

# SHRIMP dating of titanite from metasyenites in the Central Zone of the Limpopo Belt, South Africa

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## Abstract

SHRIMP dating of titanite from metasyenites in the Central Zone of the Limpopo Belt yields a mean  $^{207}\text{Pb}/^{206}\text{Pb}$  age of 2010.3 +/- 4.5 Ma calculated from twenty-three analyses. This age, combined with petrographic and field observations, suggests the metamorphism in the syenites occurred during the regional Palaeoproterozoic event.

**Keywords:** Limpopo Belt; SHRIMP; titanite; geochronology; Palaeoproterozoic.

## Introduction

A unique body of (meta)-syenite intrudes the Alldays Gneiss and outcrops in an elongate, 6.25 x 1.25 km body WNW of Alldays within the Central Zone of the Limpopo Belt, South Africa (Fig 1a + b). A recent study by Rigby et al. (2008a) reveals the metasyenites underwent a metamorphic evolution characterized by a maximum pressure of 7-8 kbar and ~770°C. The subsequent retrograde path involved a simultaneous P-T decrease along a decompression-cooling path to 4 kbar and ~550°C. These P-T estimates are 'intermediate' between the high-grade conditions reported by Zeh et al. (2004) and Rigby (2009) for metapelites near Messina and the amphibolite-facies conditions reported by Zeh et al. (2005a,b) and Chudy et al. (2008) for rocks from the Venetia area. Collectively, this data led Rigby et al. (2008a) to postulate the existence of a metamorphic field gradient. However, there are two main tectonometamorphic episodes known in the Central Zone of Limpopo Belt, one in the Neoproterozoic (e.g. McCourt & Armstrong, 1998; Kroner et al., 1998; Bumby et al., 2001; Bumby & van der Merwe, 2004; Zeh et al., 2007; Millonig et al., 2008; Perchuk et al., 2008; Van Reenen et al., 2008; Gerdes & Zeh, 2009; Zeh et al. 2009) and one in the Palaeoproterozoic (e.g. Jaeckel et al., 1997; Holzer et al., 1998; Kroner et al., 1999; Zeh et al., 2004; Rigby et al., 2008b; Chudy et al., 2008; Eriksson et al., 2009; Gerdes & Zeh, 2009; Rigby et al., 2010; Eriksson et al., 2010a and b; Millonig et al., 2010) and without robust geochronological constraints it is not clear in which event the metasyenites were metamorphosed. Additionally, due to this uncertainty, the existence of the proposed metamorphic field gradient by Rigby et al (2008a) is, at present, mere speculation. In this short communication we present new U-Pb SHRIMP data obtained from titanite in the metasyenites to delineate their age and support the metamorphic field gradient hypothesis.

