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Geochemistry and mineralogy of Early Archean spherule beds, Barberton Mountain Land, South Africa: evidence for origin by impact doubtful

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ABSTRACT

Spherule layers in the ~ 3.4 Ga Barberton Greenstone Belt, South Africa, have been interpreted as being the result of large asteroid or comet impacts on the early earth. This interpretation was based, among other arguments, on the enrichment of siderophile elements, especially the platinum group elements. We made a detailed mineralogical, petrological and geochemical study of spherule bed samples taken from drill cores and underground exposures at the Princeton, Mt. Morgan and Sheba gold mines, as well as surface localities. The macrostructure of each sample (from within different spherule layer units) shows evidence for multiple (more than five) events over about 30 cm. This would require multiple impacts within a few million years, which is unlikely. The mineral phases are almost exclusively of secondary origin. The mineralogy provides evidence for extensive hydrothermal and metasomatic alterations of the spherule beds. Geochemical analyses of alternating spherule, shale and chert layers show no correlation between the siderophile elements (e.g., Ir, Co, Ni and Au), contrary to that which would be expected if the siderophile elements had an extraterrestrial source. Furthermore, no significant variation in the content of the siderophile elements was detected between spherule layers and shale layers; however, siderophile element contents are high only in layers containing abundant sulphide minerals and having high As, Sb, Se and Cr contents. We suggest that complex mineralizations, similar to those that have formed the Barberton Archean gold deposits or the Bon Accord deposit, were responsible for the siderophile element enrichments in the spherule beds. The mineralogical and geochemical data provide no direct evidence in favour of their initial origin by impact. Nowhere else in the world have such multiple (or even single) spherule beds been observed, and none of the numerous known impact craters (or the Cretaceous–Tertiary boundary) is associated with comparable spherule beds. Known impact debris usually contains < 1% meteoritic component, if any at all, while the Barberton spherules are anomalous in being extremely enriched compared to any known impact deposits.

1. Introduction

The Barberton Greenstone belt is a 3.5–3.2 Ga old formation situated in the Swaziland Supergroup near Barberton, eastern Transvaal, South Africa. The belt includes a lower, predominantly volcanic sequence, the Onverwacht Group, and an upper, mainly sedimentary, sequence, the Fig Tree Group. Spherule beds were found throughout both the volcanic and sedimentary (Onverwacht and Fig Tree) sequences. Several authors have studied some of these spherule beds. For example, Lowe and Knauth have [1] presented evidence for the existence of extensive beds of accretionary lapilli up to 3 mm in diameter within the Onverwacht Group. The strata of the Onverwacht Group are dominated by altered quartz porphyries and diabasic lavas frequently intercalated with chert layers. Carbonates and volcaniclastic debris are also present. Lowe and Knauth [2] reinterpreted spherules within the Onverwacht Group, which were previously thought to be silicified marine carbonate ooids, to be accretionary lapilli. Heinrichs [3] studied similar spherules from the Umsoli chert and concluded that they too are accretionary lapilli, although he argued against the subaerial or shallow-water deposition origin of these layers that was advocated by Lowe and Knauth [2].

In 1986, Lowe and Byerly [4] described silicate spherules with diameters of around 0.1–4 mm occurring in a layer near the base of the Fig Tree Group. Most spherules were composed of intergrown microcrystalline quartz and sericite, with outer rims of different mineralogical compositions. The textural appearance of some rare spherules was interpreted as pseudomorphs of quench textures, similar to the textures observed in chondrules. On the basis of these and other petrological features, and their occurrence in a massive layer, Lowe and Byerly [4] interpreted these spherules to be possibly of impact origin. Later, the discovery of iridium anomalies of up to several hundred ppb in some of these spherule samples was taken as supporting evidence for an extraterrestrial origin of the spherule beds [5]. Lowe et al. [5] also reported on additional spherule beds, one of them (S1) in the Onverwacht Group, and two more (S3 and S4) in the Fig Tree Group. Abundances of the platinum group elements were reported to be of roughly chondritic proportions [5], strengthening the case for an impact origin. A more detailed recent study of different fractions of one spherule layer (S4) by Kyte et al. [6] showed that the PGEs are somewhat fractionated (40%) relative to chondritic abundances. Nevertheless, these authors maintained that the most likely explanation for the observed PGE enrichments (and interelement ratios) is a meteoritic source. If the Barberton spherule beds are of impact origin, several large-scale impacts must have occurred during a relatively short time interval at around 3.2 Ga ago [6], in order to explain the multiple occurrence of spherule layers at different stratigraphic levels.

