Earth's earliest global glaciation? Carbonate geochemistry and geochronology of the Polisarka Sedimentary Formation, Kola Peninsula, Russia

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Research highlights:

ICDP FAR-DEEP Hole 3A targeted Palaeoproterozoic diamictites of the Polisarka Sedimentary Formation of Russian Fennoscandia ► Zircon U-Pb dating of a tuff above the diamictites yielded an interpreted minimum age of 2434 Ma for the diamictites ► This new U-Pb age constrains the onset of the Palaeoproterozoic glaciation in Fennoscandia to between ca. 2430 and ca. 2440 Ma ►

carbonate $\delta^{13}C$ analyses of carbonate rocks below the diamictites revealed two excursions to ca. -5‰ ► the origins of these excursions are carefully considered

Abstract

As part of the International Continental Scientific Drilling Program's Fennoscandian Arctic Russia – Drilling Early Earth Project (ICDP FAR-DEEP), Palaeoproterozoic diamictic and associated rocks were targeted and recovered in Hole 3A on the Kola Peninsula of NW Russia. In addition to the diamictites, carbonate sedimentary rocks and volcanic ash layers (all metamorphosed to greenschist grade) were encountered. Sedimentology and geochemistry suggest deposition of the diamictites in an open-marine aragonite-precipitating environment. Sampling of the core and of outcrops from the same geographical area yielded a number of zircons for analyses, the majority of which were inherited. However a tuff at 20.01 m core depth yielded zircons dated at 2434 ± 1.2 Ma (± 6.6 Myr including decay constant uncertainties) that we interpret as a magmatic age. These data, combined with dates from underlying intrusions, indicate deposition of the Polisarka Sedimentary Formation diamictites and underlying carbonates during an interval of time from ca. 2430 to 2440 Ma. The carbonate rocks, which likely originally included aragonitic limestones, were deposited mostly in a deep-water setting (i.e, at least below storm wave base) and occur below the diamictite. They record two inorganic carbon $\delta^{13}C$ excursions, from values of ca. 0‰ to minima of ca. -5.4‰, as the contact with the overlying diamictite is approached. The older excursion occurs about 9 m below the base of the diamictic units and the younger one at 1m below. Throughout that interval, Mg/Ca ratios correlate strongly with $\delta^{13}C$ (n = 38, r = 0.85), and combined with petrographic observations, this indicates that the first (stratigraphically lower) excursion was modified by secondary alteration and the second is recorded in resedimented dolostone clasts. It is tempting to speculate that these dolostone clasts weredeposited in penecontemporaneous shallow-marine waters, and that their low $\delta^{13}C$ values might reflect input of oxidised atmospheric methane to the ocean surface (and therefore the cause of the glaciation); the dolostones were subsequently

resedimented into the deeper marine settings. However this must be left as a hypothesis to be tested when further age-constrained contemporaneous pre-glacial carbonate sections are found.

Keywords:
Huronian-age glaciation; carbon isotopes; carbonate rocks; Palaeoproterozoic; Great Oxidation Event

Introduction

During the purported global glaciation episode(s) of the Palaeoproterozoic, ice extended from the poles to low latitudes at least once (e.g. Evans et al., 1997; Mertanen et al., 1999; Melezhik, 2006; Melezhik et al., 2013a; Hoffman, 2013). These early glaciations may have been as significant for biological and geological evolution as the 'Snowball Earth' episodes in the Neoproterozoic, a billion years later. Robust geochemical testing of proposed causes for severe climatic deterioration in the Palaeoproterozoic has been hindered by lack of suitable rock types in immediately pre-glacial sections.

Varied explanations for initiation of glaciation have included atmospheric CO_2 (greenhouse gas) drawdown resulting from enhanced chemical weathering of silicate rocks because of collisional tectonics (Young, 1991), rifting at low latitudes (e.g. Evans, 2003), and a combination of tectonic and environmental factors (Melezhik, 2006). These models implicitly require lengthy (million-year timescale) durations as they involve processes operating at rates of the geological rock cycle, and all permit repeat episodes of global freezing, as observed in the rock record. Another potential driver to consider is catastrophic and rapid oxidation of Earth's proposed early methane atmosphere (e.g. Kasting et al., 1983; Pavlov et al., 2000; Kopp et al., 2005; Papineau et al., 2005; 2007). Here, the warming effect of a methane-rich atmosphere might have counteracted the relative weakness of the young Sun and a methane atmosphere was invoked to explain the relative lack of evidence for glaciation until the Palaeoproterozoic (Pavlov et al., 2000; see also corrections by Haqq-Misra et al., 2008). This state-of-affairs ended when atmospheric free oxygen first became widespread ca. 2.4 billion years ago (e.g. Pavlov et al., 2000; Kopp et al., 2005; Kasting, 2005; Melezhik, 2006; Haqq-Misra et al., 2008; Guo et al., 2009), the 'Great Oxidation Event' (GOE). Photochemical dissociation of ozone in the newly oxic atmosphere (with less free H_2) would have given rise to free OH^- radicals. These, in turn, could have reacted with methane to produce $CH_3 + H_2O$, as well as a series of short-lived organic molecules (Ravishankara, 1988), and, finally, bicarbonate ions. It has been estimated that the GOE would have shortened the lifetime of methane in the atmosphere from 10^5 to ~10^1 years (as found at present; Pavlov et al., 2003; Kasting, 2005). Although it now seems that methane alone would not have been a sufficiently strong greenhouse gas to keep the early Earth ice-free (e.g. Haqq-Misra et al., 2008), the latter authors concluded that loss of methane from the atmosphere was still a likely trigger for glaciations around 2.4 billion years ago. The methane oxidation hypothesis is testable because it implies a one-off, unrepeatable rapid transfer of a vast quantity of ^{13}C-depleted carbon from the atmosphere to the surface oceans, thereby initiatingthe first Palaeoproterozoic glaciation. This likely would have been recorded in contemporaneous marine carbonate rocks, which is why Palaeoproterozoic carbonate rocks below diamictites recently discovered in Fennoscandian Russia are important. These were found in International Continental Drilling Program (ICDP) Fennoscandian Arctic Russia – Drilling Early Earth Project (FAR-DEEP) Hole 3A which targeted the Polisarka Sedimentary Formation of the Imandra-Varzuga Belt (Fig. 1).

Evidence for Palaeoproterozoic glaciation in the Fennoscandian region includes diamictites and dropstones of the Urkkavaara Formation (Sariolian group, Marmo and Ojakangas (1984)). There are known dropstones in sediments with varve-like laminations in the Polisarka Sedimentary Formation (Imandra-Varzuga Greenstone Belt; Melezhik et al., 2013b) and its stratigraphic equivalents in the Shambozero and Lekhta Greenstone Belts (cf. Negrutsa, 1984). None of these naturally exposed Fennoscandian sections are known to include a carbonate unit below the diamictite, so the discovery of such rocks in ICDP FAR-DEEP Hole 3A was serendipitous. Stable isotopic analyses of these carbonate rocks are reported here, with the aim of illuminating the cause of the glaciation. In addition, volcanic ash beds have been sampled for U-Pb dating of zircons to constrain the age of the diamictite-containing Polisarka Sedimentary Formation, thereby aiding global correlations and geologic context.

Geological setting

ICDP FAR-DEEP Hole 3A was drilled in the Imandra-Varzuga Greenstone Belt at latitude 67.4862N, longitude 34.5404E, between the 7th and 14th September 2007, to a total depth of 254.5 m (see Fig. 1). The target was the Palaeoproterozoic Polisarka Sedimentary Formation (Fig. 2), known from outcrop to contain diamictites (Fig. 3f) that could correlate with the Huronian diamictites of North America (Melezhik, 2013). Depths given in this manuscript are in metres composite depth (MCD).

The diamictite-containing Polisarka Sedimentary Formation sits unconformably on the Seidorechka Volcanic and Sedimentary formations, both of which overly the Kuksha and Purnach formations (Fig. 2). The Kuksha Volcanic Formation lies unconformably on the Monchegorsk layered gabbro-norite pluton (Chashchin et al., 2008), and the Kuksha Sedimentary Formation seals eroded and faulted surfaces of the pluton (Melezhik, 2013; Melezhik et al. 2013a). Zircons from the Monche Pluton were radio-isotopically dated at 2504.4 ± 1.5 Ma (ID-TIMS $^{207}Pb/^{206}Pb$ weighted mean date; Amelin et al., 1995). In the mid- to upper-Seidorechka Formation, baddeleyite grains in a subvolcanic unit yield a 2442.2 ± 1.7 Ma age (ID-TIMS upper intercept date; Amelin et al., 1995). This unit is spatially and temporally associated with an intrusion (the Imandra lopolith) dated by U-Pb ID-TIMS at 2441 ± 1.6 Ma (ID-TIMS $^{207}Pb/^{206}Pb$ weighted mean date; Amelin et al., 1995).

In the western part of the Imandra-Varzuga Greenstone Belt, the Avarench locality is comprised of a komatiitic basalt – andesite – dacite – rhyolite association that is considered the lithostratigraphic equivalent of Strelna Group rocks, including the Kuksha and Seidorechka Formations. Zircons extracted from two samples of plagioclase and quartz dacitic metaporphyrites yield an age at 2429 ± 6.6 Ma (U-Pb zircon SHRIMP date; Vrevsky et al., 2010). This dated unit is considered to be the litho- and chrono-stratigraphic equivalent of the Seidorechka Volcanic Formation (e.g., Melezhik, 2013). The c. 2504 Ma age of the Monche Pluton is the maximum age for the Imandra-Varzuga belt succession, and provides one age constraint to the Polisarka Sedimentary Formation. However, if the interpretation of Amelin et al. (1995) that the subvolcanic (c. 2442 Ma) unit is a 'feeder' to the Seidorechka Volcanic Formation is correct, then the age of the spatially associated Imandra Lopolith (slightly younger than 2442Ma, at ca. 2441 Ma) can be taken as a maximum age for the Polisarka Sedimentary Formation.

ICDP FAR-DEEP Hole 3A: stratigraphic and preservational context of the carbonates

The Polisarka Sedimentary Formation in ICDP FAR-DEEP Hole 3A is sandwiched between rhyodacites of the underlying Seidorechka Volcanic Formation and mafic komatiites of the overlying Polisarka Volcanic Formation. It was informally divided by Melezhik et al. (2013b) into a lower carbonate-rich Limestone member and an upper siliciclastic Greywacke-diamictite member. The contact between these members lies at around 123.8 m depth. The first thick diamictite bed occurs at around 114 m (Fig. 2). Three smaller diamictite units have been documented in the Limestone member. The first out-sized clast associated with deformed underlying laminae occurs at 183.2m but its origin as a potential dropstone is tempered by the fact that variably developed tectonic shearing is present in ICDP FAR-DEEP Hole 3A. Clasts and dropstones (Fig. 3a; 3g) are commonly tectonically flattened or exhibit sigmoidal morphologies, with their long axes parallel to bedding and shearing (Fig. 3a). In the Limestone member, millimetre-scale laminations comprising laterally discontinuous layers of carbonate alternating with layers of siltstone might reflect an original sedimentary texture (Fig. 3b; Melezhik et al., 2013b), but bedding-parallel shearing can generate transposed bedding resulting in a metamorphic-related 'pseudo-lamination'. This greenschist facies metamorphism complicates the interpretation of depositional environments here, but sedimentary features can be distinguished in low-strain zones.

On a broad scale, Melezhik et al. (2013b) suggested that fine compositional laminae and lack of traction-bedded structures indicate a relatively deep-water setting (below effective storm and fairweather wave base) for the Limestone member (Fig. 2). They suggested that exotic and faceted diamictite clasts that in places pierce compositional layering indicate a glacio-marine origin for the Greywacke-diamictite member. The transition from the Limestone member to the overlying Greywacke-diamictite member is one of siliciclastic upward coarsening over several metres, and the contact itself is marked by a sharp-based medium to coarse-grained laminated arkosic sandstone. These relationships are consistent with glacio-eustatic sea-level fall, with the arkosic bed representing a consequent base level incision and basinward facies shift. It is difficult to assess the water depth in which the glacial diamictites were deposited, but we assume that they were deposited in at least similar and likely shallower settings than the carbonate rocks.

Melezhik et al. (2013b) briefly described several igneous bodies encountered in the Limestone member (Fig. 2). These include a thin alkaline ultramafic body (225.15 to 225.97 m) that is best interpreted as a dyke belonging to the Palaeozoic alkaline province of the Kola Peninsula; 0.2 to 4m thick mafic bodies that have been interpreted as Palaeoproterozoic lava flows (212 to 189 m); and a 44 m thick massive ultramafic peridotite (175.68 to 131.17 m). Diagnostic features that would allow the latter to be ascribed as either intrusive or extrusive seem to be lacking. Igneous bodies including komatiites are also encountered above the diamictite sediments (Fig. 2).

Methodology: stable isotopes and elemental geochemistry

Methods used in the sampling and analyses of rock samples for their stable isotopic and elemental compositions are given in detail in the Supplementary Information.

Methodology: U-Pb geochronology

Targeted for chronology were 14 samples from drill core 3A; one field specimen containing dropstones from the Polisarka Sedimentary Formation; one field sample from the Ahmalahti Formation that stratigraphically overlies the Polisarka Sedimentary Formation; and three samples from the Seidorechka Volcanic Formation that stratigraphically underlies the Polisarka Sedimentary Formation. For U-Pb dating an analytical approach combining laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) with subsequent isotope dilution thermal ionisation mass spectrometry (ID-TIMS) of grains of interest (i.e., likely younger than the existing maximum age constraint) was employed. Further details are given in Supplementary Information.