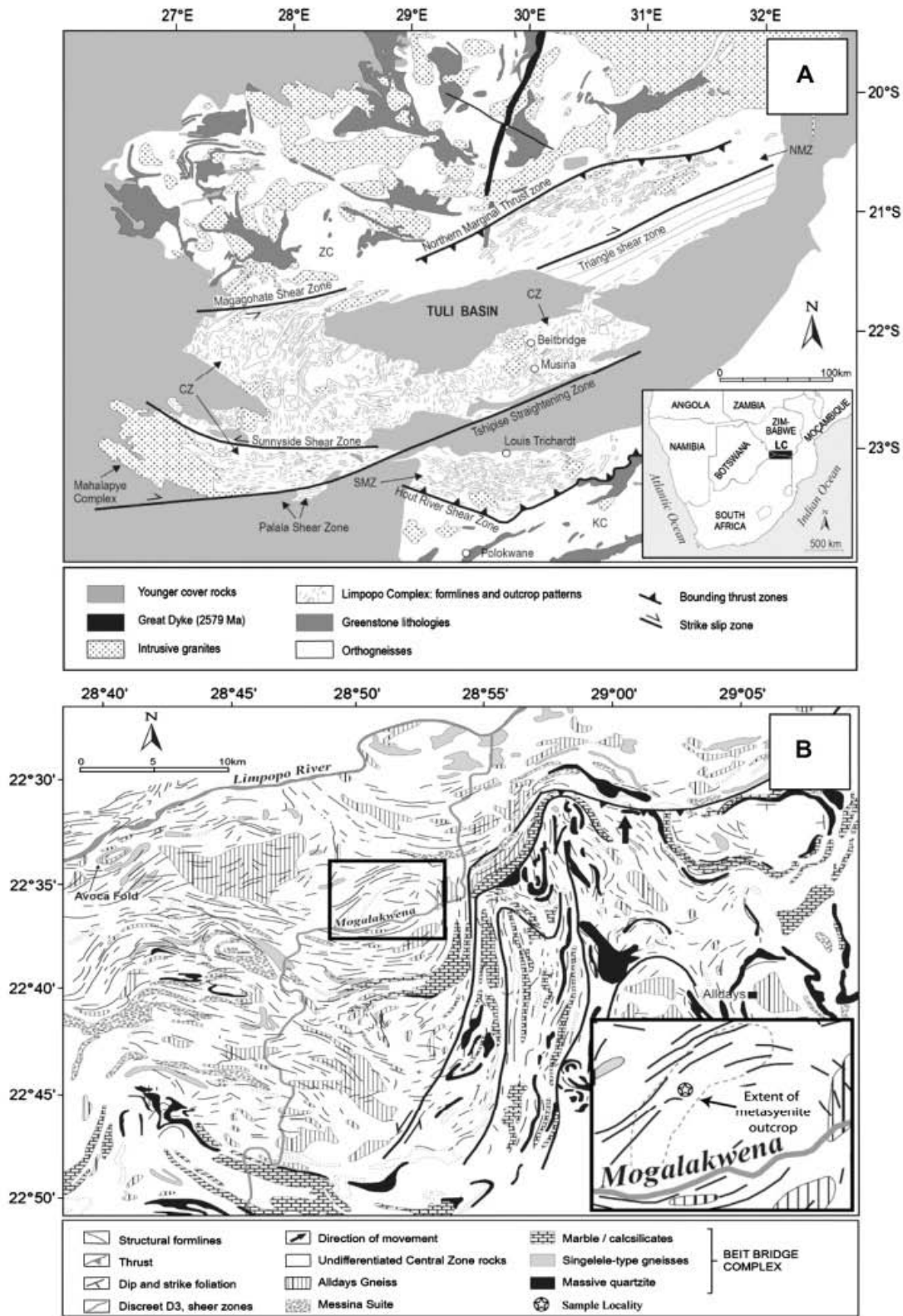


Fig. 1. (A) A map of the Limpopo Belt (after Boshoff et al. (2006)). (B) A detailed geological map of the field area (after Boshoff et al. (2006) and Rigby et al. (2008a)).

## **Geological Context**

### *Regional*

The Limpopo Belt of southern Africa (Fig. 1a) is a predominantly high-grade terrane composed of three distinct zones, each with a distinctive geological history and tectono-metamorphic evolution. The Southern Marginal Zone (SMZ) represents a high-grade equivalent of the granite-greenstone successions that prevail in the adjacent Kaapvaal Craton (KC). The SMZ is separated from the KC by the inward-dipping strike-slip ductile shear zone known as the Hout River Shear Zone. Similarly, the Northern Marginal Zone (NMZ) is a high-grade equivalent of the Zimbabwe Craton, which is separated from the NMZ by the North Limpopo Thrust Zone. Conversely, the Central Zone (CZ) forms a unique and distinct supracrustal block, which is bound to the north and south by the Magohapote and Triangle Shear Zone and Zoefontein-Palala Shear Zones respectively. The P-T-t evolution of the CZ of the Limpopo Belt is a vast and contentious issue too lengthy to be discussed here, however, the reader is referred to Perchuk et al. (2008), Zeh & Klemd (2008) and Rigby (2009) and references therein for a comprehensive description and discussion of this topic.