Impacts have played an important role in the development of the early earth: during the first few hundred million years after the formation of the earth, large impacts contributed to the accretion of our planet. There is some evidence for an extensive late-stage bombardment of the earth (and other bodies in the inner solar system) around 3.9–3.8 Ga ago—the so-called late heavy bombardment. Later, the frequency of impacts dropped considerably, when at about 3 Ga the currently observed level was reached. The study of impacts in the early history of the earth is therefore of great importance. If the Barberton spherules are truely of impact origin, their study would provide data on distal ejecta and their preservation. A more detailed investigation of the Barberton spherule beds is therefore warranted. So far no detailed mineralogical study (including secondary mineralization) or a comprehensive discussion of the geochemical stratigraphy has been available. We report here on the first results from such a study.

2. Samples and methods

We have collected samples from drill cores from the Princeton and Mt. Morgan gold mines, and underground exposure samples from the Princeton and Sheba mines near Barberton. Our spherule beds were sampled within a banded iron formation (BIF) comprising interbedded chert, sideritic shale and carbonaceous shale units. The BIF unit occurs within the Fig Tree greywackes (Fig. 1), which represent tectonic slices on the southern boundary of metavolcanic units within the Oerschot-Weltevreden schist belt. The southern boundary of the Fig Tree greywackes is structurally complex and is represented by mafic rock wedged against Moodies sediments. The mafic rocks are tectonically emplaced wedges and therefore may not represent the Onverwacht-Fig Tree contact [M. van den Berg, pers. commun., 1992]. We must accordingly conclude that the spherule bed samples from the Princeton and Mt. Morgan locations cannot be derived from the S2 layer at or near the contact with the Fig Tree Group, but that they are equivalent to the S3 bed [G. Byerly, pers. commun.]. The underground samples from the Sheba locations are believed to be equivalent to the S2 layer (Fig. 1). The exact placement of the S3 and S4 layers in the stratigraphic column is not well defined [9, and G. Byerly, pers. commun., 1993]. Kyte et al. [6] (their fig. 1) gave a placement in the stratigraphic column that was different from that of Lowe et al. [5] (their fig. 1). In addition, we have also analyzed samples from the type surface locality of the S2 spherule bed from the location described by Lowe [7]. Two samples, BA-1 and PS13, which were collected at the Princeton mine at depths of 1053 m (underground exposure) and 307.20 m (drill core) respectively, were selected for detailed chemostratigraphic work.

Petrographic thin sections were prepared for optical and electron microscopy. Layers with thicknesses of the order of 2–10 mm were separated for detailed geochemical analyses. The other samples were also subdivided into several units (usually spherule bands and host shale or chert). Trace element analyses for 35 elements were performed by neutron activation analysis (for details of the methods, see, for example, Koeberl [8]), while the major elements were determined by X-ray fluorescence (XRF) spectrometry. The mineralogical composition of the samples was determined by X-ray diffraction, optical microscopy and electron microscopy (using a Jeol JSM-6400 scanning electron microscope with a Kevex EDX system for mineral identifications).

3. Mineralogy and petrography of the spherule beds

The samples consist of alternating bands of BIF, chert, sideritic shales and spherule layers. Most samples contain several distinct spherule beds separated by a few millimetres (or at a maximum a few centimetres) of sedimentary rocks. In some samples up to seven different spherule layers can be recognized over a stratigraphic height of about 30 cm. Some spherules have clearly been deposited on top of a sedimentary unit because the shale layer shows indentations from the overlying spherules (Fig. 2). Some of this repetition may be due to tectonic overprint because some shale layers and several spherule layers are strongly deformed, and some shales are mylonitized. Lowe and Byerly [4] suggested that reworking due to currents or submarine landslides may be responsible for some of the repetition. However, most other layers clearly represent distinct units, separated by shale or chert layers, with a distinct settling pattern (i.e., higher spherule density at the bottom of a layer, and lower spherule density with smaller average spherule size at the top; see Fig. 2). It is very difficult to accept this pattern as that of a turbidite. Cyclic deposition is a more realistic possibility to explain the spherule bed repetition. In

