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'Premier' evidence for prolonged kimberlite pipe formation and its influence on diamond transport from deep Earth

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Table DR1 and DR2

Supplementary File 1

Methods and Materials

Sample acquisition and preparation

The kimberlite samples investigated during this study were obtained in 2016 by the senior author over the course of several visits to the underground extension of Cullinan Diamond Mine (Gauteng, South Africa). At the University of Johannesburg, the freshest samples were cut into centimetre thick slabs with a rock saw, and all surficial crusts were removed and discarded. Small blocks were reserved for each kimberlite sample for preparation of polished petrographic thin sections at 25 µm thickness (University of Johannesburg). The kimberlite slabs were thoroughly washed under running water, and only material visibly free of crustal and mantle rock fragments was further processed. The contamination-screened kimberlite slabs (approximately 500 to 800 grams per sample) were then wrapped in thick plastic bags and crushed with a hammer into mm-sized rock chips (<8 mm). The kimberlite chips were again contamination-screened and approximately 200 grams per sample were then processed in an automated agate mill at the University of Johannesburg to obtain analytical grade rock powder. The remaining 300 to 600 grams of kimberlite chips were processed by High-Voltage-Pulse-Power-Fragmentation (SELFRAG) at the University of Pretoria to ensure non-abrasive mineral liberation of the <1mm grain size fractions. These fractions were further sieved to collect grains within the target size range between 75 and 150 µm. The 75-150 µm grain size fractions were then processed through a Frantz isodynamic separator, and the obtained non-magnetic fractions were prepared for heavy liquid mineral separation at the

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University of Johannesburg. The use of methylene iodide (diiodomethane) heavy liquid with a density of ~3.33 g/ml at 25°C proved to be most successful for concentrating abundant euhedral perovskite crystals (mainly resorbed octahedrons) from the fine-grained groundmass of kimberlite. Five kimberlite samples were most suitable for our high-precision geochronology study, and approximately 100 perovskite crystals per sample were mounted (Figure DR4), together with grains of two mineral standards (Tazheran-3 and Afrikanda-5 perovskite), into a single epoxy puck (Mount# A4242). After polishing of the epoxy puck all exposed crystals were inspected under a Cameca SX100 electron microprobe in BSE mode to identify at least 20 crystals that are most suitable for SIMS spot analysis; i.e., inclusion and zonation free (Figure DR4; see below).

Electron microprobe analysis (EPMA)

Fully quantitative major and minor element compositions of rock-forming minerals were determinded in situ on polished petrographic thin sections of the kimberlite dykes with a Cameca SX100 electron microprobe at the University of Johannesburg. Optimal conductivity of the thin sections was achieved with 25 nm thick carbon layers produced under vacuum in a Quorum Q3OOT ES coater. The instrument was operated at an acceleration voltage of 20 kV and a beam current of 20 nA. The electron beam was adjusted daily and optimized for 1 µm spot analysis. Counting time varied between 12 and 40 s on peak, depending on the chemical element. During phlogopite analysis, F and Cl were measured for 50 and 30 s on peak, respectively. The electron microprobe was calibrated using the following natural and synthetic international reference materials: diopside (Si), almandine garnet (Al), hematite (Fe), wollastonite (Ca), olivine (Mg), rhodonite (Mn), orthoclase (K), jadeite (Na), fluorite (F), and halite (Cl), as well as pure TiO_2, Cr_2O_3, and NiO. All elements of interest were measured on their X-ray Kα lines utilizing four wavelength dispersive spectrometers. Data reduction and matrix correction was done applying the 'X-PHI' method, which is a φ(ρz)-type off-line analytical protocol.

X-ray fluorescence analysis (XRF) and CO_2 determination

The bulk rock major and minor element compositions of the kimberlite dykes were analyzed using a PANalytical MagiX PRO X-ray fluorescence spectrometer at the University of Johannesburg (Table DR1). Rock powders of <20 µm grain size were dried in an oven at 105°C prior to fusion into glass discs with the aid of a $Li_2B_4O_7$-$LiBO_2$ flux (50/50). In addition, a small amount of LiBr was added to the flux to avoid stickiness between the produced glass discs and the platinum moulds. The lower limit of detection for all elements of interest is approximately 0.05 wt.%. Instrument calibration was conducted using mixtures of pure metal oxides, and the accuracy of the XRF method was monitored by analysis of certified reference materials (BE-N, JSy-1, SARM-2, SARM-16), as well as of in-house carbonatite standards (ST199 and ST220II). For the in-house carbonatite standards, all major and minor elements reported in Table DR1 reproduced within 2% of the values reported in Tappe et al. (2006).

Loss on ignition (LOI) was determined for all bulk rock powders at the University of Johannesburg after heating of the samples to 930°C in air and holding at this temperature for 30 minutes. Bulk rock CO_2 contents were determined by liberation of CO_2 gas from the

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sample powders in a reaction with 15% $HClO_4$ and subsequent photo-coulometry analysis, with a lower limit of detection of 0.02 wt.% CO_2 (AcmeLabs, Bureau Veritas Group).

U/Pb perovskite age determinations by Secondary Ion Mass Spectrometry (SIMS)

The U/Pb perovskite isotope analyses were performed on a Cameca IMS-1280 ion-microprobe mass spectrometer at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing (IGGCAS). The U/Pb data for groundmass perovskites from four kimberlite dykes (CIM15-72, CIM15-74, CIM15-76, CIM15-80) and a massive volcaniclastic kimberlite unit (CIM15-83; 'Grey' kimberlite) of the Premier/Cullinan pipe are listed in Table DR2, and displayed in Figure 2 and online in Figures DR2 and DR5. BSE images of polished thin sections of kimberlite samples for which geochronology data were obtained are shown in Figure DR4 to document perovskite crystals in petrographic context. The complete dataset, including the analyzed Afrikanda-5 perovskite mineral standard, is provided in Table DR2.

Li et al. (2010) provided a detailed account of the SIMS U/Pb isotope analytical protocol for perovskite at IGGCAS in Beijing, and the following description is only a brief method summary. The O^{2-} primary ion beam was accelerated at 13 kV, with 10 to 18 nA intensity. Analysis spot size was approximately 20×30 μm. Positive secondary ions were extracted with a 10 kV potential. For each sample, between 11 and 23 fresh euhedral and inclusion-free perovskite grains (75-100 μm across) were analysed. Each spot analysis on a single perovskite crystal consisted of 10 cycles, and data were collected for 16 minutes per grain. The U-Th-Pb isotope ratios and elemental abundances of sample and secondary standard grains were calibrated against the Tazheran-3 perovskite standard with a TIMS-determined $^{206}Pb/^{238}U$ age

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of 463±2 Ma (Kinny et al., 1997). This primary matrix-matched calibration standard was measured at the beginning and at the end of the analytical session on 11/12 May 2017, as well as after every three 'unknown' perovskite crystals. The U/Pb ages reported in Table DR2 were calculated with Isoplot 2.2 (Ludwig, 2000) using the decay constants recommended in Steiger and Jäger (1977): $9.8485*10^{-10}$ a^{-1} for ^{235}U and $1.55125*10^{-10}$ a^{-1} for ^{238}U. The presence of initial common Pb was corrected utilizing the measured amount of ^{204}Pb and the terrestrial Pb evolution model of Stacey and Kramers (1975). It should be noted that the Pb isotopic compositions of the Stacey and Kramers (1975) model between 1.1 and 1.15 Ga are very similar to those of galena crystals recovered from the Premier kimberlite (Allsopp et al., 1967). However, provided that the measured galena Pb isotopic compositions show significant heterogeneity (i.e., $^{206}Pb/^{204}Pb$ range from 15.3 to 16.2), application of the Stacey & Kramers model for initial common Pb correction is preferred. In general, we report final U/Pb perovskite results as $^{206}Pb/^{238}U$ ages, because this decay scheme is less sensitive to the common Pb correction, which can be significant for perovskite analyses (Heaman, 1989; Kinny et al., 1997; Tappe and Simonetti, 2012).