### *Local*

The metasyenites outcrop within the farms of Rietfontein 217 MR and Mietjiesfontein 220 MR, approximately 25km W-N-W of Alldays (S22°35'19.2" E028°50'12.4") (inset Figure 1B). Field relationships indicate the (meta)syenites intruded into the Alldays gneiss (Brandl & Pretorius, 2000). In hand-specimen the metasyenite is a coarse-grained, crystalline rock composed primarily of K-feldspar, quartz and amphibole. The amphiboles are aligned forming a weak but macroscopically-prominent foliation that strikes approximately NE-SW and dips steeply towards the NW. The metasyenites also contain 20-30 cm-scale, asymmetric folds that have fold-axes trending NW-SE. A large number of quartzo-feldspathic veins, interpreted to represent mobilized melt from the surrounding Alldays gneiss, cross-cut the metasyenite and manifest in various forms; (1) as single, linear veins measuring from 0.2cm-30cm in diameter (2) as linear conjugate pairs intersecting at ~60/120° measuring up to 15cm in diameter (3) as folded veins measuring up to 10cm in diameter (Figure 2A) (4) as linear veins, offset by small-scale normal faults and (5) as inter-connected, mesh-like networks (Rigby et al. 2008a).

## **Samples & Methodology**

### *Sample description*

The rock contains amphibole in two distinct textural settings; (1) weakly aligned, parallel prismatic grains measuring up to 8mm in length that form a weak foliation. (2) as randomly oriented blocky grains measuring up to 4mm in diameter. The amphiboles are set in a coarse grained, inter-locking crystalline matrix consisting of predominantly K-feldspar with interstitial clinopyroxene, plagioclase, quartz, titanite and magnetite (Figure 2B). K-feldspar forms randomly oriented, euhedral-blocky grains, measuring up to 10mm in diameter and commonly exhibiting micro-perthitic exsolution textures. Plagioclase and K-feldspar show signs of sericitization. Quartz, commonly exhibiting sub-grain development, is found only in contact with K-feldspar and plagioclase where it forms relatively small (<2mm) interstitial patches between the blocky grains. Clinopyroxene forms randomly oriented subhedral-euhedral grains that are interstitial between large

