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Sulfur Sources of Buckshot Pyrite in the Auriferous Conglomerates of the Mesoarchean Witwatersrand and Ventersdorp Supergroups, South Africa

B. M. Guy\textsuperscript{a}, S. Ono\textsuperscript{b}, J. Gutzmer\textsuperscript{c}, Y. Lin\textsuperscript{b,1}, A. Bauer\textsuperscript{b} and N. J. Beukes\textsuperscript{a}

\textsuperscript{a}Department of Geology, University of Johannesburg, Auckland Park, 2006, South Africa
email: nbeukes@uj.ac.za
\textsuperscript{b}Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts, 02139, USA
email: sono@mit.edu, annbauer@mit.edu
\textsuperscript{c}Helmholtz-Institute Freiberg for Resource Technology, Halsbrücker Str. 34, 09599 Freiberg, Germany.
email: j.gutzmer@hzdr.de

\textsuperscript{1}Present address: Mineral Services, SGS South Africa, 58 Melville Street, Booyens, Johannesburg, 2091, South Africa.
email: bradley.guy@sgs.com

\textsuperscript{1}Present address: School of Earth and Space Sciences, University of Science and Technology of China, Hefei, 230026, P. R. China
email: yinglin@ustc.edu.cn

Abstract

Large rounded pyrite grains (>1 mm), commonly referred to as ‘buckshot’ pyrites, are a characteristic feature of the auriferous conglomerates (reefs) in the Witwatersrand and Ventersdorp supergroups. Detailed petrographic analyses of the reefs indicated that the vast majority of the buckshot pyrites are of reworked sedimentary origin, i.e., that the pyrite originally formed in the sedimentary environment during sedimentation and diagenesis. Forty-five of these reworked sedimentary pyrite grains from the Main, Vaal, Basal, Kalkoenkrans, Beatrix and Ventersdorp Contact reefs were analyzed for their multiple sulfur isotope compositions (δ\textsuperscript{34}S, Δ\textsuperscript{33}S and Δ\textsuperscript{32}S) to determine the source of the pyrite sulfur. In addition, four epigenetic pyrite samples (pyrite formed after sedimentation and lithification) from the Middelvlei and the Ventersdorp Contact reefs were measured for comparison. The δ\textsuperscript{34}S, Δ\textsuperscript{33}S and Δ\textsuperscript{32}S values of all 45 reworked sedimentary pyrite grains indicate clear signatures of mass-dependent and mass-independent fractionation and range from −6.8 to +13.8‰, −1.7 to +1.7‰ and −3.9 to +0.9‰, respectively. In contrast, the four epigenetic pyrite samples display a very limited range of δ\textsuperscript{34}S, Δ\textsuperscript{33}S and Δ\textsuperscript{32}S values (+0.7 to +4.0‰, −0.3 to +0.03‰ and −0.3 to +0.1‰, respectively).

Despite the clear signatures of mass-independent sulfur isotope fractionation, very few data points plot along the primary Archean photochemical array suggesting a weak photolytic control over the data set. Instead, other factors command a greater degree of influence such as pyrite paragenesis, the prevailing depositional environment and non-photolytic sulfur sources. In relation to pyrite paragenesis, reworked syngenetic sedimentary pyrite grains (pyrite originally precipitated along the sediment-water interface) are characterized by negative δ\textsuperscript{34}S and Δ\textsuperscript{33}S values, suggesting open system conditions with respect to sulfate supply and the presence of microbial sulfate reducers. On the contrary, most reworked diagenetic sedimentary pyrite grains (pyrite originally precipitated below the sediment-water interface) show positive δ\textsuperscript{34}S and negative Δ\textsuperscript{33}S values, suggesting closed system conditions. Negligible Δ\textsuperscript{33}S anomalies from epigenetic pyrite suggest that the sulfur was sourced from a mass-dependent or isotopically homogenized metamorphic/hydrothermal sulfur reservoir.

Contrasting sulfur isotope compositions were also observed from different depositional environments, namely fluvial conglomerates and marine-modified fluvial conglomerates. The bulk of the pyrite grains from fluvial conglomerates are characterized by a wide range of δ\textsuperscript{34}S values (−6.2 to +4.8‰) and small Δ\textsuperscript{33}S values (+0.3‰). This signature likely represents a crustal sulfate reservoir derived from either volcanic degassing or from weathering of sulfide minerals in the hinterland. Reworked sedimentary pyrite grains from marine-modified fluvial conglomerates share similar isotope compositions, but also produce a positive Δ\textsuperscript{33}S/Δ\textsuperscript{34}S array that overlaps with the composition of Archean barite, suggesting the introduction of marine sulfate. These results demonstrate multiple sources of sulfur, including atmospheric, crustal and marine sulfur reservoirs. The prevalence of the mass-dependent crustal sulfur isotope signature suggests that sulfate concentrations were probably much higher in terrestrial settings in comparison to marine environments, which were sulfate-deficient. However, the optimum conditions for forming sedimentary pyrite with a crustal sulfur isotope signature were probably not during fluvial progradation but rather during the early phases of flooding of low angle unconformities, i.e., during retrogradational fluvial deposition, coupled in some cases with marine transgressions, immediately following inflection points of maximum rate of relative sea level fall.
Introduction

Pyrite in the gold-bearing conglomerates of the upper Witwatersrand Supergroup has traditionally been classified into three groups, namely ‘compact rounded’, ‘porous rounded’ and hydrothermal (Ramdohr 1958; Saager 1970; Utter 1978; Hirdes and Saager 1983; England et al. 2002). The use of descriptive terminology for the first two groups is primarily a reflection of genetic uncertainty, i.e., whether the rounded pyrite grains represent clastic components of the conglomerate or whether they represent post-depositional pseudomorphs after rounded Fe-oxide minerals (Barnicoat et al. 1997; Law and Phillips 2005). Despite this uncertainty, most authors regard ‘compact rounded’ pyrite and ‘porous rounded’ pyrite as fragments of pyrite that were derived from the erosion of granitic-greenstone and sedimentary sources, respectively (Hallbauer 1986; England et al. 2002).

Reworked pyrite grains of a sedimentary origin have been documented by most Witwatersrand researchers, i.e., the so-called ‘buckshot’ pyrites, which are generally large rounded pyrite grains (>1 mm in size). However, the bulk of the literature has focused on compact rounded pyrite (<1 mm in size) and hydrothermal pyrite because of their significance in gold exploration in the Witwatersrand Supergroup (McLean and Fleet 1989; Phillips and Myers 1989; Myers et al. 1993; Barnicoat et al. 1997; Fleet 1998; Kirk et al. 2001; England et al. 2002; Frimmel et al. 2005). Consequently, reworked sedimentary pyrite grains are routinely overlooked, despite the fact that they comprise the bulk of total pyrite in several auriferous conglomerates of the Witwatersrand Super group (Ramdohr 1958; Utter 1978; Tucker 1980; Hirdes and Saager 1983; Hallbauer 1986; Hutchinson and Viljoen 1987; England et al. 2002) and that they can contain substantial contents of solid-solution gold and/or nano-particle gold (Utter 1978; Koglin et al. 2010; Large et al. 2013). Considering the scientific and economic importance of this world class Au-U deposit, it is somewhat surprising that virtually no one has questioned how the substantial quantities of sedimentary pyrite could have formed if the Archean atmosphere was highly depleted in oxygen (Farquhar et al. 2000), implying that sulfide weathering would have been negligible and that both continental runoff and ocean water would have essentially been sulfate-free (Habicht et al. 2002; Frimmel 2005).

Previous authors have reported relatively small δ34S variations from Witwatersrand pyrite (−0.5 to +6.5‰) (Hoefs et al. 1968; Hattori et al. 1983; Palmer 1986; Strauss and Beukes 1991; Zhao 1998). The small range of δ34S values from barren and mineralized horizons, and between different paragenetic associations, has been used to suggest a magmatic source for the sulfur. However, recent small-scale analyses of the ‘porous rounded’ pyrite (laser ablation and micro-drilling) have revealed a much wider range of δ34S values (−17 to +16‰), indicating that a portion of Witwatersrand pyrite might have formed through microbial sulfate reduction (Englund et al. 2002; Hofmann et al. 2009; Large et al. 2013). This information, supplemented with multiple sulfur isotope data (e.g., Hofmann et al. 2009), provides further evidence for a sedimentary origin as first suggested by the petrographic studies of Ramdohr (1958), Saager (1970), Utter (1978), Dimroth (1979), Hirdes and Saager (1983) and Hallbauer (1986).

In this paper, the results of a combined petrographic and multiple sulfur isotope investigation (δ34S, δ33S and Δ34S) are presented in order to constrain the source of the sulfur for reworked sedimentary pyrite grains of the upper Witwatersrand and lower Venterdsorp supergroups (~2.9 to 2.7 Ga). In the first part of the investigation, pyrite is classified according to textural and paragenetic constraints, where it will be argued that the vast majority of the buckshot pyrite grains were derived from a sedimentary source. In the second part of the investigation, it is shown that the bulk of the sulfur isotope compositions are controlled by terrestrial geological processes with only minor atmospheric input. Finally, a model for sedimentary pyrite formation in the upper Witwatersrand and lower Venterdsorp supergroups is presented.

