# Early Archean spherule beds: Chromium isotopes confirm origin through multiple impacts of projectiles of carbonaceous chondrite type

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## ABSTRACT

**Three Early Archean spherule beds from Barberton, South Africa, have anomalous Cr isotope compositions in addition to large Ir anomalies, confirming the presence of meteoritic material with a composition similar to that in carbonaceous chondrites. The extraterrestrial components in beds S2, S3, and S4 are estimated to be ~1%, 50%–60%, and 15%–30%, respectively. These beds are probably the distal, and possibly global, ejecta from major large-body impacts. These impacts were probably much larger than the Cretaceous-Tertiary event, and all occurred over an interval of ~20 m.y., implying an impactor flux at 3.2 Ga that was more than an order of magnitude greater than the present flux.**

**Keywords:** Archean, impacts, spherules, iridium, $^{53}Cr/^{52}Cr$.

## INTRODUCTION

The oldest record of major impact events on Earth may be a number of Early Archean (3.5–3.2 Ga) spherule beds in the Barberton greenstone belt, South Africa. Lowe and Byerly (1986) first proposed that single spherule beds found in the Barberton greenstone belt, and in the Eastern Pilbara block, Western Australia, were derived from quenched silicate droplets formed by major impact events. Other workers (de Wit, 1986; French, 1987; Buick, 1987) argued that an impact origin was unlikely and proposed that the spherules could be from erosion of volcanic materials. Further work by Lowe et al. (1989) found that at least four spherule beds (labeled S1–S4) occur in the Barberton greenstone belt and that some specimens are enriched in Ir and other platinum group elements (PGEs). They cited seven specific criteria that distinguish these beds from normal clastic sediments, including the wide geographic distribution of two beds across a variety of depositional environments, presence of relict quench textures and Ni-rich spinels within the spherules, absence of juvenile volcaniclastic debris, and extreme enrichment of Ir and other PGEs. Kyte et al. (1992) reported detailed analyses of four PGEs (Ir, Os, Pt, Pd) and Au in bed S4 and found Os/Ir and Pt/Ir ratios within 20% of chondritic abundances. Although Pd and Au in S4 were depleted relative to chondrites by 59% and 98%, respectively, this is opposite to the effect expected by Au mineralization and was attributed to regional hydrothermal alteration of originally chondritic material. Byerly and Lowe (1994) showed that chemical compositions of Ni-rich spinels in spherules are unique and distinct from those in komatiites and other volcanic rocks. These spinels are now recognized to occur only in spherules from bed S3 (Lowe et al., 2003). Some researchers, however, still argued for a terrestrial origin, possibly related to volcanism and gold mineralization (Koeberl and Reimold, 1995; Reimold et al., 2000). They analyzed samples from the vicinity of gold mines in the northern Barberton greenstone belt and found extreme enrichments of Ir, a result they found difficult to reconcile with an impact origin.

Work on the $^{53}Mn$-$^{53}Cr$ isotope systematics in various solar system objects (Lugmair and Shukolyukov, 1998) has provided a method for unequivocally demonstrating an extraterrestrial component in impact ejecta with high concentrations of meteoritic Cr. All meteorite classes studied so far have excess $^{53}Cr$ relative to terrestrial samples. This fact reflects an early Mn/Cr fractionation and possibly heterogeneous distribution of the now-extinct parent radionuclide $^{53}Mn$ (half-life, $t_{1/2}$ = 3.7 m.y.) in the early solar system. The carbonaceous chondrites also have an excess of $^{54}Cr$, due to a presolar component, in addition to excess $^{53}Cr$ (Shukolyukov and Lugmair, 2000, 2001). Thus, precise measurements of Cr isotope abundances can distinguish terrestrial from extraterrestrial materials and the carbonaceous chondrites from other meteorite groups. This method provided the first isotopic proof that the Cretaceous-Tertiary (K-T) boundary contains meteoritic materials (Shukolyukov and Lugmair, 1998). We have applied this method to several spherule bed samples. In our initial study (Shukolyukov et al., 2000) we found anomalous Cr isotope abundances in bed S4. We now report that three spherule beds—S2, S3, and S4—are all enriched in extraterrestrial Cr.

