THE ORIGIN AND PALEOENVIRONMENTAL SIGNIFICANCE OF STRATABOUND BARITES FROM THE MESOARCHEAN FIG TREE GROUP, BARBERTON MOUNTAINLAND, SOUTH AFRICA

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INTRODUCTION

Information on the composition of sea water during the Archean is very limited, with much of the constraints based on the occurrence of bedded barites in Archean greenstone belts in South Africa (Heinrichs and Reimer, 1977; Reimer, 1990), Australia (Lambert et al., 1978; Buick and Dunlop, 1990) and India (Deb et al., 1991). The barites occur as thin discontinuous beds (Heinrichs and Reimer, 1977) and mounds (Nijman et al., 1998) intercalated with chert, carbonates and strongly silicified sedimentary and pyroclastic rocks, deposited in shallow marine settings.

The sulfur isotope geochemistry of these barite deposits has been used to identify sulfur sources, constrain marine sulfate concentrations (Habicht et al., 2002) and stipulate the early emergence of sulfate-reducing microbes (Shen et al., 2001). Strontium isotope ratios of Archaean barites were used by McCulloch (1994) to place an estimate on the initial Sr ratio of the Earth and as support for a hydrothermally-dominated Archean ocean. All of the above assume that barites formed along the sediment-ocean water interface, a conjecture that has remained a topic of controversial discussion. Different authors have suggested deposition as hydrothermal precipitates onto the ancient seafloor (Heinrichs and Reimer, 1977; Nijman et al., 1998), as marine evaporites (Lowe and Nocita, 1999), or as replacement of gypsum evaporites (Lambert et al., 1978, see discussion by Runnegar et al., 2001).

Here, we report on the results of a detailed investigation of stratabound barites in the Mesoarchean Fig Tree Group (Swaziland Supergroup) in the Barberton Mountainland, South Africa. Combining careful field geological and petrographic observations with mineral chemistry, fluid chemistry and isotopic ($\delta^{18}O$, $\delta^{34}S$, $^{87}Sr/^{86}Sr$) data on a set of closely spaced samples, we illustrate that barites are diagenetic, rather than syn-sedimentary in origin, and that they owe their origin to fluid mixing processes very similar to those responsible for the formation of stratabound barite deposits of younger ages (Hanor, 2000).

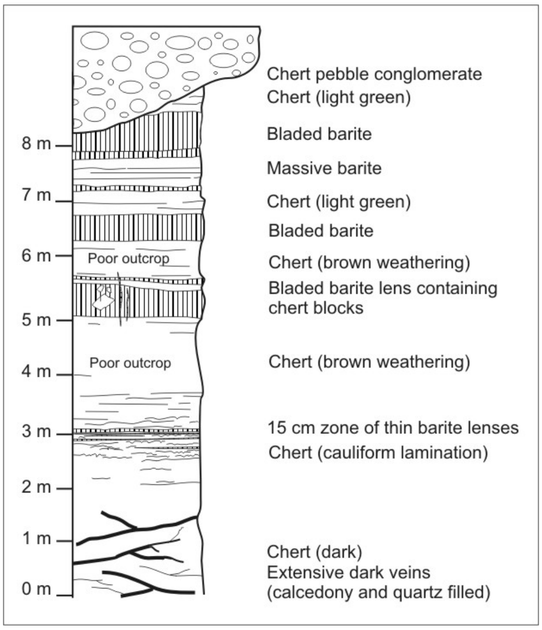

Figure 1. Lithostratigraphic log of section studied at the Conglomerate Quarry Site.

GEOLOGICAL SETTING

Samples were collected along a short profile (Fig. 1) at the Conglomerate Quarry Site (Fig. 1) to the immediate east of the well-documented Barite Syncline (Heinrichs and Reimer, 1977). Barites occur in the lower part of the 3.26-3.23 Ga Mapepe Formation, a variable succession of shale, chert-grit sandstone, and chert-clast conglomerate, interstratified with fine-grained felsic (dacitic) pyroclastic and volcaniclastic rocks, in addition to minor chert and jaspilitic iron formation (Lowe and Knauth, 1977; Lowe and Nocita, 1999). The stratabound barites are associated with strongly silicicfied siliciclastic sequences that constitute fan-delta successions (Lowe and Nocita, 1999).

The studied section is marked by an intimate association of barite with different cherty lithologies, including strongly silicified siliciclastic rock, carbonate-bearing chert and true chert (Fig. 1). Barite occurs in two distinct intervals. The first can be described as thin, discontinuous barite lenses hosted by green chert with indistinct cauliform laminations. This chert overlies strongly silicified siliciclastic rocks that are crosscut by a stockwork of chalcedony-quartz veinlets (Fig. 1). The barite lenses are up to 15 cm thick and filled by coarse white, bladed barite crystals. Distinct palisade textures suggest that these almost monomineralic barite lenses formed by open-space-fill of an already lithified host rock.