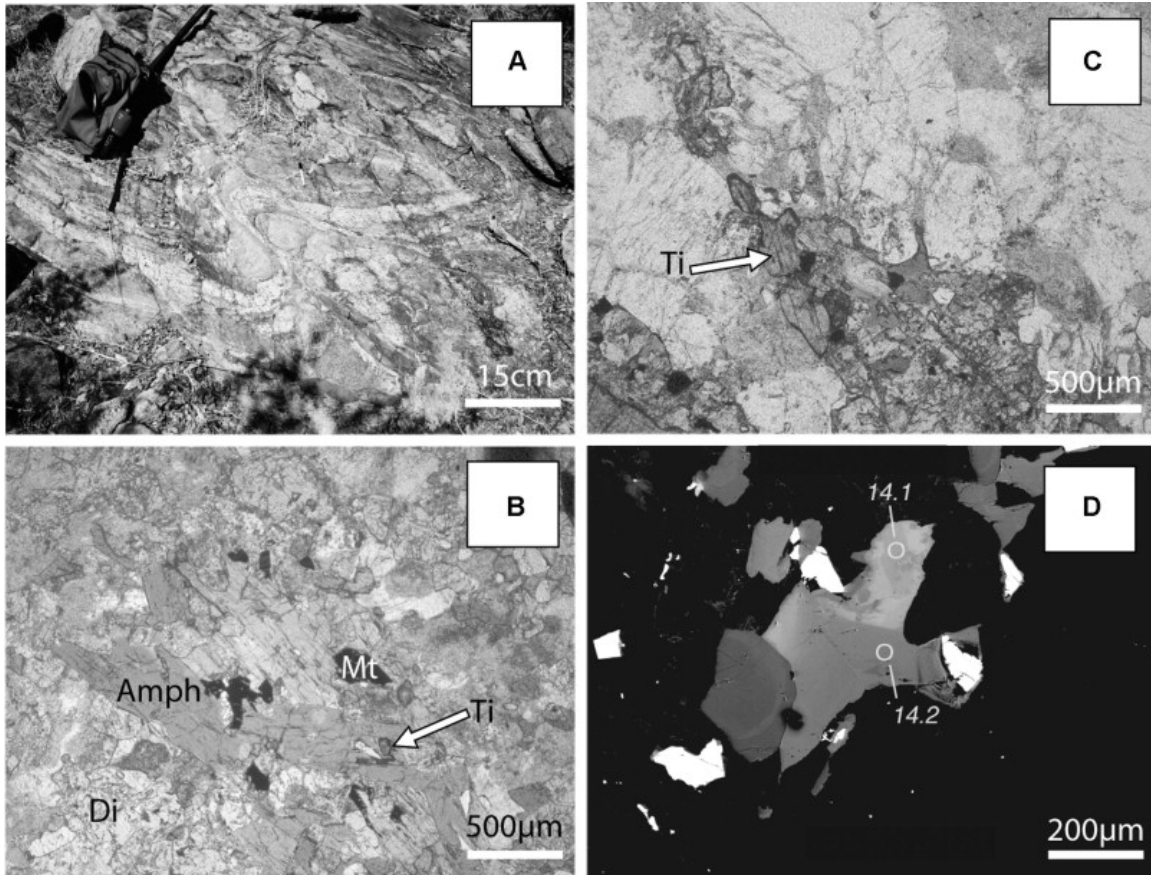


Fig. 2. (A) Field photograph small-scale folding within the metasyenite. (B) Photomicrograph of the thin-section RM06/49 illustrating the mineral assemblage (Amph = amphibole; Di = clinopyroxene; Ti = titanite; Mt = magnetite). (C) Photomicrograph of the thin-section RM06/49 illustrating large elongate titanites. (D) BSE image illustrating the zoning/internal structure of a single titanite grain.

blocky K-feldspars and elongate amphibole. Magnetite forms small equant grains measuring up to 0.5 mm in diameter, which are commonly located in contact with, or immediately adjacent to the amphiboles. Titanite is the most abundant accessory mineral, forming both large (>5mm) subhedral-to-euhedral grains (Figure 2C) and randomly oriented clusters composed of several small grains (0.1-1mm).

### *Methodology*

Photomicrographs in transmitted and reflected light were taken of the titanite thin-sections and together with back-scattered electron (BSE) images, were used to delineate the internal structures of the sectioned grains and to target specific areas within the minerals for spot analyses. BSE images of titanite reveal that specific domains of an individual grain have a contrast in the grey-scale, which may indicate compositional zoning (Figure 2D). U-Pb analyses of titanite were performed in situ from several thin-sections of the same sample at the Research School of Earth Sciences (RSES), Australian National University using a SHRIMP II. Uncertainties given for individual analyses (ratios and ages; Table 1) are at the  $1\sigma$  level, whereas uncertainties in the calculated weighted mean ages are reported at 95% confidence limits and include the uncertainties

in the standard calibration. Concordia plots and weighted mean age calculations were carried out using Isoplot/Ex (Ludwig 1999). Concordia ages were calculated using the SQUID Excel macro (Ludwig 2000) with uncertainties from the standard calibration included in the final errors quoted. On the basis of previous studies, the quadratic relationship between  $Pb^+/U^+$  and  $UO^+/U^+$  (Claoue'-Long et al. 1995) used for zircon also provides a good first-order correction for the interelement fractionation in the ion emission from titanite (Williams, 1998).

## Results and Discussion

Twenty-three analyses from different titanite grains were undertaken and the results are presented in table 1. The concordia plot (Figure 3) demonstrates most analyses are concordant. Intercepts occur at  $2012 \pm 14$  &  $64 \pm 560$  Ma with a MSWD of 0.38. The data yields a precise calculated mean  $^{207}Pb/^{206}Pb$  age of  $2010.3 \pm 4.5$  Ma.  $^{207}Pb/^{206}Pb$  ages range from  $1996.4 \pm 9.6$  to  $2057 \pm 49$  Ma and there is no discernible age difference between different zones within a single titanite grain.

