An Archean Impact Layer from the Pilbara and Kaapvaal Cratons

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The Barberton greenstone belt of South Africa and the eastern Pilbara block of Western Australia provide information about Earth's surface environments between 3.2 and 3.5 billion years ago, including evidence for four large bolide impacts that likely created large craters, deformed the target rocks, and altered the environment. We have obtained identical single-zircon uranium-lead ages of 3470 ± 2 million years ago for the oldest impact events from each craton. These deposits represent a single global fallout layer that is associated with sedimentation by an impact-generated tsunami and in Western Australia is represented by a major erosional unconformity.

Over the past 20 years, a growing body of evidence has emerged to support the importance of impact events in the physical and biological evolution of Earth (*1–3*). Isotopic dating of shocked minerals and glasses from the Moon indicates that the flux of large impactors to the Earth-Moon system includes intense episodes at about 3.8 billion years ago (Ga) (*4*) and 3.2 Ga (*5*). No record of the 3.8 Ga episode has been identified on Earth, but at least four major impact-related layers from 3.5 to 3.2 Ga are recognized in the Barberton greenstone belt (BGB), South Africa (*6–8*). The BGB and correlative rocks in the eastern Pilbara block (EPB), Western Australia, represent the oldest known well-preserved volcanic-sedimentary rock sequences on Earth and have been central in studies of early life on Earth and the origin and evolution of the crust, oceans, and atmosphere (*9–12*). These rocks were deposited on shallow marine platforms, but these terrains probably did not represent mature continental cratons. Mid-Archean sedimentary rock layers produced by large impacts were initially recognized in South Africa and Western Australia because they contain distinctive altered quench-textured spherules (figs. S1 and S2) interpreted to have formed by the quenching and solidification of liquid silicate droplets (*6*). Their regional distribution and the heterogeneous compositions of the spherules within individual beds suggest an impact origin rather than volcanic origin by lava fountaining. The apparent lack of ballistic materials within the beds indicates that the spherules probably formed by condensation of impact-generated, supra-atmospheric, rock vapor clouds (*7*, *13*). The geology, sedimentology, petrography, and geochemistry of these four spherule layers, numbered S1 through S4 from the base to the top, have now been studied in detail (*14*). Most sedimentary rocks from these Archean sequences have been affected by post-depositional diagenesis and metasomatism. The impact spherule layers are always altered to a secondary mineral assemblage of quartz-sericite-chlorite. Major element compositions have been modified by an apparent gain in silica and loss of iron, magnesium, and calcium. Compositions of highly charged cations Ti, Al, and Cr, along with Ir, seem to have been preserved in many samples. Enrichment of Ir, and of Cr isotope anomalies, which indicate the presence of extraterrestrial Ir and Cr, have been measured in these beds (*7, 15*). The S1 impact layer in South Africa contains up to 3 parts per billion Ir, which is a factor of 10 greater than that in background black cherts, and a Ir/Cr ratio of 6×10^{-6}, which is a factor of 6 greater than that in South African komatiites (*14*). No chemical analyses are available from the Australian layer. Unusually high-temperature, but nonmagmatic, Ni-rich spinels occur in S3 (*16*). No shocked minerals have been reported from these layers, perhaps because of the late metasomatic alteration common in greenstone belts and/or impacts on oceanic rather than continental crust. Six other late Archean to Paleoproterozoic beds have been recognized with similar characteristics (*17*).

We extracted zircons from samples of the oldest impact layers in both South Africa and Western Australia (Fig. 1). In the BGB, S1 is part of a 2.5-m-thick unit of silicified sediments, H4c (*18*), interbedded with mafic to ultramafic volcanic flow rocks in the Hooggenoeg Formation of the Onverwacht Group. Here, the 30-cm-thick impact layer represents a high-energy depositional event produced by multiple tsunami waves scouring into low-energy black chert, 3 m thick, during fallout of impact spherules (*14*). In Western Australia, samples were collected from the 110-cm-thick spherule bed described by (*6*), which occurs in a 10-m-thick chert near the middle of the Apex Basalt Formation of the Warrawoona Group, about 2 km east of Miralga Creek on the east side of North Pole Dome (21°06.7′S, 119°29.2′E, North Shaw 1:100,000 Sheet). A single 2-kg sample yielded 30 zircons. The zircons were small (50 to 100 μm), euhedral, and had pale to purple-pink absorption, normal birefringence, fine zoning, and no inclusions. Several grains had distinct rounded cores, but no grains displayed either the granular textures or the planar deformation features found in