Geological setting

The Witwatersrand Supergroup represents a ~7 km thick siliciclastic sequence that was deposited between 2.985 and 2.780 Ga over the central parts of the Archean Kaapvaal Craton (Fig. 1a) (Kositcin et al. 2003; Kositcin and Krapez 2004; SACS 2006). The succession unconformably overlies a granitoid-greenstone basement (3.48 to 3.03 Ga) and the volcanic-sedimentary rocks of the 3.09 to 3.07 Ga Dominion Group (Armstrong et al. 1991; Robb et al. 1992; Poujol et al. 2003). The Witwatersrand Supergroup has experienced only low-grade greenschist facies regional metamorphism, although certain areas have experienced higher grades (e.g., the northwestern parts of the basin, the overturned collar of the Vredefort Dome and the northeastern part of the Evander gold field) (Gibson and Wallmach 1995; Frimmel 1997; Phillips and Law 2000; Law and Phillips 2005). Stratigraphically, the Witwatersrand Supergroup is divided into the lower West Rand Group (~5 km thick) and the upper Central Rand Group (~2 km thick) (Fig. 1b).
Fig. 1.

The West Rand Group is composed of arenite and shale, with minor banded iron formation (BIF), conglomerate, diamicite and lava. Marine shelf deposacies are prominent in the lower parts of the group, whereas fluvial braided plain and distal marine shelf deposacies characterize the middle to upper parts (Watchorn 1981; Tankard et al. 1982; Beukes 1995). Most authors agree that the lower Hospital Hill Subgroup was deposited in a passive margin setting, with an open ocean to the southeast. However, there is little consensus regarding the tectonic setting of the middle and upper parts of the West Rand Group. Whilst some authors have argued for a passive margin setting for the entire West Rand Group (Kositcin and Krapez 2004; Koglin et al. 2010), others have suggested that the change to a foreland basin setting occurred at the junction between the Hospital Hill and Government subgroups (Beukes et al. 1995; Coward et al. 1995; Schmitz et al. 2004). Alternatively, Catuneanu (2001) proposed a foreland basin setting for the entire Witwatersrand Supergroup, where the West Rand and Central Rand groups represent the underfilled and overfilled stages, respectively. The maximum age of the West Rand Group is 2985 ± 14 Ma (detrital zircon grains, Kositcin and Krapez 2004) and the minimum age for most of the group is 2914 ± 8 Ma (the age of the lavas in the Crown Formation, Armstrong et al. 1991).

In contrast to the West Rand Group, the Central Rand Group contains a greater proportion of arenaceous and rudaceous lithotypes, with minor argillaceous and volcanic units such as the Booyens Formation and the Bird Lava, respectively. The Central Rand Group is dominated by fluvial braidedplain sedimentary rocks that were deposited in a restricted retroarc foreland basin setting (Catuneanu 2001; Kositcin and Krapez 2004; Schmitz et al. 2004; Frimmel et al. 2005). Fluvial sedimentation was controlled by deep-seated thrust faults along the basin margin, which led to synsedimentary folding and progressive uplift, source area rejuvenation, erosion and recycling of older sediments (Myers et al. 1990; McCarthy 1992; Coward et al. 1995). Marine incursions are recorded at various times during deposition of the Central Rand Group in the form of laterally continuous mudstones (Booyens Formation) and transgressive shallow marine quartz arenites. A number of prominent gold-bearing conglomerates are overlain by transgressive shallow marine quartz arenites (e.g., the Main, Carbon Leader, Vaal, Basal and Denny’s reefs; Fig. 2). Marine modification of these fluvial conglomerates, via winnowing and wave reworking, likely played a crucial role in upgrading their gold and heavy mineral content (Minter 1972; Verrezen 1987; Watchorn and O’Brien 1991; Beukes and Nelson 1995; Catuneanu and Biddulph 2001). The maximum age of the Central Rand Group is 2902 ± 13 Ma (detrital zircon grains, Kositcin and Krapez 2004) and the minimum age is 2780 ± 3 Ma (authigenic xenotime, Kositcin et al. 2003). However, based on stratigraphic correlations between the Mozaan Group and the Witwatersrand Supergroup, and indications that the two successions were deposited in the same basin, i.e., the Greater Witwatersrand basin (Beukes and Cairncross 1991), it is possible that Central Rand Group sedimentation came to an end around 2837 Ma (Gutzmer et al. 1999).

The auriferous Ventersdorp Contact Reef (VCR) overlies the Witwatersrand Supergroup with an erosional contact. Deposition probably took place around 2780 Ma based on the erosional event that preceded the correlative Derdepoort, Dennilton and Kanye-Lobate volcanic successions (Beukes and Nelson 1995; Hartzer 2000). The reef forms part of the Venterspost Formation and represents terraced fluvial and debris-flow deposits (Krapez 1985; Frimmel et al. 2005).

Methods and samples

Forty-four pyrite-bearing conglomerate samples of the Central Rand Group and Ventersdorp Contact Reef were collected from fresh drill-core and underground mine workings from the East Rand, Central Rand, West Rand, Carletonville, Klerksdorp and Welkom gold fields (Fig. 1b). Sampled reefs include the North, Carbon Leader, Main Reef Leader, Main, Middelvlei, Basal, Vaal, Saaiplaas, Kalkoenkrans, Kimberley, Beatrix, Kloof, Elsburg and the Ventersdorp Contact reefs (Fig. 2). From these samples, polished blocks were prepared and examined using reflected light and scanning electron microscopy (SEM). Minerals were identified in the SEM by energy-dispersive spectroscopy (EDS). Petrographic studies indicated that seven conglomerates contained reworked sedimentary pyrite grains suitable for micro-drilling (i.e., grains larger than 500 μm) (Fig. 2):

Fluvial conglomerates

- a. Beatrix Reef, Welkom gold field (Minter et al. 1988; Genis 1990)
- b. Kalkoenkrans Reef, Welkom gold field (H Brouwer 2013, pers. comm.)
- c. Middelvlei Reef, Carletonville gold field (Myers et al. 1993)
- d. Ventersdorp Contact Reef, Carletonville gold field (Krapez 1985)
Marine-modified fluvial conglomerates

e. Vaal Reef, Klerksdorp gold field (Catuneanu and Biddulph 2001)
f. Basal Reef, Welkom gold field (Frimmel et al. 2005)
g. Main Reef, Carletonville gold field (Beukes and Nelson 1995)

From these seven reefs, 45 reworked sedimentary pyrite grains and four epigenetic pyrite samples were selected for multiple sulfur isotope analyses ($^{33}$S/$^{32}$S, $^{34}$S/$^{32}$S and $^{36}$S/$^{32}$S). Sulfur was extracted by conventional Cr reduction and Ag$_2$S precipitation (Canfield et al. 1986). Ag$_2$S was then heated to 300°C, in the presence of F$_2$, to form SF$_6$. The SF$_6$ (3 to 6 μmol) was purified by a gas chromatography (GC) system similar to that described in Ono et al. (2006), and introduced to an isotope ratio mass spectrometer using a dual-inlet mode for measurements of masses 127, 128, 129, and 131. The mass spectrometry measurement consists of three runs, with each run consisting of eight cycles of reference versus sample injection. Reproducibility for complete analysis, from fluorination, GC purification, and isotope ratio analysis are 0.1, 0.2 and 0.4‰ (1σ) for δ$^{33}$S, δ$^{34}$S and δ$^{36}$S, respectively, and 0.01 and 0.1‰ (2σ) for Δ$^{33}$S and Δ$^{34}$S, respectively. Sulfur isotope values are reported relative to the Vienna Canyon Diablo Troilite Standard (V-CDT) by defining IAEA S-1 to be: δ$^{33}$S = −0.055‰, δ$^{34}$S = −0.300‰ and δ$^{36}$S = −1.14‰.

Fig. 2.

Classification of pyrite

The auriferous conglomerates contain a wide variety of paragenetic and morphological types of pyrite, which are typically concentrated on footwall contacts along with other detrital heavy minerals and gold (Ramdohr 1958; Saager 1970; Utter 1978; Hirdes 1979; Hirdes and Saager 1983; Hallbauer 1986; Fleet 1998; England et al. 2002). In this contribution, pyrite is classified according to its position in the paragenetic sequence (e.g., Hallbauer 1986), where each paragenetic association is further subdivided according to textural constraints. For ease of reference, the genetic classification system employed by Guy et al. (2010) for pyrite in the West Rand Group is utilized in the current contribution (Table 1). Application of this classification to the conglomerates of the Central Rand Group and Ventersdorp Supergroup required two minor adjustments, namely:

1) the inclusion of a syngenetic (synsedimentary) pyrite association (SYN) and
2) the allocation of certain diagenetic pyrite textures (e.g., banded and bladed pyrite), which were not observed in the West Rand Group, into the nodular and concretionary category (DIA-5).