The following age result for the Afrikanda-5 perovskite mineral standard for which 13 grains were analyzed as unknowns during the analytical session on 11/12 May 2017 were obtained (all uncertainties are reported at the 2-sigma level; see Table DR2 and Figure DR3): $^{206}Pb/^{238}U$ age of 383.5±3.0 Ma (recommended TIMS-determined $^{206}Pb/^{238}U$ age: 381.6±1.4 Ma; Wu et al., 2013).

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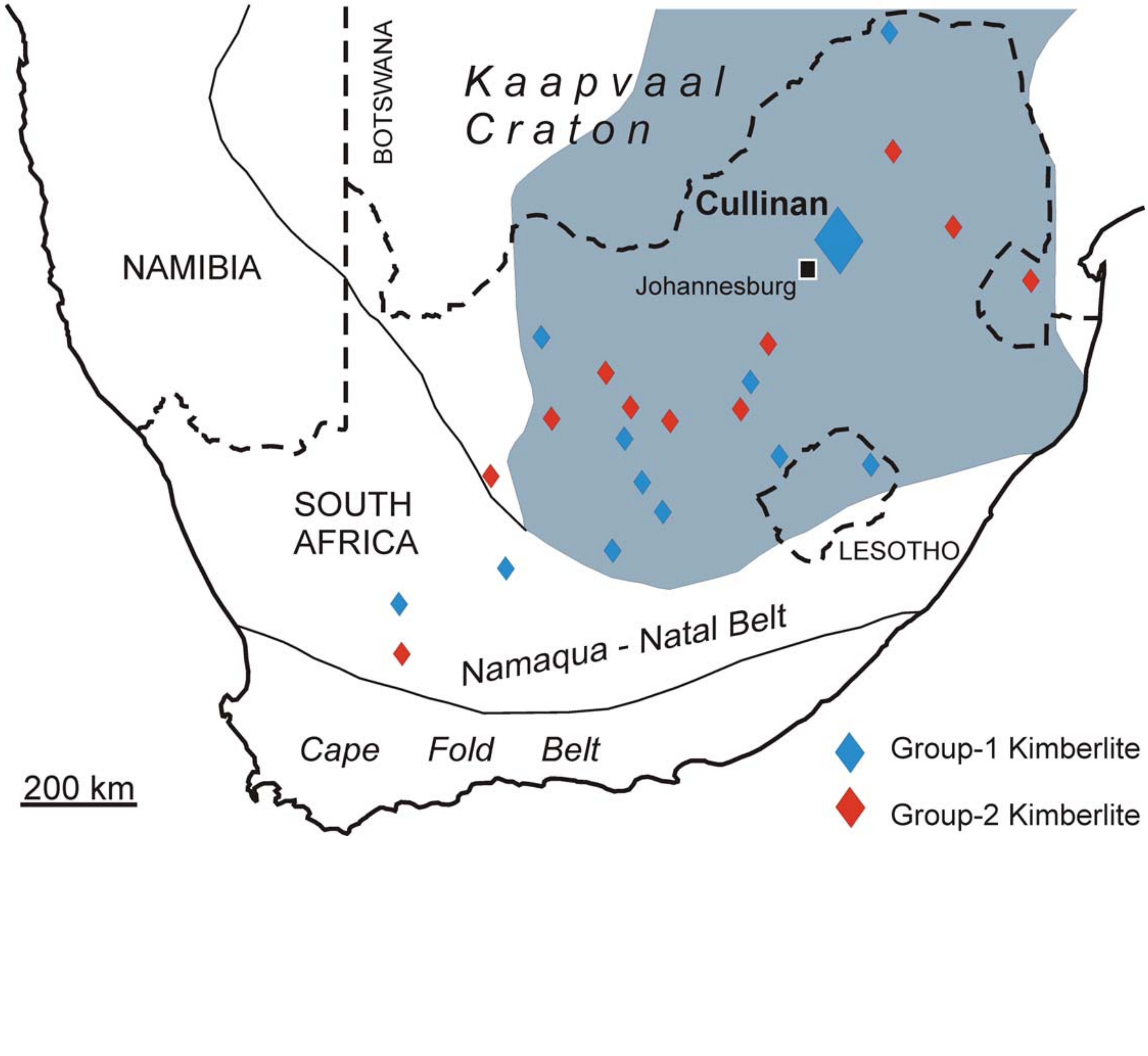
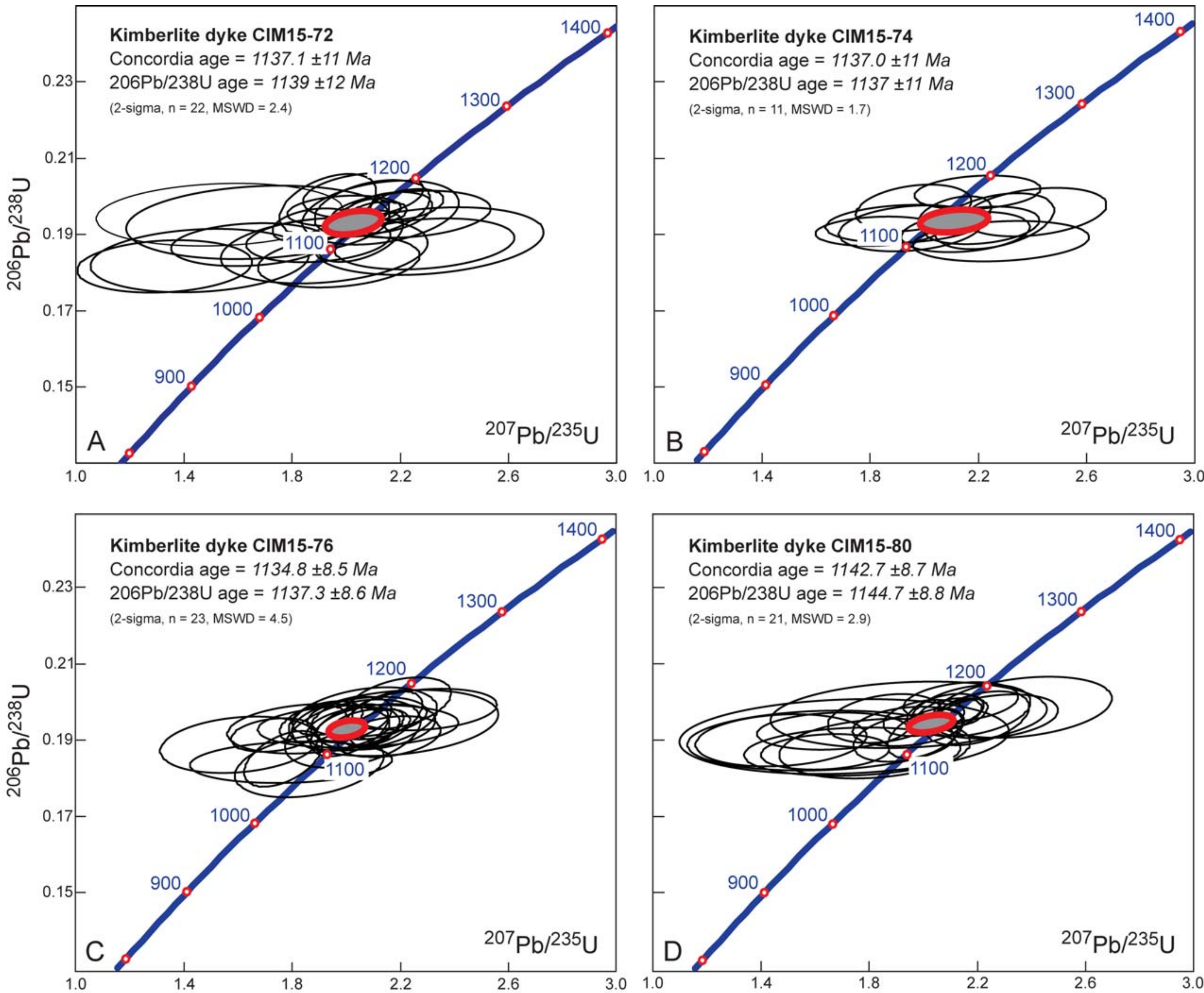
Figure DR1