Several closely stacked barite-rich units, up to 1 m thick, constitute the second barite-bearing unit in the studied profile. It is separated from the first by an approximately 2 m thick unit of carbonate-bearing chert (Fig. 1). Barite-rich units in this second interval contain fragments of host rock chert; they vary in thickness and can be followed in outcrop for no more than a few tens of meters, suggesting a flat lensoid geometry, rather than a sedimentary bedform.

Medium-grained, massively-textured and very coarse bladed barite are the two most important textural varieties of barite that occur at the studied site. Massive barite has a granular appearance. The barite-rich rock has a green colour that is very distinct from the surrounding chert (Fig. 2). Massively-textured barite is often surrounded by large bladed barite crystals that displace (rather than replace) the bedded chert above and below (Fig. 2).

The distinct green colour of the barite can be attributed to an abundance of Cr-bearing muscovite, and the local occurrence of Fe-silicate. These two silicates form at the expense of chromite and pyrite, respectively. Minute amounts of euhedral and subhedral pyrite occurs enclosed in and along grain contacts of barite blades in a few of the samples.

Barite with coarse-bladed texture occurs as up to 10cm long white barite crystals that constitute sheaf-like aggregates (Fig. 1; detailed description in Heinrichs and Reimer, 1977). Locally, several stages of growth of these barite blades can be distinguished. Preferential compaction around the large barite blades suggests formation prior to final compaction and lithification.

A prominent lens-shaped body of strongly silicified chert-pebble conglomerate defines the top of the studied section. It cuts into and partly erodes the uppermost barite unit. Small cauliflower-shaped aggregates of barite are found along the erosional contact between this conglomerate and light green chert. Petrographic studies also reveal the presence of barite in the strongly silicified conglomerate matrix.

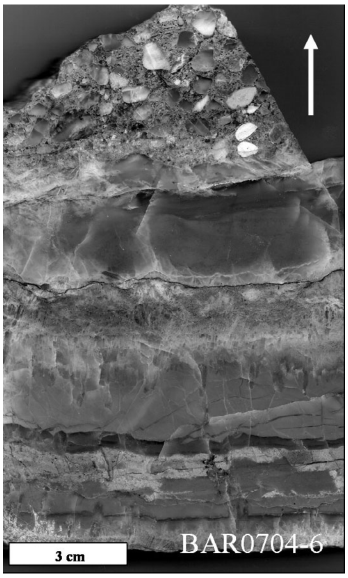

Figure. 2: Thin barite unit enclosed in chert. Euhedral, tabular barite crystals penetrate into chert above and below. Note erosive contact with silicified chert pebble conglomerate. Arrow points in stratigraphic up direction.

MINERAL CHEMISTRY

Energy-dispersive electron microprobe analysis was carried out on 10 samples representing all barite-rich units. On average (N=121), barite was found to contain 64.2±1.1 wt% BaO, 33.9±0.5 wt% SO_3, 1.3±0.7 wt% SrO, 0.8±0.1 wt% Na_2O, and 0.3±0.1 wt% SiO_2. Only SrO yields distinct variations in concentration between different samples. However, these variations appear unrelated to differences in texture or isotopic composition.

ISOTOPE GEOCHEMISTRY

Twelve samples, representing all barite-rich units and mesoscopically recognizable textural types of barite from the studied section were selected for radiogenic ($^{87}Sr/^{86}Sr$) and stable ($\delta^{34}S$, $\delta^{18}O$) isotope analyses. $^{87}Sr/^{86}Sr$ ratios are very similar to values reported for analogous barite occurrences in the Mapepe Formation at other sites (0.7009-0.7017, Strauss, 1993). A tight compositional range is also observed for $\delta^{34}S_{CDT}$ values again in excellent agreement with literature data (3.4±0.3 ‰, Perry et al, 1971). In comparison, $\delta^{18}O_{SMOW}$ values are more variable, ranging from 9.6‰ to 12.7‰ (average: 11.5±0.9‰).

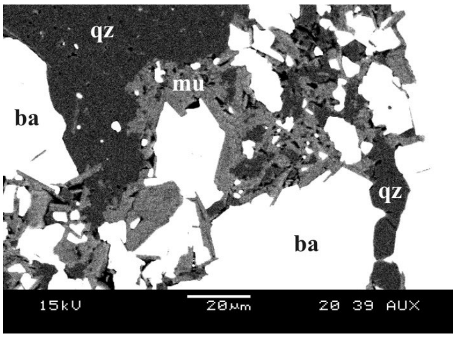

Figure. 3: BSE-SEM image of blocky barite (ba). Note textural relationships that suggest recrystallization or co-genetic formation of barite, quartz (qz) and muscovite (mu).