It should be noted that the syngenetic and diagenetic pyrite grains in the auriferous conglomerates occur as reworked fragments of earlier sedimentary pyrite aggregates, and not as components formed in situ as reported for the West Rand Group (Guy et al. 2010). Furthermore, many of the delicate pyrite types that were observed in the shales of the West Rand Group were not observed in the conglomerates of the Central Rand Group and lower Ventersdorp Supergroup. These include finely disseminated pyrite (DIA-3), pyrite aggregates (DIA-4), dendritic skeletal pyrite (DIA-7), pyrite laths (DIA-8), phyllosilicate pyrite (DIA-9) and pyrite whiskers (DIA-10). Chert pebbles with bands of finely disseminated pyrite, as documented by Hirdes and Saager (1983), are not included in this classification system since they were not observed during the petrographic examinations. However, this particular type of pyrite will be revisited in the discussion.

Pyrite descriptions

In the descriptions that follow, each type of pyrite will be discussed, with specific reference to pyrite texture, stratigraphic occurrence and other salient aspects, including mechanisms of formation and a review of previous literature (where applicable).

Detrital pyrite

The detrital pyrite association (DET) pertains to pyrite that was initially eroded and transported from an external source area, and then incorporated into the auriferous conglomerates. There are two types of detrital pyrite: compact rounded pyrite (DET-1) and pyrite in composite lithoclasts (DET-2) (Table 1).

Table 1.
Compact rounded pyrite (DET-1) represents inclusion-free, non-porous euhedral pyrite crystals (usually as single crystals; Fleet 1998) that have been rounded to various degrees (Fig. 3a). The average grain size ranges from 0.1 to 1.5 mm in diameter, although grains as small as 10 µm and as large as 5 mm have been documented (Feather and Koen 1975; Utter 1978). The majority of compact rounded pyrite grains identified in this study were less than 0.5 mm in diameter. Detrital grains of compact pyrite and cobaltite are common in the Main, Main Reef Leader, Carbon Leader and Elsburg reefs. Conversely, detrital grains of compact pyrite are less common in hydrothermally altered reefs (e.g., the Middelvlei Reef) and in reefs dominated by reworked sedimentary pyrite grains (e.g., the Beatrix, Kalkoekrans and Ventersdorp Contact reefs). Most authors agree that compact rounded pyrite was derived from an Archean granite-greenstone hinterland (Utter 1978; Hirdes and Saager 1983). However, recent chemical and Pb-Pb isotopic studies have shown that compact rounded pyrite could also represent rounded fragments of diagenetic and/or metamorphic pyrite (Guy et al. 2010; Large et al. 2013). Thus, compact rounded pyrite could have been derived from a variety of geological source areas. It is also acknowledged that an unknown percentage of compact rounded pyrite grains may represent pseudomorphs after detrital iron-oxide/iron-titanium-oxide minerals (Ramdohr 1958; Saager 1970) but also rutile, chlorite, shale, chert, quartz and other lithic fragments (Myers et al. 1993; Zhou et al. 1995). Note that compact rounded pyrite grains were not analyzed for their multiple sulfur isotope compositions since they were not the focus of this investigation (due to small grain sizes and uncertainties relating to provenance).

The second type of detrital pyrite relates to pyrite situated in lithoclasts (DET-2). The designation of this type of pyrite into the detrital paragenetic association is appropriate since the host rock or mineral particle from which it came was lithified, eroded and transported to its current position (Hallbauer 1986; Fig. 7A of England et al. 2002). The term is generally applied when the provenance of the pyrite-bearing lithoclast is equivocal.

**Reworked syngenetic pyrite**

The reworked syngenetic pyrite association (SYN) refers to pyrite that originally formed in the water column or at the sediment-water interface (i.e., synsedimentary pyrite). This contrasts with diagenetic pyrite that formed below the sediment-water interface. There are two types of reworked syngenetic pyrite present in the auriferous conglomerates, namely oolitic pyrite (SYN-1) and fine-grained micro-porous pyrite (SYN-2) (Table 1).

Oolitic pyrite, or concentrically laminated pyrite (SYN-1), are spherical to near-spherical pyrite grains (up to 7 mm in size, Hallbauer 1986) that contain fine concentric pyrite laminae ranging between 5 and 50 µm in size. Some examples may possess a core of radiating pyrite crystals (Fig. 3b, c; Figs. 5A and 15A of England et al. 2002). Oolitic pyrite has been documented from the Vaal, Kimberley, Elsburg, Composite, Ventersdorp Contact and Black reefs (Ramdohr 1958; Utter 1978; Hirdes 1979; Tucker 1980; Hallbauer 1986; England et al. 2002). In this study, oolitic pyrite grains were observed in the Carbon Leader, Middelvlei, Elsburg and Ventersdorp Contact reefs. Petrographic studies reveal the presence of galena, chalcopyrite and gold inclusions within the cortical laminae of the pyrite oolites (Fig. 3d). A replacement origin of precursor carbonate or ironstone ooids has been suggested by previous authors (e.g., England et al. 2002). However, these explanations are unlikely considering that carbonate detritus has not been reported from the auriferous conglomerates and that phyllosilicate minerals occur within the pyrite laminae (Tucker 1980; Agangi et al. submitted; this study). Furthermore, variable δ³⁴S signatures across the cortical envelope would argue against post-depositional sulfidation (England et al. 2002; Schieber and Ricciuto 2005). Schieber and Ricciuto (2005) envisaged that oolitic pyrite formed via the accretion of iron sulfide laminae under shallow burial conditions, which were subject to periods of intermittent reworking, grain abrasion and reburial.

Only one example of fine-grained, micro-porous pyrite (SYN-2) was observed, namely in the Ventersdorp Contact Reef (Fig. 3e, f). The micro-porous pyrite occurs in a laminated pyrite grain. Individual laminae are generally less than 500 µm thick. The pyrite is very fine-grained and contains numerous microscopic pores (~0.5 µm in size), as well as inclusions of galena. These features, together with the absence of siliciclastic mineral inclusions, suggest that pyrite nucleation was rapid and that precipitation occurred from highly supersaturated fluids (Scott et al. 2009). The most interesting feature, however, is the occurrence of micro-spherical structures (Fig. 3f). These micro-spherical structures, which are composed of quartz, are orientated parallel to the pyrite laminae and exhibit a uniform size range between 10 to 20 µm. Although speculative, they may represent pseudomorphs after gaseous fenestrae associated with microbes or decaying organic matter.

**Reworked diagenetic pyrite**

Diagenetic pyrite (DIA) refers to pyrite that formed below the sediment surface after sedimentation but before lithification and metamorphism. Six major types of reworked diagenetic pyrite were observed, namely...
Frambooidal pyrite (DIA-1) was observed in samples from the Vaal, Beatrix and Kalkoenkrans reefs (Fig. 3g). The individual pyrite framboids are relatively large (10 to 20 µm) and together form sizeable aggregates (1 to 2 mm in size). Thin compact overgrowths were commonly observed around the framboids. Putative astolite structures, which are thought to reflect the diagenetic transformation of frambooidal pyrite (England and Ostwald 1993), were observed in the Kalkoenkrans Reef (Fig. 3h). An early diagenetic origin for the frambooidal pyrite is inferred by the large diameter of the pyrite frambooids (~10 µm), as syngenetic framboids that form in euxinic water columns are generally much smaller (<5 µm) (Wilkin et al. 1996; Wilkin et al. 1997). However, the uniform size range of the framboids, their close packing and lack of clastic mineral inclusions may point towards an earlier stage of formation (i.e., syngenetic). Pyrite framboids in carbonaceous chert have also been reported by Hirdes (1979) and Hirdes and Saager (1983) in the Evander gold field. It is interesting to speculate on the source area of the above-mentioned pyrite-chert pebbles, since a greenstone belt provenance has been inferred for much of the detritus in the Kimberley Reef (e.g., a high proportion of BIF pebbles, chromite grains and platinum group minerals; Hirdes and Saager 1983).

Small (<30 µm) euhedral pyrite crystals (DIA-2) were observed in reworked and rounded carbonaceous lithoclasts in the Basal, Vaal, Elsburg and Ventersdorp Contact reefs (Fig. 3i). In situ analogues of this type of pyrite were also observed in carbonaceous shale units from the West Rand Group (Guy et al. 2010) and generally form during the early stages of diagenesis (Taylor and Macquaker 2000).

Pyrite nodules and concretions (DIA-5) constitute the bulk of the reworked and rounded diagenetic pyrite in the auriferous conglomerates (Saager 1970). Volumetrically, pyrite nodules are subordinate to pyrite concretions. Pyrite nodules have been interpreted to form during the earliest stages of diagenesis in shallow burial depths where the sediment is characterized by a high degree of plasticity, high fluid content and an isotropic stress field (Selles-Martinez 1996). The defining criterion for pyrite nodules is the general lack of silicilastic mineral inclusions. Three broad subtypes of pyrite nodules are recognized: a) dendritic, b) bladed, radial and c) banded.

Dendritic pyrite nodules are characterized by cone-in-cone or branching structures, and are common in the Basal (Fig. 3j, k) and Steyn reefs (Fig. 6a of England et al. 2002). Similar in situ dendritic pyrite nodules have been reported from the West Rand Group (Guy et al. 2010) and from Phanerozoic black shale successions (Woodland 1975; Carstens 1985; Carstens 1986; Ruppert et al. 2005).