BOTSWANA
Kaapvaal
Craton
Cullinan
Johannesburg
NAMIBIA
SOUTH
AFRICA
LESOTHO
Namaqua - Natal Belt
Cape Fold Belt
200 km
Group-1 Kimberlite
Group-2 Kimberlite

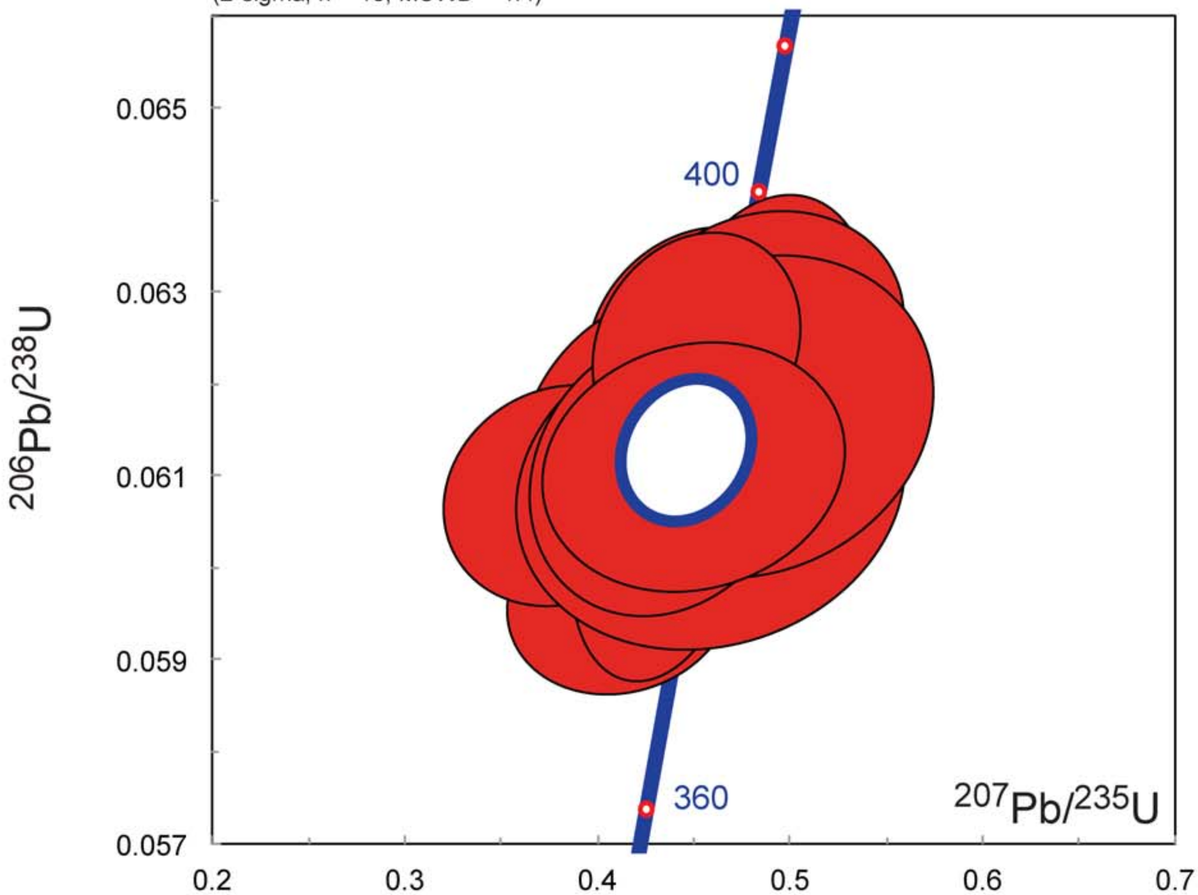
Figure DR2



Kimberlite dyke CIM15-72
Concordia age = *1137.1 ±11 Ma*
206Pb/238U age = *1139 ±12 Ma*
(2-sigma, n = 22, MSWD = 2.4)
A
Kimberlite dyke CIM15-74
Concordia age = *1137.0 ±11 Ma*
206Pb/238U age = *1137 ±11 Ma*
(2-sigma, n = 11, MSWD = 1.7)
B
Kimberlite dyke CIM15-76
Concordia age = *1134.8 ±8.5 Ma*
206Pb/238U age = *1137.3 ±8.6 Ma*
(2-sigma, n = 23, MSWD = 4.5)
C
Kimberlite dyke CIM15-80
Concordia age = *1142.7 ±8.7 Ma*
206Pb/238U age = *1144.7 ±8.8 Ma*
(2-sigma, n = 21, MSWD = 2.9)
D
$^{206}Pb/^{238}U$
$^{207}Pb/^{235}U$
900
1000
1100
1200
1300
1400
0.15
0.17
0.19
0.21
0.23
1.0
1.4
1.8
2.2
2.6
3.0

Figure DR3

'Afrikanda-5' perovskite in-house standard
Concordia age = ***383.4 ±3.1 Ma***
(2-sigma, n = 13, MSWD = 1.4)



'Afrikanda-5' perovskite in-house standard
weighted average 206Pb/238U age = ***383.5 ±3.0 Ma***
(2-sigma, n = 13, MSWD = 1.15)