Results

Sedimentary rock petrography

Sedimentary rocks of the Limestone member (Melezhik et al., 2013b) include finely laminated ‘limestone and siltstone couplets’ (Fig. 3). Some of the carbonate layers are continuous across the core width (Fig. 3b), while others form discontinuous lenses (see Figs. 3c and 3d; also Melezhik et al., 2013b). The sedimentary protoliths of these layered carbonate-siliciclastic rocks were likely carbonate and quartz-rich siltstones, now metamorphosed to marbles with interlocking crystal fabrics. Some marbles are relatively pure carbonate rocks, like those found at 128.35 m (Fig. 4a), while others include layers of quartz and talc found at 182.44 m and 201.14 m (Figs. 4b and 4c).

Layered carbonate-siliciclastic rocks both below and above the peridotite body (Fig. 2) commonly contain laminae of a soft metallic grey mineral with a blue sheen in hand-specimen. In thin-section this mineral shows pleiochroism from light brown to colourless (Fig. 4d), with birefringence to 2nd order red. The mineral is therefore deduced to be talc, and this concurs with bulk rock XRD analyses (Table S1 in supplementary information). In thin-sections, several crenulated talc layers are cross-cut (replaced) by euhedral rhombs of dolomite (Fig. 4d). Talc-replacement carbonate rhombs (shown as they appear in the core in Fig. 3e) are found in abundance in other sections of the stratigraphy, particularly within the serpentinised peridotite body between 175.68 m and131.17 m (Fig. 4e). Petrographic examination reveals that komatiites at 81.69 m are also carbonatised and serpentinised (Fig. 4f).

Distinctly different in appearance to the secondary dolomite rhombs are dusty-looking and more rounded carbonate clasts conclusively identified only around 126.97 m depth (Fig. 5). These clasts are found in at least four 3 cm-thick beds separated by foliated thin carbonate layers. Staining with Alizarin Red S revealed that the clasts are dolomitic, and the sheared carbonate layers are dominantly calcitic. These rocks lack talc, but do contain laths of white mica aligned parallel layering (Fig. 5) and interpreted as the metamorphic product of clay minerals. This mica is most prominent in calcitic foliated layers (these layers lack quartz) and also occurs with small quartz crystals around the margins of dolostone clasts (but is absent in the clasts). The mineralogy deduced from petrography is consistent with bulk rock XRD analysis (Table S1; quartz, calcite, dolomite, muscovite).

Veins and veinlets comprised of quartz and carbonate, some of which are ptygmatically folded, are found in several places (Figs. 3d, 4b and 7). Their presence raises the prospect that circulating meteoric, burial or metamorphic fluids might have altered carbonate stable isotope compositions. Following acquisition of bulk rock stable isotope data (Fig. 6), carbonate rocks around a quartz vein that occupies approximately 20cm of the core at ca. 125 m depth (Figs. 2 and 7), and a 1 cm thick quartz veinlet at ca. 126.85 m, were targeted for sampling, to assess whether carbonate stable isotopic compositions were affected by vein-associated fluids. Carbonate veins were also analysed for their stable isotopic composition and include those sampled from above and below, as well as within, the peridotite body. The final phase of carbonate present is as mm-thick brown weathering alteration rims around diamictite clasts; these, too, were sampled for stable isotopic analyses using a hand-drill.

Elemental chemistry results

Elemental concentrations of powdered samples measured by XRF give data applicable to the whole rock, whereas the ICP-AES data should relate more specifically to the carbonate component. Magnesium concentrations (measured by ICP-AES) of the carbonates range from 1410 to 97600 ppm, and Mg/Ca molar ratios up to a maximum of 47% Mg (vs 53% Ca). The carbonates are therefore limestones to calcitic dolostones. Elemental analyses of bulk rock powders have not revealed any stoichiometric dolostones in these cores. On the basis of available elemental data, the main intervals of dolostone in FAR-DEEP Hole 3A are from 221 to 225 m; immediately above the peridotite at 130.94m; and from ~124 to 127.4 m. However some samples have 'out of sequence' Mg/Ca values if the trend from ~124 to 127.4 m is interpreted as purely depth- and time- related (Fig. 6). Importantly, Mg/Ca molar ratio correlates very strongly with $\delta^{13}C$ over the interval of the carbon isotope excursions (Fig. 7): the lowest $\delta^{13}C$ values are undoubtedly from Mg-rich carbonates ($n = 38$, $r = 0.85$).

Cr and Ni concentrations of acetic-acid soluble ('carbonate') components (measured by ICP-AES) also correlate very strongly with $\delta^{13}C$ between 130.82 and 124.33 m depth (see Table S2 in supplementary information). Chromium and nickel concentrations of the first carbonate sample above the peridotite are very high (38 and 12 ppm, respectively). Whole-rock Cr and Ni concentrations (measured by XRF) do not show the strong correlation with carbonate $\delta^{13}C$ between 130.82 and 124.33 m .

Strontium concentrations (ICP-AES) range from 13 to 1180 ppm. Manganese concentrations (ICP-AES) range from 8 to 3980 ppm. Mn/Sr molar ratios (ICP-AES) range from 0.33 to 23 with the highest ratio from any sample below the peridotite (Fig. 8) being 8.1. Mn/Sr (ICP-AES) molar ratios > 9 are found at 130.94 m (the first carbonate sample above the peridotite) and in all measured bulk rock samples from ~127.8 m upwards (Fig. 8). The maximum Mn/Sr ratio of 23 at 126.01 m is exceptional. Whole-rock Mn/Sr ratios (measured by XRF) are mostly lower (< 5, with a maximum measured value of 8.7). Overall Mn/Sr trends in the XRF bulk rock data are similar to those found in the ICP-AES 'carbonate' data.

Carbonate stable isotope results

Measured bulk carbonate rock $\delta^{13}C$ values in FAR-DEEP Hole 3A range from +0.9 to -5.4‰ (VPDB). The minimum $\delta^{13}C$ value from the 44 'hand-drilled' carbonate powders was -7.5‰, with a maximum of +0.6‰. Below 177 m depth, almost all $\delta^{13}C$ values fall in the range 0 ± 1 ‰. Above 178 m, at least two $\delta^{13}C$ excursions to minima of around -6‰ are seen (Fig. 6). The first begins at ~177.5 m, with $\delta^{13}C$ falling to -2.7‰ from a starting position 2 m below the base of the peridotite. Carbon isotopic compositions of secondary dolostone crystal growths within the peridotite were measured at -6.4‰ (sample from 135 m), while veins in the peridotite are less negative at the base of the body (-4.0‰; 150.49 m) than at the top (-6.6‰; 132.8 m). All other secondary carbonates obtained from within the peridotitic section gave $\delta^{13}C$ compositions within this range.

The first 'bulk' carbonate rock sample above the peridotite (at 130.94 m) has low $\delta^{13}C$ of -5.4‰, and this was confirmed by a value of -5.8‰ from a sample of the same brown discoloured carbonate taken from 131.1 m (Fig. 6). The carbon isotope trend is towards 0‰ in the overlying carbonate rocks, reaching 0‰ at129.78 m before declining to a nadir of -5.9‰ in dolostones at

125.60 m. There is a recovery to -1.9‰, although there is considerable scatter (Fig. 6). A final negative swing to -7.4‰ at 122.32 m is based on only one data point.

Carbonate rocks that appear least likely to be altered on the basis of their petrography and distance from potential fluid conduits such as veins gave the least negative $\delta^{13}C$ compositions, mostly near 0‰, *except* for the dolostone clasts (those of 126.97 m, shown in Fig. 5), plus one diamictite clast and one sample of 'marble' from 126.87 m. The latter comes from very close to the preserved dolostone clasts. The 'clastic' dolostone grains from 126.97 m (Fig. 5) themselves exhibit significantly more negative $\delta^{13}C$ values (-4.9 to -5.0‰) than the intervening calcite-containing sheared layers (-3.0 to -4.0‰).

All veins or likely secondary carbonate rocks below the peridotite body gave 'normal' or 'near normal' $\delta^{13}C$ compositions, similar to the surrounding carbonate rock. The majority (but not quite all) veins and metamorphosed sedimentary carbonate rocks judged to be in proximity to veins above the peridotite gave negative $\delta^{13}C$ values. In one case (129.97 m), a carbonate sample from within a few millimetres of a vein gave $\delta^{13}C$ of -4.3‰ while carbonate rock 15 cm above the vein gave a value of -0.7‰. Brown-coloured (dolomitic?) alteration rims around clasts in the diamictite all gave very low $\delta^{13}C$ values, typically around -7‰.

The oxygen isotope data are all isotopically light. Bulk samples gave a $\delta^{18}O$ range from -16.2 to -23.8‰ (VPDB), while 'hand drilled' sample data range from -14.7 to -25.0‰. Except for the two extreme values all other data from the hand-drilled samples lie between -16.4 and -22.3‰. It should be recalled that none of these oxygen isotope data are corrected for their Mg content.

A cross-plot of $\delta^{18}O$ vs $\delta^{13}C$ (Fig. 9) reveals some significant trends. First it is clear that the majority of all samples have $\delta^{18}O$ values between -20 and -22‰. Some of the more Mg-rich carbonates have slightly elevated $\delta^{18}O$ (Fig. 6), particularly those near the base of the hole (affecting carbonates with $\delta^{13}C$ ca. 0‰) and not correcting for Mg content (by up to -1.4‰) could partly explain this. However the population of very low $\delta^{13}C$, Mg-rich carbonates exhibits $\delta^{18}O$ compositions comparable to the majority of the 'normal' $\delta^{13}C$ carbonates, or perhaps slightly more negative than the modal value (particularly if a dolomite correction were applied). Most intriguing are a sub-set of 'calcites' (as determined by Alizarin Red S staining) with elevated $\delta^{18}O$ (up to -16.4‰) and $\delta^{13}C$ from -3.0 to -4.0‰. These seem to form a mixing line trend with 'dolomites' from the same sample (126.97m) that have low $\delta^{13}C$ and low to modal $\delta^{18}O$ compositions (Fig. 9). One sample of secondary quartz extracted from the ICDP FAR-DEEP Hole 3A cores at 223.30 m has $\delta^{18}O_{sil}$ of 11.4 ‰ (VSMOW) most likely indicating a relatively high temperature of precipitation.

U-Pb geochronology: results and interpretation

The samples targeted for chronology are summarised in Table S3 in the supplementary information, and sample depths for ICDP FAR-DEEP Hole 3A are shown on Fig. 10. Of the 19 studied samples, only eight yielded zircons. A total of 218 zircons were obtained, and all were subjected to LA-ICPMS screening. Relative probability plots of $^{207}Pb/^{206}Pb$ ages from LA-ICP-MS for all zircon-bearing samples are shown in Fig. 10 (excluding Sample 3A 207.85 m which yielded only two Archaean dates). The maximum age of the Polisarka Sedimentary Formation (ca. 2441 Ma) is shown on each plot (Fig. 10). Samples 3A 22.90m and Ru1310 show nine grains whose $^{207}Pb/^{206}Pb$ ages are younger than 2441 Ma. When each of the nine grains was picked and further analysed by U-Pb ID-TIMS they were shown to have Archaean ages > 2600 Ma. This discrepancy can be attributed to the larger errors associated with the LA-ICP-MS method, masking Pb-loss in the nine grains. Only zircons from an andesitic fine tuff, Sample 3A 20.01 m from ICDP FAR-DEEP Hole 3A (Fig. 11), were shown to have ages < 2441 Ma (and therefore of potential geochronological use here) when analysed by U-Pb ID-TIMS. The results of dating of all sixteen zircon crystals obtained from Sample 3A 20.01m (Fig. S1 in supplementary information) are shown in Table 1. Of these sixteen crystals, ten yielded $^{207}Pb/^{206}Pb$ dates at ca. 2700 Ma. These grains have a prismatic nature, reflecting their xenocrystic incorporation of older material. The remaining six ID-TIMS analyses yielded $^{207}Pb/^{206}Pb$ dates from ca. 2410 to 2436 Ma (Fig. S1 and Table 1). Four of these grains (z2, z7, z8 and z9) are discordant and display correlations between $^{207}Pb/^{206}Pb$ age and magnitude of discordance (Table 1), suggesting non-zero age Pb-loss. As such, these four $^{207}Pb/^{206}Pb$ dates are likely to be inaccurate. The two remaining analyses (z11 and z12) are concordant (Fig. 12), giving overlapping $^{207}Pb/^{206}Pb$ dates of 2432.8 ± 2.1 and 2435.9 ± 1.5 Ma and an error weighted mean $^{207}Pb/^{206}Pb$ date of 2434.8 ± 1.2 Ma (assuming age equivalence of the two dated zircons and using a value of 137.88 for $^{238}U/^{235}U$ for consistency with older studies; see supplementary information). Incorporation of the uncertainties in $\lambda^{235}U$ and $\lambda^{238}U$ (Jaffey et al., 1971), required only when comparing $^{207}Pb/^{206}Pb$ dates with those from other decay schemes like Re-Os, increases the uncertainty to 6.6 Myr.