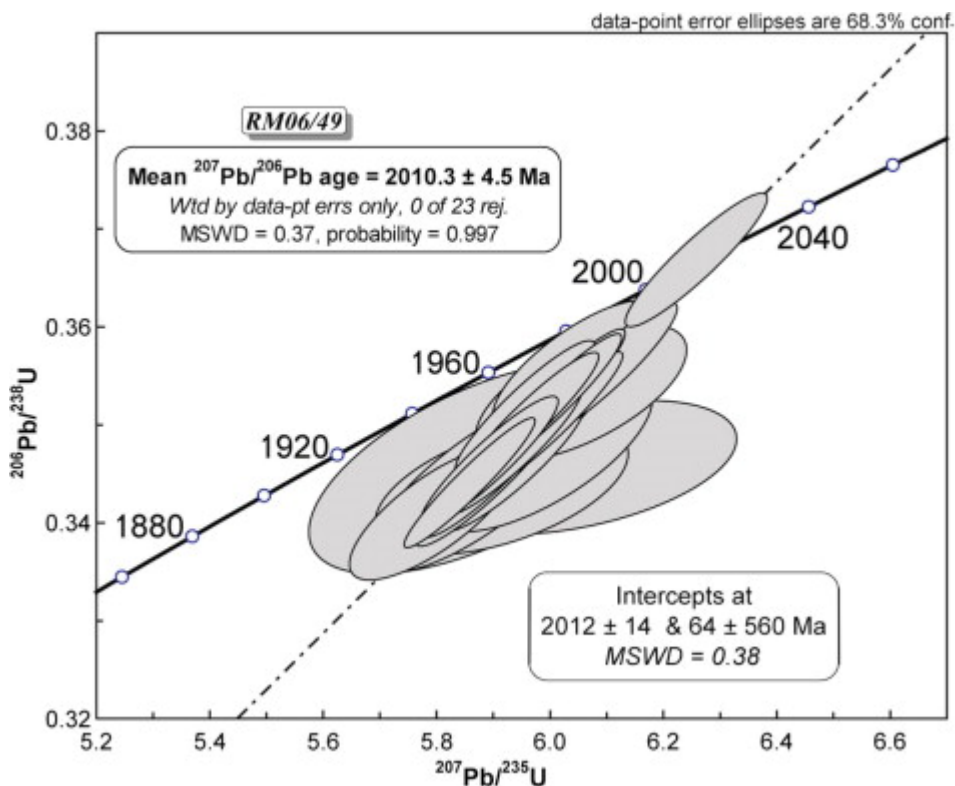


Fig. 3. U-Pb Concordia diagram for sample RM06/49.

The calculated mean  $^{207}Pb/^{206}Pb$  age of  $2010.3 \pm 4.5$  Ma suggests the titanite formed during the Paleoproterozoic event and is agreement with the data from the following studies: Chudy et al. (2008) who determined U-Pb dating of monazite yields an age of  $2015 \pm 8$ Ma; Pb stepwise leaching data obtained by Holzer et al. (1998) from garnet and titanite, which yield ages of  $2010 \pm 17$  Ma and  $2007 \pm 5$  Ma, respectively; Zircon ages from Gerdes & Zeh (2009) at  $2021 \pm 10$  Ma and Van Reenen et al. (2008) who dated

syntectonic anatectic material by U–Pb monazite ( $2017.1 \pm 2.8$  Ma) and PbSL garnet ( $2023 \pm 11$  Ma).

