 laser ablation areas (Appendix A), 3–6 ablation areas per sample (Figure 5, Figure 6), data table in

180 Supplementary Table 2. For age calculation, we used the IsoplotR program (Vermeesch, 2018) version 3.5

181 running in R version 3.6.0. Ages are calculated for individual ablation areas by linear regression in a Tera–

182 Wasserburg plot. From the 839 single spot ablation data only 16 had to be omitted due to U content below the

183 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 spary 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, four 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 a 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. Ninty-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)

221   compared to the breccia calcite cement (8 ppm in 17NP436a and 12 ppm in 17NP436b). LREE are enriched over

222   MREE (La_n/Sm_n) and negatively correlate with enriched MREE over HREE values (Dy_n/Yb_n) in all samples.

223   The vesicle-filling calcite shows both positive and negative Ce/Ce* values between 0.75 and 1.4; the breccia

224   calcite cement shows negative values between 0.18 and 0.92. Negative Ce anomalies are usually associated with

225   oxidizing conditions producing Ce^{4+} instead of Ce^{3+} (e.g., Alibo and Nozaki, 1999). We observe positive to

226   slightly negative Gd anomalies (Gd/Gd* = $Gd_n/sqrt(Eu_n \times Tb_n)$; Figure 7a). Positive Y_n/Ho_n anomalies are

227   common (Figure 7b). Negative Ce/Ce* and Eu/Eu* anomalies together with higher Gd/Gd* and Y_n/Ho_n in the

228   calcite cement of the volcanic breccia are interpreted to reflect a stronger influence of infiltrating seawater

229   (Ce/Ce* = $Ce_n/sqrt(La_n \times Pr_n)$; Eu/Eu* = $Eu_n/sqrt(Sm_n \times Tb_n)$).

230   **5   Discussion**

231   **5.1   Calcite age data and its significance**

232   In newly formed submarine volcanic rocks, calcite formation marks the phase of alkalinity-generating reactions.

233   Alkalinity describes the acid neutralizing capacity by formation of alkali and alkaline earth metal ion species

234   during rock weathering (e.g., Spivack and Staudigel, 1994). This is crucial for interpreting OFA calcite U-Pb

235   ages, implying that these ages should be no older than the "true" rock formation age. High temperature

236   hydrothermal alteration is also a common phenomenon in submarine volcanic environments. This is, in contrast,

237   restricted to discrete zones, such as veins, shear zones, and hydrothermal upflow zones (Harlov and Austrheim,

238   2013; Honnorez, 2003). It changes the mineral composition of the volcanic host rock completely, such that

239   primary igneous textures are obliterated (e.g. epidosites, Honnorez, 2003). Such rock types must be avoided as

240   they are unlikely to produce ages related to OFA. By dating isolated calcite, far from hydrothermal upflow

241   zones, we determine the age range of OFA that occurred shortly after rock consolidation. This gives a minimum

242   age estimate for ocean floor formation, if not the actual age of formation. This must not be mistaken for the

243   radiometric ages of the volcanic rock itself (e.g., ages from zircon U-Pb dating).

244   We observed one botryoidal to spary calcite phase in the vesicular basalts (Figure 3a, Figure 4a, b). Four stages

245   of mineralization were observed in the basaltic breccia: (1) hydrothermal clay, (2) radial-fibrous calcite, (3)

246   coarse equant-spary calcite and (4) fissure filling calcite crosscutting the entire fabric (Figure 3b-g). The

247   presence of radial-fibrous and sparry, equant calcite crystals is typical of continuous calcite precipitation in a

248   porous substratum (Gonzalez and Carpente, 1992). In a first phase, radial-fibrous calcite grows along the wall of

249   the voids and successively reduces the porosity of the substratum, thereby hindering fluid flow. This reduces the

250   calcite precipitation rate and the amount of nucleation, leading to larger, equant calcite crystals in the center of

251   the voids. This model can be adopted for a first calcite phase (2 and 3 in Figure 3d). As the radial-fibrous and the

252   equant calcite growth reflects one process, both calcite phases were chosen for ablation. The phase 4 fine-sparitic

253   filled fissures are interpreted to reflect a later tectonic event, expressed by differential stress, pressure solution

254   and reprecipitation of calcite in open joints (Figure 3g).

255   To explore the geologic significance of our age data, we first applied a very conservative filter, closely

256   examining ages with MSWD < 2 and 2σ-error < 10%, as their isotope ratios are most likely measured from

257 single homogenous domains (e.g., Lan et al. (2022)). Subsequently, we also discuss all ages for a full view of the

258 age spectrum.

259 Our samples generally show a low variability in ablation area ages and initial Pb values (Figure 5 and Figure 6).

260 2σ-errors with propagated systematic uncertainties are typically around 5%; only vesicular basalt sample

261 15NP236 shows high 2σ-errors. However, multi-stage calcite formation and possible subsequent alteration lead

262 to MSWD values above two and elevated age errors. Primary calcite was eventually affected by alteration and

263 crystallization of calcite with differing chemistry even within microscopically identified seemingly homogenous

264 phases (e.g. phase 2 and 3 in Figure 3d). This is made visible by CL imaging of yellow-luminescent subzones

265 penetrating non-luminescent phase 2 and 3 calcite zones in Figure 4f. However, ablation spots placed on ablation

266 areas 17NP436a_A, 17NP436b_A and 17NP436b_C largely fall on what we interpret as phase 2 and 3, radial-

267 fibrous to equant calcite, characterized by non-luminescence (Figure 4c-e). The lower intercept ages are 331 ±

268 2/15 Ma (17NP436a_A), 339 ± 6/17 Ma (17NP436b_A) and 328 ± 4/16 Ma (17NP436b_C), which consistently

269 constraints the volcanic breccia to the Visean-Serpukhovian boundary. All ablation areas of basalt breccia

270 samples 17NP436a and 17NP436b and vesicular basalt sample 15NP233 overlap within propagated 2σ-errors.

271 Their scatter reflects either the mixed ages of multiple calcite formation events during the late Mississippian to

272 Pennsylvanian which cannot be resolved, or minor isotope disturbance (by heating and/or fluid flow) during a

273 much younger event. Vesicular basalt sample 15NP236 yielded less defined regressions, thus high age errors,

274 caused by the small spread of the limited number of ablation spots. However, two ablation areas, 15NP236_B

275 and 15NP236_D, gave MSWD values of 1.4 and 0.84 respectively, while yielding much different lower intercept

276 ages. 15NP326_B gave an age of 306 ± 64/65 Ma, which overlaps with the ages of 15NP326_A (351 ± 29/33

277 Ma, MSWD = 2.2) and 15NP326_C (350 ± 15/22 Ma, MSWD = 2.2). 15NP236_D gave an age of 206 ± 73/73

278 Ma, which is apparently younger. This leads us to conclude that Carboniferous primary ages were affected by

279 young events causing isotope disturbance and shift of the apparent, yet mixed ages towards younger values. This

280 might be true to a limited degree for all samples with MSWD > 2.

281 Calcite ages are consistent with published radiometric ages of correlative rock units in the North Pamir arc,

282 including two hornblende $^{40}Ar/^{39}Ar$ ages of ~350 Ma from a meta-andesite, zircon U-Pb ages of ~329 Ma from

283 felsic to intermediate volcanics in Altyn Darya valley (Schwab *et al.*, 2004), and zircon U-Pb ages of ~360 to

284 314 Ma from island arc granites (Ji et al., 2018; Rembe et al., 2021) (Figure 8). All these ages are interpreted by

285 the aforementioned authors to be primary magmatic ages and reflect the age of emplacement of those units.

286 **5.2   Calcite REE + Y geochemistry**

287 Whole rock geochemical data from altered basalt has a flat C1-normalized REE pattern (Boynton, 1984),

288 implying an intra-oceanic arc origin (Jiang et al., 2008; Rembe et al., 2021). We suggest a possible control of the

289 basalt geochemistry on calcite REE patterns; any process altering this signal would significantly change the

290 calcite REE pattern (Debruyne et al., 2016).

291 REE partition coefficients between aqueous solution and precipitating calcite have been experimentally studied

292 (e.g., Perry and Gysi, 2018; Voigt et al., 2017); results suggest that variable physicochemical conditions could

293 lead to strongly differing integration of rare earth elements into the calcite lattice. We show that calcite cements

294 of samples 17NP436a and b are distinguishable from vesicle fillings in samples 15NP233 and -236 (Figure 7a,
295 b).

296 Calcite must be the major REE + Y sink as our samples do not show any intergrowing, co-precipitated mineral
297 phase. The dominance of calcite hints at precipitation from CO_2-rich seawater derived hydrothermal fluids under
298 low temperature conditions (Talbi and Honnorez, 2003; Honnorez, 2003). This happened in the upper few 100
299 meters of the oceanic crust. We assume a low mineralization temperature. Under this condition, Eu is trivalent
300 and negative Eu/Eu* is directly inherited from the fluid reservoir (Debruyne et al., 2016). Pronounced negative
301 Ce/Ce* values are a typical inherited signal of oxidizing seawater (e.g., Alibo and Nozaki, 1999); in correlation
302 with increasing Y_n/Ho_n values, they trace back to oxidative sorption by Fe-Mn O(OH) species (Debruyne et al.,
303 2016). Positive Gd/Gd* values may be interpreted as a seawater signal (e.g., Baar et al., 1985). However,
304 markedly positive Gd anomalies together with positive Y_n/Ho_n values are less commonly reported. Similar
305 features were observed in high salinity waters from Jordan graben lakes (e.g., Möller et al., 2007). Because
306 ocean floor aquifer porosities are highly heterogenous (e.g., Fisher and Becker, 2000), the higher porosity of
307 volcanic breccias 17NP436a and 17NP436b may have promoted seawater infiltration, leading to lower REE
308 concentrations and more pronounced Ce/Ce*, Eu/Eu*, Gd/Gd* and Y_n/Ho_n anomalies compared to amygdaloidal
309 basalt samples. We note that Gd anomalies strongly correlate with REE concentration. Although, LA-ICP-MS
310 data acquisition was done according to international standards, we cannot completely exclude the possibility of
311 polyatomic interference of the measured ^{157}Gd isotope with $^{141}Pr^{16}O^+$ (May and Wiedmeyer, 1998).

5.3 Implications on tectonic models of the Pamir

313 The results from petrological thin section examination, showing primary calcite fabrics, together with LA-ICP-
314 MS trace element geochemistry, which reflect sea water infiltration, typical for OFA, are major arguments for
315 preserved, primary U-Pb isotopic ratios. Our studies constrain the emplacement age of arc volcanic rocks in the
316 NE Pamir to Middle-Upper Mississippian (Visean-Serpukhovian) (Figure 8), significantly younger than
317 correlative lithologies in the West Kunlun, which are dated to the Cambrian (e.g. Yixieke dacite, Xiao et al.
318 (2005), Kudi ophiolite, Wang et al. (2021)). The results carry significant implications for the interpretation of the
319 Mesozoic and Cenozoic geodynamic evolution of the Tibet-Pamir orogen. Since the pioneering works of
320 Burtman et al. (1963), Burtman and Molnar (1993), Pan (1994), Mattern et al. (1996), Xiao et al. (2002) and
321 references therein, the Kudi-Oytag suture, or the "Paleozoic suture", has been hypothesized to be a single, once
322 continuous, E–W-striking feature that was bent towards the north by Cenozoic indentation of the Pamir into a
323 postulated Tarim-Tajik block.