Given the potential global significance of the U-Pb date obtained, the context and petrography of the sample is described here. Rock sample 3A 20.01 m was intersected around 100 m above the top of the carbonate-bearing interval (and ca. 80 m above the diamictites), between 20.01 and 20.30 m in ICDP FAR-DEEP Hole 3A (Fig. 2). In hand specimen (Fig. 11a), altered and compacted pumice fragments (0.5 to 1 mm) have a common alignment, giving the rock a discontinuous, streaky appearance. Lithic fragments (0.25 mm) and crystals (0.1 mm) are also present. In thin section (Fig. 11b), the altered pumice clasts (constituting 5% volume of the rock) are uniformly aligned with a eutaxitic texture, suggesting welding or in-situ diagenetic compaction. Fragments observed include volcanic quartz (3% volume) with small embayments and straight extinction, and less commonly plagioclase (1% volume). Rare lithic fragments, composed of plagioclase and pyroxene, are found in a fine groundmass of feldspar, quartz, and opaque minerals. Weak chlorite alteration is evident in the groundmass. This rock is best classified as an andesitic fine tuff (White and Houghton, 2006) on the basis of the presence of quartz and feldspar; a light to moderate colour index; the presence of pumice and fragments of crystals and (rare) lithics; and a fine groundmass. The clast type, clast morphology, and grain size range indicate that this fine tuff has not experienced interim storage prior to lithification. The morphologies of the zircon crystals (30 – 70 µm) recovered varied, with some large prismatic grains (albeit visibly metamict) with aspect ratios up to 8, and some smaller faceted grains with aspect ratios of 1.5 to 2. However there is a distinct morphological sub-population of prismatic crystals and crystal fragments with medial melt inclusion 'tunnel' traces: a feature that typifies volcanic zircon (z1, z2, z7 z8 and z11 in Fig. S1) and is characteristic of the ca. 2435 Ma population. Although post-depositional re-working is likely to have been restricted, we must also consider whether the ca. 2435 Ma zircons were inherited into the magma prior to eruption, and thus reflect a maximum age. Whilst we cannot categorically rule this out, making the age strictly a maximum age, however we note that (1) the dated zircons are distinctly younger than the known ca. 2441 Ma dates from underlying intrusions; and (2) numerous levels were sampled for zircon (fig. 10) and whilst a number of samples did contain inherited zircons they were all >2.5 Ga; the ca. 2435 population only occurs in Sample 3A 20.01, a distinct andesitic fine tuff. Therefore, based upon the concordant U-Pb systematics, the morphology of the dated zircons, and their geological context, the ^{207}Pb/^{206}Pb date of 2434.8 ± 1.2/6.6 Ma (analytical/total uncertainty) is interpreted to approximate the age of the andesitic fine tuff and inferentially the age of the sampled stratigraphic level.

Discussion

U-Pb chronology and chronological correlations

Zircon grains from an andesitic fine tuff (Sample 3A 20.01m) yield a ^{207}Pb/^{206}Pb age at 2434.8 ± 1.2 Ma; this is interpreted as an eruption age, contemporaneous with sedimentation at this stratigraphic level. The age of the Polisarka Sedimentary Formation below 20.01 m in ICDP FAR-

DEEP Hole 3A is therefore constrained between the inferred age of the underlying Seidorechka Volcanic Formation at 2441 ± 1.6 Ma, and the newly derived age of Sample 3A 20.01 m at 2434.8 ± 1.2 Ma. This age range encompasses deposition of the carbonate rocks and the diamictite units in ICDP FAR-DEEP Hole 3A (Fig. 6). The SHRIMP zircon date of 2429 ± 6.6 Ma (Vrevsky et al., 2010) from units in western part of the Imandra-Varzuga Greenstone Belt that have been inferred to represent the top of the Seidorechka Volcanic Formation are broadly consistent with the ID-TIMS age from the eastern sector, the slightly younger age perhaps being biased by non-zero age Pb-loss and/or analytical calibration.

These age constraints on deposition of the Polisarka Sedimentary Formation diamictite allow confident comparison with diamictite units deposited elsewhere. Palaeoproterozoic diamictite sections crop out in the Great Lakes region of North America, including the Huronian Supergroup in Canada and the Marquette Range Supergroup in the USA. Palaeoproterozoic diamictites are also known from the Transvaal Supergroup of South Africa, and the Meteorite Bore Member of Western Australia. Whilst the sedimentology of these sections is relatively well understood, the age constraints on these sections remain relatively poor.

There are three diamictite-bearing formations in the Huronian Supergroup (from oldest to youngest): Gowganda, Bruce, and Ramsay Lake. These three formations are underlain by the Thessalon Formation where zircons in the Copper Cliff rhyolite member have been dated at 2450 ± 25 Ma (ID-TIMS; Krogh et al., 1984); providing a maximum age constraint to diamictite deposition. The three diamictite-bearing formations are cross-cut by the Nipissing intrusions, dated at ca. 2200 Ma (for example 2217 ± 9 Ma; ID-TIMS on baddeleyite and rutile fractions; Corfu and Andrews, 1986). This date is therefore a minimum age constraint to diamictite deposition in the Huronian Supergroup sections. It has been noted that the diamictite-bearing Gowganda Formation is cross-cut by dykes with peperitic margins (Young et al, 2001), suggesting the youngest of the

Huronian Supergroup diamictites may have been deposited at ca. 2200 Ma (if the cross-cutting dykes are equivalent to the Nipissing intrusions) or older. The Polisarka Sedimentary Formation diamictite could therefore be equivalent in age to any of the Huronian Supergroup diamictites.

The Marquette Range Supergroup, in the Menominee and Iron River – Crystal Falls Ranges area, includes the diamictite-bearing Fern Creek Formation that is in turn overlain by the Sturgeon Quartzite. The youngest detrital zircons in this latter formation yield a 2306 ± 9 Ma date (SHRIMP; Vallini et al., 2006), providing a minimum age constraint to deposition of the Fern Creek Formation diamictite. There is no maximum age. The temporal relationship between the Fern Creek Formation diamictite and the Polisarka Sedimentary Formation diamictite remains to be clarified.

In the Marquette Range Supergroup (Marquette Range area) the diamictite-bearing Enchantment Lake Formation has yielded detrital zircons whose youngest age is 2317 ± 6 Ma (SHRIMP; Vallini et al., 2006), providing a maximum age constraint to the formation's deposition. Furthermore, hydrothermal xenotime has been dated in the same formation at 2133 ± 11 Ma (SHRIMP; Vallini et al., 2006), giving a minimum age constraint for deposition. The Polisarka Sedimentary Formation diamictite was therefore deposited earlier than the Enchantment Lake Formation diamictite.

In South Africa the diamictite-bearing Duitschland and Boshoek Formations crop out in the Transvaal basin. The Rooihoogte Formation is commonly considered the lithostratigraphic equivalent to the Duitschland Formation (Hannah et al., 2004) and contains authigenic pyrite that has been dated by the Re-Os method at 2316 ± 7 Ma (Hannah et al., 2004); this is a maximum age constraint to deposition of the Boshoek Formation diamictite. Rocks several units above the Boshoek Formation are intruded by the Bushveld Complex, where zircons have yielded a 2054 ± 2 Ma date (SHRIMP; Scoates and Friedman, 2008), considered a suitable minimum age constraint to the Boshoek Formation diamictite. The Polisarka Sedimentary Formation diamictite was therefore deposited before the Boshoek Formation diamictite. The 2316 ± 7 Ma date for the Rooihoogte Formation is also a minimum age constraint to diamictite deposition in the Duitschland Formation. A concordant U-Pb SHRIMP age on a zircon in the upper part of the Duitschland Formation yields a $^{207}Pb/^{206}Pb$ age at 2424 ± 12 Ma that is a maximum age to this formation (Dorland, 2004). Several igneous units beneath the Duitschland Formation have been dated, with a zircon age at 2480 ± 6 Ma (SHRIMP; Nelson et al., 1999) on the Penge Formation also providing a maximum age constraint to the diamictite-bearing Duitschland Formation. Contemporaneous deposition of the Duitschland and Polisarka Sedimentary formation diamictite units is thus permissible, given the current age constraints on the African section.

The diamictite-bearing Meteorite Bore Member crops out in Australia's Hammersley Basin. Underlying the Meteorite Bore Member by several units, zircons in a lava flow of the Woongarra Rhyolite Formation have yielded a 2449 ± 3 Ma date (ID-TIMS; Barley et al., 1997). This is a maximum age constraint to diamictite deposition in the Hammersley Basin. Baddeleyite grains from a mafic sill that cross-cuts the Meteorite Bore Member have been dated at 2208 ± 10 Ma (SHRIMP Müller et al., 2005) and are a minimum age constraint to deposition of the diamictite. The diamictite deposition ages of the Meteorite Bore Member and the Polisarka Sedimentary Formation overlap, which is not surprising, given that the Australian diamictite could have been deposited at any time during a ca. 240 Myr interval.

The Polisarka glacial deposits could be equivalent to any of the three Huronion Supergroup diamictite-bearing strata, but the loss of mass-independent fractionation of sulphur isotopes (MIF) recorded in Canada, Africa and Fennoscandia may provide further independent constraints. The permanent disappearance of sulphur MIF occurs between the first and second diamictite in South Africa (Guo et al., 2009) and Canada (Papineau et al., 2007), suggesting that one can correlate the lower Duitschland with the Ramsay Lake, the upper Duitschland with the Bruce, and the

Makganyene-Timeball Hill with the Gowganda diamictites (e.g., Melezhik et al. 2013a). If correct, then the presence in Fennoscandia of both MIF and mass-dependent fractionation in the pre-Huronian rocks (Reuschel et al., 2009), and a pronounced mass-dependent fractionation in the Huronian interval (Melezhik et al., 2013b), could reflect that the Polisarka glacial deposits correlate either with the Gowganda/Makganyene-Timeball Hill or with the upper Bruce/Duitschland diamictites. In any case the Polisarka Sedimentary Formation diamictites were certainly deposited prior to the Enchantment Lake (Marquette Range Supergroup) and Boshoek (Transvaal Supergroup) diamictite-bearing units. We suggest here that the age of the diamictite-bearing Polisarka Sedimentary Formation is constrained to between 2434.8 ± 1.2 Ma (tuff in the Polisarka Volcanic Formation) and 2441 ± 1.6 Ma (subvolvanic intrusions in the Seidorchka Formation), indicating this represents an early (perhaps the earliest) Palaeoproterozoic glaciation.

Carbonate geochemistry

Sr abundances

All analysed carbonate rock samples from the Polisarka Sedimentary Formation contain high Sr contents, ranging between 560 and 1030 ppm (767 ppm on average, n = 14). Several limestones have Sr concentrations higher than 800 ppm with a few samples containing 900–1030 ppm. Inorganic aragonites and calcites in equilibrium with modern seawater contain approximately 9000 and 1000 ppm Sr, respectively (Veizer, 1983), and Sr content in seawater has likely remained near-constant through time (Steuber and Veizer, 2002). Hence the values measured from the Polisarka carbonates are close to equilibrium concentrations of modern marine calcites (Veizer, 1983; Schlanger, 1988). However, the recrystallisation textures strongly argue for post-depositional alteration of most of the analysed samples, hence for a significant Sr loss from these rocks. It has been shown that each recrystallisation step in an open system reduces Sr content in the newly formed calcite by a factor of 10, and in dolomite by a factor 20 (Veizer, 1983; Banner, 1995). Since diagenetic and metamorphic alteration rarely takes place in an open system, the loss of Sr is commonly less. Taking into account the strong petrographic evidence for recrystallisation throughout the hole, the samples with 900–1000 ppm Sr are likely products of a precursor phase with a very high initial Sr content, hence much of the carbonate was likely originally deposited as aragonite.

Oxygen isotopes

The evidence for deformation fabrics throughout the core and likely Sr loss from the carbonate rocks do not require that every geochemical proxy has been entirely overprinted, because the requisite water/rock ratios differ for each tracer (Banner, 1995). However, the invariably low (for Palaeoproterozoic marine carbonates; e.g. Schidlowski et al., 1975) oxygen isotopic compositions of the ICDP FAR-DEEP Hole 3A carbonates are intriguing. Veizer et al. (1992) reported carbonate $\delta^{18}O$ values between -5 and -10‰ (VPDB) from the Transvaal Supergroup (South Africa) and Duck Creek Dolomite (Western Australia), but from -13 to -18‰ (VPDB) in the Bruce Member limestones of North America. They suggested that such low values might either reflect a non-marine depositional environment for the Bruce Member, or a contribution from high latitude or altitude glacial melt waters. In the case of the Polisarka Sedimentary Formation data, the interpretation of these $\delta^{18}O$ values (mostly between -19 and -22‰ vs VPDB) must be left open, but noting that the carbonate rocks have recrystallised in the presence of a hot fluid, such that their $\delta^{18}O$ values may no longer be representative of the original carbonate oxygen isotopic composition. Quartz extracted from a carbonate layer at a depth of 223.30m with $\delta^{18}O_{sil}$ of 11.4‰ VSMOW is also consistent with silica precipitation from a hot fluid (ca. 300 ^{o}C, for fluid $\delta^{18}O$ of 4‰ VSMOW; Matsuhisa et al., 1979). A second overprinting of carbonate oxygen isotopic compositions by a late stage meteoric or shallow burial fluid that preferentially affected calcites relative to dolomites would provide an explanation for the sub-set of ‘calcites’ around 126 m depth with elevated $\delta^{18}O$

(up to -16.4‰) and $\delta^{13}C$ from -3.0 to -4.0‰. The possible oxygen isotope mixing line trend in this sample (Fig. 9) would then result from mixing between 'calcite' and 'dolomite' end-members.

Robustness of the carbonate carbon isotope signal

The carbonate carbon isotopes are here of special interest because of the possibility they could reflect marine dissolved inorganic carbon (DIC) prior to one of the early Palaeoproterozoic glaciations, potentially aiding understanding of its cause. Interpreting the carbon isotopes in this way first requires an assessment of the extent of secondary alteration and whether there might still be a primary signal retrievable from the data.