Bladed and radial pyrite nodules were observed in the Kalkoenkrans, Basal and Ventersdorp Contact reefs (Fig. 3b, l, m), but have also been reported from the Kimberley, Steyn, Composite and Elsburg reefs (Tucker 1980; Hirdes and Saager 1983; Hallbauer and von Gehlen 1983; England et al. 2002; Reimold et al. 2004). Although pyrite can develop extremely elongated habits (Ohiyui and Rickard 2005), previous authors have suggested that the bladed and radial forms of pyrite were initially derived from marcasite that had converted to pyrite during greenschist facies metamorphism (Hallbauer and von Gehlen 1983; Hallbauer 1986; England et al. 2002; Falconer 2003; Falconer et al. 2006). For example, the radial pyrite of Hirdes and Saager (1983, Plate 10E and F) displays a striking resemblance to the radial marcasite of Falconer et al. (2006, Fig. 6D). In this study, marcasite ancestry is supported by the observation of a conspicuous texture that resembles the recrystallized marcasite of Falconer et al. (2006) – compare Fig. 3n and Fig. 54 of Ramdohr (1958) with Fig. 6F of Falconer et al. (2006). Interestingly, abiogenic dissolution or microbial tunneling is documented from one of these samples (Fig. 3o). Alternative explanations for the bladed and radial textures include derivation from massive sulfide deposits and replacement of precursor evaporitic gypsum (England et al. 2002). However, the lack of massive sulfide detritus (e.g., detrital base metal sulfides) and evaporitic gypsum in the Witwatersrand Supergroup, coupled with the recognition of sedimentary equivalents, supports a sedimentary provenance.

Banded pyrite nodules are characterized by various textures associated with growth banding, i.e., the banding does not reflect pyritized sedimentary layers (see replacive pyrite, DIA-12). Banded pyrite nodules have been recorded from the Kimberley, Steyn and Black reefs (Ramdohr 1958; Hirdes and Saager 1983; England et al. 2002). The ‘chevron-textured’ and ‘vein-fill’ pyrite of England et al. (2002) probably represents two varieties of banded pyrite (Fig. 6E of Falconer et al. 2006). In this study, only a small number of banded pyrite nodules were identified from the Kalkoenkrans, Basal and Ventersdorp Contact reefs (Fig. 4a) and only one example of colloform pyrite was observed (Fig. 4b). Interestingly, Ketzer et al. (2003) observed similar colloform pyrites in a paralic sandstone bed overlying coal layers. Hirdes and Saager (1983) and England et al. (2002) suggested that banded pyrite was derived from sulfidic-banded iron formations and volcanogenic massive sulfides, respectively. However, we prefer an early diagenetic origin due to the lack of massive sulfide
An explanatory text about the geology and mineralogy of the auriferous conglomerates and the recognition of comparable early diagenetic pyrite textures in shale, sandstone and conglomerate of different ages (Frizzo et al. 1991; Ketzer et al. 2003; Falconer et al. 2006).

Pyrite concretions, in contrast to pyrite nodules, incorporate the surrounding host rock material by filling in the pore spaces between silicilastic grains (Selles-Martinez 1996). Concretions that form during early diagenesis are characterized by few point contacts between quartz grains, whereas those concretions that form during the latter stages of diagenesis, replace the silicilastic framework (Selles-Martinez 1996). In this study, pyrite concretions were observed in a range of sedimentary rock types, which include sandstone, siltstone and mudstone. Pyrite concretions that formed in sandstone were observed in the Main, Kimberley and Ventersdorp Contact reefs (Fig. 4c). Previous authors have documented this type of pyrite in the proximal facies of several Witwatersrand and Ventersdorp reefs (e.g., quartz-pyrite aggregates of Ramdohr 1958; Hirdes and Saager 1983; Hallbauer 1986). Although Ramdohr (1958) advocated a replacement origin (i.e., of magnetite and hematite quartzite), comparable pyrite and marcasite concretions in recently deposited sandstone and conglomerate suggest a sedimentary origin (Ketzer et al. 2003; Falconer 2003). The bulk of the pyrite concretions in the auriferous conglomerates are characterized by silt-sized quartz grain inclusions and not clay- or sand-sized quartz grain inclusions (Fig. 4d, e). Mineral inclusions such as quartz, chlorite, muscovite, feldspar, rutile and chromite infer a sedimentary protolith. Note that concretions are characterized by mineral inclusions and not round/elliptical pores. (Hence, the frequent usage of the term ‘porous pyrite’ for concretionary pyrite is a misnomer.) Interestingly, polygonal syneresis cracks were observed in one concretion from the Vaal Reef. These cracks subsequently became filled with compact pyrite (Fig. 4f). Pyrite concretions with negligible rounding reflect a local source, but not an in situ origin as suggested by England et al. (2002), since the mineralogy and small size of the inclusions (fine-grained phyllosilicate minerals) is not consistent with their formation in quartz-pebble conglomerates (Fig. 4e and Table 2).

Diagenetic euhedral pyrite crystals (DIA-6) are relatively uncommon in the auriferous conglomerates of the Central Rand Group and Ventersdorp Supergroup. However, it is possible that many of the euhedral pyrite crystals have been rounded to form of compact rounded pyrite grains (e.g., Guy et al. 2010). Only one example was observed from the Carbon Leader Reef as part of a larger reworked composite grain (Fig. 4g; compare with an in situ example in supplementary Fig. S1j).

Diagenetic pyrite overgrowths (DIA-11) are also uncommon in the auriferous conglomerates of the Central Rand Group and Ventersdorp Supergroup. Nevertheless, they were observed as thin coatings (~10 µm) around framboidal pyrite and small euhedral pyrite crystals in the Basal and Kalkoenkrans reefs (Fig. 3g). Diagenetic pyrite overgrowths are generally much smaller than epigenetic overgrowths and occur in sediments that show little evidence of metamorphic/hydrothermal fluid flow.

Replacive pyrite (DIA-12) was observed in a small number of sedimentary lithoclasts in the Kalkoenkrans and Beatrix reefs (Fig. 4h, i, j). There are two types, namely variably-pyritized black shale clasts and ‘mineralized bacteria’. Interestingly, Tucker (1980) found that the former type was common in samples with high gold grades. Historically, the term ‘mineralized bacteria’ has been applied to pyrite morphologies that exhibit small microspherical structures (10-45 µm in size). These structures were interpreted to represent pyritized bacterial colonies or the remains of primitive life forms (Ramdohr 1958; Schidlowski 1965; Saager 1970). However, following the work of numerous authors (e.g., Scott et al. 2009 and references therein), it has become apparent that a large proportion of the ‘mineralized bacteria’ textures represent framboidal pyrite or structures derived from framboidal pyrite (England and Ostwald 1993). Nevertheless, not all of these textures represent pyrite framboids or atoll structures. In one sample from the Beatrix Reef, small 5 to 20 µm-sized elliptical microstructures and wrinkled pyrite laminae were observed (Fig. 4h, i; Figs. 31 and 32 of Saager 1970). These features are consistent with the morphology of bacterial debris (Fig. 3A of Lott et al. 1999) and may represent the pyritized remains of ancient organic material (Bubela and Cloud 1983; Schieber 2002). SEM-EDS analyses of the minerals inside the elliptical structures indicate the presence of quartz, galena, chalcopyrite, Fe-Mg-Mn carbonates, pyrophyllite and muscovite.

**Epigenetic pyrite**

The epigenetic pyrite association (EPI) consists of pyrite that formed after sedimentation and lithification, during regional metamorphism and local hydrothermal events. There are five types of epigenetic pyrite: euhedral crystals (EPI-1), overgrowths (EPI-2), veinslets (EPI-3), replacive pyrite (EPI-4) and pyrrhotite and base metal sulfides (EPI-5) (Table 1). Although epigenetic pyrite is not the primary focus of the investigation, some important observations are noted below.
Euhedral pyrite and pyrite overgrowths (EPI-1 and EPI-2) (both porous and compact) comprise the largest proportion of epigenetic pyrite in the auriferous quartz-pebble conglomerates (Fig. 4k, l). The crystals are generally coarse-grained and can reach several millimeters in size (Feather and Koen 1975). They commonly occur in aggregates, and overgrow compact rounded pyrite grains and reworked sedimentary pyrite grains. They are particularly abundant in reefs that contain an appreciable amount of reworked diagenetic pyrite (e.g., the Basal and Venterdorp Contact reefs). Hirdes and Saager (1983) and Hallbauer and von Gehlen (1983) observed that epigenetic euhedral pyrite crystals in the Kimberley and Venterdorp Contact reefs were commonly associated with local heat sources, such as dykes and lavas of the Venterdorp Supergroup. Similar occurrences were reported from the Promise Formation in the West Rand Group, where epigenetic euhedral pyrite crystals were closely associated with diabase sills and early diagenetic pyrite (Guy et al. 2010; see also Wagner and Boyce 2006). Rounded fragments of putative epigenetic porous pyrite were observed in the Beatrix, Kalkoenkranz, Elsburg, North and Vaal reefs (Fig. 4k), but also in the Basal Reef (Fig. 47 of Saager 1970) and in the Coronation Formation, West Rand Group (Fig. 71 of Guy et al. 2010). In situ analogues of this type of pyrite have been reported from a number of metamorphosed sedimentary successions (Large et al. 2009; Guy et al. 2010; Thomas et al. 2011).