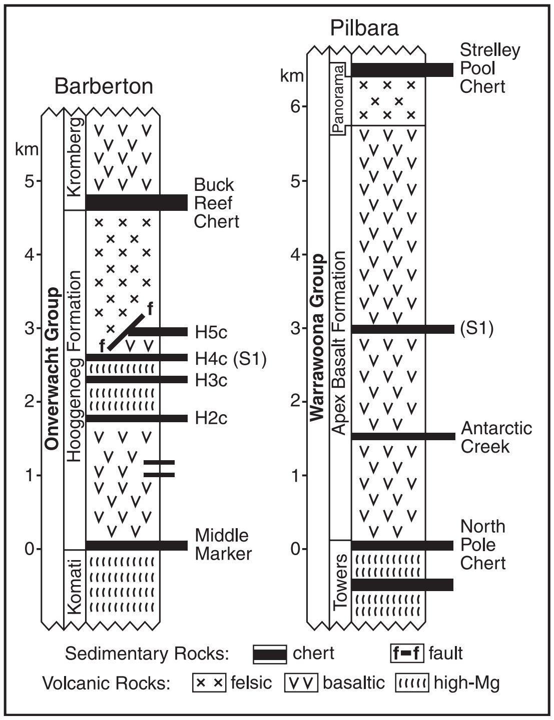

Fig. 1. Generalized stratigraphic diagrams compare portions of the (**left**) Onverwacht Group from the west side of the Onverwacht Anticline and the (**right**) Warrawoona Group from the east side of the North Pole Dome. The S1 impact layer is found within the H4c member of the Hooggenoeg Formation, Onverwacht Group (*18*), and within an unnamed chert within the Apex Basalt Formation, Warrawoona Group (*6*).

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Table 1. Compositions and ages of zircons determined by SHRIMP RG analysis. Percent concordancy (% cc) is used to select zircons for the weighted mean $^{207}Pb/^{206}Pb$ age. In the last column, grains are labeled as "a," accepted; "d," discordant; or "x," xenocryst. ppm, parts per million.

Zircon grain	U (ppm)	Th (ppm)	206/238	±	207/235	±	207/206	±	% cc	Grains
Pilbara greenstone belt										
B1	357	603	1903	13	2786	10	3507	9	54	d,x
B2	153	50	3405	35	3451	15	3477	8	98	a
B3	205	78	3030	35	3297	16	3464	8	88	a
B4	177	71	3322	27	3407	11	3457	7	96	a
B5	228	213	2451	18	3078	13	3517	14	70	d,x
B6	161	97	2762	32	3194	16	3478	10	79	a
B7	345	386	2138	20	2906	13	3492	10	61	d
B8	182	105	3085	23	3336	12	3491	9	88	a
B9	462	354	2153	8	2857	6	3400	6	63	d
B10	233	135	2853	21	3220	10	3457	6	83	a
B11	122	78	3447	32	3471	12	3484	5	99	a
B12	341	156	2604	21	3130	11	3488	6	75	d
G1	124	113	3520	43	3494	17	3480	6	101	a
G5	315	170	3174	29	3341	12	3442	6	92	a
G7	144	83	3027	33	3298	16	3468	10	87	a
G8	249	220	3241	31	3382	13	3466	6	94	a
G10	121	81	2879	33	3248	16	3485	12	83	a
G11	100	51	2822	32	3214	16	3468	12	81	a
G12	207	111	3374	89	3436	38	3472	23	97	a
G13	113	96	3304	44	3414	18	3480	8	95	a
Weighted mean: 3470.1 ± 1.9 Ma										
Barberton greenstone belt										
2	496	360	1783	99	2712	74	3501	20	51	d,x
3	246	190	3343	41	3420	16	3465	6	97	a
14	217	124	3083	52	3319	22	3464	6	89	a
15	288	257	2406	22	2982	12	3397	7	71	d
17	233	169	3307	23	3412	10	3474	6	95	a
18	149	125	3133	15	3341	9	3468	9	90	a
21	101	54	3220	37	3378	19	3473	17	93	a
23	263	208	2127	34	2872	22	3446	17	62	d
22	123	72	3319	17	3418	9	3476	8	96	a
26	118	81	2375	48	2989	26	3432	14	69	d
26a	129	116	3280	53	3410	22	3487	10	94	a
30	327	352	1948	37	2783	23	3460	9	56	d
33	177	137	3179	34	3356	15	3464	8	92	a
35	242	217	2905	39	3249	19	3470	11	84	a
36	113	95	3359	19	3429	10	3470	9	97	a
37	441	288	1739	24	2694	16	3516	7	50	d,x
38	71	55	3247	51	3386	22	3470	13	94	a
39	104	66	3238	33	3395	15	3490	10	93	a
40	128	92	3287	96	3397	38	3463	9	95	a
Weighted mean: 3470.4 ± 2.3 Ma										