324 Recent publications outline an early Paleozoic history of the West Kunlun arc magmatism (Figure 9a). The
325 southward subduction of the Proto-Tethys started in the Terreneuvian, dated by the 531 Ma Nanpingxueshan
326 pluton in the Tianshuihai Group (Yin et al., 2020). As a consequence of the development of the Yixieke volcanic
327 arc (Xiao et al., 2005) and the Yierba arc, the South Kunlun was intruded by the Yierba adakitic diorite at ca.
328 513 Ma (Yin et al., 2020). In response to slab roll-back, the Kudi ophiolite formed in a back-arc position
329 between 513–516 Ma (Wang et al., 2021). The Proto-Tethys closed in the Silurian between 431–420 Ma (Wang
330 et al., 2020) with exhumation of metamorphic units starting from ca. 440 Ma, as dated by monazite U-Pb from
331 the Saitula Group (Zhang et al., 2018). 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 hiati 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 Kyzylkum 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. Although systematic errors of lower intercept ages could be small (as low as <1 % at 2σ), we focus on propagated errors because they include the long-term variance of the reference materials, the analytical error of the monitor standard, and other important sources of errors. 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 2σ-error < 10%, which we interpret as representing the 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 2σ-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 on the

369   timing of volcanism. We note that these calcite ages do not directly date the formation of these volcanic rock but

370   provide minimum age constraints within a timespan of about 25 Ma of ocean floor alteration.

371   Age data must be evaluated in the light of detailed petrographic analysis, including petrographic microscopy and

372   cathodoluminescence microscopy, as well as geochemistry of the investigated calcite. Geochemical data

373   supports our hypothesis of an ocean floor alteration-related origin of the investigated calcite. However, we

374   underline that interpretation of REE content in calcite is not straight forward, since the trace element uptake by

375   calcite is dependent on a multitude of factors.

376   The presence of Middle to Upper Mississippian ocean floor in the North Pamir argues against models invoking a

377   continuous, early Paleozoic Kunlun belt, stretching from the West Kunlun far into the North Pamir. Instead, they

378   support the presence of a mid to late Carboniferous volcanic arc system, tying the North Pamir more to

379   comparative units in the Tien Shan.

7   Appendices

381   Appendix A: Reflected light images, Fig.A1–A4

382   Appendix B: X-ray fluorescence microscopy (XFM) maps, Fig. B1–6

383   Appendix C: REE data of each ablation area, Fig.C1

8   Code and data availability

385   Whole rock geochemistry data used from literature (Rembe et al. (2021), S1) as well as LA-ICP-MS isotope data

386   (S2) and geochemistry (S3) will be uploaded to UQ eSpace (https://espace.library.uq.edu.au/), run by the

387   University of Queensland.

9   Author contribution

389   JR, RZ, ERS, and JK conceptualized the project. Fieldwork was carried out by JR, ERS, JK, and CJ.

390   Methodological concept preparation, laboratory work and data interpretation was done by RZ, JR, JXZ, YF, and

391   DLH. JR prepared a first draft of the manuscript and all authors contributed to the review and editing procedure.

10   Competing interests

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

11   Acknowledgement

395   We thank Langtao Liu for help with field work, and Antje Musiol and Baiansuluu Terbishalieva for support with

396   laboratory work at the University of Potsdam. We are thankful for suggestions and constructive comments of

397 Dimitry Konopelko, Alexander Robinson and an anonymous reviewer. We also thank the editor Daniela Rubatto

398 for the assistance and the handling of the manuscript.

12   Funding statement

400 The project was funded by Deutsche Forschungs Gesellschaft e.V. (DFG) grant SO 436/12-1 to Sobel and DFG

401 grant KL 495/27-1 to Kley. Additional support was provided by grants to Sobel, Zhao and Zhou through the

402 Australia-Germany Joint Research Cooperation Scheme, to Howard and Zhou through the Australian

403 Synchrotron Access Program and to Zhou through a UQ ECR grant. Chen was supported by grants through the

404 2nd Tibetan Plateau Scientific Expedition and Research Program (STEP, 2019QZKK0901) and State Key Lab. of

405 Earthquake Dynamics of China (LED2016A05).

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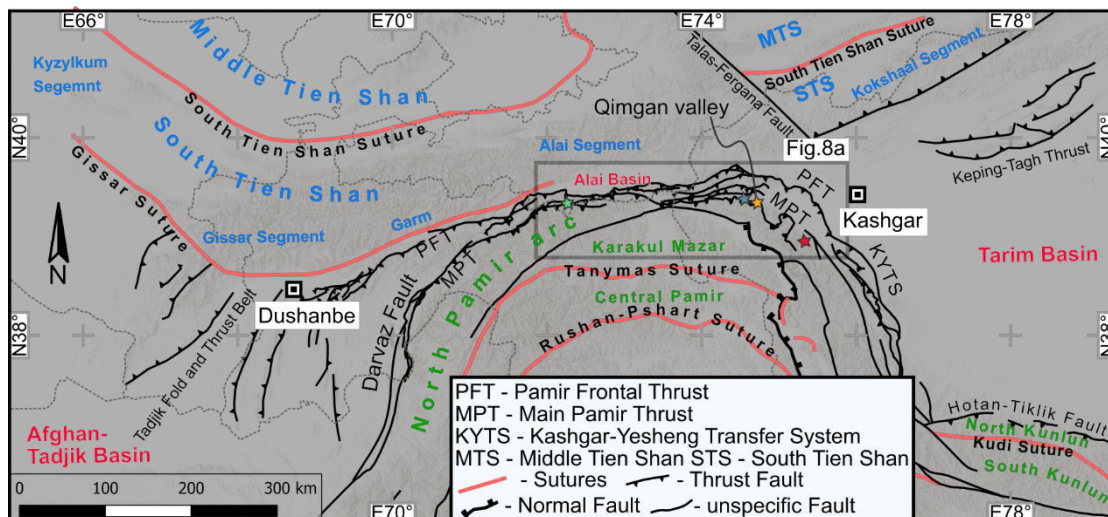
408 *Figure 1: Overview map of the North Pamir and surroundings. The yellow star marks the position of the Qimgan valley, as*
409 *noted. The meaning of the other star symbols are explained in Figure 8. Map drawn after Konopelko et al. (2019), Li et al.*
410 *(2020), and Henan Institute of Geological Survey (2014).*

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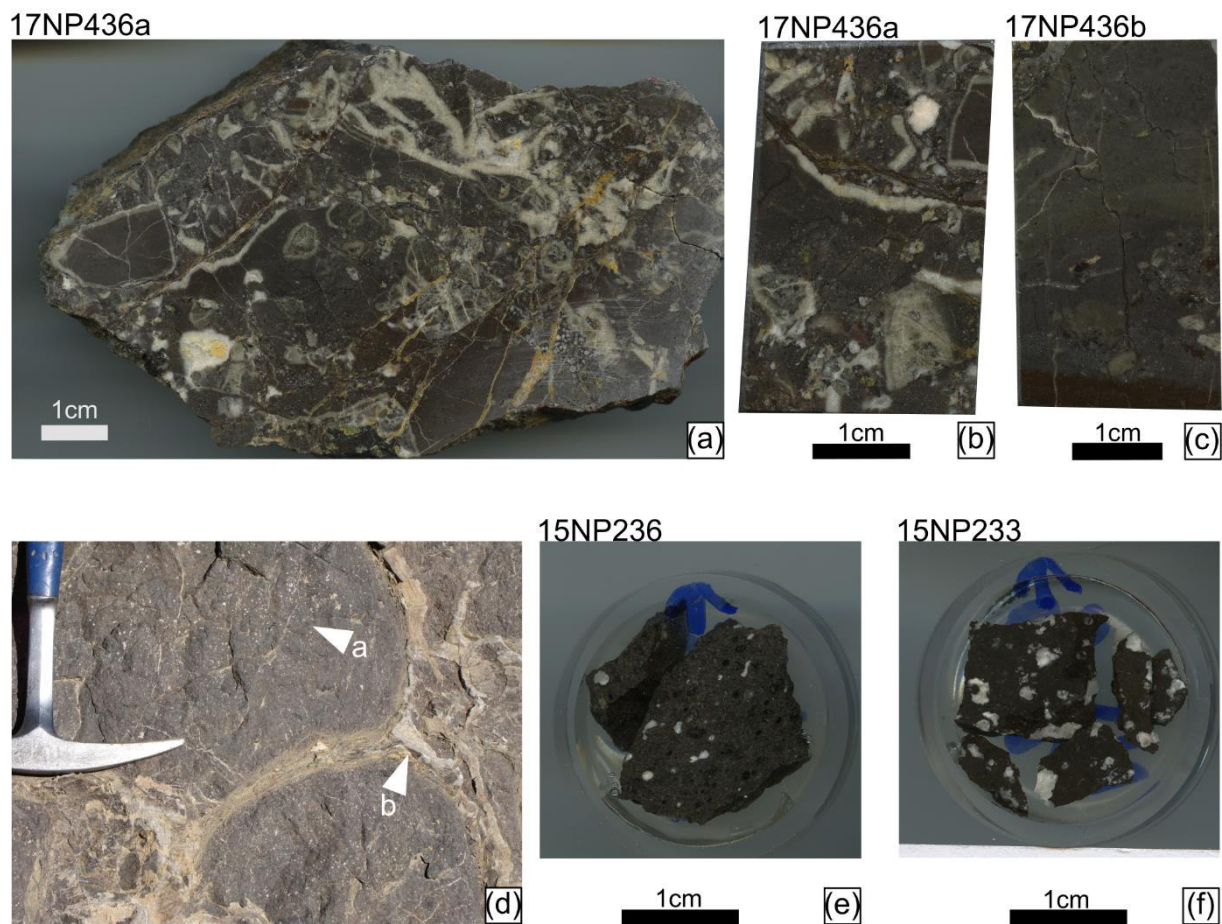
Figure 2: Photographs of hand specimen of sample 17NP436a (a) and polished rock block used for LA-ICP-MS

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 rock, were used for LA-ICP-MS.