Pyrite veinlets (EPI-3) are relatively uncommon in comparison to euhedral pyrite crystals and pyrite overgrowths. The vast majority of veinlet-associated pyrite occurs in micro-fractures within quartz and chert pebbles (Fig. 4m). However, one sample consisting of brittle and granular pyrite was collected from a major auriferous and carbonaceous vein from the Klerksdorp gold field (Cloete 2009).

Only a small number of replacement textures (EPI-4) were observed during this study (e.g., Reimer and Mossman 1990; Fleet 1998). These include pyrite replacing quartz grains, shale fragments and Fe-Ti oxide minerals from the Basal, Kalkoenkranz and Venterdorp Contact reefs (Fig. 4n). In each case, however, the replacement was partial and the precursor mineral was recognizable. Previous researchers have documented pyrite and pyrrhotite replacing hematite, magnetite, titaniferous magnetite, ilmenite, rutile, phyllosilicates, chert, quartz pebbles and other lithic rock fragments (Ramdohr 1958; Saager 1970; Hirdes and Saager 1983; Phillips et al. 1987; Myers et al. 1993; Phillips and Dong 1994; Zhou et al. 1995; Barnicoat et al. 1997; Phillips and Law 2000). However, some of these examples probably reflect textural varieties of diagenetic pyrite (e.g., the quartz-pyrite aggregates of Ramdohr 1958).

Epigenetic pyrrhotite and base metal sulfides (EPI-5) were rarely observed in this study (Fig. 4o). However, the scarcity of pyrrhotite and base metal sulfides probably reflects the sampling bias towards unaltered reef sections that contained well-preserved sedimentary pyrite grains. Zhou et al. (1995) reported that pyrrhotite was common in the northern parts of the basin (West Rand and Carletonville gold fields) but less common in the East Rand gold field and absent in the Evander and Welkom gold fields. In addition, Zhou et al. (1995) also documented pyrrhotite in areas that were unaffected by contact metamorphism and suggested a regional metamorphic influence. However, a close relationship between pyrrhotite and carbonaceous lithologies in the Witwatersrand Supergroup (Tweedie 1968; Guy 2012) suggests that the pyrite to pyrrhotite transformation may also be linked to the presence of organic carbon and is not only dependent on regional metamorphism (Ferry 1981; Thomas et al. 2011).

Fig. 3.

Fig. 4.

Multiple sulfur isotope data

The δ34S, Δ33S and Δ34S values of the entire sample set range from −6.8 to +13.8‰, −1.7 to +1.7‰ and −3.9 to +0.9‰, respectively (Figs. 5, 6 and Table 2). Sulfur isotope compositions vary according to paragenetic association, pyrite type and depositional environment.

Variation according to paragenetic association

Reworked syngenetic pyrite grains display negative δ34S values (−6.2 to −1.5‰) and small negative Δ33S anomalies (average −0.3‰) (Fig. 5a). In contrast, the majority of reworked diagenetic pyrite grains display more positive δ34S values (most between +0 and +5‰) with variable Δ33S anomalies (−1.7 to +1.7‰) (Fig. 5a). Not all diagenetic samples exhibit positive δ34S values, as a few samples are characterized by negative δ34S values (down to −6.8‰). In addition, reworked diagenetic pyrite grains display much larger Δ34S offsets in comparison
to reworked syngenic pyrite grains (relative to the Archean $\Delta^{34}S/\Delta^{33}S$ array of $-1 \pm 0.2$). Epigenetic pyrites, which include both in situ samples and putative reworked fragments (Fig. 4k), are characterized by highly attenuated $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ values (average $+2.5$, $-0.1$ and $-0.1\%$, respectively) (Figs. 5a and 6a).

Variation according to pyrite type

Connections between sulfur isotope composition and textural pyrite type are most pronounced for oolitic pyrite (SYN-1), fine-grained, micro-porous pyrite (SYN-2), dendritic pyrite nodules (DIA-5), pyrite concretions with sand-sized quartz inclusions (DIA-5) and reworked epigenetic porous pyrite aggregates (EPI-1) (Fig. 5b). However, many other diagenetic pyrite types, such as small euhedral crystals (DIA-2) and concretions with fine-grained mineral inclusions (DIA-5), lack appreciable systematic isotope variation (Fig. 5b).

Oolitic pyrite (SYN-1) yields negative $\delta^{34}S$ excursions (down to $-6.2\%$) and small negative $\Delta^{33}S$ anomalies (average $-0.4\%$) (Fig. 6b, d, i). The single fine-grained, micro-porous pyrite sample (SYN-2) from the VCR exhibits negative $\delta^{34}S$ and negligible $\Delta^{33}S$ values ($-5.2$ and $-0.07\%$, respectively) (Fig. 6e). Dendritic pyrite nodules (DIA-5) are marked by small negative $\delta^{34}S$ values (average $-1.3\%$) but relatively large negative $\Delta^{33}S$ anomalies (average $-1.4\%$). Pyrite concretions with sand-sized quartz grain inclusions (DIA-5) display the most variable $\delta^{34}S$ and $\Delta^{33}S$ compositions ($-6.6$ to $+13.8\%$ and $-0.6$ to $+1.7\%$, respectively) (Fig. 6h). Dendritic pyrite nodules and pyrite concretions with sand-sized quartz grain inclusions also exhibit some of the largest offsets in $\Delta^{36}S$ ($-3\%$). Reworked porous pyrite aggregates (EPI-1) display limited variations in $\delta^{34}S$ and $\Delta^{33}S$, and average $+3.2$ and $-0.02\%$, respectively.

Variation according to depositional environment

Excluding two outliers, reworked sedimentary pyrite grains from the fluvial-dominated Beatrix, Kalkoenkrans and Ventersdorp Contact reefs display low magnitude $\Delta^{33}S$ ($\pm 0.3\%$) and variable $\delta^{34}S$ values ($-6.2$ to $+4.8\%$) (Fig. 5c). Conversely, pyrite grains from the marine-reworked conglomerates of the Main, Vaal and Basal reefs are characterized by a wider range of $\Delta^{33}S$ anomalies ($-1.7$ to $+0.9\%$) and a $\Delta^{33}S/\delta^{34}S$ array that intercepts the $\Delta^{33}S$ and $\delta^{34}S$ axes at $-1.5$ and $+12\%$, respectively (Fig. 5c).

Discussion

Detailed petrographic analysis of the buckshot pyrite from the gold-bearing conglomerates of the upper Witwatersrand and lower Ventersdorp supergroups suggest that the majority of the large pyrite grains were derived from a sedimentary source rock. In the discussion that follows, we expand on this premise and use the multiple sulfur isotope data to provide further constraints on their origin.

Sedimentary provenance for buckshot pyrite

A number of source terranes have been proposed to account for the abundance and startling morphological variety of the large rounded pyrite grains in the auriferous conglomerates of the Witwatersrand and Ventersdorp supergroups. These include volcanogenic massive sulfide deposits, carbonate platforms, evaporites (Hutchinson and Viljoen 1987; England et al. 2002) and sulfidic-banded iron formations (Hallbauer and von Gehlen 1983; Hirdes and Saager 1983; Hutchinson and Viljoen 1987; Koglin et al. 2010). However, the requisite bulk rock detritus from these terranes is conspicuously absent and evidence for pre-burial sulfidation is lacking, e.g., detrital clasts of partially pyritized carbonates were not observed (Myers et al. 1993). Similarly, it is also unlikely that the large quantity of pyrite in the auriferous conglomerates was sourced from Paleoproterozoic granite-greenstone belts, as these typically contain little pyrite (Köppel and Saager 1974; Phillips and Powell 2011). Rather, it may be suggested that the majority of the buckshot pyrite was derived from an intrabasinal sedimentary setting, i.e., that they are of endoclastic origin and were not transported over very long distances (Dimroth 1979; Hallbauer 1986; Large et al. 2013). In support of this interpretation, virtually every single one of the pyrite morphologies observed in the Witwatersrand conglomerates possesses an in situ modern or ancient textural equivalent from a sedimentary setting (Fig. 7). Additional lines of evidence for an intrabasinal sedimentary source includes immature grain shapes, fragile internal textures, siliciclastic mineral inclusions,
presence of shale clasts and trace element compositions (Minter 1976; Dimroth 1979; Hallbauer and von Gehlen 1983; Hirdes and Saager 1983; Hallbauer 1986; Phillips and Law 2000; Agangi et al. submitted; Large et al. 2013). Possible source rocks of this affinity include sediments of the stratigraphically lower West Rand Group and contemporaneous Central Rand Group.

Note that at least two types of rounded pyrite were probably derived from an extrabasinal source area. These include rounded fragments of epigenetic porous euhedral pyrite and pyrite-bearing chert clasts. The former probably reflects a metamorphic provenance and the latter, a greenstone belt provenance (Hirdes and Saager 1983; Phillips and Dong 1994).