## SAMPLES AND PROCEDURES

Detailed descriptions of the spherule bed deposits, including precise sample locations, are provided by Lowe et al. (2003). All three beds studied are from the Fig Tree Group of the Barberton greenstone belt, which consists of terrigenous sedimentary units, felsic volcaniclastic rocks, and cherty strata. The underlying Onverwacht Group consists largely of ultramafic and mafic volcanic rocks with thin interflow cherty sedimentary layers. In the southern Barberton greenstone belt, both S4 and S3 occur in the middle of the Fig Tree and S2 occurs at its base, marking the Onverwacht–Fig Tree contact. Zircon dating has shown that this contact is diachronous (Byerly et al., 1996), and in northern areas of the Barberton greenstone belt, bed S3 is found at the base of the Fig Tree.

S4 is known in only one locality, named Jay's Chert, at 25°54.9′S, 31°01.13′E, on the west limb of the Onverwacht anticline where it is only 6.5 m above S3 (see stratigraphic section in Fig. 12 of Lowe et al., 2003). Kyte et al. (1992) analyzed the uppermost 7.5 cm of this bed at 0.5 cm intervals and found Ir concentrations ranging from 7 to 450 ng/g. They also analyzed six lithic sandstones from 0.2 m above to 9.5 m below S4 with Ir concentrations from 0.13 to 0.31 ng/g. Shukolyukov et al. (2000) reported Cr isotope data on two of the spherule bed samples analyzed by

TABLE 1. Cr ISOTOPE COMPOSITION WITH Cr AND Ir CONCENTRATIONS FOR BARBERTON SPHERULE BEDS, BACKGROUND ROCKS, AND CARBONACEOUS CHONDRITES

| Samples | Normalized $\epsilon_{53}$ | Raw $\epsilon_{53}$ | Raw $\epsilon_{54}$ | Cr (mg/g) | Ir (ng/g) |
|---|---|---|---|---|---|
| **Bed S2** | | | | | |
| SAF-275-4C | −0.09 ± 0.03 | nd | nd | 0.16 | 6 |
| **Bed S3 (Sheba Mine)** | | | | | |
| SAF-381-10B | −0.37 ± 0.07 | nd | nd | 0.98 | 104 |
| SAF-381-10G | −0.41 ± 0.08 | +0.08 ± 0.18 | +0.89 ± 0.23 | 3.67 | 725 |
| **Background (Sheba Mine)** | | | | | |
| SAF-381-5 (chert) | +0.01 ± 0.08 | nd | nd | 0.09 | <0.6 |
| **Bed S3 (Jay's Chert)** | | | | | |
| SAF-380-5B | −0.41 ± 0.10 | nd | nd | 2.45 | 519 |
| **Bed S4 (Jay's Chert)*** | | | | | |
| SAF-349-3, C | −0.26 ± 0.11 | | | 1.36 | 154 |
| SAF-349-3, D4 | −0.32 ± 0.06 | | | 1.63 | 240 |
| C + D4 | | −0.1 ± 0.2 | +0.4 ± 0.3 | | |
| **Background (Jay's Chert)*** | | | | | |
| SAF-380-18 | −0.03 ± 0.09 | nd | nd | 0.50 | 0.31 |
| SAF-380-21 | −0.01 ± 0.09 | nd | nd | 0.33 | 0.13 |
| **Komatiite, Barberton, South Africa** | | | | | |
| BARB-1 | +0.02 ± 0.09 | nd | nd | 2.35 | 1.8 |
| **Carbonaceous chondrites**† | | | | | |
| Orgueil (CI) | −0.43 ± 0.09 | +0.39 ± 0.10 | +1.51 ± 0.20 | 2.65 | 456 |
| Murray (CM) | −0.31 ± 0.07 | +0.27 ± 0.09 | +1.13 ± 0.21 | 3.23 | 604 |
| Kainsaz (CO) | −0.30 ± 0.09 | +0.20 ± 0.13 | +1.02 ± 0.24 | 3.53 | 760 |
| Allende (CV) | −0.35 ± 0.08 | +0.10 ± 0.09 | +0.85 ± 0.17 | 3.63 | 785 |

*Note*: nd—not determined.
*From Kyte et al. (1992) and Shukolyukov et al. (2000).
†Carbonaceous chondrite isotopic data (except for Kainsaz) from Shukolyukov and Lugmair (2001), and Cr and Ir concentrations from Kallemeyn and Wasson (1981). Allende $\epsilon_{53}$ updated since Shukolyukov and Lugmair (1998).