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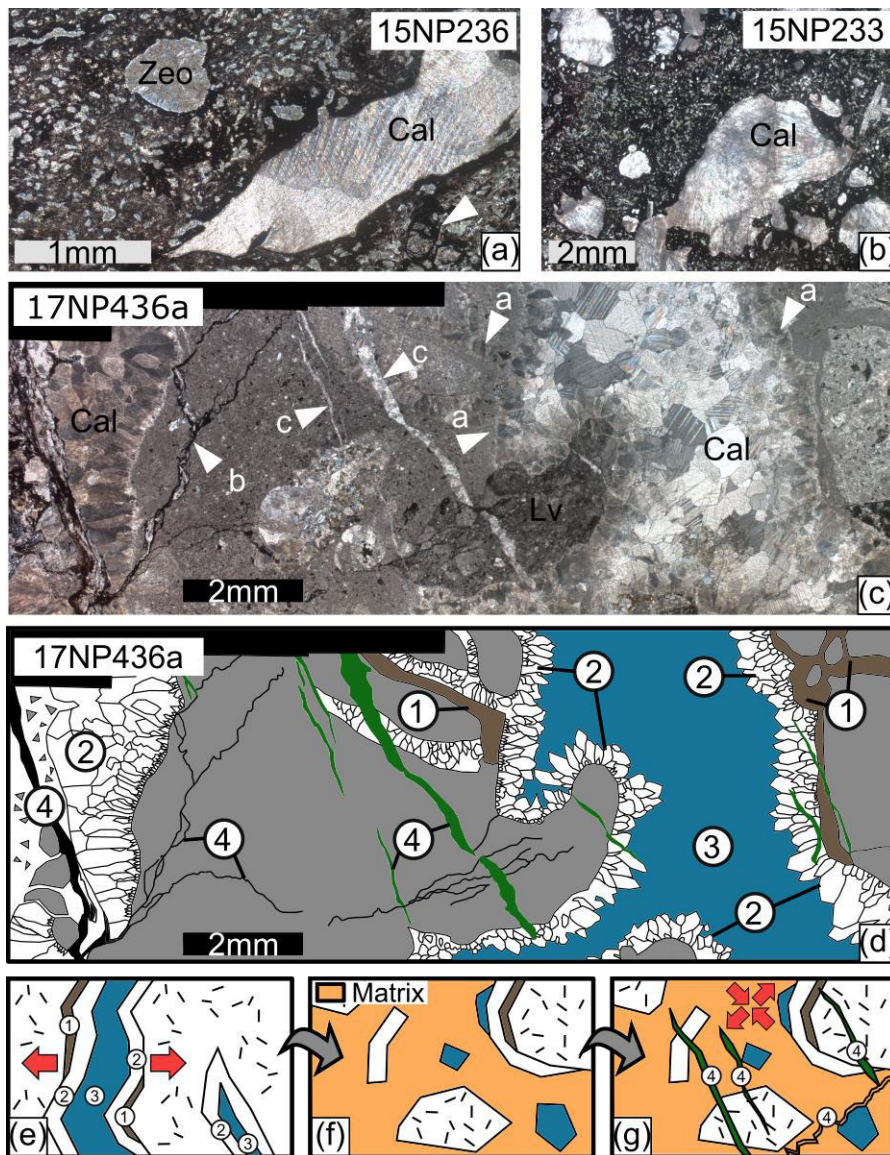
Figure 3: Typical calcite-filled vesicles from sample 15NP236 (a), in this case with spary calcite and zeolite mineralization. The white arrow marks preserved perlitic structures. Botryoidal calcite was found in both amygdaloid-basalt samples, the example in (b) is from 15NP233. Figure 3c shows a thin section photograph of sample 17NP436a. White arrows indicate radial fibrous calcite (a), dark stylolites (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 stylolites (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 indicate stress regime.

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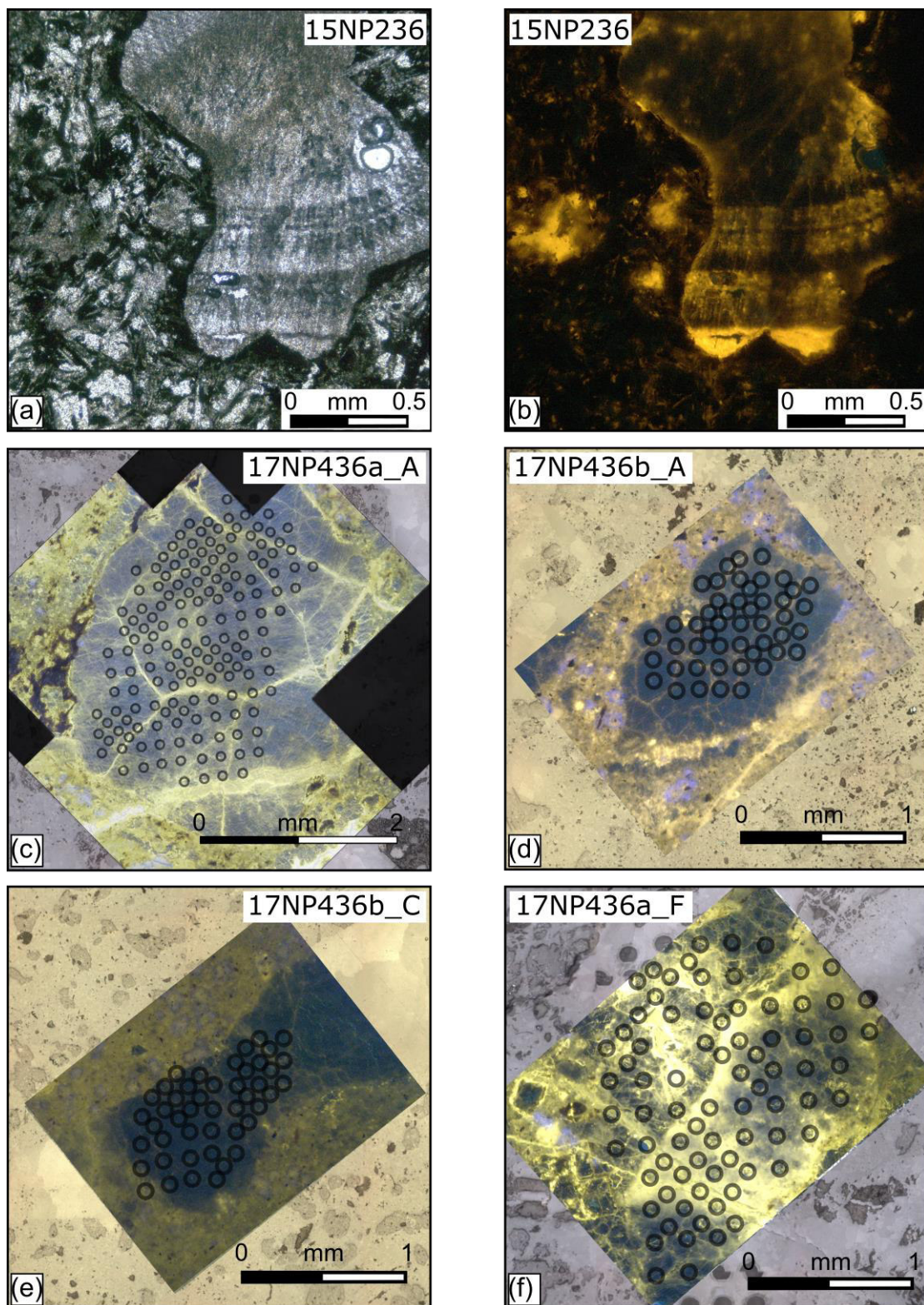
Figure 4: Microphotographs under plain light (a) and cathodoluminescence (b) of an exemplary vesicle from sample
15NP236 show primary botryoidal structure of the calcite. Primary calcite seems non-luminescent to dull-luminescent.
Cathodoluminescence images of ablation areas 17NP436a_A (c), 17NP436b_A (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.

441

Basalt breccia sample 17NP436a

17NP436a_A
331±2/15 Ma, MSWD = 1.7
$(^{207}Pb/^{206}Pb)_0 = 0.876 \pm 0.011$
n = 119

17NP436a_B
325±4/16 Ma, MSWD = 2.3
$(^{207}Pb/^{206}Pb)_0 = 0.880 \pm 0.021$
n = 82

17NP436a_C
308±7/16 Ma, MSWD = 2.5
$(^{207}Pb/^{206}Pb)_0 = 0.874 \pm 0.027$
n = 64

17NP436a_D
307±6/15 Ma, MSWD = 4.2
$(^{207}Pb/^{206}Pb)_0 = 0.846 \pm 0.034$
n = 40

17NP436a_E
298±10/17 Ma, MSWD = 4.7
$(^{207}Pb/^{206}Pb)_0 = 0.774 \pm 0.046$
n = 37

17NP436a_F
304±7/16 Ma, MSWD = 3.5
$(^{207}Pb/^{206}Pb)_0 = 0.864 \pm 0.014$
n = 61

Basalt breccia sample 17NP436b

17NP436b_A
339±6/17 Ma, MSWD = 1
$(^{207}Pb/^{206}Pb)_0 = 0.974 \pm 0.100$
n = 38

17NP436b_B
322±3/15 Ma, MSWD = 4.8
$(^{207}Pb/^{206}Pb)_0 = 0.866 \pm 0.017$
n = 47

17NP436b_C
328±4/16 Ma, MSWD = 1.7
$(^{207}Pb/^{206}Pb)_0 = 0.893 \pm 0.045$
n = 29

17NP436b_D
316±9/17 Ma, MSWD = 2.4
$(^{207}Pb/^{206}Pb)_0 = 0.830 \pm 0.058$
n = 23

442

443 *Figure 5: Tera-Wasserburg plots of ablation area ages on basalt breccia samples 17NP436a and 17NP436b. All errors are*
444 *given as 2σ.*

445

Vesicular basalt sample 15NP236

15NP236_A
351±29/33 Ma, MSWD = 2.2
$(^{207}Pb/^{206}Pb)_0 = 0.889 \pm 0.059$
n = 14

15NP236_B
306±64/65 Ma, MSWD = 1.4
$(^{207}Pb/^{206}Pb)_0 = 0.854 \pm 0.056$
n = 15

15NP236_C
350±15/22 Ma, MSWD = 2.2
$(^{207}Pb/^{206}Pb)_0 = 0.904 \pm 0.038$
n = 10

15NP236_D
206±73/73 Ma MSWD = 0.84
$(^{207}Pb/^{206}Pb)_0 = 0.715 \pm 0.068$
n = 10

15NP236_E
272±57/58 Ma, MSWD = 4.3
$(^{207}Pb/^{206}Pb)_0 = 0.746 \pm 0.077$
n = 18

Vesicular basalt sample 15NP233

15NP233_A
324±4/16 Ma, MSWD = 2.4
$(^{207}Pb/^{206}Pb)_0 = 0.869 \pm 0.041$
n = 60

15NP233_B
327±5/16 Ma, MSWD = 2.5
$(^{207}Pb/^{206}Pb)_0 = 0.861 \pm 0.086$
n = 99

15NP233_C
337±7/17 Ma, MSWD = 9.8
$(^{207}Pb/^{206}Pb)_0 = 0.901 \pm 0.081$
n = 58

Figure 6: Tera-Wasserburg plots of ablation area ages on vesicular basalt samples 15NP236 and 15NP233. All errors are given as 2σ.