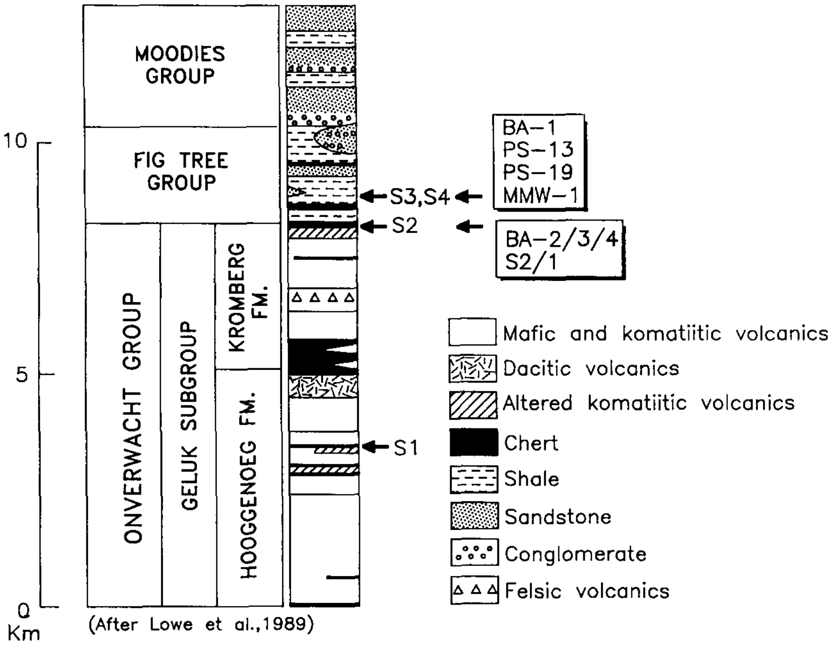

Fig. 1. Schematic stratigraphy of the upper part of the Barberton Greenstone Belt, showing the locations of the spherule beds described by Lowe et al. [5], and the locations of the samples taken for the present study. Samples BA-1, PS-13 and PS-19 are samples from the Princeton mine, MMW-1 is from the Mt. Morgan mine, BA-2, 3 and 4 are from the Sheba mine, and S2/1 is from a surface exposure of the S2 layer.

the impact interpretation, every spherule bed would represent the signature of a separate impact event, requiring multiple impacts within a limited time interval.

Table 1 summarizes the mineralogical composition of individual layers from the BA-1 subsample series and identifies characteristics of the distinct subsamples used in the geochemical studies. The general mineralogy of all samples containing spherule layers is, without doubt, the result of secondary processes. The main mineral constituents present are siderite, quartz, pyrite, sericite and some minor sphalerite. A few subsamples also contain minor baryte. No K-feldspar, cited by Heinrichs [3] as possible evidence for a volcanic origin of the spherule-rich bed, was observed in our samples. No primary phases except a few angular quartz grains and the occasional chromite were recognized. Like Byerly and Lowe [9] we too found some Ni-rich chromites, and we also found some chromites without Ni. However, it is not clear if the chromites are truely a primary phase, as our SEM studies showed that some chromites contain several weight percent Zn. Besides pyrite (in some spherule layers up to 15 vol%), we found several other opaque phases, including chalcopyrite and a relatively abundant Ni-As sulphide, probably gersdorffite. Pyrite was observed to grow both in spherules and matrix as a secondary phase, and it forms overgrowths on all other minerals. No relics of primary pyrite were found. Quartz clasts are generally not annealed and none show any evidence for shock metamorphism.

It is important to compare our samples with the petrographic descriptions of the spherule layers by Lowe et al. [4–6], as well as with the descriptions of volcanic spherule-rich horizons studied by Lowe and Knauth [1,2] and Heinrichs [3] in order to ascertain without doubt that a comparison between our results and earlier work [4–6] is permissible. This comparison yields the following results:

(1) With regard to the shapes and internal textures and the size distribution and textural arrangement of the spherules, and also with regard to the fabrics observed in petrographic thin sections from spherule layers, our samples are directly comparable to those described by Lowe et al. [4,5].

(2) No mineralogical evidence for the presence of volcanic or volcaniclastic material was found in our samples, although growth structures resembling some accretionary lapilli [10] were occasionally observed.

(3) Having said this, on the macroscopic scale (and from macroscopically examining the deposition fabrics), our spherule layers closely resemble examples of accretionary lapilli beds that have been discussed previously [e.g., 3,10].

Relict textures showing pseudomorphs of quench textures are very rare (as also observed by [4]). It has been questioned [G. Byerly, pers. commun., 1993] whether samples collected from zones of gold mineralization would not be more

Fig. 2. Multiple spherule layers in two saw slabs of specimen BA-1. Shale layers are dark or medium grey; ductile deformation is clearly visible in several layers. Note the grain-size variations within spherule layers, and indentations in shale caused by individual spherules.

hydrothermally altered than those samples originally described by Lowe et al. [4,5]. The petrographic characteristics of Lowe et al.'s spherule layers [4,5] are very similar to those of our samples, and the original publications [i.e., 4,5] do not provide enough mineralogical information for assessing a difference in alteration. It should be noted, however, that the whole Barberton area shows a severe hydrothermal overprint, and that all surface samples (including our samples) are severely altered.