shocked zircons (*19–21*). The South African samples were collected 2 km south of the Buck Reef Ridge on the west side of the Onverwacht Anticline (25°56.2′S, 30°53.7′E, Nelshoogte 1:50,000 Sheet). Three 5-kg samples were collected from the base, middle, and top of this coarse detrital layer. Zircons were found in the basal and upper samples but were rare in the middle of the bed. About 50 zircons were picked and mounted for study. Most of the zircons were euhedral, small (50 to 100 μm), and finely zoned; displayed pale pink absorption and normal birefringence; and contained few inclusions. No cores or shocked features were recognized. Thus, zircons from both the South African and Australian layers are best interpreted as locally derived detritus produced by the impact tsunami waves and not as materials from the impact target. We performed the U-Th-Pb zircon analyses on the Stanford-USGS Sensitive High-Resolution Ion Micro-Probe Reverse Geometry (SHRIMP RG) instrument (Table 1). A weighted mean $^{207}Pb/^{206}Pb$ age was calculated for each sample after excluding grains that yielded U/Pb ages that were <80% concordant. The Warrawoona impact layer yielded a $^{207}Pb/^{206}Pb$ age of 3470.1 ± 1.9 million years ago (Ma) (15 grains averaged, 3 excluded, 2 xenocrysts), and the Onverwacht impact layer yielded a $^{207}Pb/^{206}Pb$ age of 3470.4 ± 2.3 Ma (13 grains averaged, 4 excluded, 2 xenocrysts). Four zircons with markedly older ages of about 3510 Ma are interpreted to represent a population of older xenocrysts. A concordia plot for the samples from the two layers (Fig. 2) shows that all the zircons fall on a modern Pb-loss trend. These results suggest that both beds represent a single fall-deposited impact layer, S1.

The 3470 Ma age determined for S1 is stratigraphically consistent with known ages of overlying and underlying rocks in both the BGB and EPB. The Komati Formation, about 2.6 km lower in the BGB sequence, is dated at 3481 ± 2 Ma (*22*), and felsic volcanic rocks 0.4 to 0.5 km above S1 are 3445 million years old (*23*). In the North Pole Dome area of the EPB, the measured age of S1 is stratigraphically consistent with an age of 3457 ± 3 Ma for felsic volcanic rocks overlying the Apex Basalt 2 to 3 km higher in the sequence. The section underlying S1 has not been dated in the North Pole Dome and correlations are disputed (*24*), but elsewhere in the Pilbara, the rocks correlated with those beneath S1 are at least 3471 million years old (*25, 26*).

We suggest that the 3470 Ma age of zircons in S1 represents coeval or only slightly older felsic igneous activity and thus is an approximate depositional age for these cherts and S1. In both areas, spherules in S1 are mixed with non–impact-produced detrital material, and the beds show structures indicating major wave and/or current activity associated with spherule deposition (*14*). We suggest that the zircons were derived through erosion of exposed or shallow marine rocks by impact-generated tsunamis. It is not known whether the 3510 Ma zircons were xenocrysts within the 3470 Ma volcanic units or whether they represent a separate suite of exposed and eroded rocks. Thus, the two layers have the same basic zircon populations, one reflecting volcanism at 3470 Ma, nearly coeval with the impact, and the other a minor population possibly reflecting the presence of rock ages of about 3510 Ma in the BGB and EPB.

A major unconformity has been found in the EPB Archean sequence west of the North Pole Dome (*27*). An intrusive microgranite cut by the unconformity is 3467.6 ± 3.7 million years old, which may date the unconformity. Volcanic rocks below this unconformity are dated at 3515.2 ± 2.7 Ma. This unconformity may be the result of the S1 impact and tsunami in the EPB. In the BGB, similar lithologies lie beneath S1. A plagioclase porphyry intruding the Komati Formation and the nearby trondhjemitic Steynsdorp Pluton, which intrudes lower portions of the BGB sequence, have been dated at 3470 +39/–9 Ma and 3509 +9/–7 Ma, respectively (*28*). No unconformity has been identified associated with S1 in the BGB.