Kyte et al. (1992) as well as two of the background samples. These are discussed here for completeness.

We analyzed samples of S3 from two localities. SAF-380-5 is a 2.5-cm-thick piece from 10 to 15 cm above the lowest exposed part of S3 at Jay's Chert. S3 is 78 cm thick here, but the base is not exposed. Spherules and textures are better preserved here than at any other site. Iridium was measured in three slices from the rock, and one specimen was analyzed for Cr isotopes. SAF-381-10 is the lower ~7 cm of S3 from the Sheba Mine locality in the northern Barberton greenstone belt (25°42.86′S, 31°08.09′E), where this bed is ~17 cm thick. At this locality, S3 was thinned by shearing and was the site of significant sulfide mineralization. This ~7 cm thickness of the bed was partially replaced by carbonate minerals and has high concentrations of pyrite throughout, particularly at the top where there is a nearly pure layer of pyrite. The upper 10 cm of the bed was silicified. Sample SAF-381-10 was cut into 1-cm-thick slices that were analyzed for Ir, along with six background samples that included chert, shale, and sandstone from the overlying Fig Tree Group and silicified ultramafic rock from the top of the underlying Onverwacht Group. Cr isotope measurements were on the S3 samples with the lowest (S3 B) and highest (S3 G) measured Ir contents and on a chert (SAF-381-5) from 3 m above S3 at this locality.

Ir and Cr isotopes were investigated in only one locality of bed S2 during this study, at 25°54.47′S, 31°00.93′E. SAF-275-4 is a 3.5-cm-thick specimen from the upper ~20 cm of a 120-cm-thick bed of S2. This sample was cut into four slices for Ir determination, and a piece with the highest Ir content was analyzed for Cr isotopes. We also analyzed a sample of komatiite (Barb-1) for Ir and Cr isotopes.

Ir and Cr concentrations were measured by instrumental neutron activation analysis using procedures similar to those of Kyte et al. (1992). Detection limits are ~1 ng/g for Ir in the types of rocks in this study. The Ir in background samples at the Jay's Chert locality was radiochemically purified to achieve lower detection limits (Kyte et al., 1992). Cr isotope measurements were by thermal-ionization mass spectrometry (Lugmair and Shukolyukov, 1998). Isotopic ratios are presented as deviations from terrestrial values in epsilon ($\varepsilon$) units, where $1\varepsilon$ is 1 part in $10^4$, and terrestrial ratios of $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ are defined as $\varepsilon \equiv 0$. Measurement of high-precision $^{53}Cr/^{52}Cr$ ratios requires a second-order mass-fractionation correction based on the $^{54}Cr/^{52}Cr$ ratio. This procedure assumes no excess of $^{54}Cr$, which is the case for most of the meteorite classes studied (at least within an uncertainty of ~$0.1\varepsilon$ to $0.3\varepsilon$), including ordinary and enstatite chondrites, angrites, HEDs, aubrites, main-group pallasites, mesosiderite clasts, primitive achondrites, brachinites, and martian meteorites (Lugmair and Shukolyukov, 1998). Because the carbonaceous chondrites (and the Bencubbin and CH-like meteorites Hammadah Al Hambra 237 and QUE 94411) also have a $^{54}Cr$ anomaly (Shukolyukov and Lugmair, 2000, 2001), the fractionation correction shifts the observed $^{53}Cr/^{52}Cr$ ratio in the negative direction. In this paper we report analyses with fractionation corrections as "normalized" $^{53}Cr/^{52}Cr$ ratios ($\varepsilon_{53}$). For completeness, we also report raw, uncorrected $\varepsilon_{53}$ and $\varepsilon_{54}$ values, which are less precise, but provide significant insights into the results.

## RESULTS

Both localities of bed S3 had exceptionally high Ir and Cr concentrations. In the Sheba Mine samples, Ir and Cr ranged from 104 to 725 ng/g and from 0.98 to 3.66 mg/g, respectively. The background sediments had Ir concentrations below detection limits, from <0.6 to <1.6 ng/g, and Cr concentrations from 0.09 to 0.91 mg/g. Two silicified ultramafic samples from this area had Ir concentrations of <1.6 and 2.6 ng/g and Cr concentrations of 3.85 and 0.94 mg/g. In the three S3 samples from Jay's Chert, Ir and Cr ranged from 426 to 519 ng/g and from 2.06 to 2.45 mg/g, respectively. The samples from bed S2 were less enriched in Ir and Cr; the concentrations ranged from 2 to 6 ng/g and from 0.12 to 0.60 mg/g, respectively.