4. Geochemical stratigraphy

The geochemical studies revealed a large degree of variability between individual layers that are only a few millimetres or centimetres apart. Table 2 gives the results for some key elements, using as an example the detailed chemostratigraphy of sample BA 1, which consists of alternating shale, chert and spherule layers. Interelement correlations were studied for all subsamples. The surprising result is that there are no statistically

TABLE 1

Stratigraphy and mineralogy of sample BA-1 (see Fig. 2), based on optical microscopy of thin sections. Subsample nomenclature identical to the nomenclature used in Table 2 (brackets indicate that two or more similar millimetre-thick layers were combined into one subsample)

Layer	Subsample	Formation	Mineral composition
1	–	SL	Qz-Ser-Pyr
2	1	Shale	Qz-Sid-Pyr-(Ser)
3	2	SL	Qz-Sid-Pyr-(Ser)
4a	3	Shale	Qz-Sid-(Pyr)-(Ser)
4b		SL	Pyr-Qz-(Sid)
5	–	SL	Qz-Sid-Pyr-(Ser)
6	4	Shale	Pyr-Qz-(Sid)-((Ser))
7		SL	Sid-Qz-(Pyr)-(Ser)
8		Shale	Pyr-Sid-Qz-((Chr))-((Sph))
9	5	SL	Ser-Sid-Qz-(Pyr)
10		Shale	Pyr-Sid-(Qz)
11	–	SL	Ser-Qz-Sid-(Pyr)
12a	–	Shale	Pyr-Sid-Qz
12b	–	Shale	Pyr-Qz-Sid
13	6	SL	Qz-Sid-(Ser)-(Pyr)-((Sph))
14	–	ASL	Sid-(Qz)-(Ser)-((Pyr))
15a	7	ASL	Sid-Qz-Ser-Pyr-(Bio)-(Cpy) ((Chr))-((Montm))
16		Clast	(Breccia) Montm-Qz
15b	8	ASL	(U-Myl) Ser-Sid-Qz-((Pyr))-((Chr))
17	9	ASL	(Myl) Ser-Sid-Qz-(Pyr)-((Cpy))
18		SL	Ser-Qz-Sid-(Pyr)-((Cpy))
19		SL	(Myl) Sid-Qz-Ser-((Pyr))
20	10	SL	Sid-Qz-Ser-(((Pyr)))
21	11	SL	Qz-Sid-(Ser)-(((Pyr)))
22	12	Shale + chert	Sid-Qz-(Ser)-(Montm)-(((Pyr)))
23	13	Chert	Qz
24	14	Shale + pyrite L.	Qz-Sid-(Pyr)
25	15	Shale	(Myl) Sid-Qz-(Bio)-(Mu)-(((Pyr)))
26		Shale	Qz-Bio-Sid-(((Pyr)))
27		SL	Sid-Qz-(Pyr)
28		Chert	Qz

SL = Spherule layer; *ASL* = altered Sph. layer; *Qz* = quartz; *Ser* = sericite; *Sid* = siderite; *Pyr* = pyrite; *Bio* = biotite; *Cpy* = chalcopyrite; *Chr* = chromite; *Sph* = sphalerite; *Mu* = muscovite; *Montm* = montmorillonite; *U-Myl* = Ultramylonite.

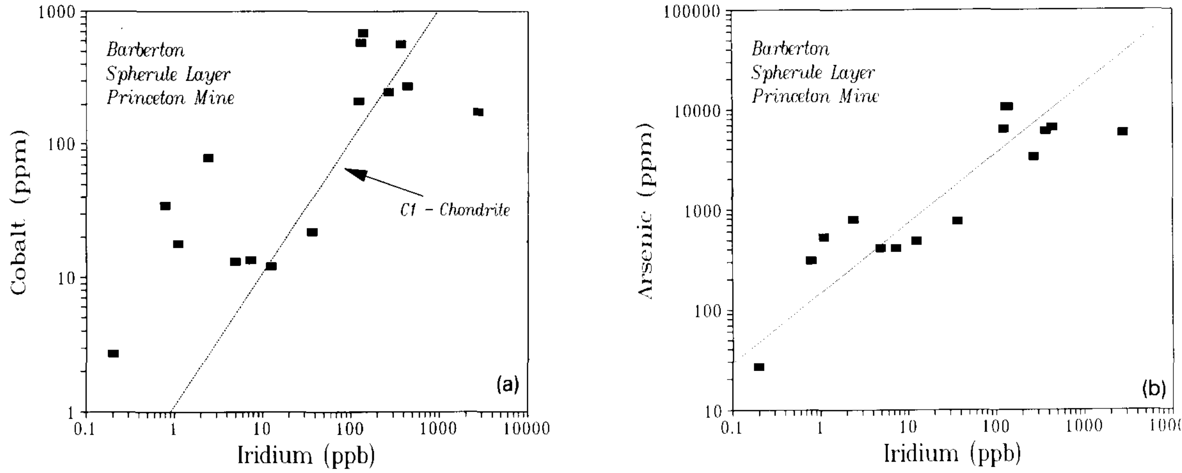

Fig. 3. (a) Iridium vs. Co abundances in subsamples from BA-1, showing the absence of any statistically significant correlation ($r = 0.10$). (b) Iridium vs. As abundances in the same sample, showing a better ($r = 0.8$) correlation.

significant correlations between the siderophile elements (e.g., Ir/Co, Ir/Ni, Ir/Au and Ni/Co). An example is given in Fig. 3a, which shows the Ir/Co diagram (correlation coefficient $r = 0.10$). However, statistically significant correlations do exist between siderophile and some chalcophile/lithophile elements (e.g., Au and As ($r = 0.87$), Ir and Cr ($r = 0.99$), and Au and Sb ($r = 0.93$); see also Fig. 3b).