The carbonate rocks are all to varying extents recrystallised, but recrystallisation alone is not necessarily an indicator that the carbon isotopes of these carbonates are reset: note that carbonates with 'normal' $\delta^{13}C$ are as affected by this pervasive recrystallisation as those containing the low $\delta^{13}C$ signal. Because interaction between carbonates and meteoric fluids commonly increases Mn concentrations and decreases Sr concentrations of the rocks, marine carbonates with Mn/Sr ratios <3 (e.g. Derry et al., 1992) or <10 (Kaufman and Knoll, 1995) are commonly believed to have retained original seawater DIC signals in their $\delta^{13}C$. Carbonate rocks here would all meet the Mn/Sr <10 criterion (mostly being between about 3 and 5) except for the first sample immediately above the peridotite, and all samples from above ca. 127.8 m (Fig. 8). Using the ICP-AES Mn/Sr ratio data, the $\delta^{13}C$ of all samples associated with the second and most prominent $\delta^{13}C$ excursion could be considered suspect. However, these ICP-AES data are from 'bulk carbonate' so do not discriminate between calcite of clear secondary origin and the primary dolostone clasts. The Mn/Sr values cannot be reliably used as an indicator of carbonate carbon isotope alteration in these mixed dolomite – calcite samples that contain the second prominent negative carbon isotope excursion. The XRF elemental data reflect only the whole rock (i.e. including silicate) composition. The Mn/Sr molar ratios calculated from these XRF data are all < 10, although the XRF dataset is more limited than the ICP-AES dataset here.

Correlation between carbonate oxygen isotopes and carbon isotopes can also be indicative of post-depositional alteration in cases where the oxygen isotopes have been altered. A complicating factor to using this approach here is the variable mineralogy of the carbonate rock samples. Correlation between carbonate $\delta^{13}C$ and $\delta^{18}O$ (Fig. 9) is best explained as the result of mixing between low $\delta^{13}C$, low $\delta^{18}O$ dolostone and high $\delta^{13}C$, high $\delta^{18}O$ secondary calcite end-members. This approach cannot therefore be used to distinguish primary from altered carbon isotope signals in this case. It is however encouraging that the dolostone clasts and secondary calcite yield different values, testifying that the carbonate carbon isotopes of ICDP FAR-DEEP Hole 3A have not been entirely overprinted by any late-stage secondary fluid interaction.

Carbon isotopes and magnesium abundances

Strong correlation between increasing Mg/Ca ratios and decreasing $\delta^{13}C$ values in some sections of ICDP FAR-DEEP Hole 3A (Fig. 6) means the origin(s) of the Mg/Ca trend may bear directly on the interpretation of the carbon isotope data. The elevated Mg in samples from 221 to 225 m is due to the presence of dolomite, although the reasons for its occurrence in this section of the core are unclear. The petrography of these sheared and recrystallised rocks is very similar to those of surrounding carbonate rocks with more calcitic compositions. Elevated Mg/Ca values are also seen from ~124 to 127.4 m, and there are several possible explanations for this. First is the possibility that the Mg derives from the adjacent ultramafic igneous rocks, perhaps during and following metamorphism at greenschist facies (ca. 300ºC). This seems an attractive explanation for samples taken from brown stained and chlorite-rich sections immediately above the peridotite at 130.94 m. While the $\delta^{13}C$ is very low in this sample (as it is in dolomite crystals that have replaced talc in the peridotite below), elemental concentrations of Ni and Cr are very high, perhaps due to alteration by fluids circulating between the (Mg, Ni and Cr-rich) peridotite and overlying carbonate. However it is worth noting that serpentinisation and carbonatisation of peridotite consume and do not produce CO_2, although of course CO_2 flux may accompany emplacement. The isotopically negative carbon isotope signatures of these carbonates (including the dolomite crystals replacing talc) must here be explained either by carbon from Palaeoproterozoic sea- or meteoric water, or perhaps decarbonation reactions during metamorphism, or by local alteration involving externally sourced (perhaps magmatic and/or hydrothermal) fluids.

Analysis of the prominent and smoothly curved excursion to low $\delta^{13}C$ that reaches a nadir around 125.60 m depth shows alteration by fluids interacting with the peridotite to be untenable. This second excursion occurs away from obvious bedding or structural contacts and entirely within a sedimentary carbonate section (Fig. 7), separated from the peridotite body by several metres of carbonate rock with $\delta^{13}C$ of 0 to -1‰. There are no obvious features consistent with preferential channelling of diagenetic fluids through the low $\delta^{13}C$ section except some quartz veins (see Fig. 12). But their siliceous composition implies hot basinal fluids were silica-rich and carbon-poor, so unlikely to dramatically alter $\delta^{13}C_{carb}$.

Above 130 m depth the Mg/Ca values are consistent with calcitic carbonate compositions, except for between ca. 124 and 127.4 m. Here the petrography suggests the presence of (primary) dolomitic clasts with some secondary calcite (Fig. 5). It seems most likely that these dolostone clasts were resedimented from shallower settings. It is possible that they were derived from erosion of a much older carbonate platform, although older formations in this area are not known to contain any likely dolostone sources. Hence it seems reasonable to suggest that the clastic dolostone likely formed in shallow waters penecontemporaneously with deeper water calcites, in the run-up to the Huronian glaciation. If correct, then the carbon isotopic composition of the allochthonous dolostone clasts records the pre-Huronian shallow-water marine DIC, while the deeper-water DIC is recorded by the majority of the (calcitic) carbonates in ICDP FAR-DEEP Hole 3A. Correlation between Mg/Ca and $\delta^{13}C$ in the carbonates between ~124 and 127.4 m (Fig. 6) could then be explained by mixing lines between deep water calcites with near-zero per mil $\delta^{13}C$ and shallow-water-derived, isotopically light dolostone clasts. There are clearly several plausible reasons for why the dolostone clasts exhibit low $\delta^{13}C$ values. One speculative hypothesis that we cannot conclusively rule out is oxidation of isotopically light methane, and its incorporation into shallow dolomite-precipitating waters.

Conclusions

1. The new U-Pb data reported here likely constrain the onset of the Palaeoproterozoic glaciation recorded by the Polisarka Diamictite to a narrow time-window between ca. 2441 ± 1.6 Ma and 2434.8 ± 1.2 Ma. Considering constraints from other cratons, this glacial deposit likely records one of the earliest Palaeoproterozoic glaciations, and perhaps the earliest.
2. The ICDP FAR-DEEP Hole 3A carbonate carbon isotope data imply Palaeoproterozoic seawater DIC shallow-to-deep trends in which lighter values characterise the shallower water settings. We speculate that this reflects atmospheric methane oxidation. However this interpretation must be viewed with circumspection in that the carbonate carbon isotope profile includes resedimented dolostone clasts that we infer were derived from contemporaneous shallower settings. Further, at least some of the carbon isotope values have been affected by post-depositional processes. Resolving these issues will likely require discovery of another section containing pre-glacial carbonates of the same age, either in Fennoscandia or elsewhere.

3. Geochemical data, such as the high Sr-content in the Polisarka limestones, strongly suggest aragonite precipitation from penecontemporaneous marine waters. A Polisarka "aragonite sea" might have been associated with an elevated Mg content in contemporaneous seawater.

Acknowledgements

ATB and AM were supported by NERC grant NE/G00398X/1 to AEF, ARP and DJC. VAM is supported by NFR grant 191530/V30 (projects 331000 and 802795).

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Figure captions

Fig. 1 Map showing the location of ICDP FAR-DEEP Hole 3A in Fennoscandian Russia

Fig. 2 Stratigraphy (based on ICDP FAR-DEEP Database) and stratigraphic context of ICDP FAR-DEEP Hole 3A

Fig. 3 Images of Polisarka Sedimentary Formation rocks, mostly from cores of ICDP FAR-DEEP Hole 3A. A) Sheared and flattened lonestones (some denoted by arrows) in a diamictite at 114.36m. Note the yellow-discoloured dolomitic alteration rims of some of these clasts: these gave low $\delta^{13}C$ values. B) Layered siltstone-carbonate couplets of possible ‘varve-like’ origin (178.93m depth). C) Deformed layered siltstone-carbonate rocks showing discontinuous lenses of carbonate (one example arrowed; 190.52m). D) Sheared and folded carbonate-siliciclastic rock, including a ptygmatically folded quartz vein (arrowed; 180.25m. E) Talc-rich rock containing numerous dolostone crystals of secondary origin (dolostone crystals are white spots, one of which is arrowed; 212.19m). F) Dropstone from an outcrop of the Polisarka Sedimentary Formation. G) Andesitic dropstones in diamictite (ICDP FAR-DEEP Hole 3A, 101.4 m depth; core width is 5 cm). Coin for scale (A-E) is 20mm diameter. Photographs 3F and 3G reproduced with kind permission of Springer Science+Business Media from Victor A. Melezhik, Grant M. Young, Patrick G. Eriksson, Wladyslaw Altermann, Lee R. Kump, and Aivo Lepland (2013) 7.2 Huronian-Age Glaciation. In: V.A. Melezhik, L.R. Kump, A.E. Fallick, H. Strauss, E.J. Hanski, A.R. Prave, A. Lepland (eds.), Reading the Archive of Earth’s Oxygenation, Volume 3: Global Events and the Fennoscandian Arctic Russia - Drilling Early Earth Project, pp. 1059-1109. Copyright Springer Science+Business Media 2013.

Fig. 4. Thin-sections of carbonate rocks in ICDP FAR-DEEP Hole 3A. A) Relatively homogenous carbonate rock from 128.35m as seen in cross-polarised light. B) Carbonate rock from 182.44m, in cross-polarised light. Note the quartz patches between some of the carbonate crystals (arrowed). C) Carbonate rock with layers of talc (arrowed) from 201.14m in cross-polarised light. D) A layer of talc (brown crenulated mineral) overgrown with a dolomite rhomb (arrowed) (212.19m). E) A dolomite rhomb that has overgrown talc within the peridotite body (147.23m). F) A carbonate rhomb from a carbonatised komatiite at 81.69m.

Fig. 5 The clastic dolostone found at 126.97 m depth in ICDP FAR-DEEP Hole 3A. A) Hand-specimen, stained with Alizarin Red S to distinguish calcite (red-stained layers) from dolomite (unstained). B) Thin-section showing a dolomitic clast under cross-polarised light. Note that quartz grains surround the dolostone clast in the centre. C) Same dolomitic clast viewed in plane polarised light.

Fig. 6. Carbonate rock geochemistry, including carbon isotopes, oxygen isotopes, and Mg/Ca ratios. For symbols see the legend and Fig. 2. Note that the data inside the red box belong to the carbonate unit between the peridotite and diamictite. Two excursions to low $\delta^{13}C$ values are seen as the base of the diamictite is approached. Secondary carbonate within the peridotite body also gives low $\delta^{13}C$ values. The second excursion at 126.97m is linked to resedimented dolostone clasts. Secondary calcite layers in that same area give higher $\delta^{13}C$ values. Mg/Ca ratios correlate strongly with $\delta^{13}C$ in the area of the excursions. Oxygen isotope values are invariably low, and trends seem to reflect carbonate Mg content.

Fig. 7 Photograph of the rocks between 128.47 m and 124.75 m depth in ICDP FAR-DEEP Hole 3A. Note that this section starts with laminated calcites, and includes low $\delta^{13}C$ allochthonous dolostone clasts. Note also the quartz veins, around which the carbonates also have low $\delta^{13}C$ values.

Fig. 8 Carbonate $\delta^{13}C$ (bulk rock samples) and Mn/Sr ratios (for the same bulk-rock samples). For stratigraphic symbols see Fig. 2. Mn/Sr ratios shown in yellow were determined by ICP-AES and those in pink were determined by XRF. Note that the data within the red box belong to the carbonate unit between the peridotite and diamictite.

Fig. 9 A cross-plot of carbonate $\delta^{18}O$ (x-axis) vs $\delta^{13}C$ (y-axis). For symbols see the legend. Oxygen isotope values are not corrected for their Mg content (data presented as if samples were all calcite). Their oxygen isotope values are relatively invariant, hence the trend mostly runs parallel to the Y axis. A possible mixing-line trend (black line) likely reflects mixing between 'calcite' and 'dolomite' end-members. See text for discussion.

Fig. 10 $^{207}Pb/^{206}Pb$ histogram plots of LA-ICPMS data for samples targeted for chronology and the location of samples from drill core 3A. Sample Ru1310 was collected in the field at 67° 11.984 N and 35° 46.361 E. Lithological column is based on FAR-DEEP Database.

Fig. 11 Petrography of drill core sample 3A 20.01 m (ash from which zircons were obtained). A) Hand specimen. L = lithic. P = pumice. C = crystal. B) Thin section. P = pumice. Qtz = quartz (volcanic).

Fig. 12: Conventional concordia plot for zircons analysed from sample 3A 20.01 m.