Results of the Cr isotope analyses in $\varepsilon$ notation, along with Ir and Cr concentrations for each sample analyzed isotopically, are given in Table 1. As was observed previously in S4 (Shukolyukov et al., 2000), samples of beds S2 and S3 have Cr isotope compositions distinctly different from the terrestrial value with negative normalized $\varepsilon_{53}$ (Fig. 1). All background samples, including the Barberton komatiite, have $\varepsilon_{53}$ indistinguishable from terrestrial values. The normalized $\varepsilon_{53}$ for S2, $(-0.09 \pm 0.03)\varepsilon$, is a relatively small but significant deviation from the terrestrial value and took an extremely long analysis to achieve. However, the $\varepsilon_{53}$ values in S3 and S4, as large as $(-0.41 \pm 0.08)\varepsilon$ and $(-0.32 \pm 0.06)\varepsilon$, respectively, approach the magnitude of isotopic anomalies observed in carbonaceous chondrites. The less precise, raw $\varepsilon_{53}$ and $\varepsilon_{54}$ values for one sample from S3 and for a combined sample from S4 show that both S3 and S4 have distinctly elevated $\varepsilon_{54}$ values.

## DISCUSSION AND CONCLUSIONS

These data confirm the highly anomalous character of Early Archean spherule beds and leave no doubt that they contain an extraterrestrial component (ETC). This is best illustrated in the samples studied from the Jay's Chert locality, where we examined two spherule beds and six interbedded lithic sandstones. Although Jay's Chert has been subjected to significant hydrothermal alteration, as is typical of many of the rocks in the Barberton

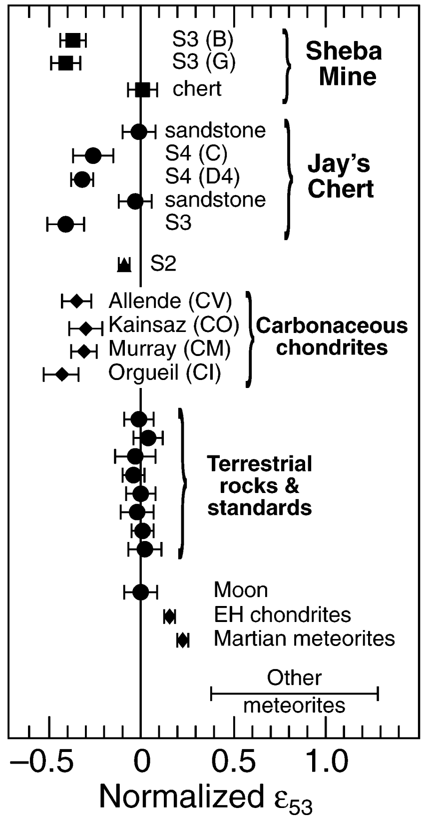


**Figure 1. Plot of normalized (see text) $\varepsilon_{53}$ values of spherule beds and background samples discussed in this study compared to terrestrial rocks and meteorites (for abbreviations, see Table 1). Only carbonaceous chondrites and spherule beds have negative normalized $\varepsilon_{53}$ values.**