In general, samples with high abundances of Ir or Au also have high Cr, As, Sb and Se contents. On a macroscopic scale, there is a clear positive

TABLE 2

Selected chemical and mineralogical data for subsamples of an Archean spherule bed at Princeton mine (BA samples) and for a sample from the surface type locality [7] (S2 sample), Barberton, South Africa

		Cr	Co	Ni	Zn	As	Se	Sb	Ir	Au	Mineralogy
BA 1-1	Shale	443	580	9480	111	10540	58.5	1066	131	712	Qz-Sid-Pyr-(Ser)
BA 1-2	Spherule L.	1631	273	5770	121	6550	41.8	404	437	133	Qz-Sid-Pyr-(Ser)
BA 1-3	Spherule L.	360	685	9020	35	10620	56.1	813	138	712	Pyr-Qz-(Sid)
BA 1-4	Shale	1070	212	6020	85	6310	37.4	410	123	126	Pyr-Sid-Qz-((Chr))-((Sph))
BA 1-5	Shale	1280	564	5450	88	6040	148	455	372	547	Pyr-Sid-(Qz)
BA 1-6	Spherule L.	1070	248	3130	99	3330	26.1	253	271	149	Qz-Sid-(Ser)-(Pyr)-((Sph))
BA 1-7	Clast	59.8	22.1	650	103	754	1.33	43.7	37.2	3.1	Montm-Qz
BA 1-8	ASL	16400	174	6080	2190	5735	9.4	245	2730	52	Ser-Sid-Qz-((Pyr))-((Chr))-((Cpy))
BA 1-9	Spherule L.	2065	12.1	394	107	477	1.12	38.5	12.7	1.5	Ser-Qz-Sid-(Pyr)-((Cpy))
BA 1-10	Spherule L.	407	13.5	362	97	407	1.11	21.8	7.4	1.6	Sid-Qz-Ser-((Pyr))
BA 1-11	Spherule L.	325	13.1	330	93	412	1.04	38.9	4.9	1.2	Qz-Sid-(Ser)-((Pyr))
BA 1-12	Shale+Chert	121	18.1	395	93	529	0.59	31.1	1.1	2.8	Sid-Qz-(Ser)-(Montm)-(((Pyr)))
BA 1-13	Chert	9.34	2.71	20	13	27.1	0.13	15.2	0.2	2.4	Qz
BA 1-14	Shale	40.2	34.6	186	44	309	1.11	11.4	0.8	6.8	Qz-Sid-(Pyr)
BA 1-15	Spherule L.	438	78.9	475	57	790	1.35	72.4	2.4	4.7	Sid-Qz-(Pyr)
S2-2	Spherule L.	244	1	13	16	37.9	0.45	7.08	3.1	1.1	Qz-Pyr-Sid

Elemental abundances measured by instrumental neutron activation analysis. All data in ppm except Ir and Au which are in ppb. *ASL* = altered spherule layer; *Qz* = quartz; *Ser* = sericite; *Sid* = siderite; *Pyr* = pyrite; *Chr* = chromite; *Cpy* = chalcopyrite; *Sph* = sphalerite; *Montm* = montmorillonite. Minerals given in order of abundance as derived by optical microscopy of thin sections.