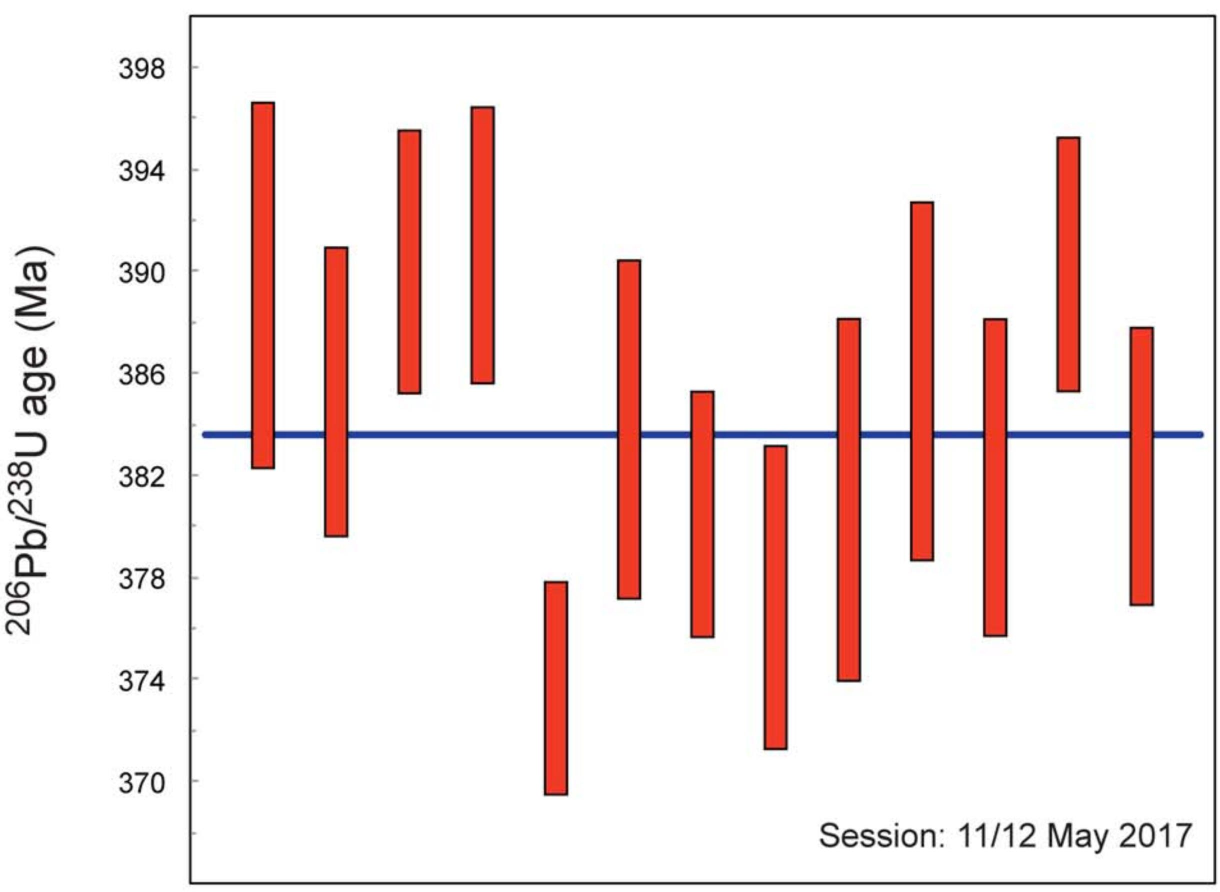
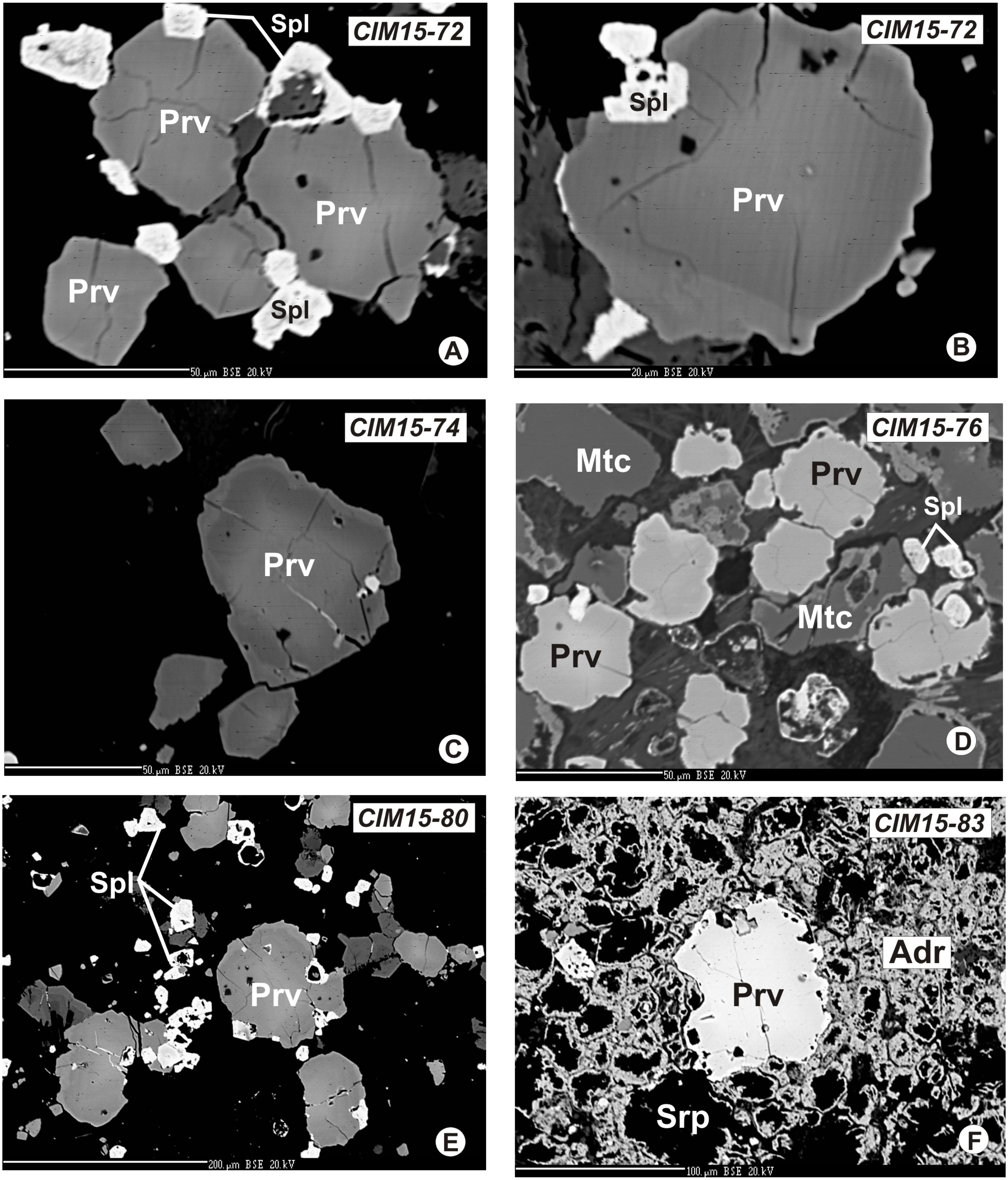