FLUID CHEMISTRY

Fluid inclusions were studied in seven barite samples. Inclusions are typically <10µm and found as isolated groups, pseudosecondary or occasionally secondary trails. There were no differences in ice melting temperatures between primary and pseudosecondary inclusions. The great majority of the inclusions contain only a single aqueous liquid phase, and those with a vapour bubble probably originated due to leakage. The absence of a vapor phase suggests that barite formed at low temperature, certainly less than 60^{o}C. Salinities determined by microthermometry reveals the presence of two fluids of different salinity, one of high salinity (18-23wt% NaCl$_{equiv}$) and the other of moderate salinity (9-16wt% NaCl$_{equiv.}$). Only one of these fluids was identified in each of the samples studied. The fluids are thought to represent mixtures of two compositional end members, one of very high salinity (≥ 23wt% NaCl), the other one of low salinity (< 9 wt% $_{\text{NaClequiv.}}$).

The fluid composition of single inclusions was analysed by laser ablation ICP-MS (Allen et al. 2005).

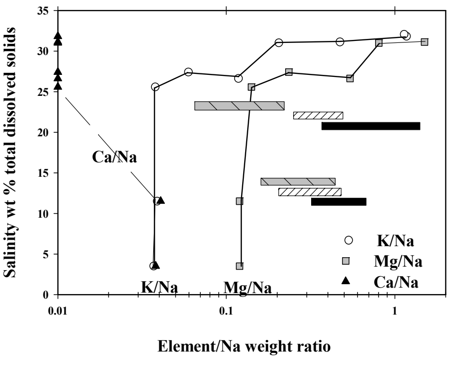

Figure 4: Elemental ratios vs. Na for the high and low salinity fluid inclusions determined by LA-ICP-MS. The evolution of modern seawater, during surface evaporation, is shown for comparison.

The high salinity fluid has K/Na and Mg/Na ratios that would be consistent with evaporation of modern seawater if the salinity was slightly higher (Fig. 4). The lower salinity fluid's composition reflects a contribution from the high salinity fluid that has increased the K/Na and Mg/Na ratios. The Ca/Na ratios in both fluids are inconsistent with seawater evaporation and probably reflect extensive WRI. However it is not impossible that the early oceans were Ca-rich.

DISCUSSION

Modern sea water is saturated in $BaSO_4$ and the precipitation of barite in modern marine environments is attributed to the mixing of sulfate-rich sea water ($[SO_4^{2-}] = 2.8x10^{-2}$ Mol/kg) with sulfate-poor fluids of hydrothermal or diagenetic origin that are enriched in Ba (and Sr) (Hanor, 2000). Large synsedimentary concentrations of barite along the sea floor occur only where barite precipitation is considerably faster than siliciclastic deposition. Alternatively, barite may form along suitable lithological horizons that permit mixing of the two fluid reservoirs in the sub seafloor (McClung et al., in press; Canals et al., 1992).

There is ample evidence that the latter scenario applies to the formation of stratabound barite in the Mapepe Formation at the Conglomerate Quarry site. Field geological and petrographic evidence suggests that thin, laterally discontinuous lenses of coarse crystalline barite at the studied site are of diagenetic origin; barite formation appears to postdate deposition of the host rock succession, but pre-dates final compaction and at least some of the extensive silicification. There is no evidence in favor of replacive formation of barite at the expense of Ca-sulfate evaporites.

The intimate association of barite with Cr-bearing muscovite and chromite suggests that porosity for fluid mixing and barite precipitation was provided by thin Cr-bearing pyroclastic beds, intercalated with less permeable chert beds. The mixing of two low-T aqueous fluids (as recorded by fluid inclusions) along these porous intervals is thought to be a key factor for barite deposition.

Strongly evaporated sea water is regarded as the source for the high-salinity fluid end member identified in barites from the Mapepe Formation. Mesoarchean sea water is thought to have contained no more than $2x10^{-4}$ Mol/kg sulfate (Habicht et al., 2002). This concentration may, however, well have greatly increased during evaporation, without reaching concentrations required for the precipitation of Ca-sulfate (gypsum). Mixing of the evaporated sea water with an aqueous fluid enriched in Ba by water-rock interaction processes in the sub seafloor can explain all of the observed characteristics of barite in the Mapepe Formation.

CONCLUSION

The genesis of Mesoarchean stratabound barite related to diagenetic fluid mixing has profound implications for their paleoenvironmental significance. Diagenetic barite may indeed reflect the sulfur isotope composition of

Mesoarchean sea water, if we assume that the high-salinity fluid is indeed strongly evaporated sea water and the source of sulfate. $^{87}Sr/^{86}Sr$ ratios of barite, on the other hand, can not be expected to reflect the composition of contemporaneous sea water and thus provides no constraint on an early 'hydrothermal ocean' (McCulloch, 1994). Instead, they approach the composition of the source rocks that interacted with the low salinity fluid end member. Possible source rocks are mantle-derived volcanic rocks of the Onverwacht Group and, more importantly, pyroclastic rocks of felsic (dacitic) composition of the basal Fig Tree Group.

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