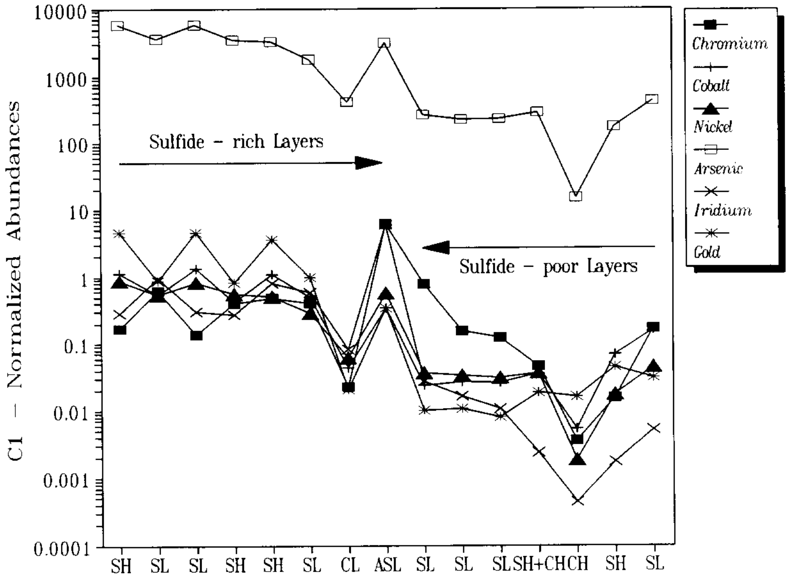

Fig. 4. Chemostratigraphy of selected elemental abundances (chondrite-normalized [43]) across layers of sample BA 1. Layer BA 1-1 is on the left, BA 1-15 on the right. For mineralogy and elemental abundances, see Tables 1 and 2. Layers BA 1-1 to BA 1-8 are enriched in sulphide minerals, which is reflected in high abundances not only of the chalcophile, but also of the siderophile elements. No difference is obvious between siderophile element contents in spherule, chert or shale layers. *SH* = shale; *SL* = spherule layer; *CL* = clast; *ASL* = altered spherule layer; *CH* = chert.

correlation between the abundance of sulphides (pyrite, chalcopyrite and gersdorffite) and high contents of Au, Ir, As, Cr, Sb and Se. For example, layers BA 1-1 to BA 1-8 are sulphide-rich, while layers BA 1-9 to BA 1-15 are sulphide-poor. Figure 4 shows that all sulphide-rich layers also have high abundances of some siderophile and chalcophile elements. This observation is also confirmed by a bulk analysis of the sulphide-poor surface sample (S2-2) from the type locality [5,7]. This sample is less enriched in the siderophile elements than the sulphide-rich samples from BA 1, but is similar to the sulphide-poor BA 1 samples (Table 2).

Another important result of the chemostratigraphic studies is the observation that high siderophile element contents are not restricted to spherule layer samples, but are also found at similar concentration levels for chert and shale layers, as demonstrated in Fig. 4. In detail, spherule layers as well as shale layers show similar abundances of the siderophile and chalcophile elements, and the absolute abundances of these elements are high in sulphide-rich zones and low in the sulphide-poor zones. A similar lack of a chemical distinction between spherule layers and shale or chert layers is found in subsamples of sample PS13 [Koeberl et al., in prep.], where the highest concentrations of siderophile elements (including Ir) are found in pyritic shales, while the spherule and chert layers show lower abundances.

5. Discussion

From field relationships and petrographical and mineralogical work it is clear that we are dealing with samples similar to those described by Lowe et al. [4–6]. We differ, however, in our interpretation of the spherule layers. The stratigraphic evidence shows that a relatively large number of distinct spherule beds exists in the Barberton Greenstone Belt. Although Lowe et al. [5] mention only four distinct spherule beds, which they interpreted to be of impact origin, a detailed examination of samples from these spherule beds shows that each one consists of several distinct sublayers, none of which can be explained by tectonic duplication or reworking. According to the impact hypothesis, this requires quite a number of distinct impacts. Kröner et al. [11] have recently dated rocks from the Fig Tree Group, and Kyte et al. [6] concluded that at least the S2, S3 and S4 spherule beds were deposited within an interval of about 30 Ma. It is difficult to accept that three distinct impacts could occur within the same region within 30 Ma of each other, and further that all three of them would produce spherule layers that have not been recognized elsewhere as a feature of Archean or more recent impact structures. Numerous impact events that occurred in recent geological history have been recognized, and none are associated with such spherule beds. If our interpretation of distinct sublayers in each of the layers is correct (and we suggest strongly that it is), an even larger number of impacts, all within the same short time interval and at the same location, would be required. This is difficult to accept.

Other objections to the interpretation of the origin of the Barberton spherule layers by impact can be made. For example, Lowe and Byerly [4] state that some spherules show "pseudomorphs of quench textures". Although we found a few spherules with such textures, they are very rare. The overwhelming majority of spherules with relics or pseudomorphs of quench textures observed by us occur in only two subsamples (S2-1 and BA 1-3) and all the other spherule layers were devoid of such features. Lowe and Byerly [4] suggested that these textures are similar to those observed in meteoritic chondrules [e.g., 12]. However, chondrules have not originated by impact [12,43], rendering any textural argument irrelevant. In addition, it may well be that in some cases secondary minerals grow into forms that resemble quench textures, without representing pseudomorphs of primary textures [G. Graup, pers. commun., 1993]. Without observation of the primary phases interpretation as quench textures is doubtful.

Another question concerns the existence of thick beds of impact-derived spherules, as has been suggested by Lowe and Byerly [4]. For comparison, they cite (among others) the occurrence of microtektites in deep-sea sediments. However, microtektites never occur in the form of solid beds, are much smaller than the Barberton spherules, are dispersed over a relatively large area, and have petrological and chemical characteristics [e.g., 13] that are completely different from those of the Barberton spherules. Impact-derived spherule beds similar to the Barberton spherule beds are known from neither any terrestrial impact crater nor from the Cretaceous–Tertiary (K/T) boundary. The stratigraphic position (i.e., abundance in the stratigraphic column) and the petrological and chemical characteristics of rare impact-derived spherules found at Ries crater are again different from those of the Barberton spherule layers [14, and Graup, pers. commun., 1991]. A single spherule bed in Australia, which has also been suggested to be of impact origin [15], is significantly different in stratigraphy (only one well-defined layer) and petrology (very abundant quench textures) from the Barberton spherule beds.