Figure DR4

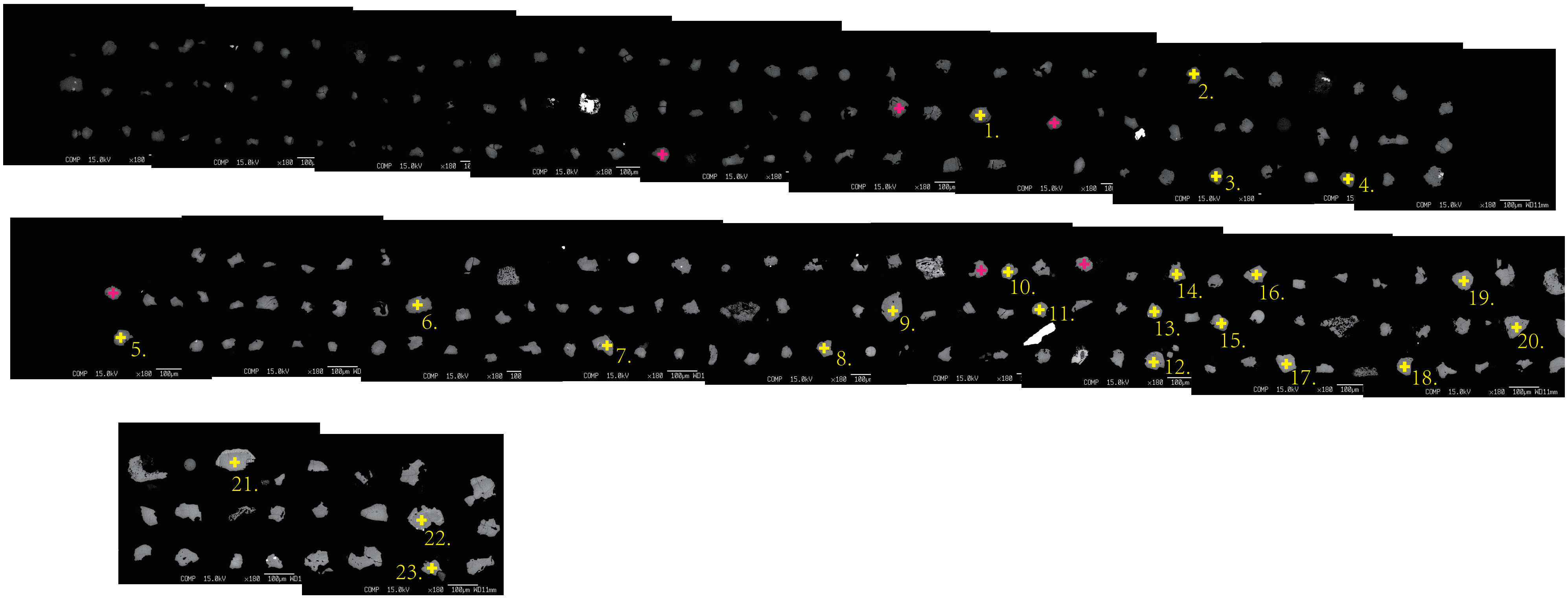


CIM15-72
Spl
Prv
Prv
Prv
Spl
A
50 µm BSE 20 kV
CIM15-72
Spl
Prv
B
20 µm BSE 20 kV
CIM15-74
Prv
C
50 µm BSE 20 kV
CIM15-76
Mtc
Prv
Spl
Mtc
Prv
D
50 µm BSE 20 kV
CIM15-80
Spl
Prv
E
200 µm BSE 20 kV
CIM15-83
Adr
Prv
Srp
F
100 µm BSE 20 kV

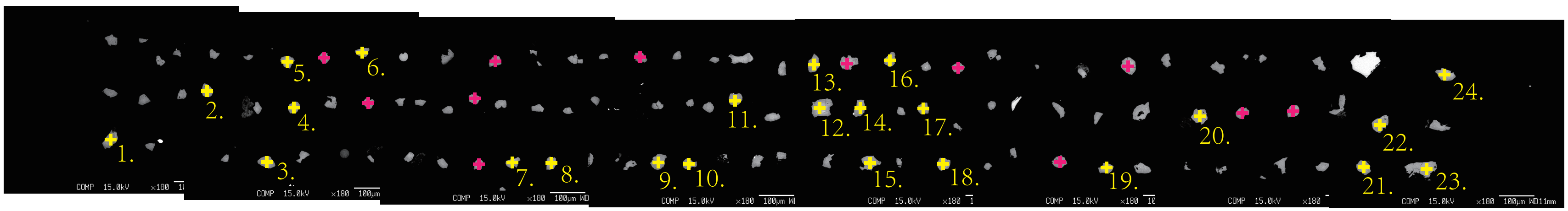
BSE images

Mount# A4242

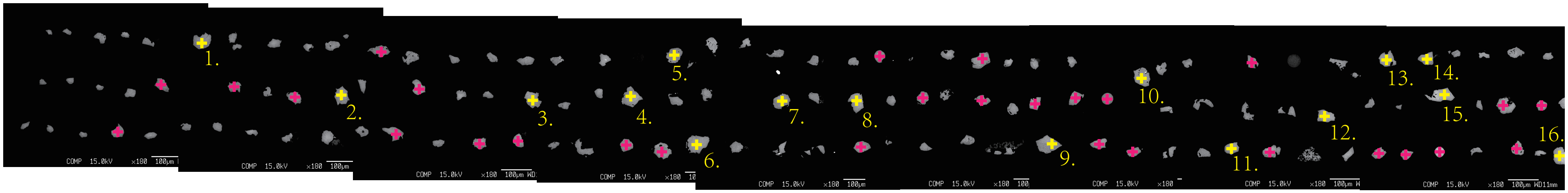
CIM15-072_Premier_Dyke *(23 perovskite grains selected in yellow)*

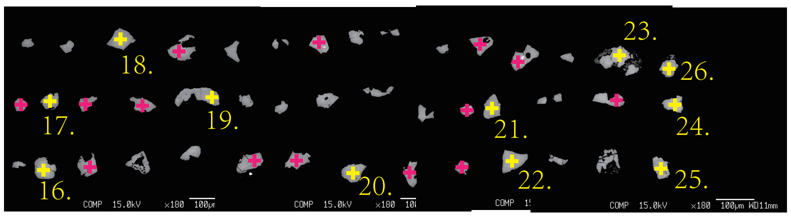


BSE images
Mount# A4242
CIM15-074_Premier_Dyke *(24 perovskite grains selected in yellow)*

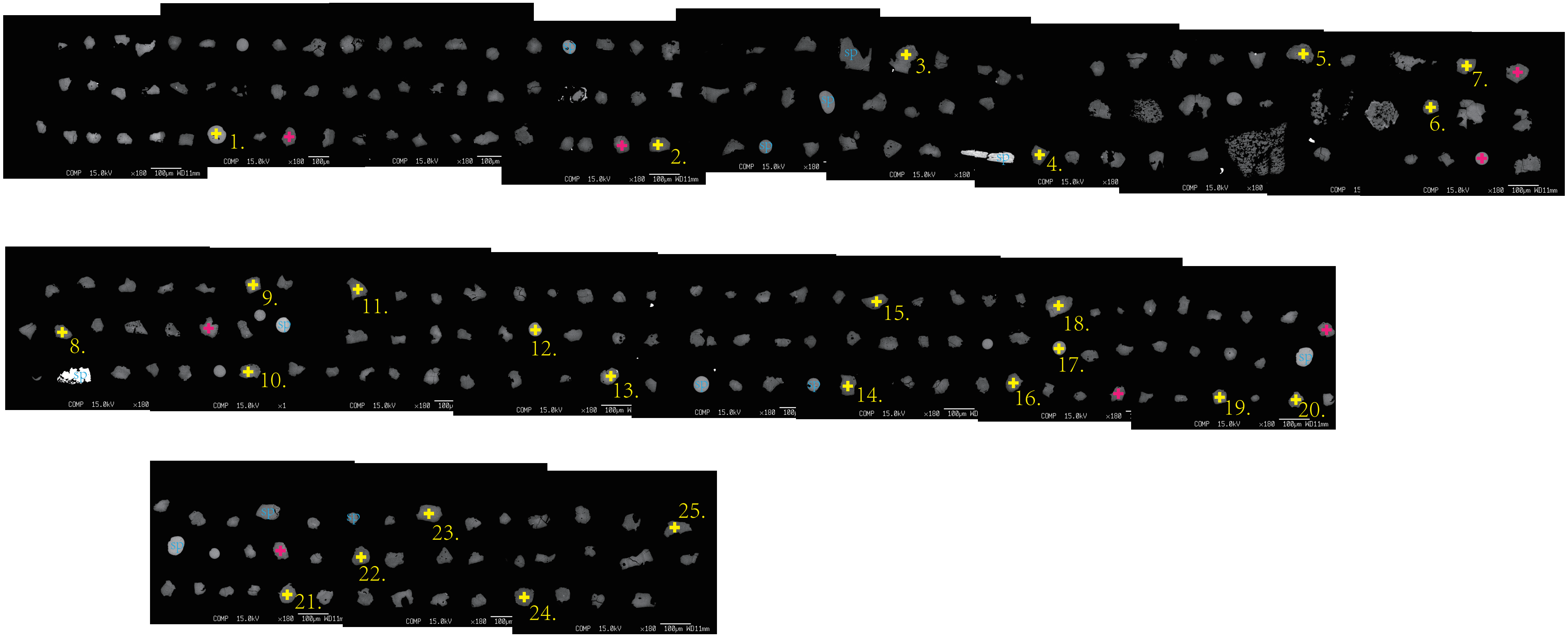


BSE images
Mount# A4242
CIM15-076_Premier_Dyke *(26 perovskite grains selected in yellow)*