Correlation of Earth's oldest documented impact layer between the EPB of Western Australia and the BGB of South Africa is consistent with our previous work indicating that these early Archean impacts were very large: 10 to 100 times more massive than the Cretaceous-Tertiary event, producing unusual impact-generated tsumanis (*3, 7, 14, 16*). This report confirms the global nature of these massive fallout layers, suggests that an early terrestrial record of large asteroidal impacts does exist, and may provide important constraints on the evolution of Earth's geological and biological systems.

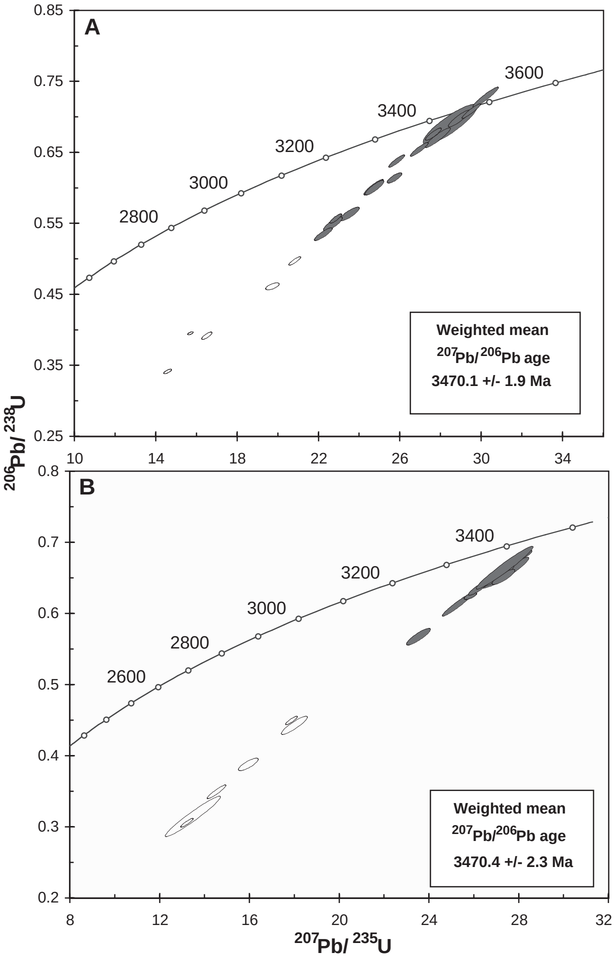

Fig. 2. Concordia diagrams for zircons from the S1 impact layers found in (**A**) the Warrawoona Group of Western Australia and (**B**) the Onverwacht Group of South Africa. Ellipses are 2σ errors, and samples that are greater than 80% concordant (Table 1) are shown shaded. The principal variation in both data sets is the result of modern Pb loss.

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Supporting Online Material
www.sciencemag.org/cgi/content/full/297/5585/1325/DC1
Figs. S1 and S2

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C–O Bond Formation by Polyketide Synthases

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Polyketide synthases (PKSs) assemble the polyketide carbon backbone by sequential decarboxylative condensation of acyl coenzyme A (CoA) precursors, and the C–C bond-forming step in this process is catalyzed by the β-ketoacyl synthase (KS) domain or subunit. Genetic and biochemical characterization of the nonactin biosynthesis gene cluster from *Streptomyces griseus* revealed two KSs, NonJ and NonK, that are highly homologous to known KSs but catalyze sequential condensation of the acyl CoA substrates by forming C–O rather than C–C bonds. This chemistry can be used in PKS engineering to increase the scope and diversity of polyketide biosynthesis.

Polyketides are natural products found in bacteria, fungi, and plants that include many clinically important drugs such as erythromycin (antibacterial), daunorubicin and epothilone (anticancer), rapamycin (immunosuppressant), and lovastatin (antihypercholesterolemic). These metabolites are biosynthesized from acyl CoA precursors by PKSs. PKSs have been the focus of intensive research in the past decade for their extraordinary structure, mechanism, and catalytic reactivity and flexibility (*1–4*). Genetic manipulation of PKSs has been increasingly recognized as an alternative strategy for the production of novel compounds that are difficult to access by traditional chemical synthesis (*5–10*). Success of the genetic approach depends on the continuous discovery and characterization of PKSs that catalyze different chemistry (*11–16*).

Three types of PKSs are known. Type I PKSs are multifunctional enzymes that are organized into modules, each of which minimally contains three domains, β-ketoacyl

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