The geochemical evidence too, based on our new studies, does not unequivocally support an impact origin for the Barberton spherules. The lack of any significant correlation between the siderophile elements (e.g., Ir, Ni, Co and Au) clearly contrasts with the siderophile element correlations observed in most impact-derived rocks at meteorite craters [e.g., 13,16–18] and at the K/T boundary [18,19]. In addition, none of the platinum group elements (PGE) enrichments found at impact craters [13,16–18] coincide with any spherule layers. Besides the absence of a correlation between siderophile elements, the elemental abundances in the spherule beds are quite different from chondritic abundances (see Fig. 4). Lowe et al. [5] have noted an apparent similarity in siderophile element abundances (especially the PGEs) between the Barberton spherule beds and chondritic abundances. However, such similarities are restricted to only some of the PGEs, and are also found in only a few samples. If a larger set of elements, including other siderophile and chalcophile elements, is considered (Table 2) [Koeberl et al., in prep.], no significant similarities remain. Samples with a smaller amount of sulphides (S2-1 and S2-2 (the surface samples from the S2 layer type locality) and PS19) show similar relative abundances (i.e., they show similar general abundances of elements, including siderophile elements, but without the extreme enrichment of Ir and other siderophiles that is present in sulphide-rich samples).

It was argued by Lowe et al. [5] and Kyte et al. [6] that the PGE enrichment in the spherule beds is most easily explained by an extraterrestrial source, although Kyte et al. [6] admitted being unable to satisfactorily explain the elemental patterns by both chondritic and iron meteorite impactors. Lowe et al. [5,6] claimed that the PGE abundance patterns of the Barberton spherule layers are almost identical to chondritic patterns. However, this is actually not the case, because even in their "best" samples differences of a factor of 2 exist. If other siderophile elements (e.g., Ni, Co or Au, which have been shown to be generally characteristic of impact products [16–18]) are taken into account, much larger differences are revealed. It is furthermore well established that impact products (e.g., impact glasses and other impact ejecta) contain, in general, $\ll 1\%$ of any meteoritic component (quite often $\ll 0.1\%$), with only a few rare exceptions bearing up to about 5% of meteoric component [e.g., 13,16–18]. In some subsamples the PGE contents in the Barberton spherule layers exceed even chondritic abundances (Table 2), requiring meteoritic contributions of up to $> 100\%$ (assuming a chondritic meteorite), which is impossible. These enrichment factors are of the order of 20 to $> 100\%$ even for contamination from an iron meteorite (some of which can have higher contents of Ir and other siderophiles, but which lacks the "near-chondritic" PGE abundance pattern that Kyte et al. [6] comment on). Therefore, the high PGE concentrations must be the result of remobilization and concentration processes, and cannot be used as direct arguments for an impact origin.

Because of the secondary nature of the pyrite, and good correlation between siderophile and chalcophile element abundances, throughout the spherule beds it can be assumed that the PGEs, Au and other siderophiles have been thoroughly redistributed. Lowe et al. [4–6] acknowledge that the spherule beds are strongly altered; taking the hydrothermal mobility of many siderophile elements into account it is hard to understand why they would even consider elemental ratios as being primary and characteristic of a meteoritic origin. There is abundant evidence for low- and medium-temperature mobilization of the PGEs under a variety of conditions [20–24], sometimes leading to the formation of minerals enriched in individual PGEs [21]. Sulphide mineralization having high contents of As and the PGEs (especially Ir) has been described in the literature [see 25]. Experimental studies indicate that the mobility of PGE hydroxide, sulphide and chloride complexes is strongly dependent on Eh/pH and temperature conditions, with maximum mobility occurring at different (i.e., low) temperatures for the various PGEs [26–28]. There are unfortunately no detailed studies on the behaviour of all the PGEs under different Eh/pH conditions, and furthermore we do not know the composition of the fluids that percolated through the Barberton area. Recently, high concentrations of Au correlating with high concentrations of As have been found to be associated with various pyrite generations at the Gold Quarry deposit in Nevada [29].

There is sufficient evidence for several phases of hydrothermal and tectonothermal activity in the Barberton Mountain Land [30,31] having repeatedly led to important noble metal depositions [31,32]. In rocks of the Fig Tree Group, hydrothermal fluids with temperatures in excess of 300°C were recorded [31], and another phase of thermal overprinting coincides with the formation of the Bushveld Complex [30]. Local geological evidence [M. van den Berg, pers. commun., 1992] indicates that rocks in the Barberton area, including the spherule beds, have been subjected to several successive stages of mineralization.