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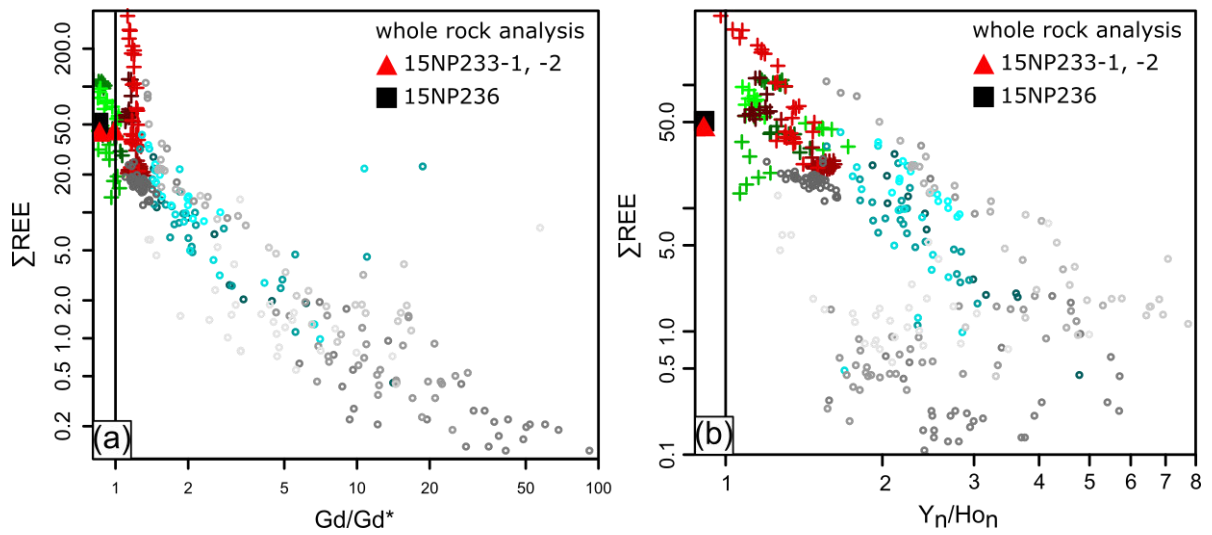
451 *Figure 7: (a) Mixing trend between high total REE—negative Gd/Gd* and low total REE—positive Gd/Gd* composition. (b)*

452 *Higher Y_n/Ho_n values correlate with low total REE. Y and Ho normalized against chondrite values of Anders and Grevesse*

453 *(1989). (e, f) + -15NP233, -236, o -17NP436A, -B; color-code see Appendix A.*

454

Stratigraphic units are C: Carboniferous, P: Permian, T1: Lower Triassic, T2: Mid Triassic, T2-3: Middle to Upper Triassic, J: Jurassic, K: Cretaceous, ⬡ hornblende 40Ar/39Ar age, ⬭ zircon U-Pb age, *340-320Ma (e.g., Ji et al., 2018; Jiang et al., 2008; Rembe et al., 2021)
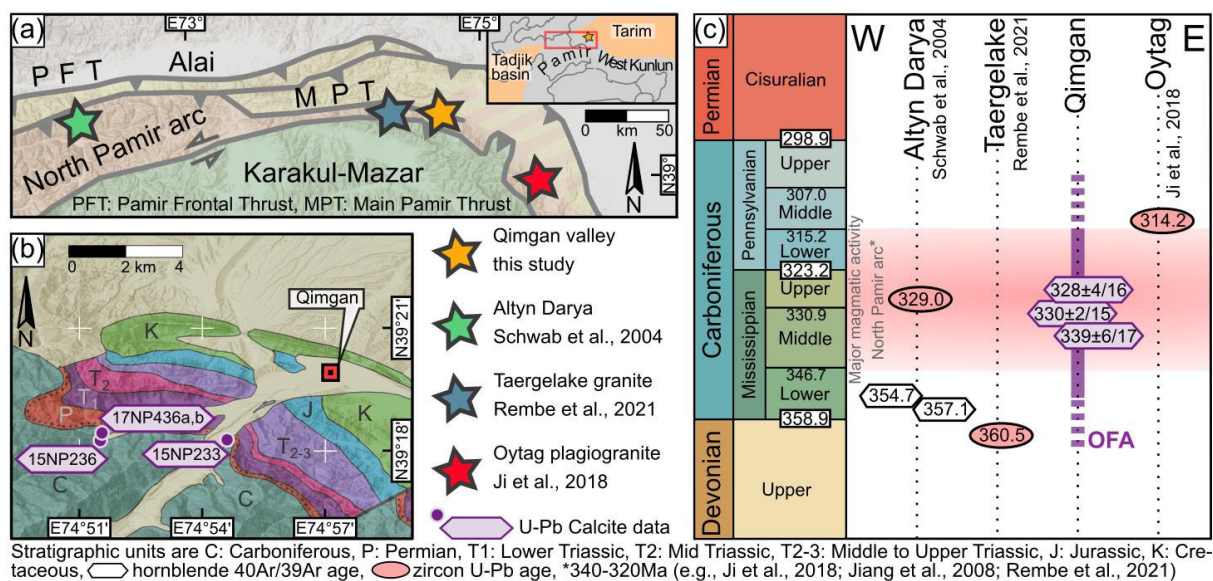
Figure 8: (a) Map of the northeastern Pamir with location of radiometric ages for the North Pamir arc volcanic rocks,

shown in c. (b) Detailed field locations of samples in the Qimgan 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. Stratigraphic

table and ages according to the International Chronostratigraphic Chart (Cohen et al., 2020).

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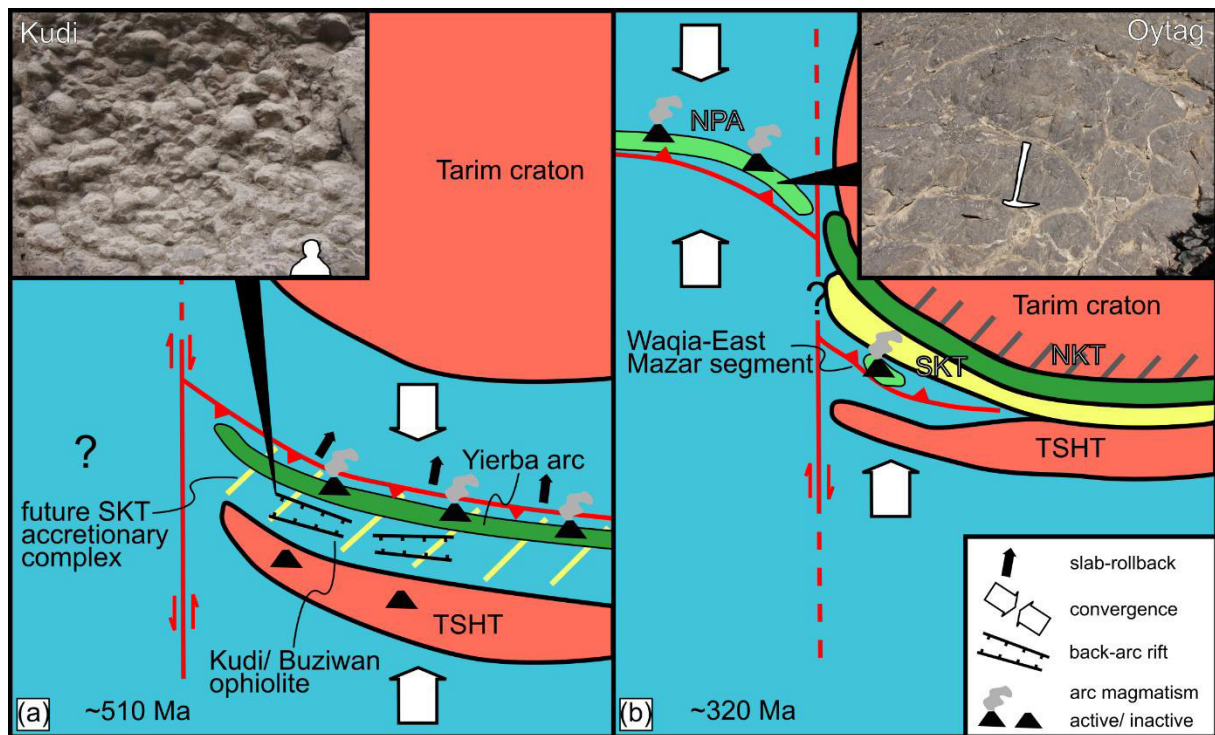
463 *Figure 9: (a) Paleogeographic situation in the mid-Cambrian: The roll-back of the Proto-Tethys slab caused the formation of*

464 *the Kudi ophiolite, exposed in the Buziwan valley (Wang et al., 2021). (b) Paleogeographic situation in the late*

465 *Mississippian: The North Pamir arc formed along an intra-oceanic subduction zone (Jiang et al., 2008) forming the Oytag*

466 *segment in its eastern branch. Subduction-related Waqia granite (Tang et al., 2020) and East Mazar granite (Li et al., 2006),*

467 *both today part of tectonic slivers, suggest the presence of a remnant oceanic basin between Tianshuihai and the South*

468 *Kunlun Terrane accretionary complex, as suggested by Zhang et al. (2018). Small photographs show pillow basalts in the*

469 *Kudi section (in a) and Oytag near Qimgan (in b). SKT-South Kunlun Terrane, TSHT-Tianshuihai Terrane, NPA-North*