Table 1: U-Th-Pb data for zircons analysed from sample ICDP FAR-DEEP Hole 3A 20.01 m

Captions for supplementary tables and figure are given in the file ‘supplementary information’

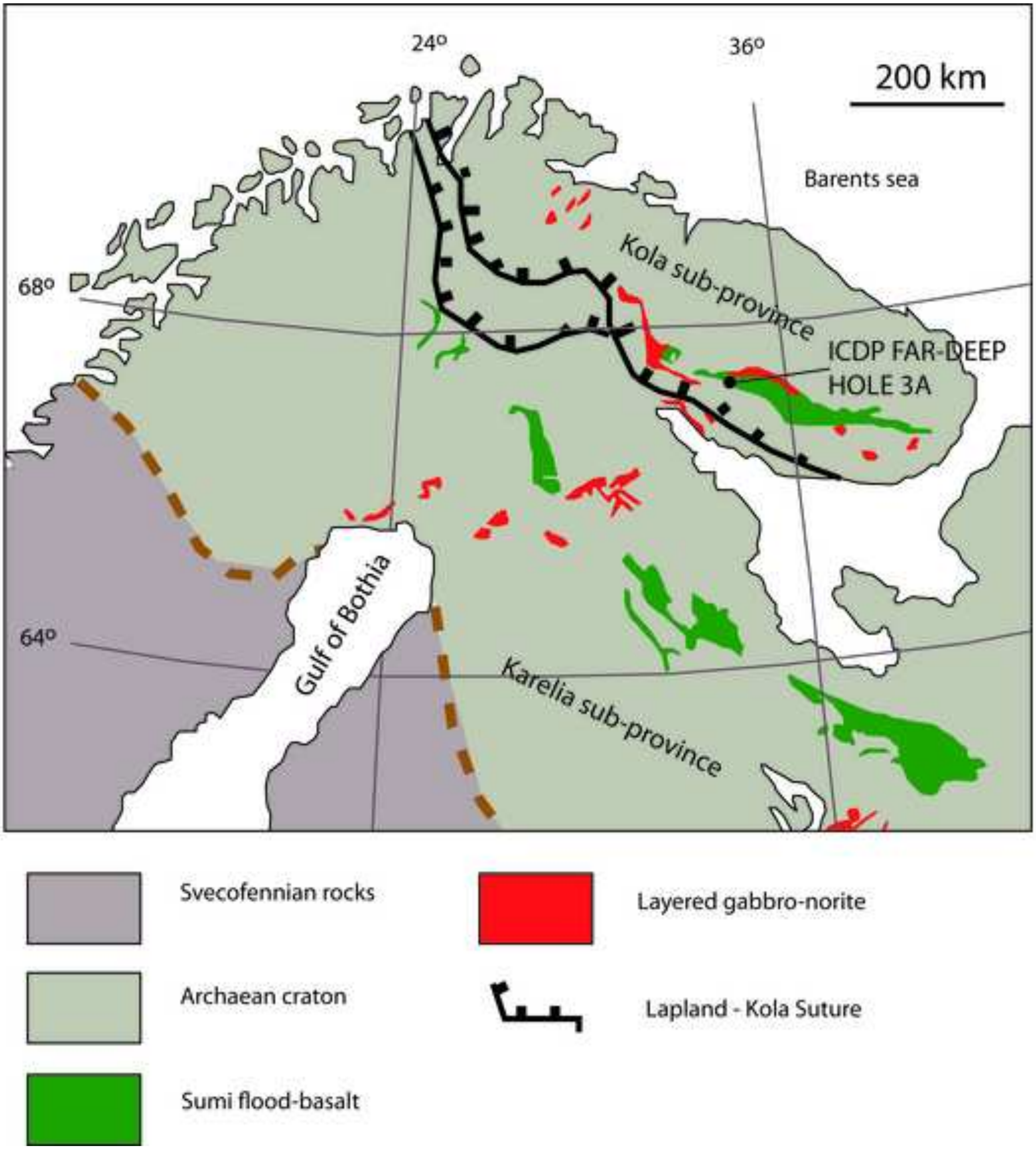
Research highlights:

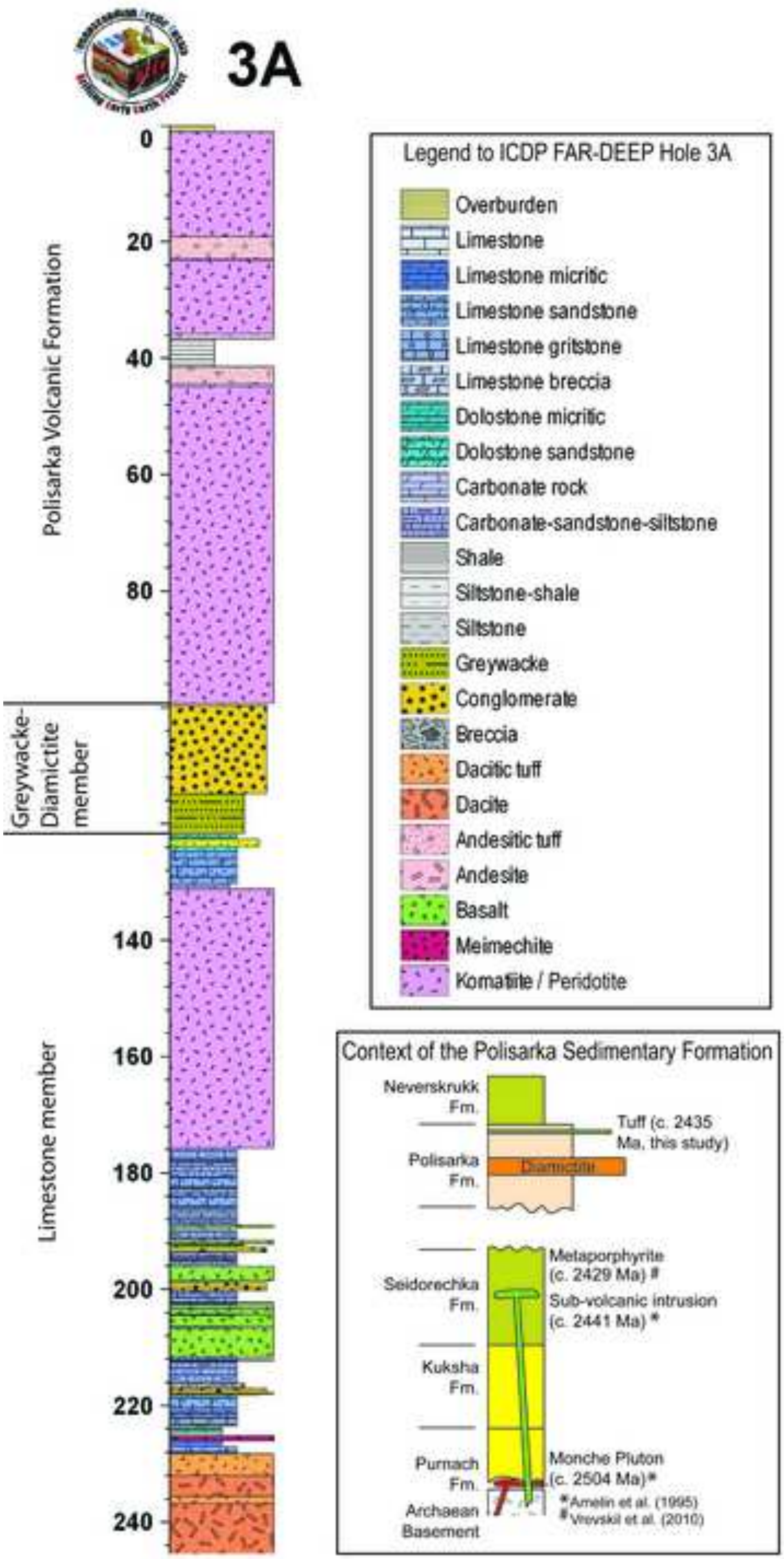
ICDP FAR-DEEP Hole 3A targeted Palaeoproterozoic diamictites of the Polisarka Sedimentary Formation of Russian Fennoscandia ► Zircon U-Pb dating of a tuff above the diamictites yielded an interpreted minimum age of 2434 Ma for the diamictites ► This constrains the onset of the Palaeoproterozoic glaciation in Fennoscandia to between ca. 2430 and ca. 2440 Ma ► carbonate $\delta^{13}C$ analyses of carbonate rocks below the diamictites revealed two excursions to ca. -5‰ ► the origins of these excursions are carefully considered

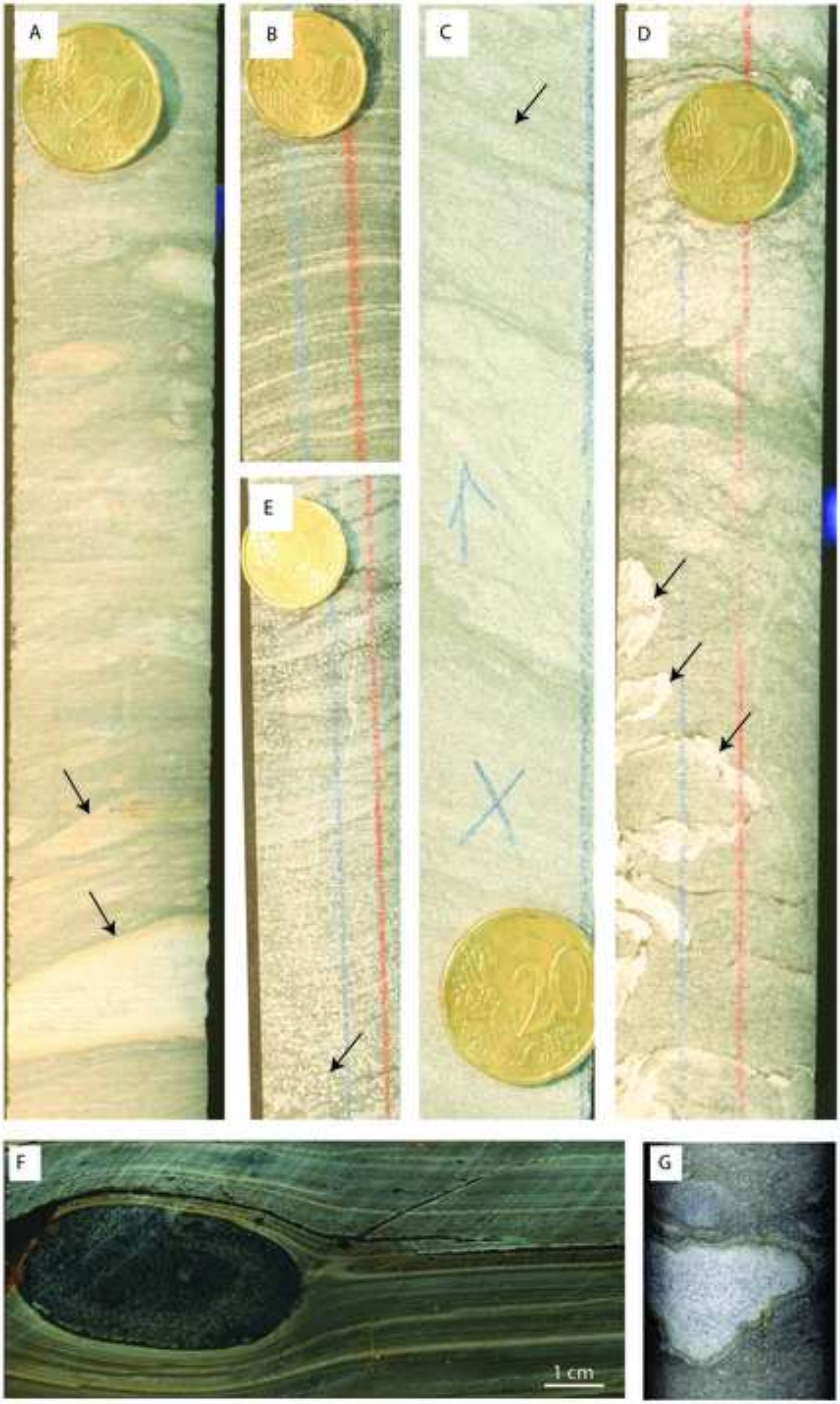
							Radiogenic Isotope Ratios								Isotopic Ages					
Fraction	Th/U	$^{206}Pb^*$ x10^{-13} mol	mol % $^{206}Pb^*$	Pb^*/Pb_c	Pb_c (pg)	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	% err	$^{207}Pb/^{235}U$	% err	$^{206}Pb/^{238}U$	% err	corr. coef.	$^{207}Pb/^{206}Pb$	±	$^{207}Pb/^{235}U$	±	$^{206}Pb/^{238}U$	±
(a)	(b)	(c)	(c)	(c)	(c)	(d)	(e)	(e)	(f)	(e)	(f)	(e)	(f)		(g)	(f)	(g)	(f)	(g)	(f)
z2	0.787	4.1196	99.61%	86	1.37	4397	0.224	0.156904	0.089	9.688111	0.293	0.447821	0.254	0.957	**2422.5**	1.5	2405.6	2.7	2385.6	5.1
z3	0.486	12.0116	99.88%	280	1.17	15203	0.135	0.189230	0.080	13.728777	0.173	0.526188	0.103	0.959	2735.4	1.3	2731.2	1.6	2725.4	2.3
z4	0.472	1.6033	99.33%	49	0.90	2718	0.131	0.189681	0.096	13.794564	0.337	0.527453	0.303	0.961	2739.3	1.6	2735.7	3.2	2730.8	6.7
z6	0.331	1.4206	98.87%	27	1.39	1499	0.101	0.198730	0.222	12.805982	0.440	0.467355	0.374	0.864	2815.7	3.6	2665.5	4.1	2472.0	7.7
z7	1.040	7.5733	99.54%	72	3.15	3346	0.296	0.157161	0.090	9.714832	0.177	0.448323	0.098	0.949	**2425.3**	1.5	2408.1	1.6	2387.8	2.0
z8	0.968	3.8219	98.99%	32	3.49	1523	0.275	0.155794	0.099	9.582447	0.224	0.446091	0.158	0.922	**2410.5**	1.7	2395.5	2.1	2377.9	3.1
z9	0.938	6.6041	99.42%	57	3.44	2664	0.266	0.158101	0.093	9.829474	0.191	0.450913	0.117	0.927	**2435.4**	1.6	2418.9	1.8	2399.4	2.3
z11	0.939	1.2339	98.17%	18	2.02	882	0.264	0.157854	0.123	9.969447	0.332	0.458051	0.275	0.935	**2432.8**	2.1	2432.0	3.1	2431.0	5.6
z12	0.461	7.0665	99.46%	54	3.47	2820	0.130	0.158146	0.089	9.967708	0.182	0.457125	0.105	0.946	**2435.9**	1.5	2431.8	1.7	2426.9	2.1
z13	0.512	9.3420	99.77%	140	1.84	7239	0.141	0.198694	0.085	15.005791	0.186	0.547739	0.120	0.935	2815.5	1.4	2815.6	1.8	2815.8	2.7
z31	0.354	1.7701	94.52%	5	9.42	268	0.100	0.194517	0.216	13.892947	0.736	0.518008	0.689	0.956	2780.7	3.5	2742.4	7.0	2690.8	15.2
z39	0.251	0.2721	91.03%	3	2.37	177	0.073	0.169418	0.858	10.483936	1.854	0.448811	1.567	0.887	2551.8	14.4	2478.5	17.2	2390.0	31.3
z43	0.146	1.2562	99.38%	49	0.65	2955	0.040	0.188104	0.096	13.695541	0.352	0.528057	0.318	0.964	2725.6	1.6	2728.9	3.3	2733.3	7.1
z44	0.581	0.5824	98.17%	18	0.90	994	0.159	0.194837	0.153	14.615500	0.689	0.544053	0.667	0.975	2783.4	2.5	2790.5	6.6	2800.5	15.1
z15	0.510	0.5825	93.76%	5	3.49	246	0.139	0.189949	0.230	14.193600	0.734	0.541943	0.691	0.949	2741.7	3.8	2762.7	7.0	2791.6	15.7
z23	0.730	2.3370	98.69%	24	2.75	1196	0.202	0.185026	0.102	13.224841	0.529	0.518391	0.504	0.981	2698.4	1.7	2695.8	5.0	2692.4	11.1