The experiments of Cherniak (1993) indicate that titanite with a diffusion domain radii of 0.005 to 0.5 cm should close to Pb diffusion between 650 and 780°C, respectively, for cooling rates typical of regional metamorphism. The studied titanite grains form crystals up to 0.5 cm in radius, compatible with a closure temperature of 780°C (Cherniak 1993); a temperature which is in agreement with the peak metamorphic conditions determined from pseudosections and conventional thermobarometry by Rigby et al. (2008a) and may suggest the titanite formed during metamorphism. Conversely, Rigby et al. (2008a) suggest that the titanites were part of the primary magmatic assemblage and that metamorphism of the syenite was not associated with neo-mineralization. Prior to the experiments of Cherniak (1993) titanite was deemed to have a very low closure temperature as it recrystallizes easily during deformation (e.g. Mezger et al. 1991). Therefore it can date deformation even under low grade conditions. In the present case the most likely interpretation is therefore that the titanite dates the tectonometamorphic episode at c. 2.0 Ga. Irrespective of arguments pertaining to closure temperatures, the data does constrain the age of the metamorphism irrespective of the whether the titanites are magmatic or metamorphic in origin. If the titanites are metamorphic in origin then the data defines a precise growth age. Alternatively, if the titanites are magmatic then the SHRIMP data, coupled with field observations and petrographic data that indicate the metasyenites are deformed, define a minimum-age constraint on the Paleoproterozoic event. Moreover, the P-T conditions determined by Rigby et al. (2008a) to be ‘intermediate’ between the amphibolite facies conditions reported by Zeh et al. (2005a) and the granulite facies conditions of Zeh et al. (2004) and Rigby (2009) are now bracketed in terms of their age, and collectively this data *may* suggest that the metamorphic field gradient hypothesis proposed by Rigby et al. (2008a) is a valid concept and that metamorphic conditions across the Central Zone of the Limpopo Belt at 2.0 Ga varied predictably. However, this hypothesis is dependent on the reliability of the P-T conditions determined by different workers using different methods (Perchuk et al., 2008 versus Zeh & Klemd, 2008 and Rigby, 2009). If the P-T estimates produced by the pseudosection approach (e.g. Zeh et al. 2004; 2005a; Rigby et al., 2008a and Rigby, 2009) are correct then the field gradient hypothesis remains a valid concept. However, if the local equilibrium estimates of Boshoff et al. (2006) and Perchuk et al. (2008) are correct then the hypothesis may be flawed. The debate over the P-T estimates is a contentious issue which has yet to be fully resolved. In regards to the ‘field gradient’ it is a working hypothesis and additional P-T-t work is required to further validate the concept.

### **Conclusion**

A mean  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $2010.3 \pm 4.5$  Ma from titanite brackets the age of metamorphism in the syenites to have occurred during the regional Paleoproterozoic event. The age, when used in conjunction with other published data *may* suggest that the Central Zone of the Limpopo Belt preserves evidence of a metamorphic field gradient at c. 2.0 Ga.

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Table 1. Summary of SHRIMP U–Pb zircon data for sample RM06/49.

Grai n. Spot	% <sup>206</sup> P b <sub>c</sub>	pp m U	pp m Th	<sup>232</sup> Th/ <sup>238</sup> U	ppm <sup>206</sup> Pb *	(1) <sup>206</sup> Pb/ <sup>238</sup> U Age	(1) <sup>207</sup> Pb/ <sup>206</sup> PbA ge	%Di s- cor- dant	(1) <sup>207</sup> Pb*/ <sup>206</sup> P b*	± %	(1) <sup>207</sup> Pb*/ <sup>235</sup> U	± %	(1) <sup>206</sup> Pb*/ <sup>238</sup> U	± %	Err. cor. r.		
2.2	0.35	342	113 5	3.43	102	191 5	±2 2	2020	±11	5	0.12438	0.6 3	5.932	1.5	0.3459	1.3	.900
2.3	0.42	344	797	2.39	109	201 5	±2 1	2011. 9	±9.1	0	0.12381	0.5 1	6.263	1.3	0.3669	1.2	.924
3.1	0.39	306	974	3.29	92.6	193 7	±2 2	2018	±8	4	0.12424	0.4 5	6.006	1.4	0.3506	1.3	.945
3.2	0.44	315	112 8	3.70	95.8	194 8	±2 2	2007. 3	±8.5	3	0.12349	0.4 8	6.009	1.4	0.3529	1.3	.939
4.1	0.51	252	494	2.03	75	190 9	±2 2	2012. 7	±9.7	5	0.12387	0.5 5	5.885	1.4	0.3446	1.3	.925
5.1	1.73	360	103 9	2.98	112	196 4	±2 1	2003	±19	2	0.1232	1.1	6.049	1.7	0.3561	1.3	.759
6.1	0.50	325	957	3.04	97.3	191 7	±2 1	2005. 4	±9.5	4	0.12336	0.5 4	5.891	1.4	0.3463	1.3	.921
7.1	0.41	310	909	3.03	94.3	194 7	±2 1	2008. 6	±8	3	0.12358	0.4 5	6.007	1.4	0.3525	1.3	.944
7.2	0.85	305	916	3.10	92.5	193 5	±2 2	2009	±12	4	0.12361	0.6 9	5.966	1.5	0.3501	1.3	.883
8.1	3.39	329	101 2	3.17	101	190 4	±2 2	2026	±38	6	0.1248	2.2	5.91	2.5	0.3436	1.3	.518