470 *Pamir volcanic arc, NKT-North Kunlun Terrane.*

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637

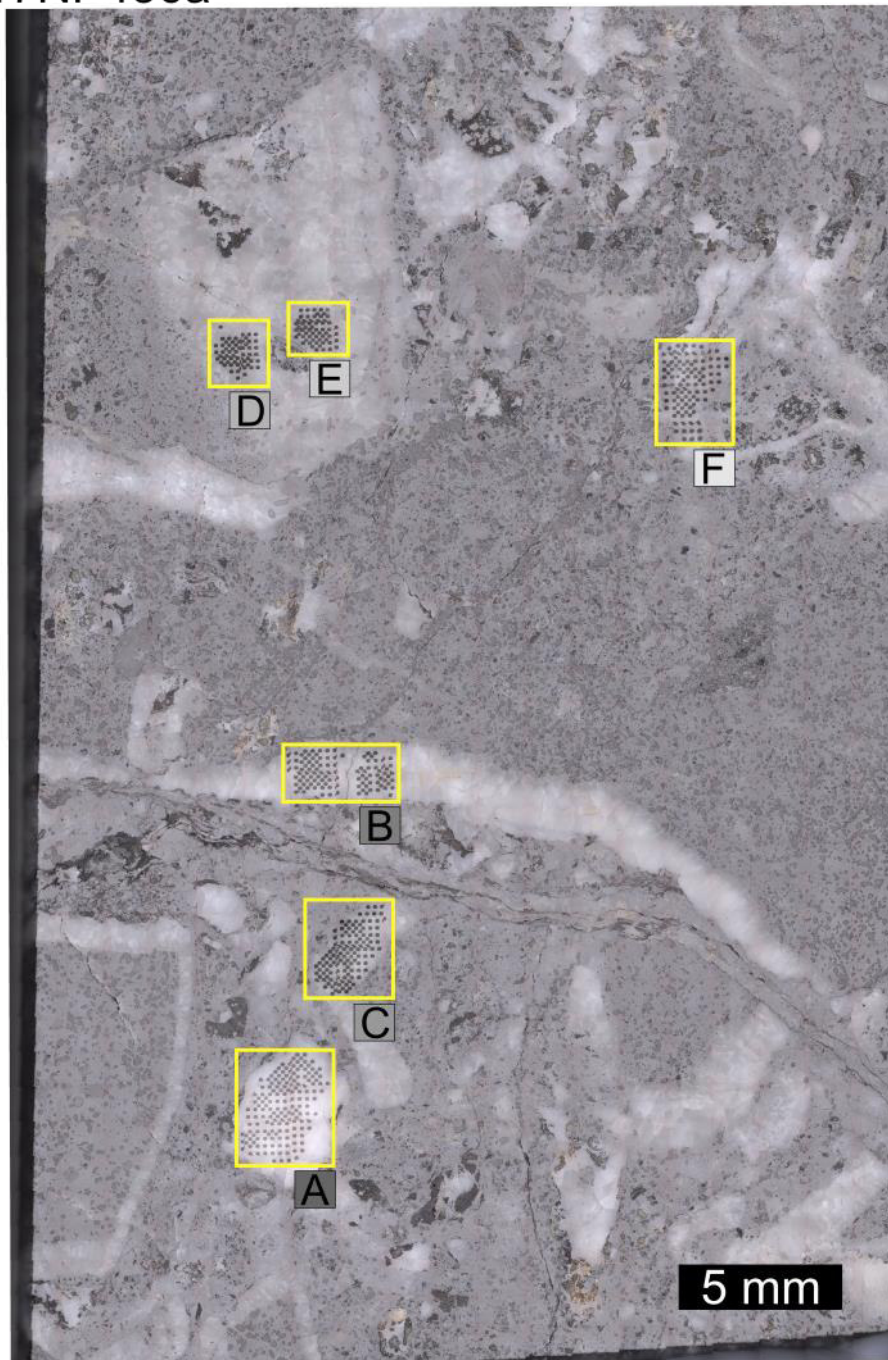
Appendix A

17NP436a

Figure A1. Reflected light image of sample 17NP436a 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.

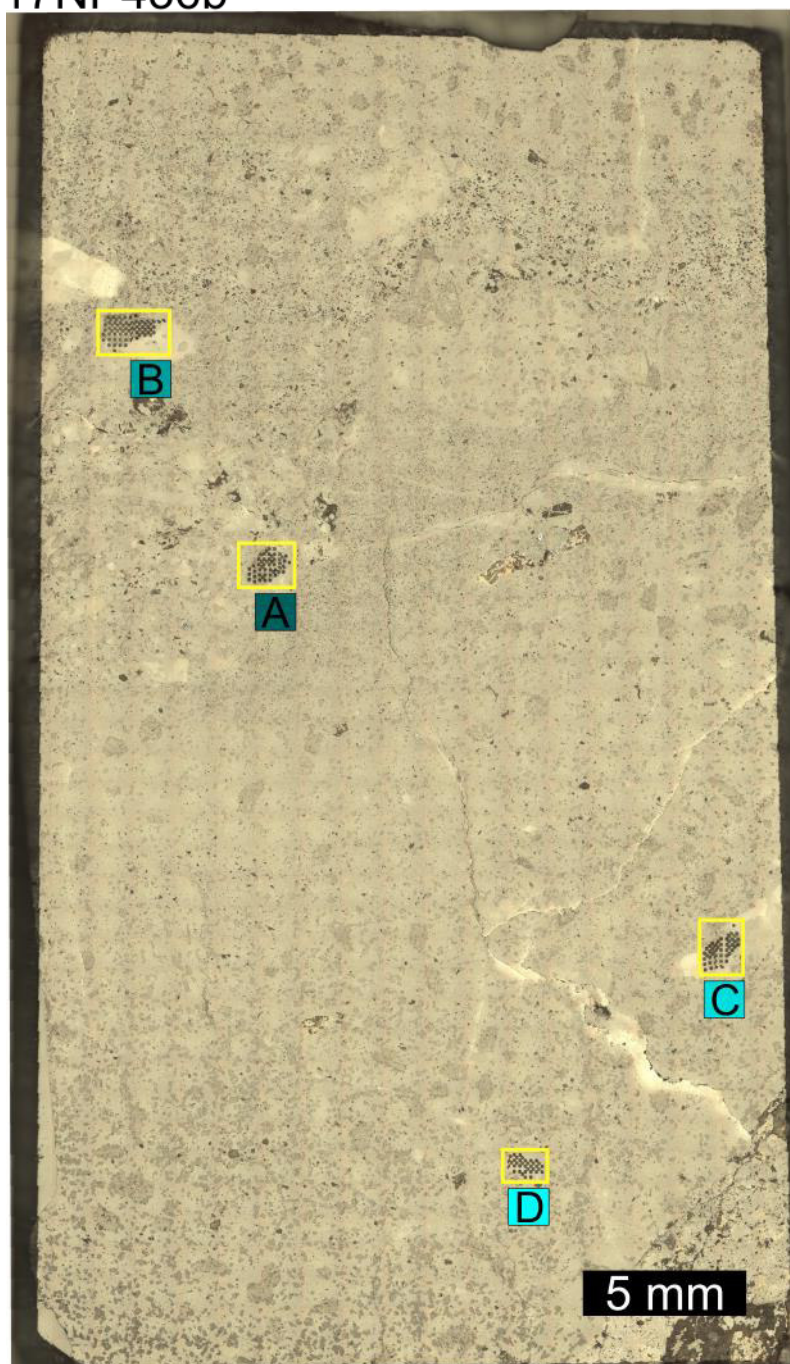
Appendix A

17NP436b

Figure A2. Reflected light image of sample 17NP436b 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.

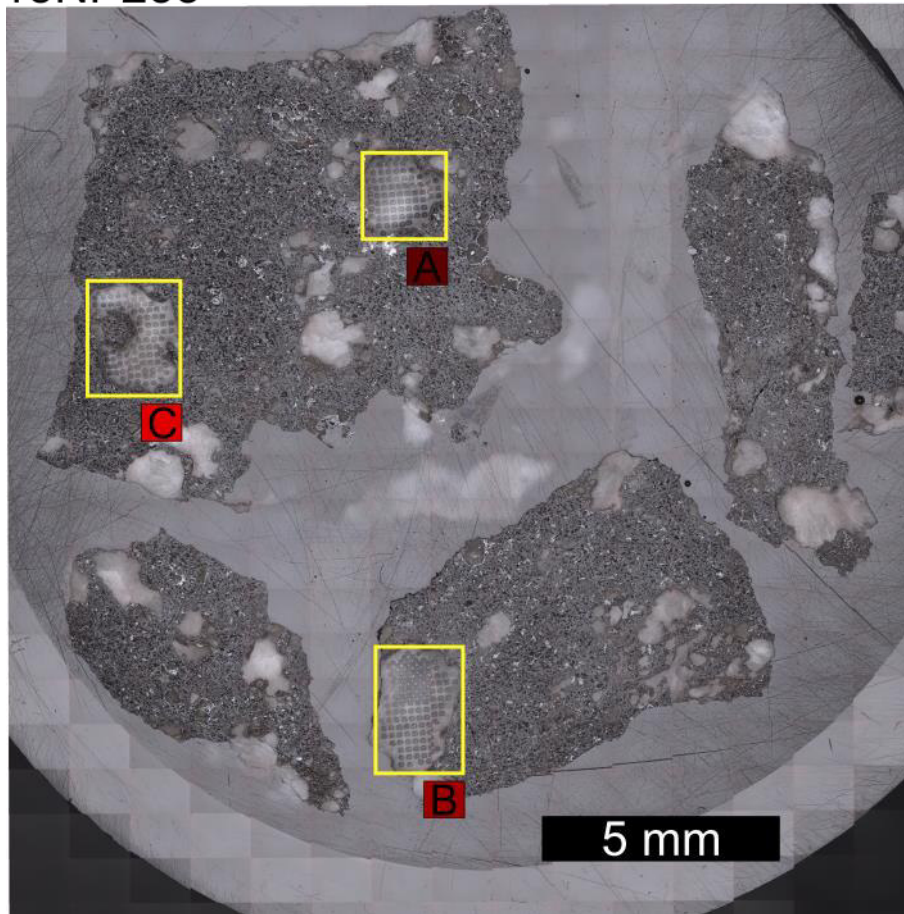
Appendix A

15NP233

Figure A3. Reflected light image of sample 15NP233 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.