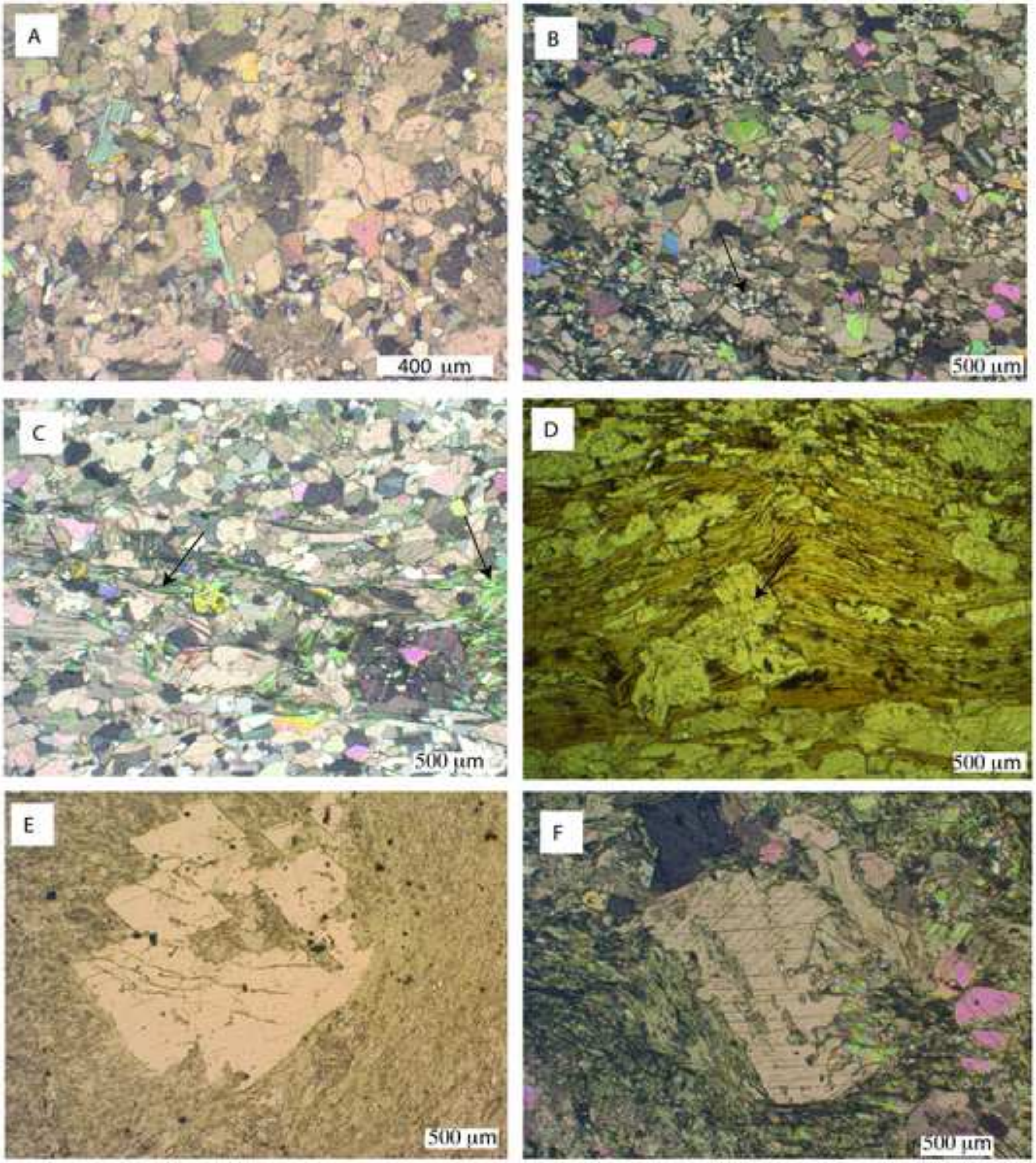
(a) z1, z2 etc. are labels for fractions composed of single zircon grains or fragments; all fractions annealed and chemically abraded after *Mattinson* [2005].
(b) Model Th/U ratio calculated from radiogenic 208Pb/206Pb ratio and 207Pb/235U age.
(c) Pb* and Pbc represent radiogenic and common Pb, respectively; mol % $^{206}Pb^*$ with respect to radiogenic, blank and initial common Pb.
(d) Measured ratio corrected for spike and fractionation only.
(e) Corrected for fractionation, spike, and common Pb; up to 1 pg of common Pb was assumed to be procedural blank: 206Pb/204Pb = 18.20 ± 0.50%; 207Pb/204Pb = 15.65 ± 0.40%; 208Pb/204Pb = 38.20 ± 0.75% (all uncertainties 1-sigma). Excess over blank was assigned to initial common Pb.
(f) Errors are 2-sigma, propagated using the algorithms of *Schmitz and Schoene* [2007] and *Crowley et al.* [2007].
(g) Calculations are based on the decay constants of *Jaffey et al.* [1971]. 206Pb/238U and 207Pb/206Pb ages corrected for initial disequilibrium in 230Th/238U using Th/U [magma] = 4.
206Pb/238U dates in bold are those used in the weighted mean zircon date calculation

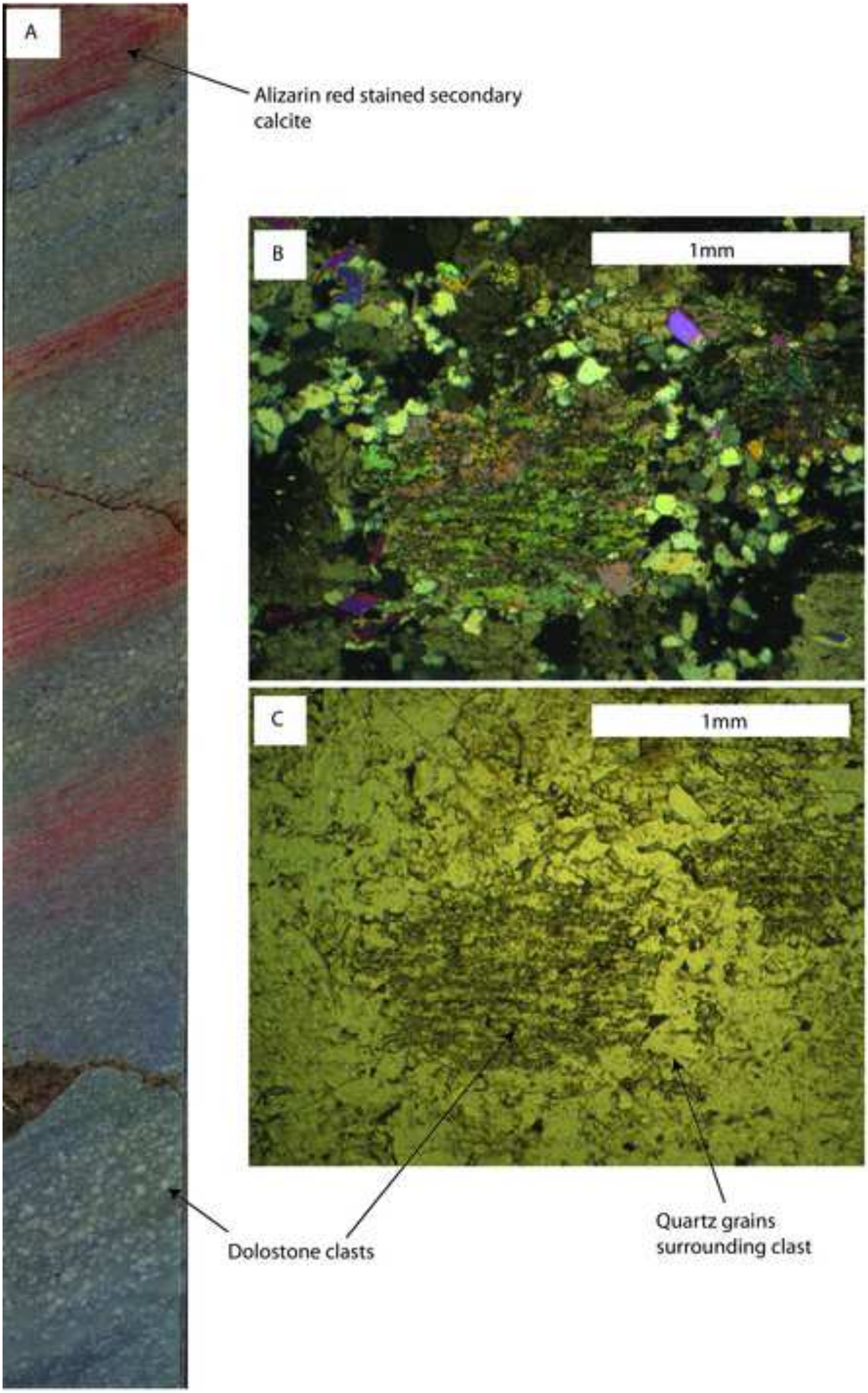
Table 1: U-Th-Pb data for zircons analysed from sample ICDP FAR-DEEP Hole 3A 20.01 m

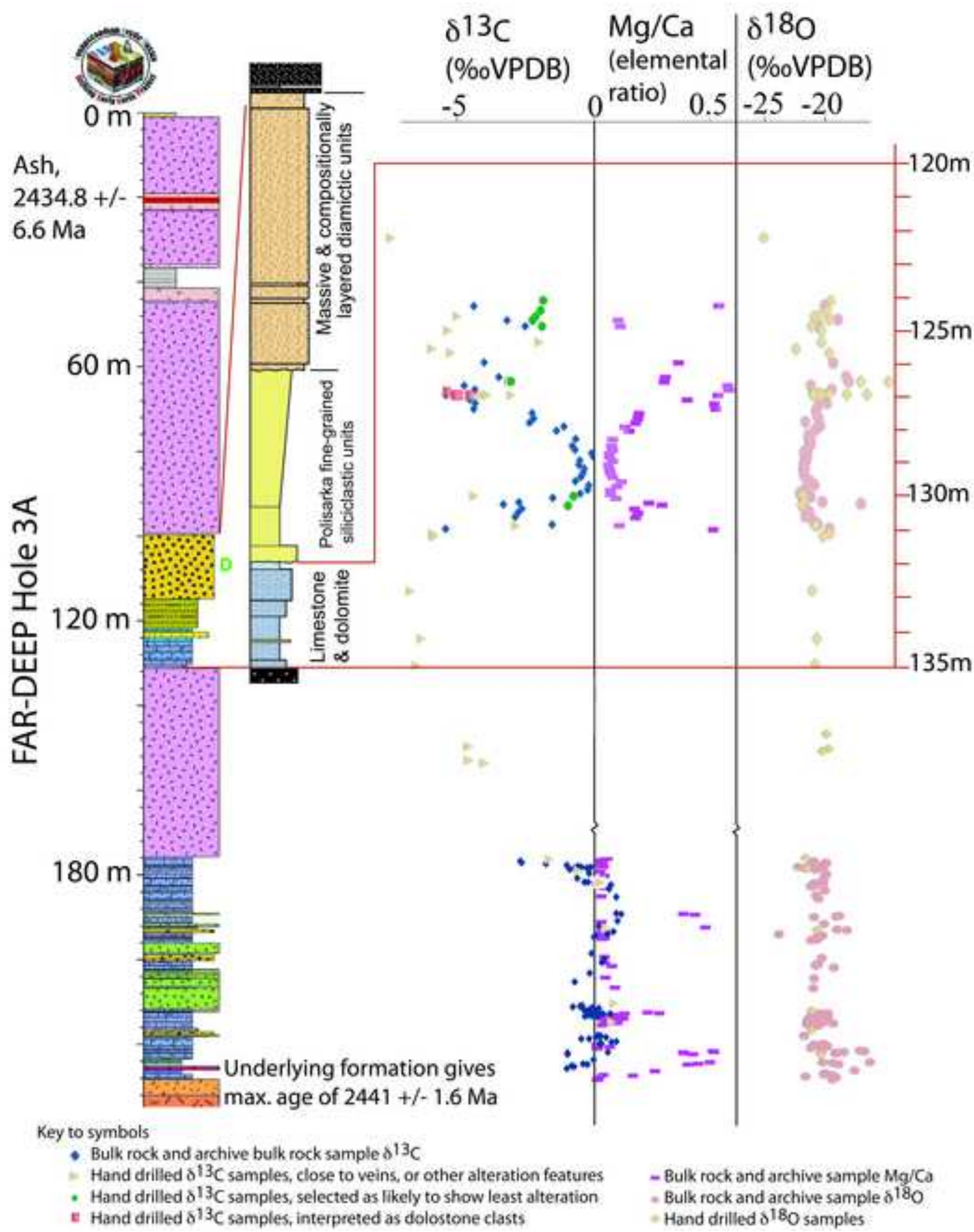

24º
36º
200 km
Barents sea
68º
Kola sub-province
ICDP FAR-DEEP
HOLE 3A
64º
Gulf of Bothia
Karelia sub-province
Svecofennian rocks
Archaean craton
Sumi flood-basalt
Layered gabbro-norite
Lapland - Kola Suture