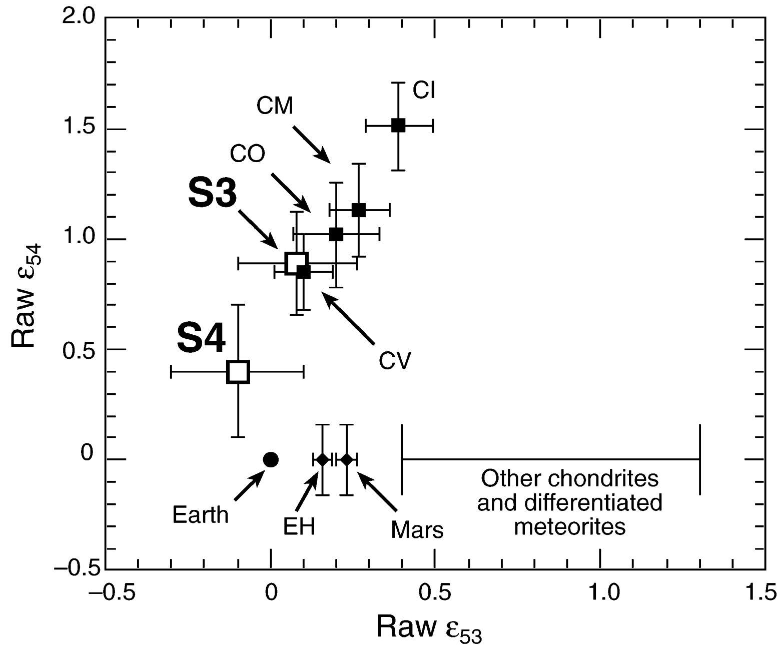


**Figure 2. Plot of raw $\varepsilon_{54}$ vs. $\varepsilon_{53}$ values. Although these data are less precise than normalized $\varepsilon_{53}$ values, they clearly distinguish beds S3 and S4 as similar to carbonaceous chondrites. CV, CO, CM, and CI groups of carbonaceous chondrites are represented by Allende, Kainsaz, Murray, and Orgueil meteorites, respectively. (See Table 1 for abbreviations.)**

greenstone belt (Lowe and Byerly, 1986; Hanor and Duchac, 1990), there is no evidence of Au mineralization or other unusual geochemical activity in this area. These rocks are silicified shale, sandstone, and conglomerate in a 30-m-thick fan-delta deposit. The background samples are silicified but otherwise normal medium- to coarse-grained lithic sandstones with relatively uniform compositions (Kyte et al., 1992), and two of these were found to have normal isotopic ratios. The unusual characters of beds S3 and S4 are only noticed on close examination that reveals high spherule contents and anomalous chemical and isotopic compositions.

A plot of the raw $\varepsilon_{53}$ and $\varepsilon_{54}$ data (Fig. 2) shows a trend of increasing $\varepsilon_{53}$ and $\varepsilon_{54}$ for the carbonaceous chondrites Allende, Kainsaz, Murray, and Orgueil, members of the CV, CO, CM, and CI groups, respectively (see Table 1). The cause of this trend is not yet understood, and more precise measurements will be necessary to properly delineate it. However, it is interesting that within error, S3 plots on the value for Allende. The fact that S4 plots outside the range of measured carbonaceous chondrites, but in a direct line with the observed trend, may reflect contamination by terrestrial Cr, but it is possible that the Cr in S4 is from a type of meteorite not yet analyzed for Cr isotopes (e.g., CK or CR). On balance, the data are consistent with an interpretation that the anomalous Cr in each of these spherule beds is derived from carbonaceous chondrites. For beds S3 and S4, the data are closest to type CV chondrites. We lack the data to make similar conclusions for S2. These results suggest an impactor flux different from the modern population of near-Earth asteroids, which contain only a small proportion of carbonaceous chondrites (Binzel et al., 2001).

TABLE 2. CALCULATED EXTRATERRESTRIAL (ET) Cr CONTENT, AND EXTRATERRESTRIAL COMPONENTS (ETC) BASED ON Cr AND Ir IN SPHERULE BED SAMPLES

| Sample | ET Cr* | ETC (Cr) | ETC (Ir) |
|---|---|---|---|
| **Bed S2** | | | |
| 275-4C | 26 | 1.1 | 0.8 |
| **Bed S3** | | | |
| 381-10B | 100 | 27 | 13 |
| 381-10G | 100 | 100 | 92 |
| 380-5B | 100 | 68 | 66 |
| **Bed S4** | | | |
| C | 74 | 28 | 20 |
| D4 | 91 | 41 | 31 |
| **Estimated bed averages**† | | | |
| S2 | 26 | 1.9 | 0.4 |
| S3 Sheba Mine | 100 | 61 | 46 |
| S3 Jay's Chert | 100 | 61 | 60 |
| S4 Jay's Chert | 80 | 30 | 15 |

*Note*: All values in percent and not allowed to exceed 100%.
*Calculated from isotopic composition of Cr.
†Calculated from average Cr and Ir concentrations of all samples.