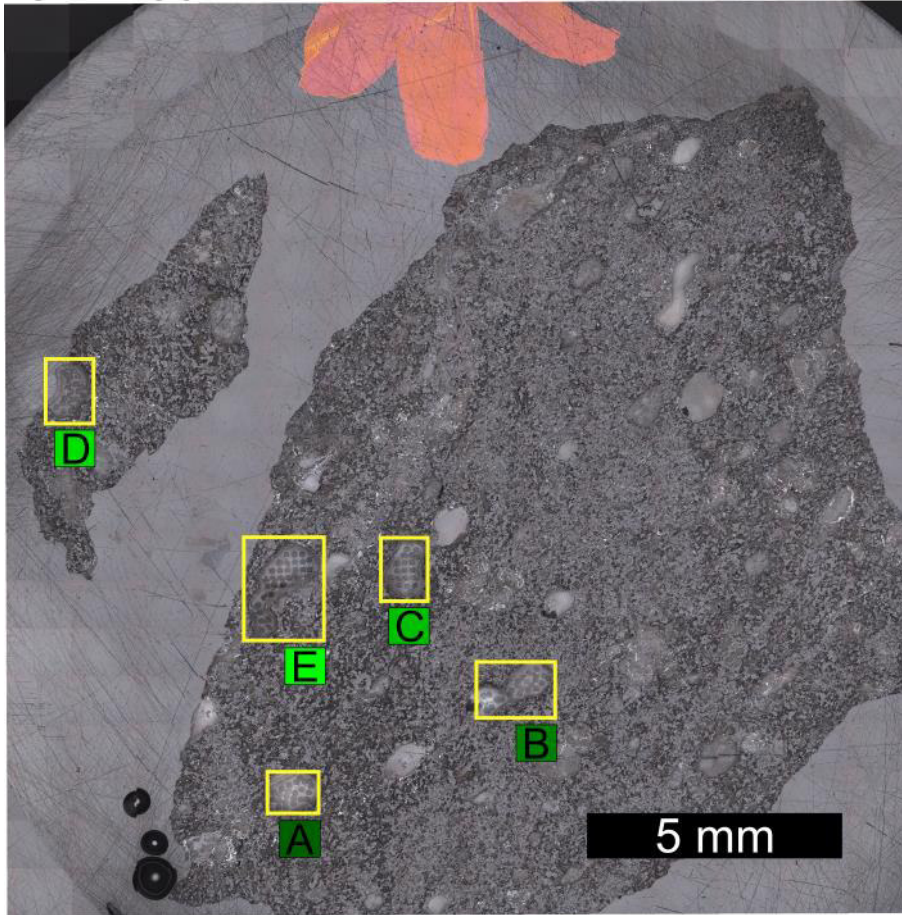
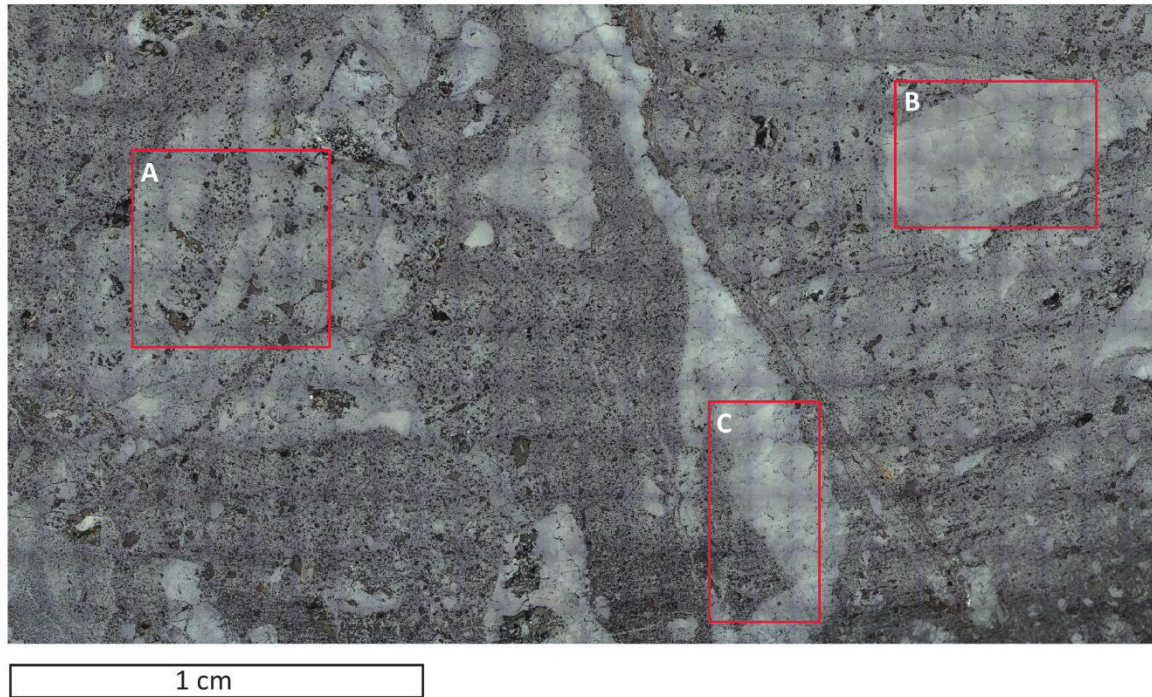
Appendix A

15NP236

Figure A4. Reflected light image of sample 15NP236 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

Reflective light photo

1 cm

Cross-polarized light photo

1 cm

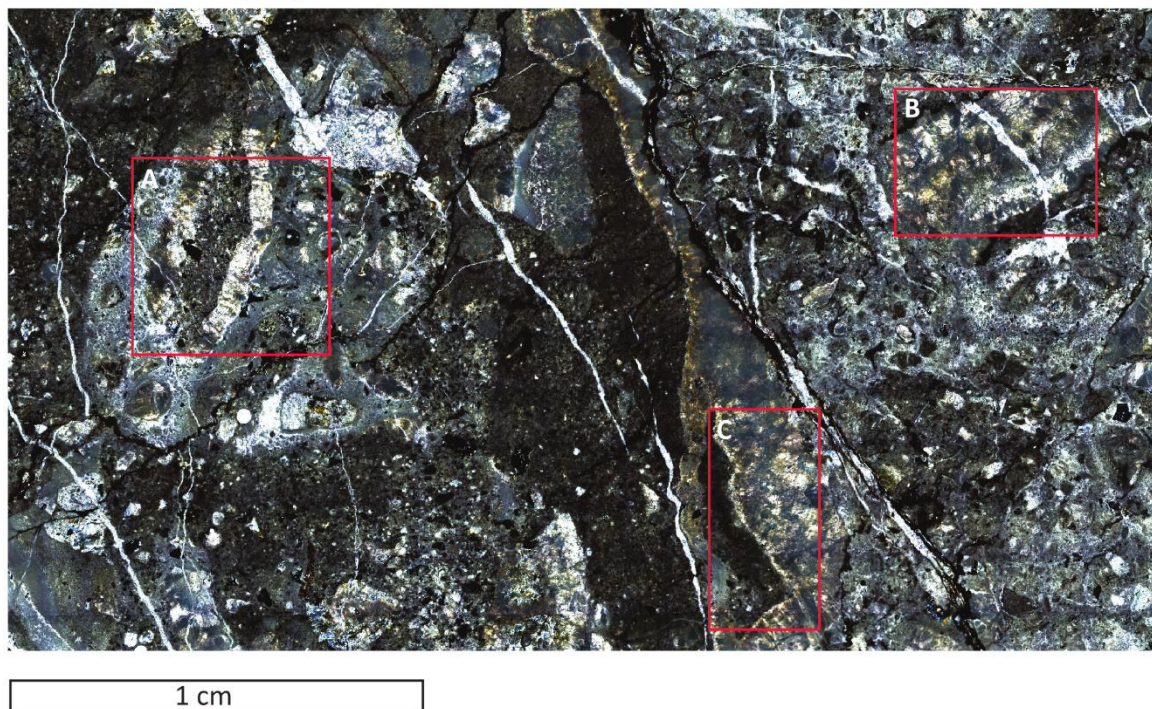



Figure B1. Reflected light image and cross-polarized light image of the investigation area on sample 17NP436a.

Appendix B

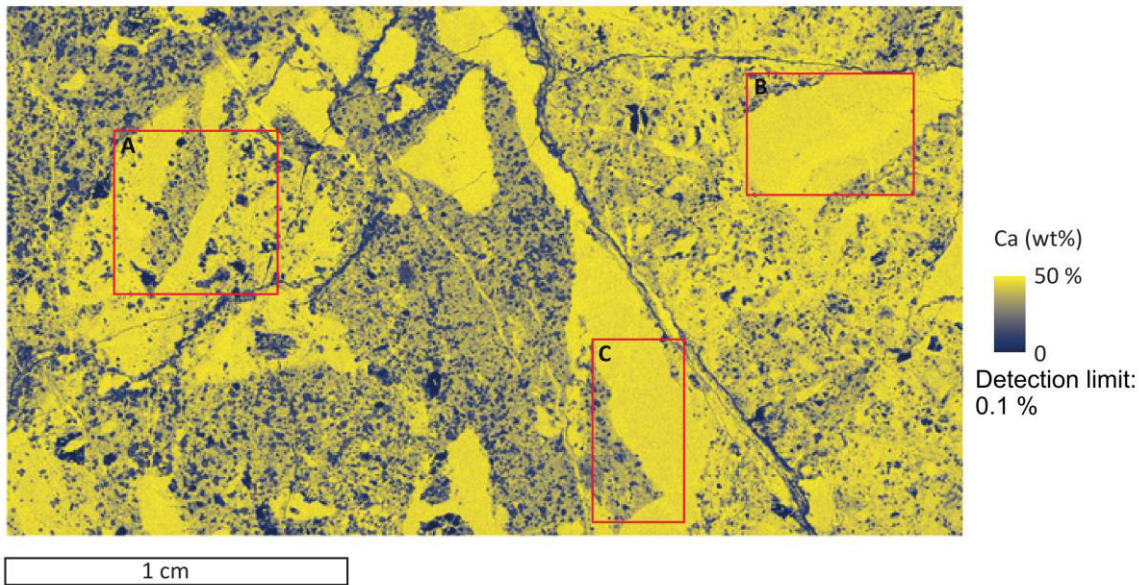
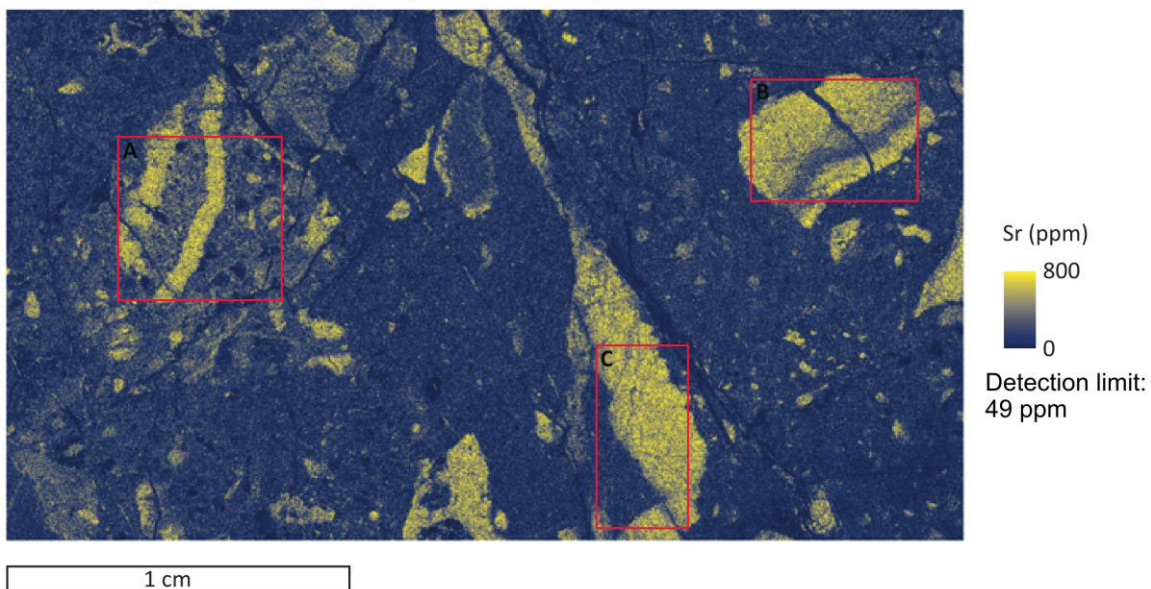



Figure B2. Coarse scan of the investigation areas on sample 17NP436a for Ca and Sr.

Area A shows a rock fragment fringed by radial-fibrous calcite cement. The right fissure shows calcite growing from both walls toward the center, showing lower Sr values in the center of the vein.

Area B shows an isolated fragment of radial-fibrous to equant cement with Sr and Ca zoning. High Sr/ low Ca values occur in the radial-fibrous calcite along the lower-right boundary with an abrupt change to low Sr/ high Ca values in the center that grade into high Sr/ low Ca values in a broad zone along the upper-left boundary. The low Sr/ high Ca values occur at the transition from radial-fibrous to equant calcite crystals. A younger calcite filled fissure crosscuts the calcite cement fragment. Crucial are the much lower Sr values. This fissure formed during tectonic straining of the rock, pressure solution and reprecipitation of calcite.

Area C shows calcite crystals with highest Sr/ lowest Ca values in the center of the single crystals.