3A
0
20
40
60
80
140
160
180
200
220
240
Polisarka Volcanic Formation
Greywacke-Diamictite member
Limestone member
Legend to ICDP FAR-DEEP Hole 3A
Overburden
Limestone
Limestone micritic
Limestone sandstone
Limestone gritstone
Limestone breccia
Dolostone micritic
Dolostone sandstone
Carbonate rock
Carbonate-sandstone-siltstone
Shale
Siltstone-shale
Siltstone
Greywacke
Conglomerate
Breccia
Dacitic tuff
Dacite
Andesitic tuff
Andesite
Basalt
Meimechite
Komatiite / Peridotite
Context of the Polisarka Sedimentary Formation
Neverskrukk Fm.
Tuff (c. 2435 Ma, this study)
Polisarka Fm.
Diamictite
Metaporphyrite (c. 2429 Ma) #
Seidorechka Fm.
Sub-volcanic intrusion (c. 2441 Ma) *
Kuksha Fm.
Purnach Fm.
Monche Pluton (c. 2504 Ma)*
Archaean Basement
*Amelin et al. (1995)
#Vrevskii et al. (2010)

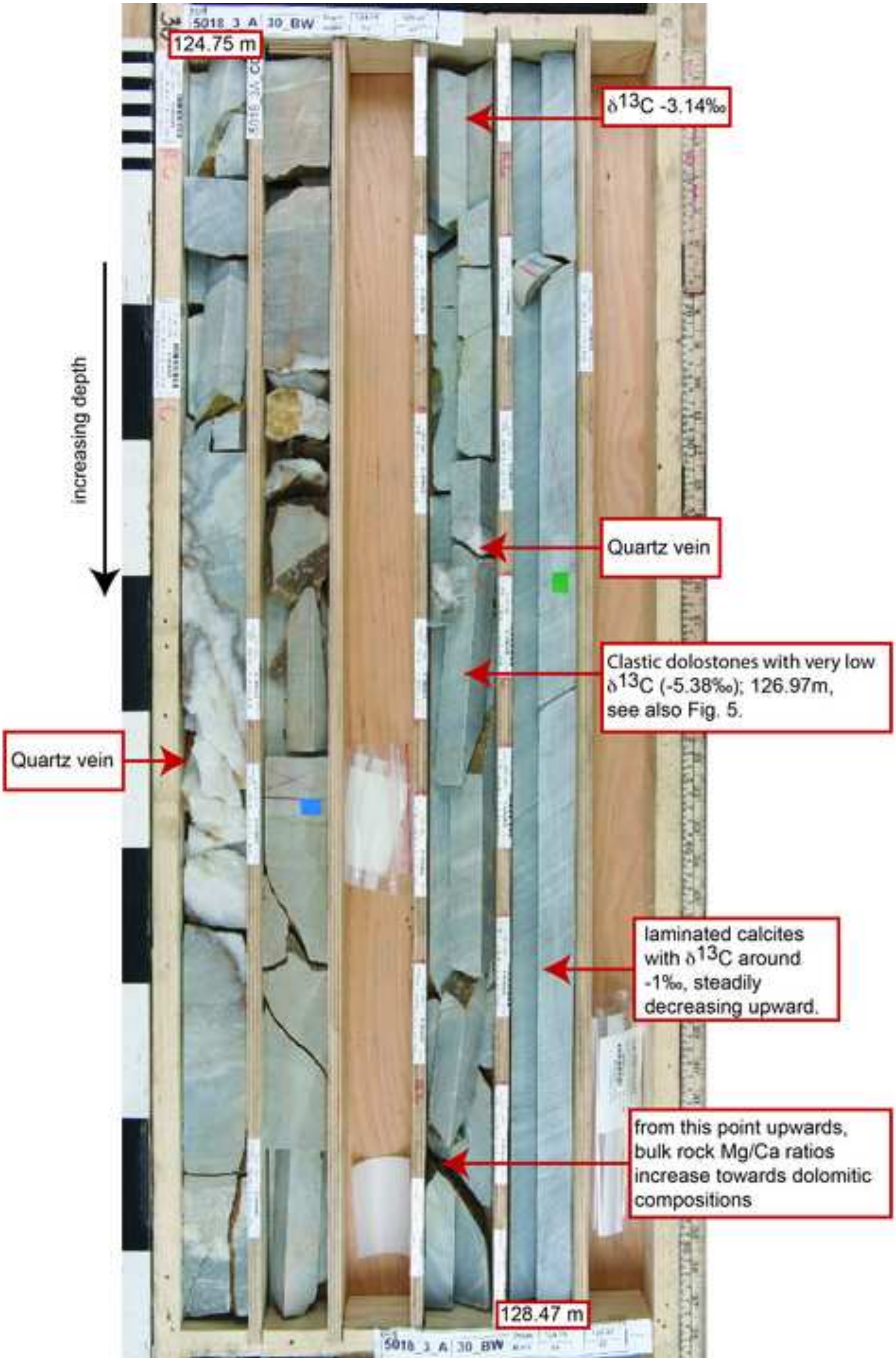

A
B
C
D
E
F
G
1 cm


A
400 µm
B
500 µm
C
500 µm
D
500 µm
E
500 µm
F
500 µm


A
Alizarin red stained secondary calcite
B
1mm
C
1mm
Dolostone clasts
Quartz grains surrounding clast



FAR-DEEP Hole 3A
0 m
60 m
120 m
180 m
Ash, 2434.8 +/- 6.6 Ma
Massive & compositionally layered diamictic units
Polisarka fine-grained siliciclastic units
Limestone & dolomite
Underlying formation gives max. age of 2441 +/- 1.6 Ma
δ13C (‰VPDB)
-5
0
Mg/Ca (elemental ratio)
0.5
δ18O (‰VPDB)
-25
-20
120m
125m
130m
135m
Key to symbols
Bulk rock and archive bulk rock sample δ13C
Hand drilled δ13C samples, close to veins, or other alteration features
Hand drilled δ13C samples, selected as likely to show least alteration
Hand drilled δ13C samples, interpreted as dolostone clasts
Bulk rock and archive sample Mg/Ca
Bulk rock and archive sample δ18O
Hand drilled δ18O samples



124.75 m
δ13C -3.14‰
increasing depth
Quartz vein
Clastic dolostones with very low δ13C (-5.38‰); 126.97m, see also Fig. 5.
Quartz vein
laminated calcites with δ13C around -1‰, steadily decreasing upward.
from this point upwards, bulk rock Mg/Ca ratios increase towards dolomitic compositions
128.47 m
5018_3_A_30_BW

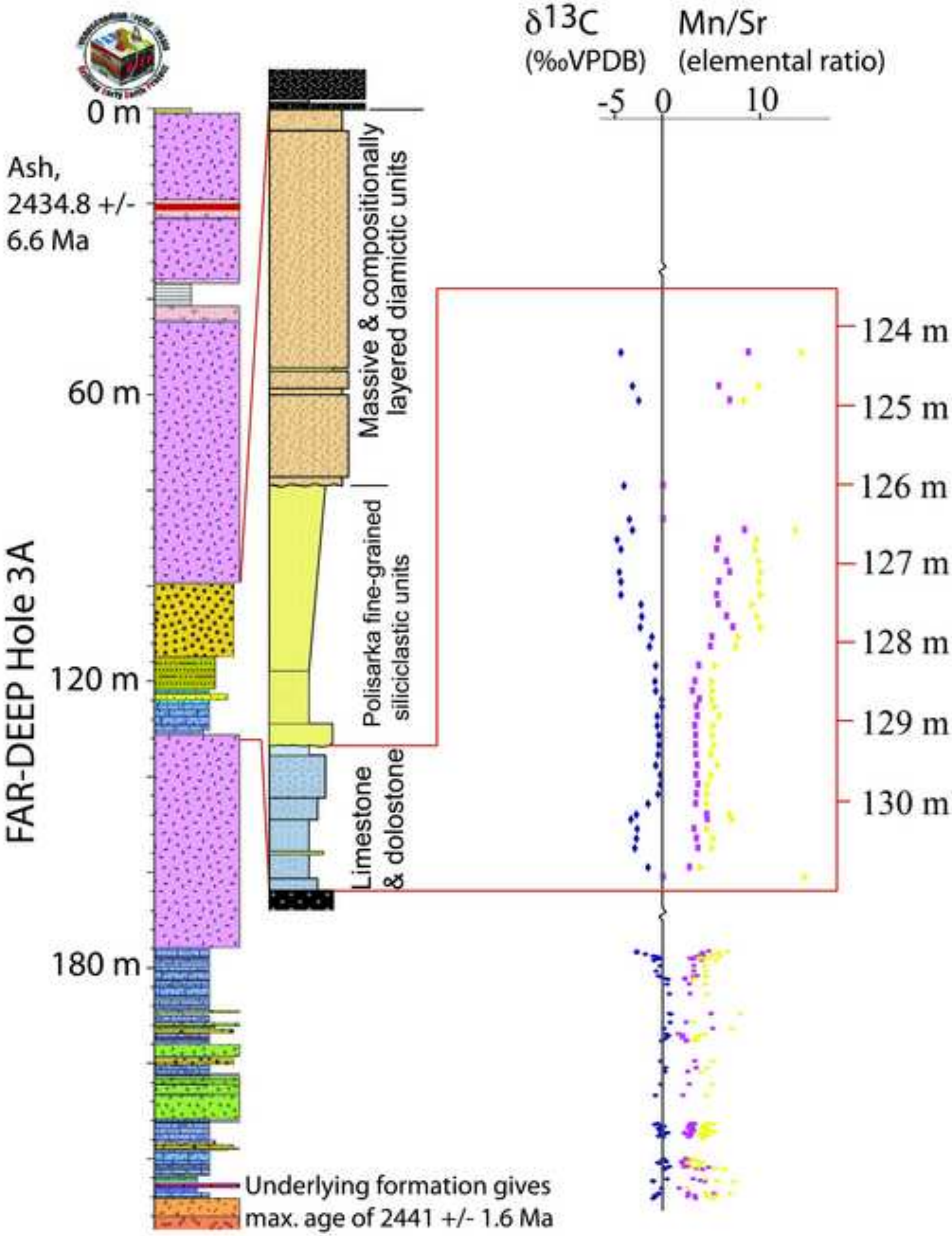
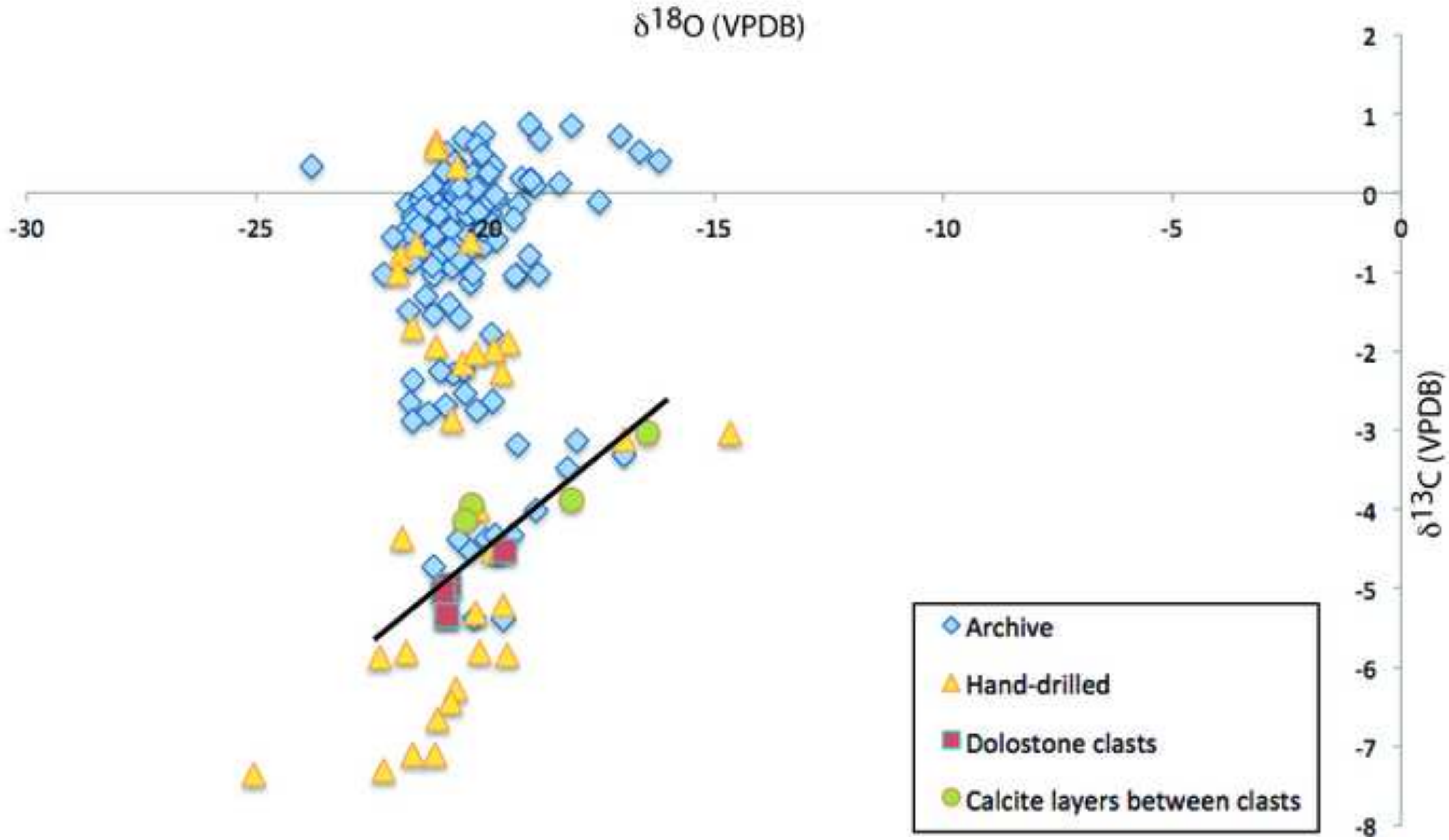