Fig. 7.

Geological context of multiple sulfur isotope signatures

Paragenetic association

Links between pyrite paragenesis and multiple sulfur isotope compositions are most pronounced for sedimentary rocks of Archean age — but less so for post-Archean sedimentary rocks that were deposited in more sulfate-rich settings (Kamber and Whitehouse 2007; Partridge et al. 2008; Ono et al. 2009b; Farquhar et al. 2013). This statement holds true for the reworked sedimentary pyrite grains in the Mesoarchean Witwatersrand and Ventersdorp supergroups. More specifically, reworked syngenetic pyrite grains are characterized by sulfur isotope values that plot to the left of the Archean Reference Array (ARA), whereas most of the sulfur isotope values from reworked diagenetic pyrite grains plot to the right of the ARA (Fig. 5a). Ono et al. (2009a) attributed this variation to reflect the openness of the system, where samples that plot to the left of the ARA represent open system conditions (i.e., abundant sulfate supply) and those that plot to the right of the ARA represent closed system conditions below the sediment-water interface (i.e., restricted sulfate supply).

Interestingly, very little data plots along the ARA in the Δ^{34}S-Δ^{33}S plot (Fig. 5a), suggesting either microbial reworking of the primary atmospheric signal (Johnston, 2011), changes in atmospheric photochemistry (Farquhar et al. 2007, Domagal-Goldman et al. 2008), existence of non-photolitic sulfur reservoirs (Guy et al. 2012; Roerdink et al. 2012) or a combination thereof. Similarly, the bulk of the multiple sulfur isotope data in the Δ^{34}S-Δ^{32}S plots below the ARA (Fig. 5a). Whereas syngenetic pyrite displays minor offsets, some diagenetic pyrites are characterized by impressive Δ^{34}S offsets of ~3‰. Deviation from this array can be explained by overprinting of mass-dependent isotope effects (Δ^{32}S/Δ^{34}S of ~6.8; Ueno et al. 2008; Ono et al. 2009b) and/or isotope self-shielding due to increased volcanic SO_{2} loading (Δ^{38}S/Δ^{34}S of ~4.6; Ono et al. 2013). Despite these offsets, the Δ^{34}S/Δ^{32}S ratio of syngenetic pyrite (~1.0) is consistent with the main Archean S-MIF reaction (Fig. 5a) (Kaufman et al. 2007; Ono et al. 2009b; Ono et al. 2013).

Pyrite type

Five morphological types of pyrite reveal unique sulfur isotopic compositions (Fig. 5b). Syngenetic oolitic pyrite (SYN-1) from the Ventersdorp Contact Reef yields relatively large negative δ^{34}S values (~1.5 to ~6.2‰) and weakly negative δ^{33}S values (~−0.4‰) (Fig. 6b, d, i). In addition to relatively large negative δ^{34}S values, England et al. (2002) observed core-to-rim δ^{34}S gradients in oolitic pyrite from the same reef (see their Fig. 15). Similar δ^{34}S gradients have been documented in modern oolitic pyrite laminae (Fig. 10 of Schieber and Riciputi 2005) and point to changes in pore water sulfate concentrations; a feature probably caused by microbial sulfate reduction in an environment subject to short-lived high-energy pulses and sedimentary reworking. In support of a microbial origin, Schieber and Riciputi (2005) found thin sheet-like structures on the cortices of modern pyrite ooids that resembled organic biofilms. They suggested that the biofilms might have facilitated in the precipitation of sulfate minerals by providing an organic substrate for sulfate-reducing bacteria and for acting as a growth template.

Although only one example of syngenetic fine-grained, micro-porous pyrite (SYN-2) was observed, the δ^{34}S value of ~5.2‰ is similar to that of oolitic pyrite (SYN-1) (Fig. 5b). Indeed, the unique textural characteristics of the sample are suggestive of elevated sulfate concentrations that may have enabled microbial discrimination of sulfur isotopes.

In contrast to the oolitic and micro-porous pyrite varieties, diagenetic dendritic pyrite nodules from the Basal Reef (DIA-5) display small δ^{34}S values (~−0.4‰) and relatively large negative δ^{33}S values (~−1.6‰), which plot near the ARA (Fig. 5b). Dendritic nodules from the West Rand Group are also characterized by large negative Δ^{33}S values that plot near the ARA (~3.1 to ~4.0‰, Guy et al. 2012). This implies that these morphological types of pyrite are adept at acquiring large Δ^{33}S fractionations with minimal mass-dependent reworking (Ono et al. 2003; Ono et al. 2009a; Johnston 2011). Although the reasons for this relationship are
unclear, it may be related to rapid disequilibrium precipitation (as indicated by the dendritic growth textures) in a closed system (e.g., Carstens 1985; Carstens 1986; Staudte et al. 2007).

Diagenetic pyrite concretions (DIA-5) with sand-sized quartz grain inclusions reveal a wide range in sulfur isotope compositions, both in relation to δ34S and Δ34S (−6.6 to +13.8‰ and −0.6 to +1.7‰, respectively) (Fig. 5b). These results contrast with the limited fractionation range of pyrite concretions with fine-grained mineral inclusions. The variability of the sulfur isotope signatures could reflect the porous and permeable nature of the host sandstone, i.e., high hydraulic conductivities and open system diagenetic conditions.

Three examples of reworked epigenetic porous pyrite aggregates (EPI-1) from the Beatrix and Kalkoenkranz reefs yield remarkably uniform δ34S and Δ34S compositions (average +3.2 and −0.02‰, respectively) (Fig. 5b). Based on the internal texture of the pyrite, the presence of silicate mineral inclusions and mass-dependent Δ34S values, it could be speculated that these porous aggregates were derived from a source area consisting of metamorphosed sedimentary rocks.

Depositional environment

Links between depositional facies and sulfur isotope compositions have contributed to a better understanding of sulfur cycles in a broader depositional context (Kamber and Whitehouse 2007; Ono et al. 2009a; Guy et al. 2012). Similarly, in the auriferous conglomerates of the Witwatersrand and Ventersdorp supergroups, there are tangible differences between the sulfur isotope ratios of pyrite from fluvial conglomerates and marine-modified fluvial conglomerates (Fig. 5c).

Reworked sedimentary pyrite grains collected from fluvial conglomerates (i.e., the Kalkoenkranz, Beatrix and Ventersdorp Contact reefs) generally yield small Δ34S values (±0.3‰) and variable δ34S values (−6.2 and +4.8‰) (Fig. 5c). With respect to δ34S-Δ34S systematics, two major trends were observed. The first trend is characterized by relatively large negative δ34S values (down to −6.2‰) and small negative Δ34S anomalies (−0.4‰). Such values are indicative of microbial sulfate reduction (Ono et al. 2003; Parquhar et al. 2013) and probably reflect elevated concentrations of sulfate in abandoned fluvial channels, stagnant pools and ephemeral ponds (Fig. 8a). The second trend is characterized by negligible Δ34S anomalies and δ34S values between ~0 and +5‰. This range of δ34S values is typical for crustal (riverine) sulfate today and may signify reservoir effects associated with microbial sulfate reduction (Turchyn et al. 2013) (solid line ‘MSR’, Fig. 8a). Alternatively, it may represent mixing between two sulfur reservoirs, i.e., a juvenile volcanogenic reservoir and a putative crustal mass-dependent reservoir (dashed line ‘V’ to ‘C’, Fig. 8a). Nevertheless, the δ34S composition of this reservoir is comparable to the inferred mass-dependent reservoir observed from fluvial deposits in the middle and upper West Rand Group (‘C’ in Fig. 8b) (Guy et al. 2012). This reservoir was initially interpreted to represent a continental-derived sulfate due to the close association of dampened Δ34S anomalies with early diagenetic pyrite, fluvial braidplain deposits and a foreland basin tectonic setting (Guy et al. 2012). Sulfate was probably supplied to the sedimentary environment via oxidation of sulfide minerals (Reinhard et al. 2009; Leichtarier et al. 2010; Wacey et al. 2011; Stuecken et al. 2012) and/or degassing from subaerial volcanoes (Kump and Barley 2007; Gaillard et al. 2011; Binder and Keppeler 2011; Philipott et al. 2012). Evidence for a terrestrial sulfur flux can be found in other parts of the Kaapvaal and Zimbabwe cratons during the Mesoproterozoic and Neoarchean eras. Reworked pyrite grains of sedimentary origin have been documented from the ~3.1 Ga Dominion Reef (Rantzsch et al. 2011), the ~3.0 Ga Mozana Contact Reef (Saager et al. 1986; Hofmann et al. 2009), the ~2.9 Ga conglomerates of the Uitkyk Formation (Saager and Muff 1986; de Wit et al. 1993; Kröner et al. 2000), the ~2.7 Ga Ventersdorp Contact Reef (Hallbauer 1986; England et al. 2002), the ~2.7 Ga Belingwe greenstone belt (Grassineau et al. 2001; Grassineau et al. 2002; Hofmann et al. 2009) and the ~2.6 Ga Black Reef (Barton and Hallbauer 1996; Hofmann et al. 2009). In contrast, reworked sedimentary pyrite grains are scarce/absent in the chert-dominated conglomerates of the ~3.5 to 3.2 Ga Barberton greenstone belt (Hessler and Lowe 2006; de Wit et al. 2011). A similar narrative applies to the temporal distribution of chert and chert-pyrite clasts in Archean conglomerates on the Kaapvaal Craton (Figs. 3.11C and 4.5D in Guy 2012; Plate 12 of Hirdes and Saager 1983; Fig. 1 of Phillips and Dong 1994).