Appendix B

Scan 66075 (resolution: 5 µm/ pixel; dwell time: 20ms)

Scan 66074 (resolution: 5 µm/ pixel; dwell time: 20ms)

Scan 66076
(resolution: 5 µm/ pixel; dwell time: 20ms)

Sr (ppm)
1000
0
Detection limit:
11 ppm

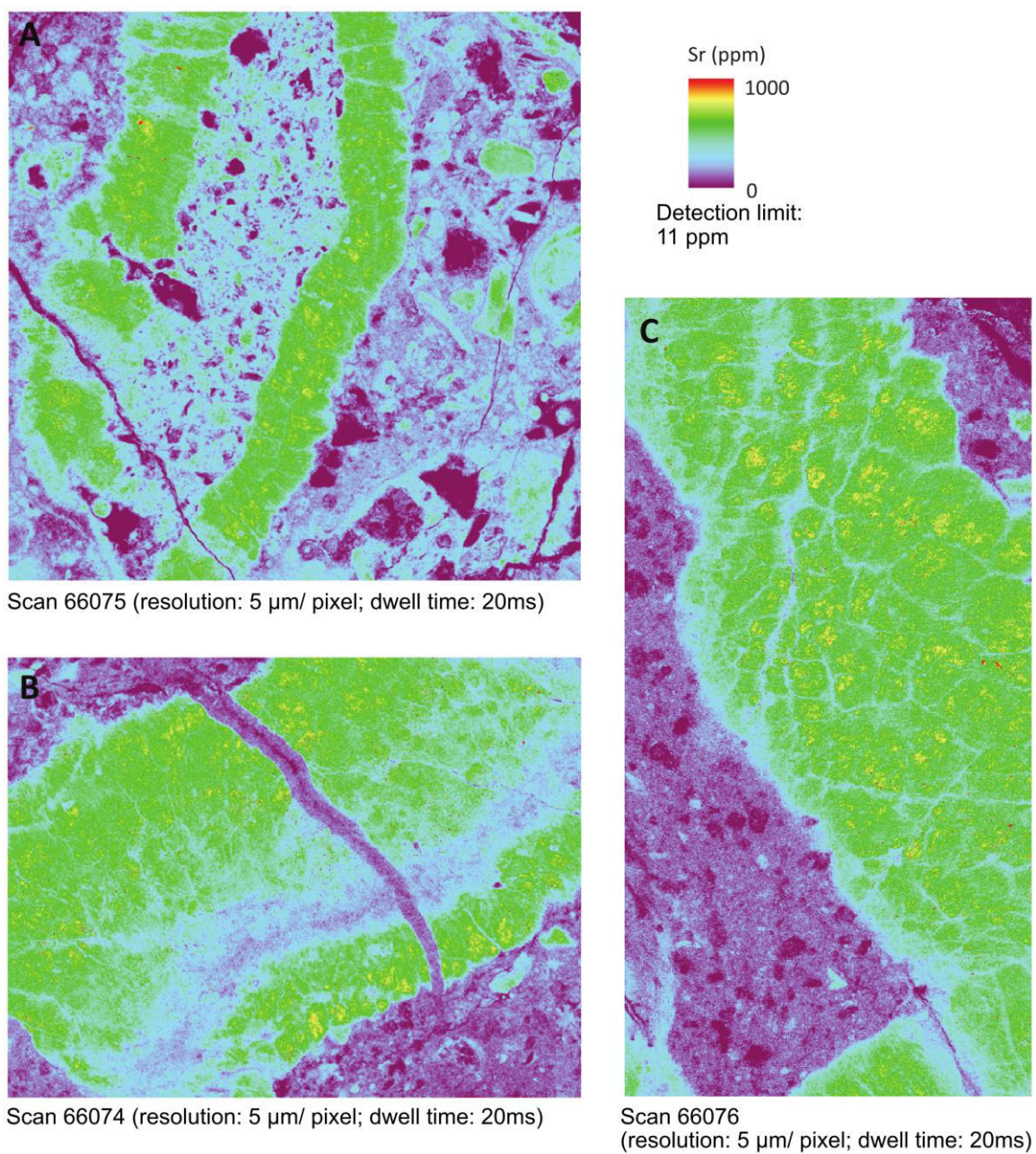



Figure B3. Fine scan of the investigation areas on sample 17NP436a for Sr.

Appendix B

Scan 66075 (resolution: 5 µm/ pixel; dwell time: 20ms)

Scan 66074 (resolution: 5 µm/ pixel; dwell time: 20ms)

Scan 66076
(resolution: 5 µm/ pixel; dwell time: 20ms)

Ca (wt%)

10 %

Detection limit:
0.03 %

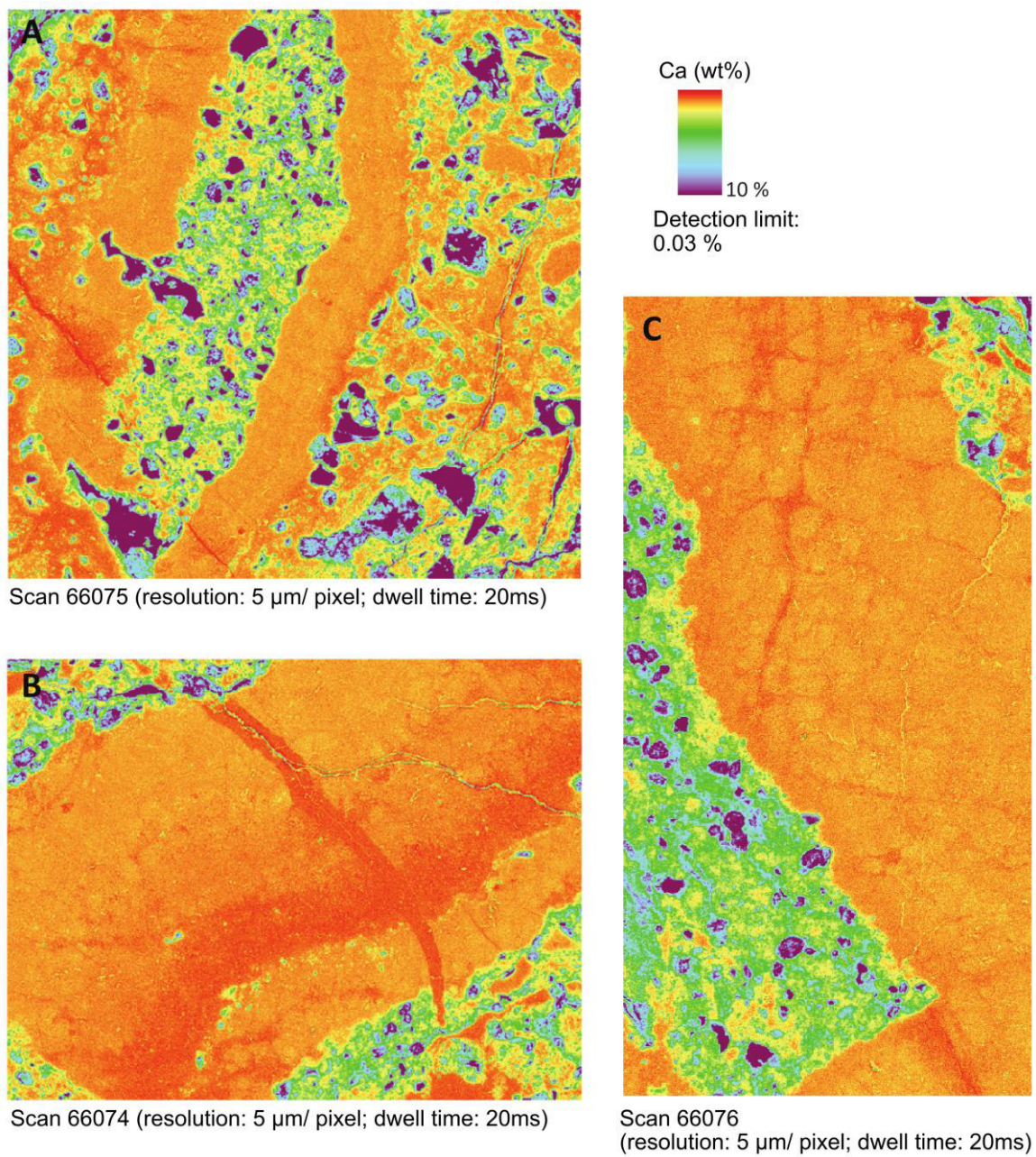



Figure B4. Fine scan of the investigation areas on sample 17NP436a for Ca.

17NP436a basalt breccia

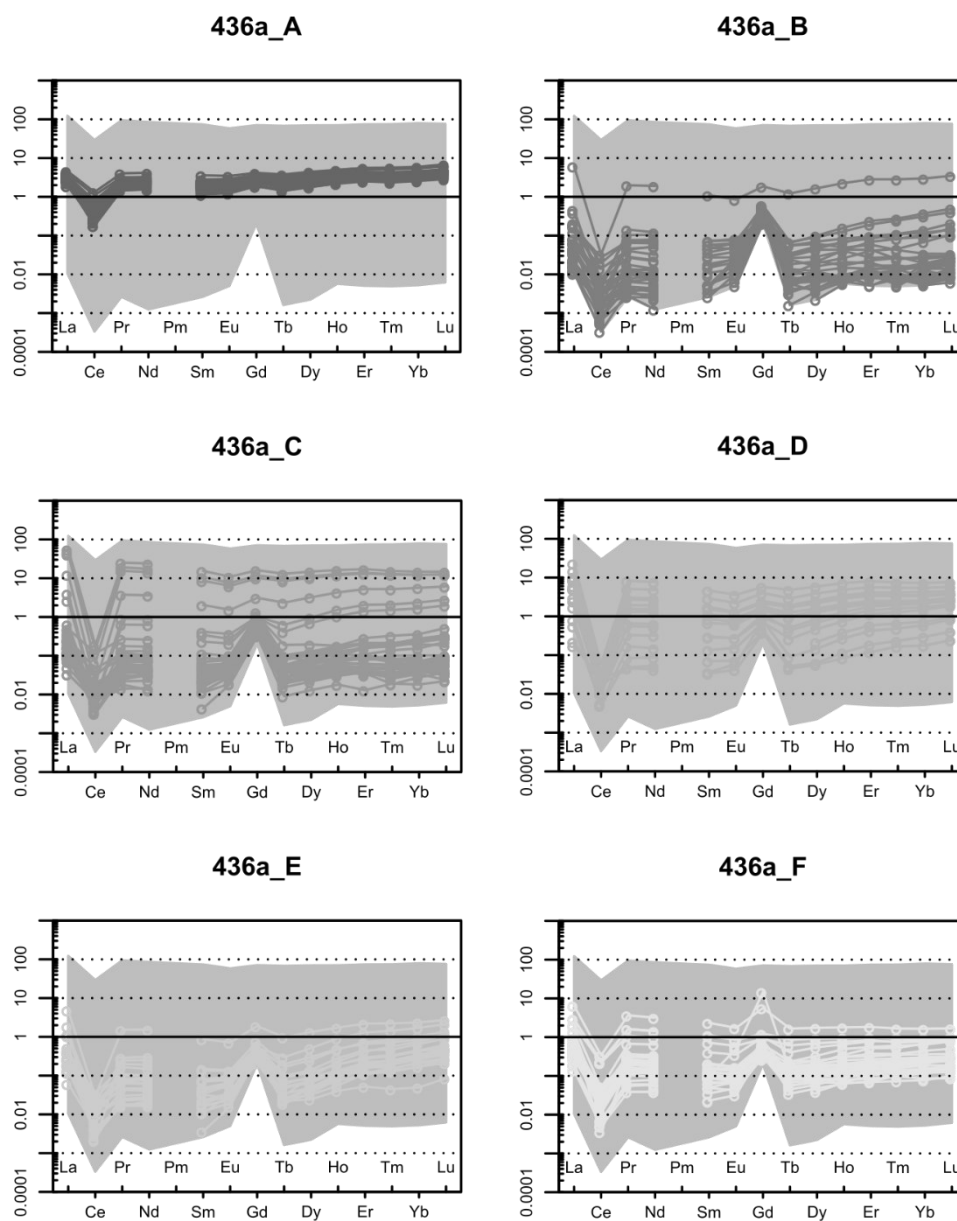



Figure C1. Rare earth element plots of each individual ablation area for sample 17NP436a. Grey shaded area in each diagram represents the range of chondrite normalized REE concentrations in all calcite ablation spots.