δ13C
(‰VPDB)
Mn/Sr
(elemental ratio)
-5
0
10
0 m
Ash,
2434.8 +/-
6.6 Ma
60 m
120 m
180 m
FAR-DEEP Hole 3A
Massive & compositionally layered diamictic units
Polisarka fine-grained siliciclastic units
Limestone & dolostone
124 m
125 m
126 m
127 m
128 m
129 m
130 m
Underlying formation gives
max. age of 2441 +/- 1.6 Ma

Fig_9_d18O_vs_d13C_final.jpg



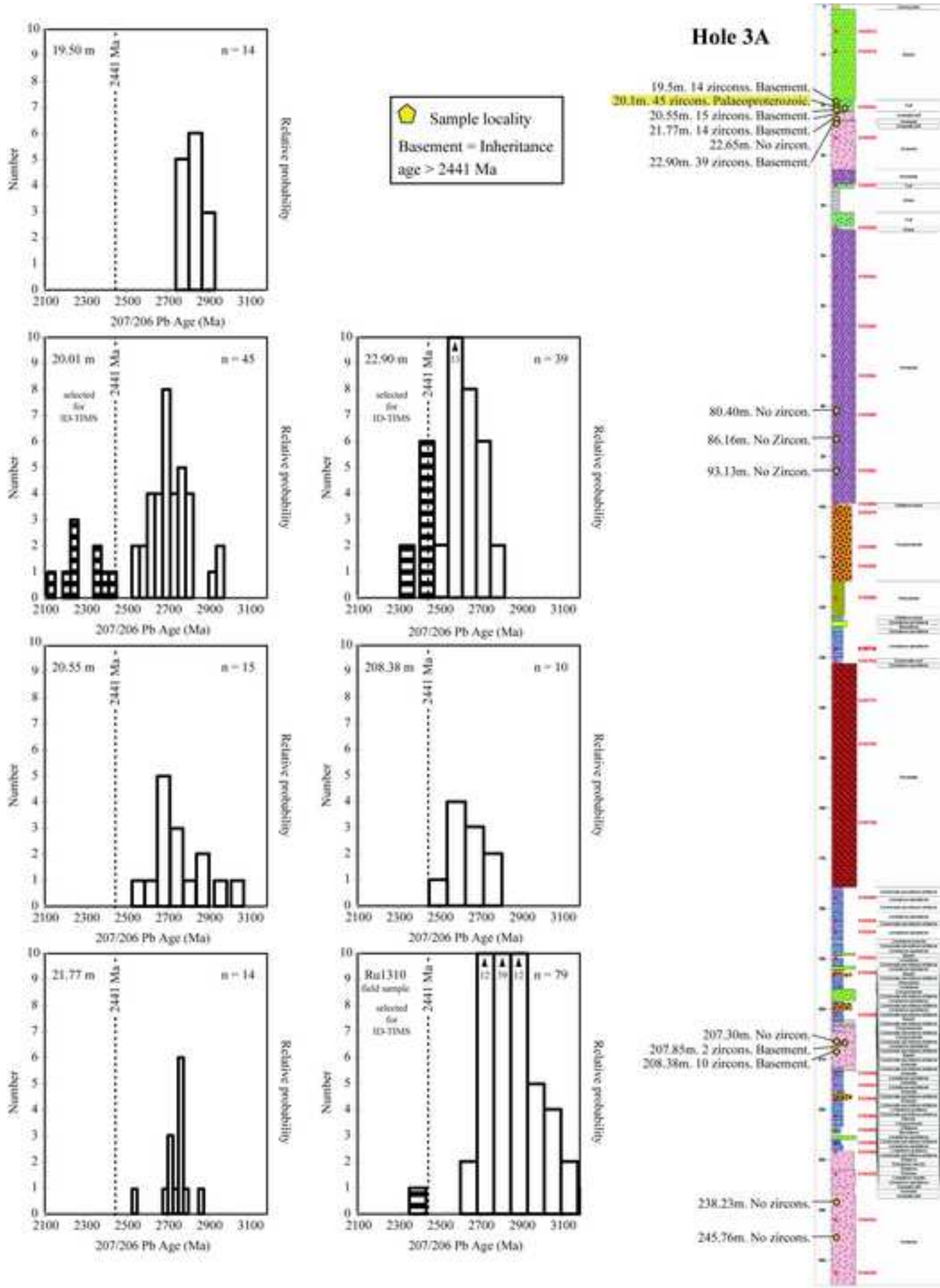

Hole 3A
Sample locality
Basement = Inheritance age > 2441 Ma
19.5m. 14 zircons. Basement.
20.1m. 45 zircons. Palaeoproterozoic.
20.55m. 15 zircons. Basement.
21.77m. 14 zircons. Basement.
22.65m. No zircon.
22.90m. 39 zircons. Basement.
80.40m. No zircon.
86.16m. No Zircon.
93.13m. No Zircon.
207.30m. No zircon.
207.85m. 2 zircons. Basement.
208.38m. 10 zircons. Basement.
238.23m. No zircons.
245.76m. No zircons.
19.50 m
n = 14
20.01 m
n = 45
selected for ID-TIMS
22.90 m
n = 39
20.55 m
n = 15
208.38 m
n = 10
21.77 m
Ru1310 field sample
n = 79
2441 Ma
Number
Relative probability
207/206 Pb Age (Ma)

Figure 11

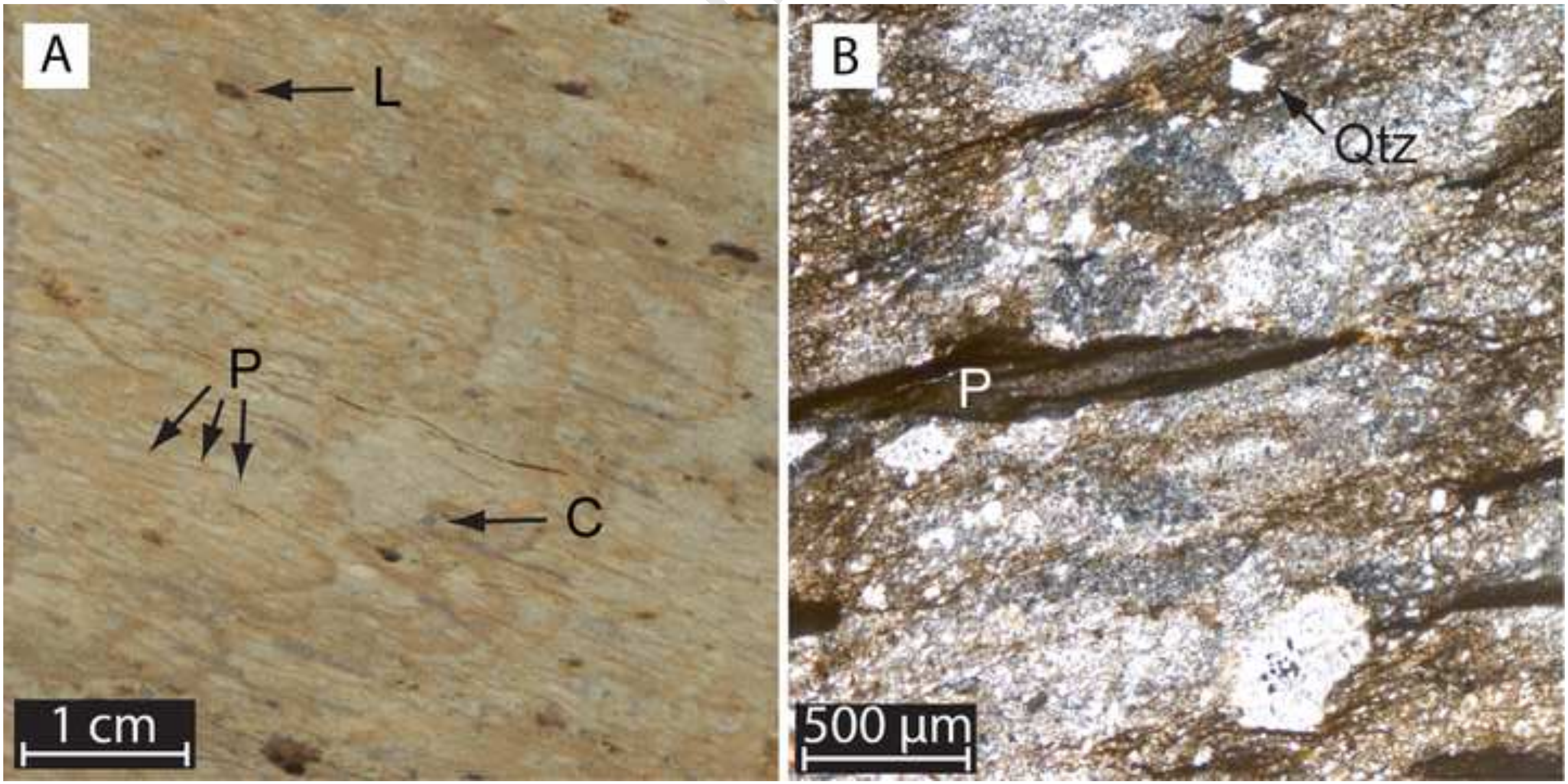
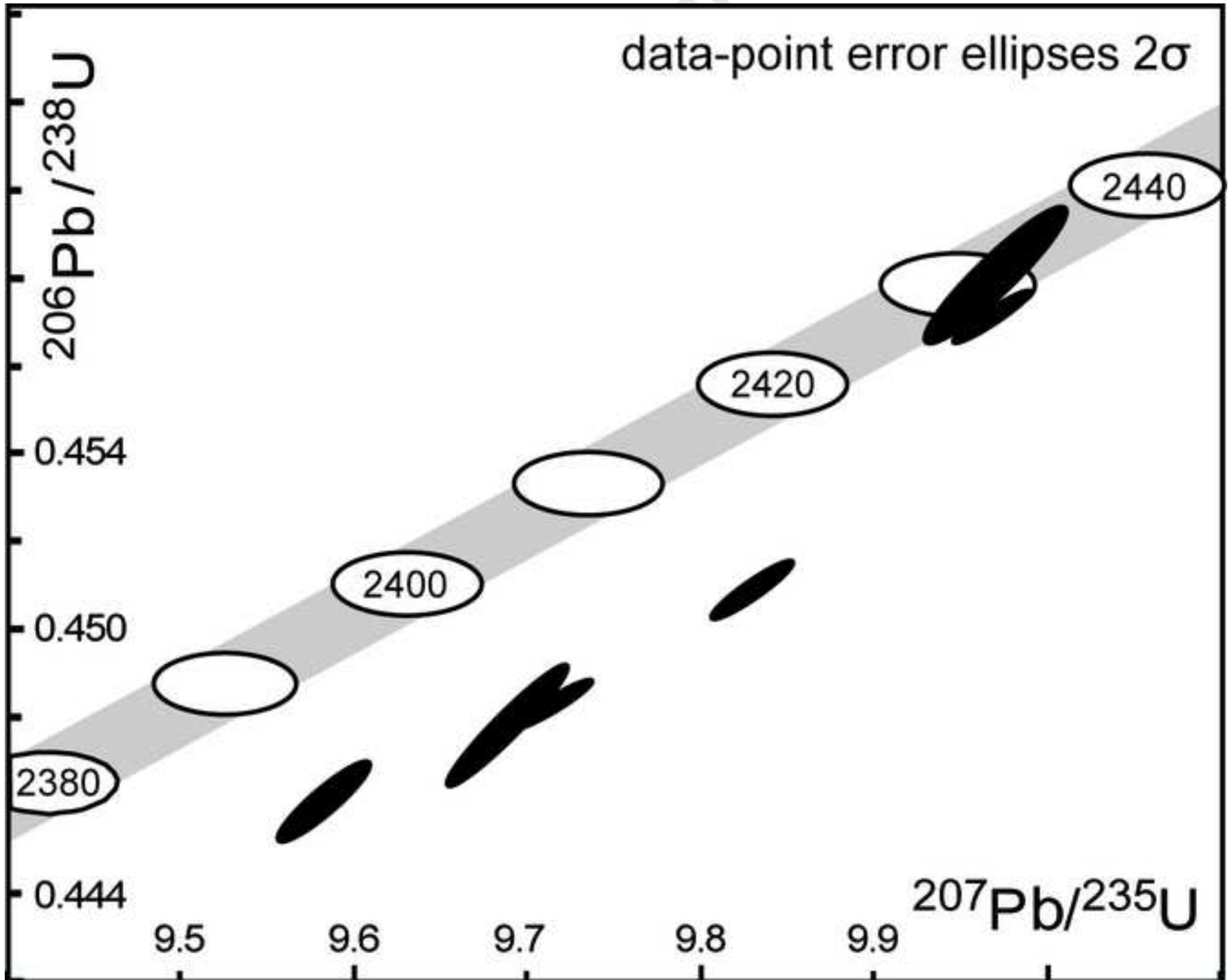


Figure 12



data-point error ellipses 2σ
206Pb/238U
207Pb/235U
0.454
0.450
0.444
9.5
9.6
9.7
9.8
9.9
2380
2400
2420
2440