BSE images
Mount# A4242
CIM15-080_Premier_Dyke *(25 perovskite grains selected in yellow)*



BSE images
Mount# A4242
CIM15-083_Premier_'Grey' volcaniclastic kimberlite *(22 perovskite grains selected in yellow)*

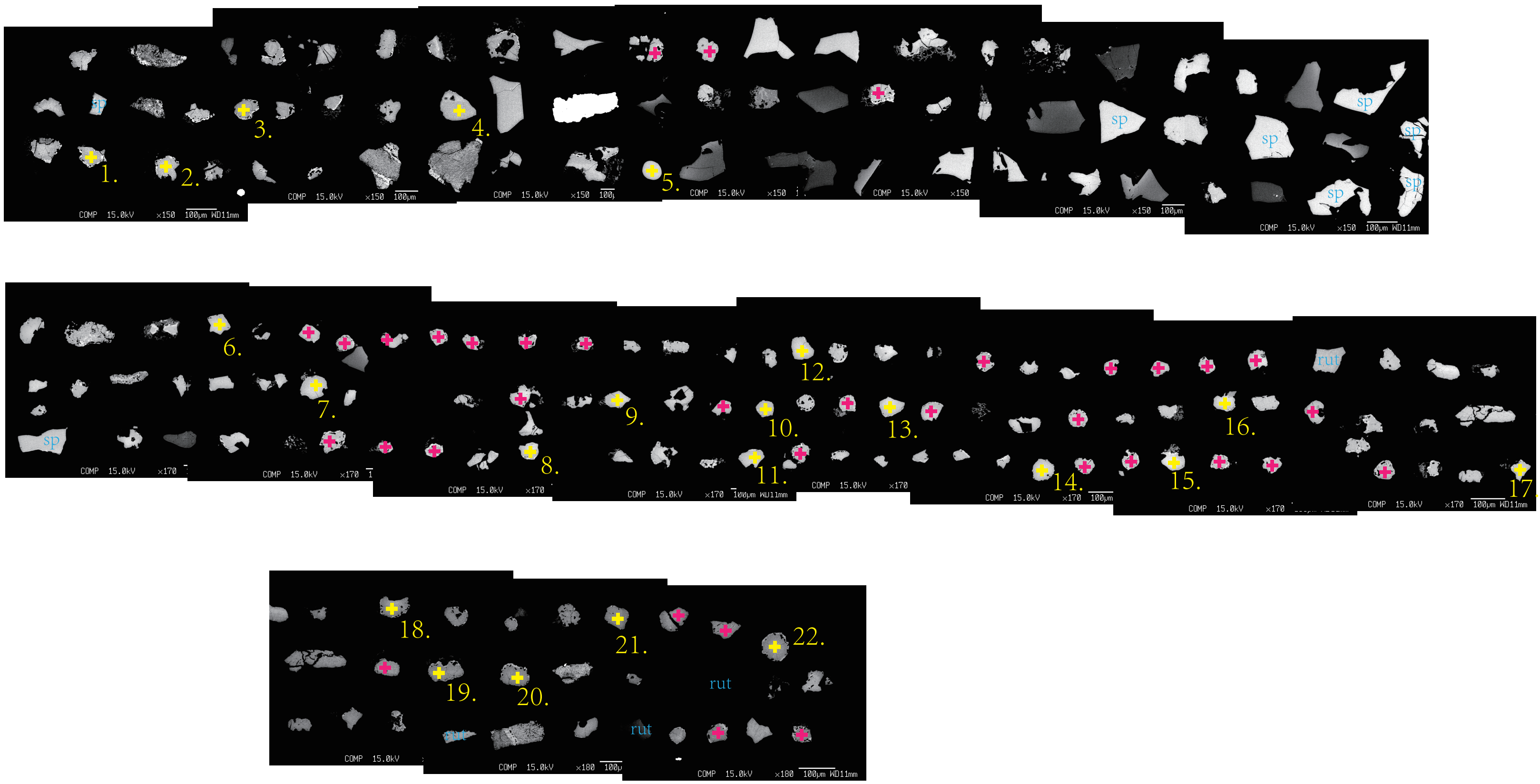
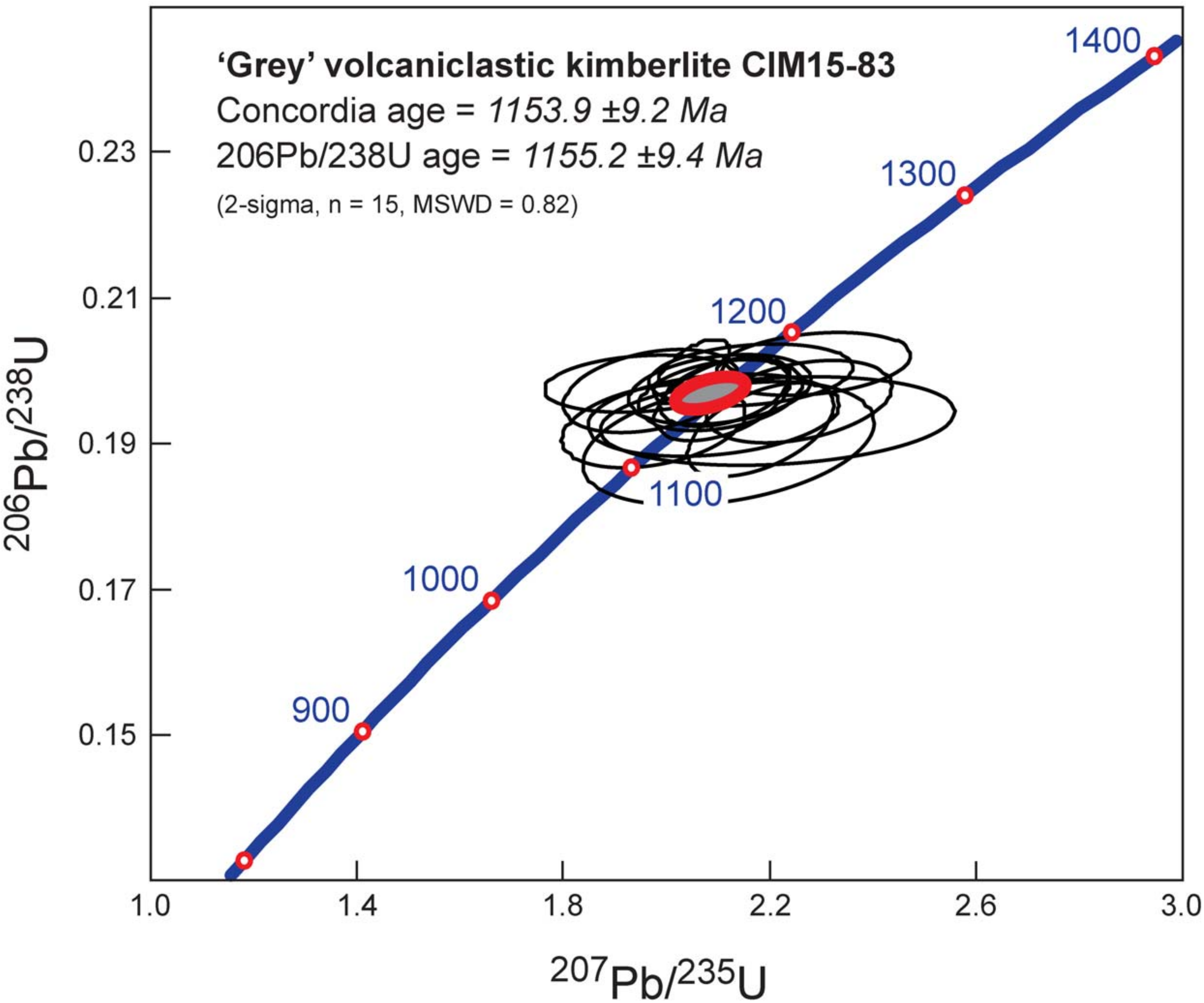
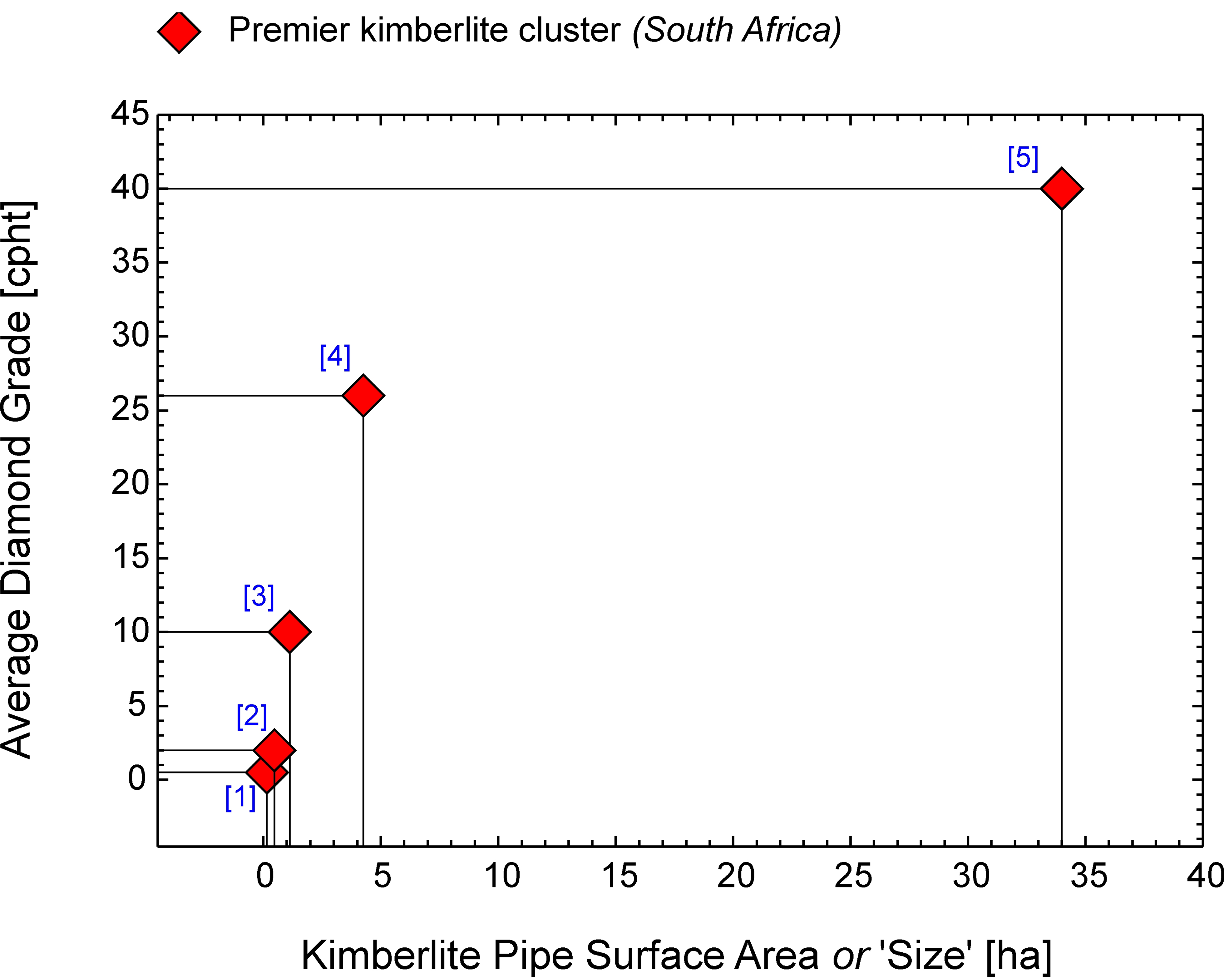