17NP436b basalt breccia

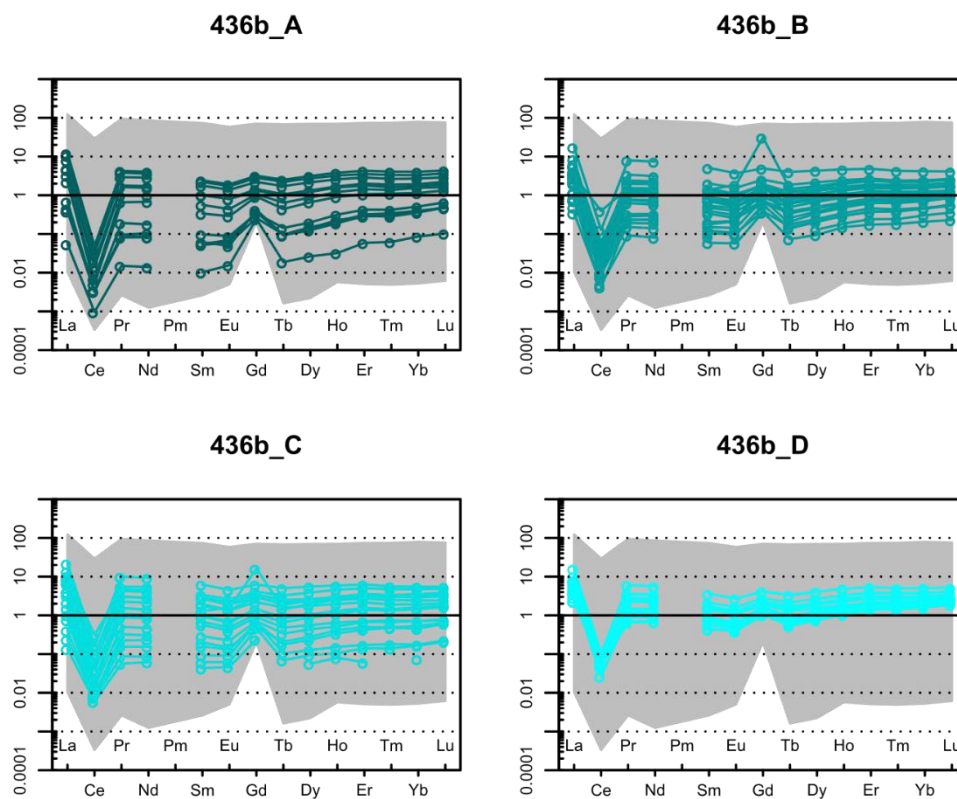



Figure C2. Rare earth element plots of each individual ablation area for sample 17NP436b. Grey shaded area in each diagram represents the range of chondrite normalized REE concentrations in all calcite ablation spots.

15NP233 vesicular basalt

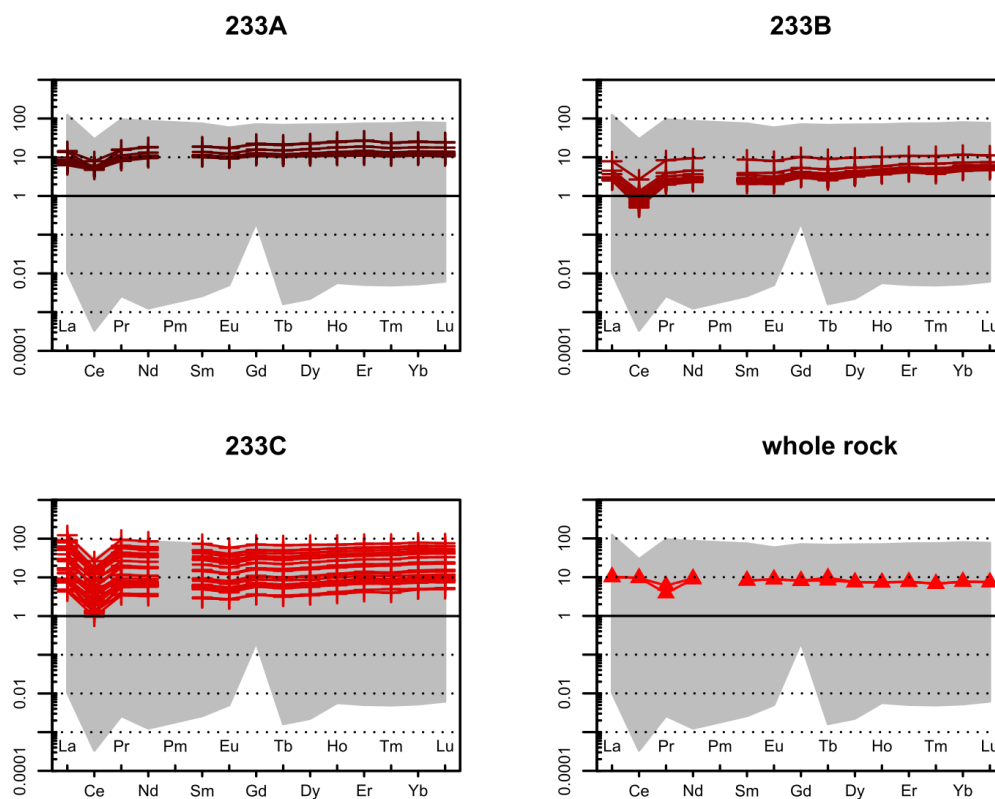



Figure C3. Rare earth element plots of each individual ablation area for sample 15NP233. Whole rock data from Rembe et al. (2021). Grey shaded area in each diagram represents the range of chondrite normalized REE concentrations in all calcite ablation spots.

15NP236 vesicular pillow basalt

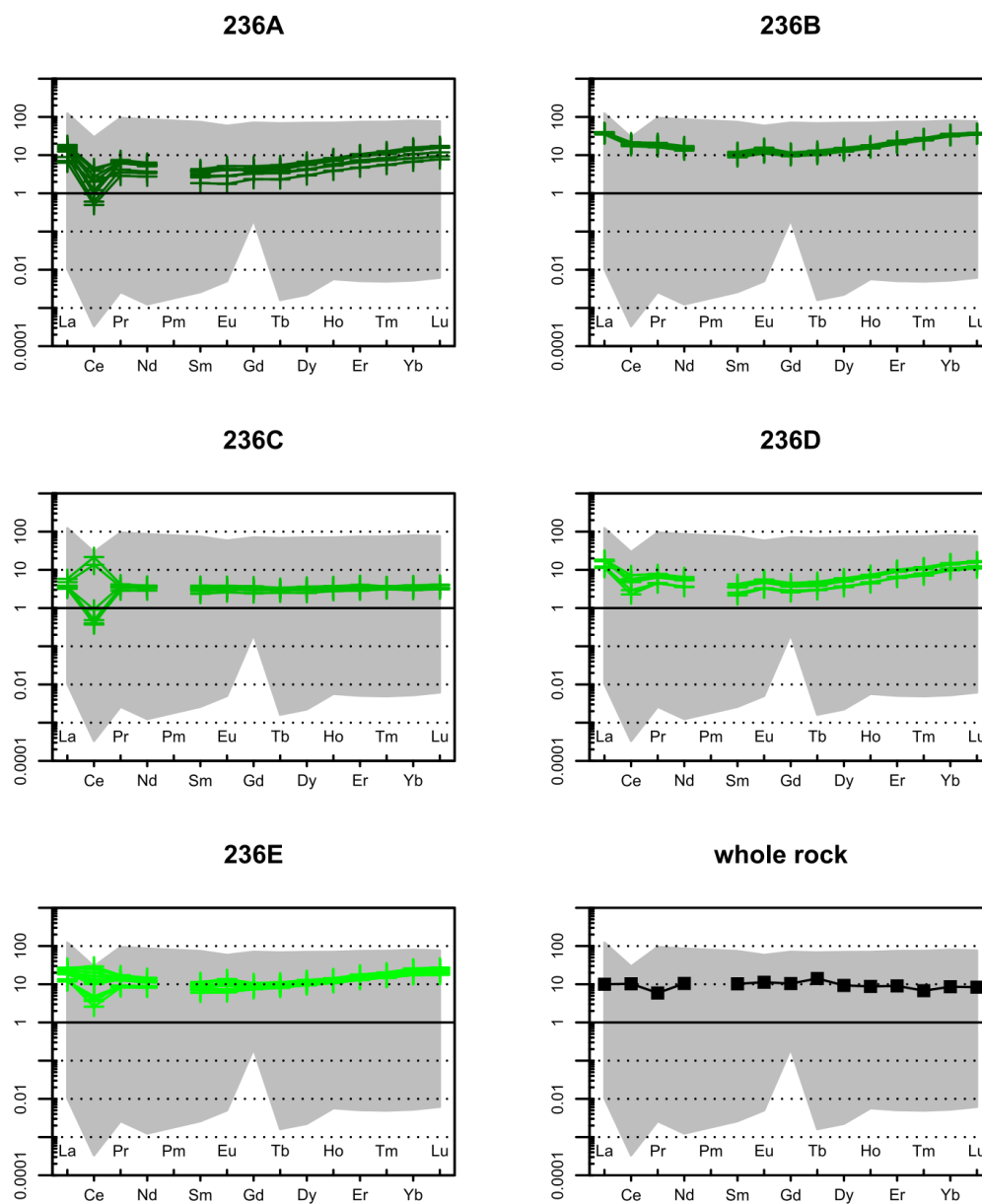



Figure C4. Rare earth element plots of each individual ablation area for sample 15NP236. Whole rock data from Rembe et al. (2021). Grey shaded area in each diagram represents the range of chondrite normalized REE concentrations in all calcite ablation spots.