A question of great importance concerns the initial source of the PGEs. Komatiites, which are common in the Barberton area [33,34], contain PGEs at levels that are much higher than those of the average crust, but still about 1–2 orders of magnitude below those observed in the spherule beds [35–37]. Chromites and chromitites from near the Barberton area and from other locations have been found to be enriched in Ir and some other siderophile elements, with variable PGE patterns [38,39]. Sulphide deposits of magmatic origin (e.g., Fe-Ni sulphide mineralizations) tend to be more enriched in Au than in Ir [38,40]. For the Barberton spherule layers, no clear pattern can be deduced because of the large variations between the layers: in some cases Au is much more abundant than Ir, and in some cases not. Kyte et al. [6] report relatively low Au values (a few ppb) but highly variable Ir and other PGE abundances. In our samples we observe two different types of behaviour: some of our samples have relatively low Au contents and variable Ir contents (but not as high as those observed by Kyte et al. [6] for their S4 bed samples), and others show very high Au (and Ir) contents but without a significant correlation between the contents of Au and Ir. It may be noted that although some of the PGEs in the study of Kyte et al. [6] show positive correlations their ratios are different from C1 ratios for several element pairs (e.g., Ir/Au and Ir/Pd). As we have not analyzed any other PGEs apart from Ir we cannot comment on their behaviour in our samples. However, the close connection between the siderophile element enrichments and the occurrence of sulphide minerals and chalcophile elements suggests a causal relationship. Kyte et al. [6] reported the occurrence of two small nuggets that are high in PGEs in a pyrite crystal. High PGE abundances (e.g., up to 1100 ppb Ir), together with roughly chondritic PGE patterns, are known, for example, from the Bon Accord deposit in the Barberton Greenstone Belt [41,42]. The Bon Accord is an unusual Ni-Fe silicate-spinel assemblage of terrestrial origin that is not associated with any spherule layers. It serves as an example that normal mineralization processes may be capable of redistributing and concentrating the PGEs (with their ultimate source most probably being the terrestrial mantle). This deposit is also important as it contains a terrestrial occurrence of the rare Ni-chromites encountered in the Barberton spherule layers by us and by Byerly and Lowe [9].

6. Conclusions

We have performed detailed mineralogical, petrological and geochemical analyses on a series of different samples taken from several locations in the Barberton Greenstone Belt representing two of the spherule layers described by Lowe et al. [4–6]. Although we have confirmed, through stratigraphic and petrological studies, that we are dealing with the same spherule beds as described before [4–6], our data do not necessarily lead to the conclusions drawn by these authors, namely that these spherule beds were formed from large-scale impact events. We observe a variety of mineralizations in our samples, ranging from very little mineralization to samples showing strong sulphide mineralization. Despite the fact that some of our samples are less affected by secondary alteration than others, the geochemical observations made are valid for all of our samples. Also, many of our samples have petrological and geochemical characteristics similar to those described by Lowe et al. [4–6], but regarding siderophile and chalcophile element abundances our samples show a distinctly wider compositional variation. An important observation is the lack of correlation between siderophile element abundances in the different layers of each sample, as well as the absence of a geochemical distinction between spherule and shale layers. Furthermore, we observed a correlation of siderophile elements with the abundance of secondary sulphides, and we conclude that the peculiar chemistry of the spherule beds is the result of a series of stages of secondary alteration, mainly through hydrothermal processes.

An origin of the spherule beds by impact may not be the most likely explanation, although we cannot categorically exclude it. In addition to our new mineralogical and geochemical data, we have tried to critically discuss the previously presented evidence for an impact origin [4–6] and conclude that there are numerous problems and inconsistencies. At least three of the four spherule beds described by Lowe et al. [5] consist of several distinct sublayers. In the impact hypothesis this would require a relatively large number of impacts at about 3.2 Ga within a geologically short time interval of about 30 Ma. Although such impacts were asserted by Lowe et al. [5,6] to record the final stages of the late heavy bombardment, it should be noted that the late heavy bombardment, as observed for example in the lunar cratering record, ended at about 3.8 Ga. Also, the Barberton spherule beds would represent a unique impact deposit, as similar impact deposits are not known from other stratigraphic sections or any of the numerous well-studied terrestrial impact craters. Although rare, somewhat similar PGE-rich mineralizations, including rare Ni minerals, have been described before from the Barberton area [41,42]. From our data we conclude that there is no unequivocal mineralogical, petrological or geochemical evidence in favour of an impact origin for the Barberton spherule beds, although again we cannot totally exclude such an origin. There is, of course, the possibility that the ultimate source of the PGEs was meteoritic. However, the high PGE contents in the Barberton spherule layers would require meteoritic contributions that are several orders of magnitude above any found at known impact deposits. Alternatively, the spherule beds may be the result of widespread volcanic activity, followed by several phases of hydrothermal and tectonothermal activity, leading to siderophile element mobilization and redistribution in the course of sulphide mineralization.

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