Grai n. Spot	% <sup>206</sup> P b <sub>c</sub>	pp m U	pp m Th	<sup>232</sup> Th/ <sup>238</sup> U	ppm <sup>206</sup> Pb *	(1) <sup>206</sup> Pb/ <sup>238</sup> U Age		(1) <sup>207</sup> Pb/ <sup>206</sup> PbA ge		%Di s- cor- dant	(1) <sup>207</sup> Pb*/ <sup>206</sup> P b*	± %	(1) <sup>207</sup> Pb*/ <sup>235</sup> U	± %	(1) <sup>206</sup> Pb*/ <sup>238</sup> U	± %	Err. cor. r.
8.2	0.90	314	101 8	3.35	95.2	193 4	±2 2	2014	±12	4	0.12399	0.6 7	5.982	1.5	0.3499	1.3	.887
9.1	4.84	354	886	2.58	111	191 4	±2 2	2057	±49	7	0.127	2.8	6.05	3.1	0.3457	1.3	.427
9.2	1.86	316	103 2	3.37	97.9	195 0	±2 2	2019	±28	3	0.1243	1.6	6.06	2.1	0.3533	1.3	.632
9.3	0.59	329	138 6	4.35	100	194 3	±2 1	1996. 4	±9.6	3	0.12274	0.5 4	5.954	1.4	0.3518	1.3	.922
10.1	0.50	292	929	3.29	87.6	192 2	±2 1	2012	±10	4	0.1238	0.5 6	5.931	1.4	0.3475	1.3	.916
11.1	0.49	303	659	2.25	91.6	193 8	±2 1	2005. 3	±8.4	3	0.12335	0.4 7	5.964	1.4	0.3507	1.3	.938
11.2	2.15	148	323	2.26	45	192 1	±2 5	2029	±28	5	0.125	1.6	5.98	2.2	0.3471	1.5	.695
12.1	0.56	267	451	1.74	79.7	191 3	±2 2	2012. 1	±9.4	5	0.12383	0.5 3	5.897	1.4	0.3454	1.3	.928
14.1	0.68	285	942	3.42	87.5	196 1	±2 2	2019. 9	±9.8	3	0.12437	0.5 5	6.098	1.4	0.3556	1.3	.920
14.2	0.99	99	151	1.57	29.6	190 6	±2 9	2012	±25	5	0.1238	1.4	5.87	2.2	0.344	1.7	.782
15.1	1.69	278	106 9	3.98	82.8	189 1	±2 2	2003	±20	6	0.1232	1.1	5.791	1.7	0.341	1.3	.761

Grai n. Spot	% <sup>206</sup> Pb <sub>c</sub>	ppm U	ppm Th	<sup>232</sup> Th/ <sup>238</sup> U	ppm <sup>206</sup> Pb *	(1) <sup>206</sup> Pb/ <sup>238</sup> U Age		(1) <sup>207</sup> Pb/ <sup>206</sup> PbA ge		%Di s- cor- dant	(1) <sup>207</sup> Pb* / <sup>206</sup> Pb b*	± %	(1) <sup>207</sup> Pb* / <sup>235</sup> U	± %	(1) <sup>206</sup> Pb* / <sup>238</sup> U	± %	Err. cor r.
						191 4	±3 4	2003	±48								
20.1	3.64	60	110	1.89	18.5	191 4	±3 4	2003	±48	4	0.1232	2.7	5.87	3.4	0.3456	2.1	.606
21.1	0.33	324	112 0	3.57	96.1	190 6	±2 1	2006. 1	±7.1	5	0.12341	0.4	5.855	1.3	0.3441	1.3	.954

Errors are 1-sigma; Pb<sub>c</sub> and Pb\* indicate the common and radiogenic portions, respectively. Error in Standard calibration was 0.30% (not included in above errors but required when comparing data from different mounts). (1) Common Pb corrected using measured <sup>204</sup>Pb.