Fig. 8.

Reworked sedimentary pyrite grains from marine transgressive conglomerates (i.e., the Main, Vaal and Basal reefs) typically yield larger Δ34S values in comparison to pyrite grains from fluvial conglomerates (Fig. 5c). With respect to δ34S-Δ34S systematics, three trends were observed. The first trend relates to the small Δ34S anomalies that overlap with the sulfur isotope compositions of reworked sedimentary pyrite from fluvial conglomerates. This trend probably reflects the incorporation of pyrite from underlying fluvial channels, i.e., pyrite with a crustal signature (Fig. 5c). The second trend is characterized by a positive Δ34S/δ34S array that intercepts the Δ34S and δ34S axes at ~−1.5 and +12‰, respectively (dashed line ‘A’ to ‘M’, Fig. 8a). These end-members have been observed in previous studies and were interpreted to represent two sulfate reservoirs,
namely a mass-independent reservoir derived from photochemical processes (‘A’ in Fig. 8a) (Farquhar et al. 2000, Ono et al. 2003; Ueno et al. 2008) and a mass-dependent reservoir derived from seafloor hydrothermal systems (‘M’ in Fig. 8a) (Bao et al. 2007; Ueno et al. 2008). The occurrence of a similar mass-dependent sulfur reservoir in the marine-dominated parts of the West Rand Group, Witwatersrand Supergroup (Fig. 8b; Guy et al. 2012) and the close compositional fit with Archean barite (Fig. 8c; Bao et al. 2007; Ueno et al. 2008; Roerdink et al. 2012) suggests that this array represents a marine sulfate signature (‘M’) (Fig. 8a). If valid, the preservation of this array is consistent with low levels of sulfate in the Archean ocean (Habicht et al. 2002; Ono et al. 2009a; Jamieson et al. 2012). The third trend is related to the data points that plot to the left of the ARA in the second quadrant (Fig. 8a). Previous studies have interpreted such data as evidence for S^0 disproportionation (Philippot et al. 2007) and oxidation of photochemical sulfur (Kaufman et al. 2007). Alternatively, the data points may also point to mixing between polysulfides derived from an elemental sulfur precursor (Δ^34S>0) and hydrogen sulphide derived from microbial sulfate reducers (Δ^34S<0 and Δ^34S<0) (e.g., Farquhar et al. 2013).

### Conceptual models for sedimentary pyrite formation

Establishing the original depositional setting and source of buckshot pyrite in the auriferous conglomerates has proven problematic since the pyrite segregations have been dislodged from their enclosing sediment. Indeed, published accounts of in situ sedimentary pyrite in the auriferous conglomerates are exceedingly scarce (see Tucker 1980 for two notable exceptions). One explanation could be that the sedimentary pyrite grains were derived from the erosion and reworking of pyrite-bearing strata from the stratigraphically lower West Rand Group. This could have happened during deposition of the Central Rand Group in a shrinking foreland basin with strata of the West Rand Group being exposed along the tectonic margins of the basin. However, such an explanation may only be partly applicable since there is a clear difference in sulfur isotope populations between fluvial and marine-modified conglomerates (Fig. 5c). If the sedimentary buckshot pyrites were exclusively derived from erosion of older strata, then the fluvial and marine-modified conglomerates should have displayed similar sulfur isotope patterns. However, because we see only partial overlap of the data (Fig. 5c), it can be concluded that a major proportion of the buckshot pyrites were formed and reworked during deposition of the two aforementioned conglomerate facies, i.e., they are syndepositional and strictly endoclastic in origin.

Reworked sedimentary pyrite grains with a crustal sulfur isotope signature are interpreted to have formed in a braided fluvial depositional environment, i.e., on the floor of abandoned fluvial channels, stagnant pools and interchannel flats (Tucker 1980; Hailbauer and von Gehlen 1983). In this continental setting, Tucker (1980) suggested that sedimentary pyrite would have formed during periods of quiescence in abandoned channels under low-energy flow conditions. However, during short-lived high-energy pulses, the pyrite would be ripped up and re-deposited. Reworked sedimentary pyrite grains with a marine sulfur isotope signature are interpreted to have formed in sedimentary rocks associated with marine transgressions.

There are, however, many caveats to this model. For instance, it is important to realize that all major auriferous conglomerates in the Witwatersrand Supergroup overlie laterally extensive and very flat erosional unconformities. The conglomerates thus represent retrogradational braided fluvial complexes, sometimes in combination with marine transgressions. It is envisaged that conditions for sedimentary pyrite formation were most favorable when accommodation space in the basin started to increase following degradation and the development of the erosional unconformities (Fig. 9). It is suggested that under such conditions, sedimentary pyrite (carrying the crustal sulfur isotope signature) formed in flooded abandoned fluvial channels and on interchannel flood plains, whereas sedimentary pyrite (carrying the marine sulfur isotope signature) formed in paralic marine embayments (Tucker 1980; Hailbauer and von Gehlen 1983; Saager and Muff 1986; Eriksson et al. 1998). As relative sea levels increased, these deposits were reworked by wave action to form the marine-modified conglomerates. (Fig. 9). This succession of events would help to explain the sheet-like architecture of the major auriferous conglomerates, the pyrite-rich matrix and the deposition of thin quartz arenites overlying many of the auriferous conglomerates (Verrezen, 1987; Catuneanu and Biddulph 2001). Note that the formation of sedimentary pyrite extended into deeper water settings, as evidenced from the Boosens Formation in the Evander gold field, where pyrite layers in carbonaceous shale can be traced for over 23 km (e.g., the upper and lower pyrite markers) (Tweedie 1968; Bailey et al. 1990). The pyrite layers are individually composed of pyrite seams, nodules and concretions that exhibit concentric and radiating growths of pyrite (Tweedie 1968; personal observation). Erosion of such strata, via fluvial or marine processes, would also help to explain the textural variations of pyrite in the auriferous conglomerates (see supplementary Fig. S1 for examples of pyrite textures in black shale) and perhaps provide a source for some of the gold (see Fig. 7.3 of Guy 2012 for an example of a gold-bearing diagenetic pyrite nodule in West Rand Group shale).

In contrast to the retrogradational fluvial conglomerates, it is informative to note that the thick successes of progradational braided fluvial deposits and associated discontinuous lenticular conglomerates formed during periods of decreasing accommodation space in the basin, prior to the development of low angle erosional unconformities (Fig. 9). These progradational fluvial deposits are typically characterized by dispersed
concentrations of buckshot pyrite (e.g., Catuneanu and Biddulph 2001). This observation supports the
conclusion that sedimentary pyrite formed preferentially during periods of increased rates of relative sealevel
rise and drowning of penepalined land surfaces. However, this is not to say that sedimentary pyrite did form not
in progradational fluvial sediments. During degradation and unconformity development, such dispersed
sedimentary pyrite accumulations may have become reworked and concentrated in heavy mineral lags or
pediment deposits along unconformity surfaces.

Fig. 9.

Conclusion

Petrographic and multiple sulfur isotope analyses were carried out on buckshot pyrite grains from auriferous
conglomerates in the Witwatersrand and Ventersdorp supergroups to determine the origin of the pyrite sulfur.
Textural and geochemical constraints indicate that the majority of the buckshot pyrite grains were derived from
a sedimentary provenance and that the wide range of pyrite morphologies are characteristic of sedimentary
pyrite, and not multiple source areas (Dimroth 1979). Forty-five of these reworked sedimentary pyrite grains
were analyzed for their multiple sulfur isotope compositions. The $\delta^{34}S$, $\Delta^{34}S$ and $\Delta^{36}S$ values range from $-6.8$ to
$+13.8_{oo}$, $-1.7$ to $+1.7_{oo}$ and $-3.9$ to $+0.9_{oo}$, respectively. Relationships between $\delta^{34}S$ and $\Delta^{34}S$ point to the
presence of three sulfur reservoirs: 1) mass-independent photochemical $SO_2$ and $S^0$ (data points on the ARA),
2) mass-dependent marine $SO_2$ (positive $\Delta^{34}S/\delta^{34}S$ array in the fourth quadrant) and 3) mass-dependent crustal
$SO_2$ ($\delta^{34}S = -0$ to $+5_{oo}$, $\Delta^{34}S = -0_{oo}$). Of these three, the latter is the most prominent reservoir and implies a
significant contribution of continentally-derived sulfur for most of the pyrite grains in the auriferous quartz
pebble conglomerates. The emergence of a continentally-derived crustal sulfur reservoir may be linked to the
colonization of land by sulfide-oxidizing microbes (Wacey et al. 2011; Stueeken et al. 2012; Turchyn et al.
2013) and/or the advent of modern plate tectonic processes and oxidized volcanic gases (Chaussidon et al. 1989;
Ohmoto and Goldhaber 1997; Kump and Barley 2007; Smithies et al. 2007; Frimmel 2008; Binder and Keppler
2011; Gaillard et al. 2011; Schneiderhan et al. 2011; Philippot et al. 2012; Roerdink et al. 2012). In contrast, the
preservation of a marine sulfur isotope signature (Fig. 8a) is consistent with low levels of sulfate in the Archean
ocean (Habicht et al. 2002; Jamieson et al. 2012) since elevated concentrations of sulfate would have erased the
photochemical signature – producing a $\Delta^{34}S$ trend resembling the modern sulfur cycle (Bekker et al. 2004; Guo
et al. 2009; Johnston 2011). The conclusion that most of the large rounded pyrite grains in the auriferous
conglomerates are of sedimentary and endoclastic origin has important ramifications regarding the cycling of
sulfur during the Archean, but also perhaps for the metallogenesis of gold in the conglomerates. More detailed
sulfur isotope studies, in the context of depositional systems tracts, are required to test the model presented here.