Figure DR5



'Grey' volcaniclastic kimberlite CIM15-83
Concordia age = *1153.9 ±9.2 Ma*
206Pb/238U age = *1155.2 ±9.4 Ma*
(2-sigma, n = 15, MSWD = 0.82)
1400
1300
1200
1100
1000
900
0.23
0.21
0.19
0.17
0.15
1.0
1.4
1.8
2.2
2.6
3.0
$^{206}Pb/^{238}U$
$^{207}Pb/^{235}U$

Figure DR6



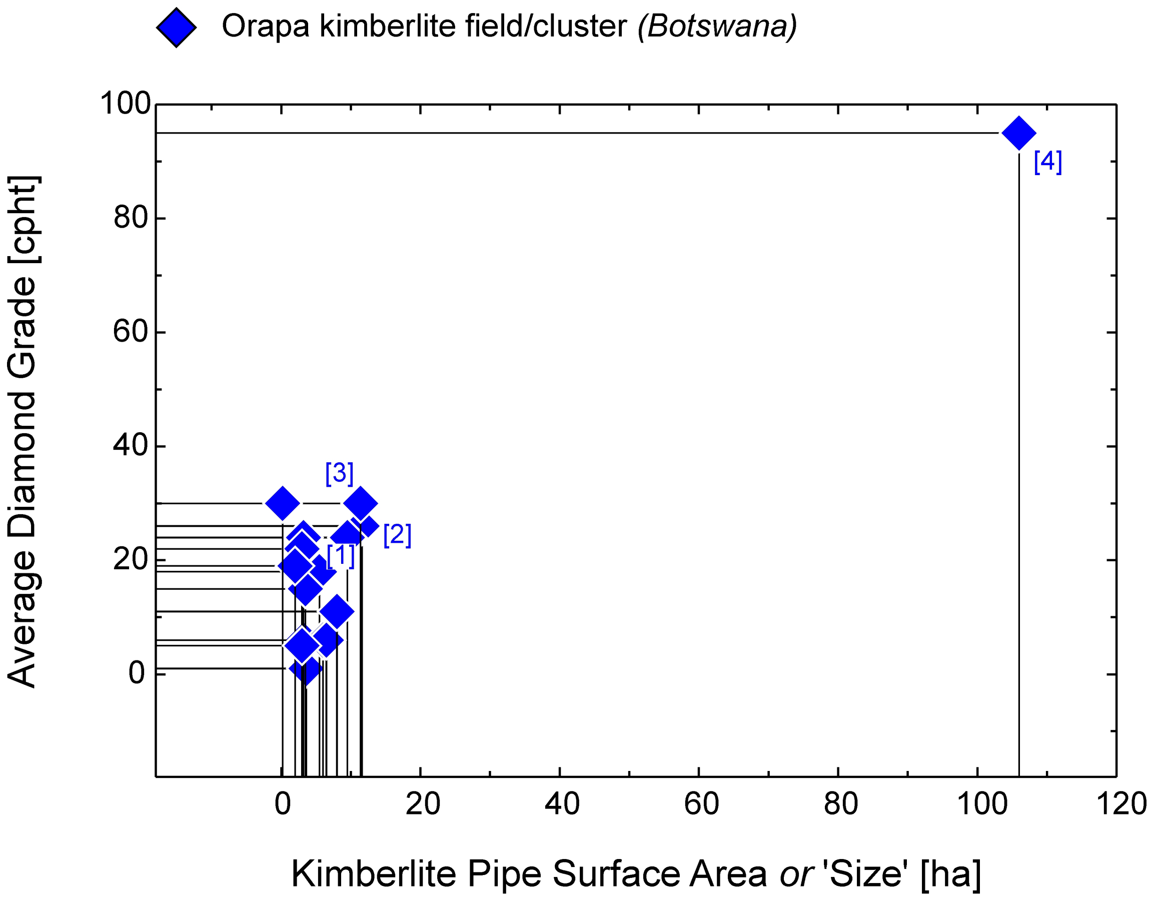
[1] Schuller Annexe

[2] National

[3] Schuller

[4] Montrose

[5] Premier / Cullinan Mine

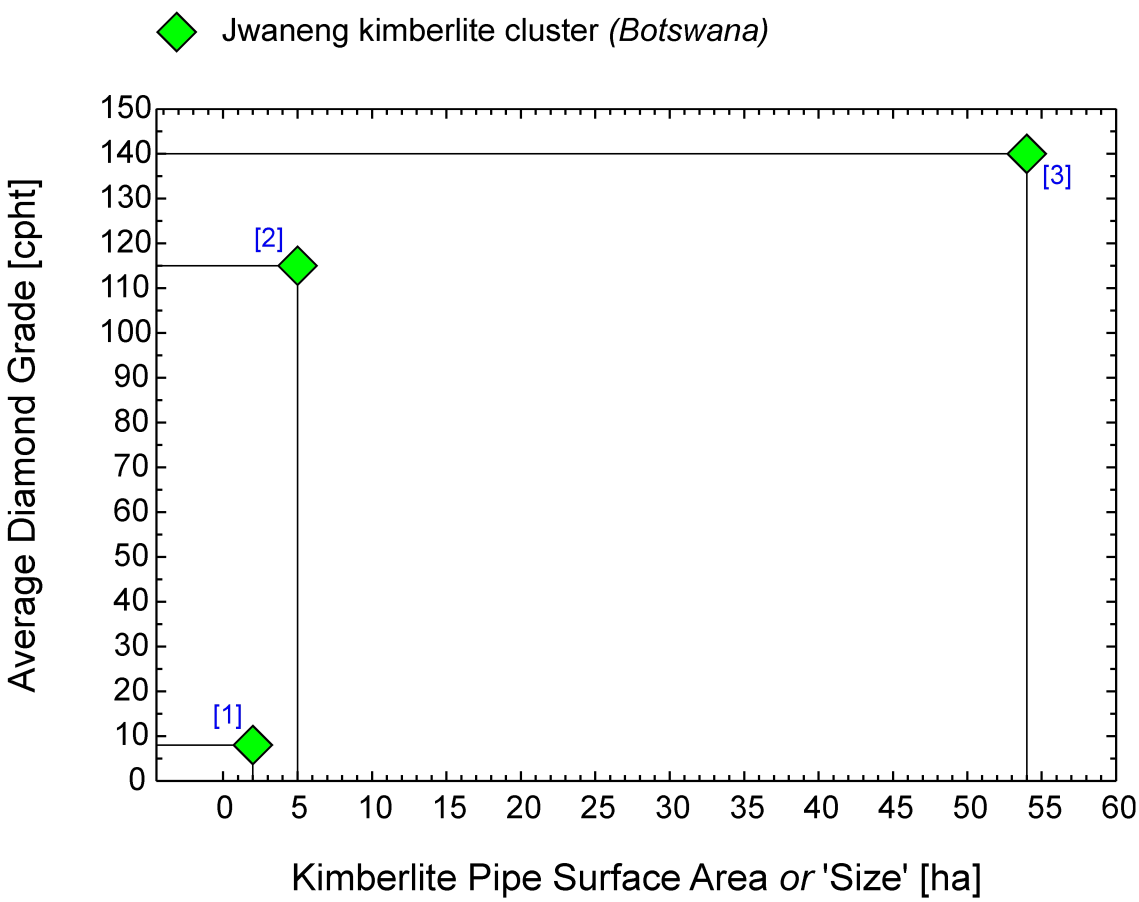


[1] AK6, Karowe Mine

[2] DK1, Letlhakane Mine

[3] BK9, Damtshaa Mine

[4] AK1, Orapa Mine

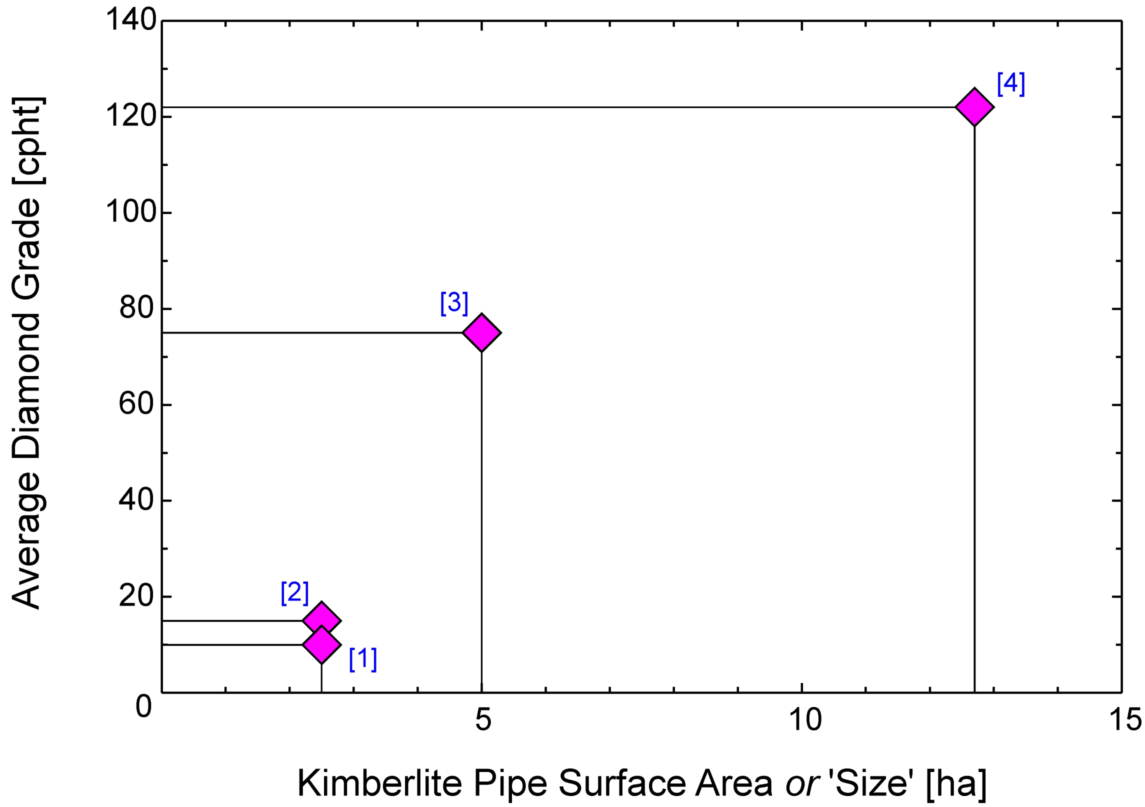


[1] DK12

[2] DK7

[3] DK2, Jwaneng Mine

Venetia kimberlite cluster *(South Africa)*



[1] K04

[2] K03

[3] K02

[4] K01, Venetia Mine