We can estimate the ETC in these spherule beds by assuming (1) that the meteoritic source had a chemical and isotopic composition similar to the Allende meteorite and (2) that all Ir is meteoritic and by using the Cr isotope composition to estimate the fraction of extraterrestrial Cr in each sample (Table 2). In general, the estimates based on Ir tend to be lower than those based on Cr. For the sample from bed S2, both estimates are ~1% ETC. Bed S4 has an intermediate ETC, estimated as 15%–30%. For bed S3, ETCs range from 13% to 100%; bed averages are as high as 60%. Some spherule bed localities that have been correlated with S3 have yielded Ir concentrations much lower than this, ~1–12 ng/g (Lowe et al., 2003). These low values may reflect dilution of the impact-produced debris by locally derived sediments, as is the case for S2 in the present study; hydraulic fractionation of low- and high-Ir components within the environment of deposition; or locally severe metasomatism, especially in areas of the northern Barberton greenstone belt. Alternatively, it is possible that additional, low-Ir spherule beds within this stratigraphic interval have not yet been recognized (Lowe et al., 2003). The ETC estimates for S3 from the Sheba Mine locality and S4 are probably representative, because we sampled ~40% of the bed at each site. For S2, and S3 from Jay's Chert, these estimates are less certain because we sampled only ~3% of these beds.

We recognize that the remarkably high concentrations of PGEs in some of these and other samples lead one to extrapolate ETCs of 100% or even much greater (e.g., Reimold et al., 2000), and that this is difficult to reconcile with a simple impact model. However, the Cr isotope data require extraterrestrial accretion as a source of materials in these beds, and we must find models that fit the data. An alternative to an impact model could be some sort of interplanetary dust storm, but this scenario is much less likely and inconsistent with large tsunamis proposed by Lowe et al. (1989, 2003). Considering that thick layers of spherules with ≤60% ETC have been subjected to current deposition, possible reworking, regional hydrothermal and metasomatic alteration, and sometimes local tectonism or Au mineralization, we should not be surprised to find local enrichments of Cr or PGEs that are much higher or lower than average. For example, the Sheba Mine bed was tectonized and exposed to severe mineralization. It is possible that this mineralization resulted in localized redistribution of Cr and PGEs, but this possibility does not contradict the impact model. In fact, only the high ETCs from bed S3 are truly exceptional, compared to other known impact deposits. The 1% ETC of S2 is well within the range of known impact deposits, such as in the late Eocene (Ganapathy, 1982). The 15%–30% ETC for bed S4 is only fractionally higher than in some K-T boundary sediments, where carbonate-free ETCs of 10%–20% have been reported (e.g., Kyte et al., 1985).

The most anomalous character of these spherule beds is not the high ETC, but the high total flux of meteoritic material that these deposits represent. The best analogue to these beds is the global ejecta deposit of the K-T boundary. This deposit is composed mainly of spherules and is highly enriched in Cr and PGEs (e.g., Smit, 1999; Kyte et al., 1985). However, the actual fallout layer of the K-T deposit is typically only ~3 mm thick, and the total amount of Ir deposited globally is only ~55 ng/cm$^2$ (Donaldson and Hildebrand, 2001). Although we are hesitant to make similar extrapolations for the Barberton beds, the inescapable fact is that at none of the multitude of well-preserved K-T boundary deposits has anything like the Archean beds been found. Regionally, thick spherule deposits (tens of centimeters) occur near the Chicxulub crater (Smit, 1999), but these are from low-velocity ejecta and lack a significant ETC.

If we conservatively estimate that S2, S3, and S4 are global deposits 20, 20, and 10 cm thick, with average Ir concentrations of 3, 300, and 100 ng/g, respectively, and densities of 2.7 g/cm$^3$, then we can compare these directly to the K-T deposits. At 162 ng/cm$^2$ Ir, the S2 impactor may have been only a few times larger than the Chicxulub projectile. However, with 2700 ng/cm$^2$ Ir in S4 and 16,200 ng/cm$^2$ Ir in S3, the implied projectile masses are 50–300 times greater. These translate into projectiles with diameters ~3–7 times larger than at the K-T boundary.

These megaimpacts occurred over a geologically brief interval of time. Zircon ages place S2 as ca. 3260 Ma (Byerly et al., 1996) and S3 as 3243 ± 4 Ma (Kröner et al., 1991; Lowe et al., 2003). To have all three impacts within 20 m.y. suggests an impactor flux at least an order of magnitude greater than the modern flux. If this is correct, then further investigation of the Barberton greenstone belt may yield evidence of other large impact events.


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