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Pyrite in the Witwatersrand Gold Fields, South Africa. (DIA 1) Small euhedral crystals (DIA 1) with compact pyrite overgrowths (DIA 2). Note scale in f. (4) Pyrrhotite in the Witwatersrand Gold Fields, South Africa. (DIA 2) in a shale clast. (5) Bladed, radiating pyrite nodule (DIA 1) (see arrows). Bright mineral is galena. e, f Fine-grained, micro-porous pyrite (SYN-2). Note scale in f. (5) Reworked diagenetic pyrite, g Framboidal pyrite (DIA-1) with compact pyrite overgrowths (DIA-11). h Putative atoll structures after framboidal pyrite (DIA-1). i Small euhedral crystals (DIA-2) in a shale clast. j Dendritic pyrite nodule (DIA-5) (cone-in-cone). k Branching dendritic pyrite nodule (DIA-5). l Bladed, radiating pyrite nodule (DIA-5). m Bladed pyrite rim on concretion (DIA-5). n Pyrite pseudomorphs after marcasite spheroids? (DIA-5). o Abiotic dissolution/microbial tunneling. Refer to Table 2 for numbers 1 to 7 (top left corner of selected photomicrographs).
conformities due to very flat land surfaces and flooding of river channels and paralic
Transvaal Supergroup).  

Reworked diagenetic pyrite. a Banded pyrite nodule (DIA-5). b Colloform banded pyrite nodule (DIA-
5). Note truncation. c Quartz-pyrite concretion (DIA-5). Note compact cement and sand-sized quartz grains. d
Rounded pyrite concretion (DIA-5). e Fine-grained pyrite concretion (DIA-5). Note lack of rounding. Vertical
line is polishing scratch. f Polygonal syneresis cracks in a rounded pyrite concretion (DIA-5). g Zoned euhedral
pyrite crystals. h, i ‘Mineralized bacteria’ (DIA-12). Note wavy contortions of pyrite laminae. j Pyritized shale
clast (DIA-12).  

Epigenetic pyrite. k Detrital fragment of porous euhedral pyrite (EPI-1, 2). l Compact euhedral
pyrite crystals (EPI-1) and overgrowths (EPI-2). m Pyrite veinlet in quartz pebble (EPI-3). n Partial pyrite
replacement of a quartz grain (EPI-4). o Pyrrhotite enveloping a compact rounded pyrite grain (EPI-5). Refer to
Table 2 for numbers 8 to 13 (top left corner of selected photomicrographs).  

Plots of $\Delta^{33}$S vs. $\delta^{34}$S (‰) and $\Delta^{36}$S vs. $\Delta^{33}$S (‰) for a paragenetic association. b pyrite type and c
depositional environment.  

Hand specimen (4.7 cm in length) from the Ventersdorp Contact Reef. a Pyrite veinlet (EPI-3). b Oolitic
pyrite or concentrically laminated pyrite (SYN-1). c Fine-grained pyrite concretion (DIA-5). d Oolitic pyrite or
concentrically laminated pyrite (SYN-1). e Fine-grained, micro-porous pyrite (SYN-2). f Pyrite concretion
(DIA-5). g Putative replacive pyrite (DIA-12/EPI-4). h Quartz-pyrite concretion. i Oolitic pyrite (SYN-1) with
core of radiating pyrite. Values in permil (‰). Scale bar corresponds to 500 µm.  

Schematic representation of the pyrite types identified in the auriferous conglomerates (left) and
examples of their in situ textural equivalents (right). References: (1) Guy et al. (2010). (2) Black shale specimen

Plots of $\Delta^{33}$S vs. $\delta^{34}$S (‰) for a conglomerates of the Central Rand Group and b non-conglomeratic
sedimentary rocks from the West Rand Group (Guy et al. 2012). Dashed lines indicate reservoir mixing,
whereas solid lines indicate microbial processing (Johnston 2011). c Comparative $\Delta^{33}$S-$\delta^{34}$S data sets of barite
(Bao et al. 2007; Ueno et al. 2008; Roerdink et al. 2012) and reworked sedimentary pyrite from the
Witwatersrand and Ventersdorp supergroups (Hofmann et al. 2009).  

Conceptual models for sedimentary pyrite formation in the upper Witwatersrand and lower Ventsersdorp
supergroups. a Highstand systems tract characterized by high accommodation space, rapid sedimentation and
progradation of braided fluvial systems. Dispersed sedimentary pyrite may have formed in the fluvial and
marine depositional environments. b Late highstand systems tract characterized by increasing degradation and
sedimentary bypassing. Sedimentary pyrite with a crustal signature may have formed in abandoned channels and
ephemeral ponds. c These sedimentary pyrite grains would have been concentrated into heavy mineral lags
during the development of low angle unconformities (e.g., Beatrix, Kalkoenkrans and Ventsersdorp Contact
reefs). d Sedimentary pyrite formation (both with crustal and marine signatures) would have followed the
development of the unconformities due to very flat land surfaces and flooding of river channels and paralic
marine embayments. e These pyrites were then reworked into marine-modified conglomerates during marine
transgressions (e.g., Main, Basal and Vaal reefs).  

Variations in pyrite texture in black shale (Transvaal Supergroup). a Radiating pyrite spheroids (DIA-
5). Note framboid core (DIA-1). b Putative atoll structures (DIA-1). c Spheroidal pyrite nodules (DIA-5).
Compare with Fig. 3n. d Bladed, radiating pyrite (DIA-5). e Banded pyrite (DIA-5). f Fine-grained radiating
pyrite (DIA-5). g, h Pyrite concretion (DIA-5). Note differential pyritization. i, j Euhedral pyrite crystals (DIA-
6). Note zoning in j and compare zoning with Fig. 4g.
## Reworked pyrite in the Witwatersrand

<table>
<thead>
<tr>
<th>QPCs</th>
<th>In situ equivalents</th>
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<tbody>
<tr>
<td>SYN-1 Oolitic</td>
<td></td>
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<tr>
<td>Framboidal</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>Atoll structures</td>
<td><img src="image2.png" alt="Image" /></td>
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<tr>
<td>Small euhehedral crystals</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>DIA-5 Dendritic (cone-in-cone)</td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>DIA-3 Dendritic (branching)</td>
<td><img src="image5.png" alt="Image" /></td>
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<tr>
<td>Bladed, radial</td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Bladed, radial</td>
<td><img src="image7.png" alt="Image" /></td>
</tr>
<tr>
<td>Bladed, radial (marcasite spheroids)</td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>Banded (textural)</td>
<td><img src="image9.png" alt="Image" /></td>
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<tr>
<td>Banded (crystallographic)</td>
<td><img src="image10.png" alt="Image" /></td>
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<tr>
<td>Banded (colloform)</td>
<td><img src="image11.png" alt="Image" /></td>
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<tr>
<td>Concretion (quartz-pyrite)</td>
<td><img src="image12.png" alt="Image" /></td>
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<tr>
<td>Concretion</td>
<td><img src="image13.png" alt="Image" /></td>
</tr>
<tr>
<td>Euhedral</td>
<td><img src="image14.png" alt="Image" /></td>
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<tr>
<td>Replacement (organic material)</td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
<tr>
<td>Replacement (shale)</td>
<td><img src="image16.png" alt="Image" /></td>
</tr>
<tr>
<td>Porous, zonal</td>
<td><img src="image17.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Legend
- Atmospheric sulfur signature
- Volcanic sulfur signature
- Crustal sulfur signature
- Marine sulfur signature

- Pyrite from ~2.9–2.8 Ga Kimberley Reef and Ventersdorp Contact Reef (Hofmann et al. 2009)
- Barite from 3.26–3.23 Ga Fig Tree Group (Bao et al. 2007; Roerdink et al. 2012)
- Barite from 3.41 Ga Kromberg Formation (Roerdink et al. 2012)
- Barite from 3.49 Ga Dresser Formation and 3.55 Ga Theespruit Formation (Ueno et al. 2008; Roerdink et al. 2012)