Isotopic composition of Pongola Supergroup limestones from the Buffalo River gorge, South Africa: constraints on their regional depositional setting

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ABSTRACT
Carbonate samples from exposures of the Pongola Supergroup in the Buffalo River gorge, South Africa, preserve high Sr contents and relatively low Mn concentrations. Some of the Buffalo River gorge samples have substantially higher Sr, lower Mn, lower $^{87}$Sr/$^{86}$Sr and similar $^3$C and $^18$O compositions relative to previously reported Pongola carbonates from the White Mfolozi inlier.

$^3$C values for the Buffalo River gorge samples do not display any variation whereas $^18$O values vary by up to 5 per mil. These variations fall within the trends previously reported for carbonate lithologies from the Pongola Supergroup. The variations noted can not be explained by metamorphic decarbonation reactions but are consistent with fluid/rock exchange systematics involving a fluid such as meteoric water. Water-rock exchange modelling demonstrates that the Sr isotope composition of high-Sr carbonate samples is substantially less prone to change than those of carbon and, particularly, oxygen.

The Sr isotope system in some of the samples probably preserves original sea water signatures. Initial $^{87}$Sr/$^{86}$Sr values at 3 Ga of ~0.70305 indicate formation from Archaean sea water with a large mantle component, consistent with formation of these carbonates in an open-sea environment.

Introduction
The Pongola Supergroup is an Archaean supracrustal succession situated on the Kaapvaal Craton of southern Africa and comprises a lower Nsuze Group overlain by the Mozaan Group. The former group is dominated by lavas whereas the latter consists mainly of sedimentary rocks. Matthews (1990) described the setting of the Pongola Supergroup and recognised, on the basis of lithological and tectonic interpretations, a northern intracratonic, rift-type facies and a southern epicratonic facies. Lavas within the Nsuze Group have been dated at 2985 ± 1 Ma (Hegner et al., 1994) whilst the minimum age of the Mozaan Group is constrained by a date of 2871 ± 30 Ma for the intrusive Usushwana Complex (Hegner et al., 1984).

This paper provides Sr, O and C isotopic data for metamorphosed carbonate lithologies from the southern Nsuze succession (Figure 1).

Sr isotopes in sea water and carbonate sediments
The composition of sea water is preserved in chemical and biochemical precipitates such as carbonate sediments (Veizer, 1984). Analysis of the resulting sedimentary rocks can provide a fairly sensitive indication of whether the water from which they were formed was open to exchange with global marine oceans or not. The three most important sources of Sr entering sea water are:

1) old, high $^{87}$Sr/$^{86}$Sr, continental crust; introduced to the oceans via rivers,

2) newly formed, low $^{87}$Sr/$^{86}$Sr, oceanic crust and fluids interacting with this crust, principally at mid-ocean ridges, and

3) sediments already in the basin, which interact with sea water or with fluids released in subduction zone environments.

Of these three potential sources, the first two are significantly more important in most instances than is the last.

For present-day oceans the average continental contribution ($^{87}$Sr/$^{86}$Sr ~0.711) is more than three times greater than that from the mantle ($^{87}$Sr/$^{86}$Sr ~0.7028), providing a global oceanic $^{87}$Sr/$^{86}$Sr signature of ~0.7092 (Veizer, 1984). If tectonic or structural controls on a
Figure 1. Map showing the locality of the White Mfolozi inlier and Buffalo River gorge relative to the main outcrop of the Pongola Supergroup.
depositional basin restrict the influence of either of the first two sources described above, then the \(^{87}\text{Sr}/^{86}\text{Sr}\) signature within the basin may be substantially different to that expected within open ocean basins. For instance, closed intracratonic basins will have a much lower, if indeed any, contribution from mantle-derived mafic volcanism and the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of water in such depositories should thus be high, close to values expected for average continental crust. Changes in \(^{87}\text{Sr}/^{86}\text{Sr}\) within a depository will occur very rapidly if, for instance, a closed basin becomes open to interchange with marine waters with mixing occurring within timescales of \(\sim 10^3-10^4\) years (Veizer, 1984; Veizer et al., 1989a).

**Alteration subsequent to deposition**

Carbonate minerals (e.g. aragonite or high-Mg calcite) which originally precipitated from sea water may subsequently partially or wholly equilibrate with meteoric water. This meteoric water dissolves the original minerals and reprecipitates low-Mg calcite or dolomite. In the process the isotopic and chemical composition of the carbonate fraction of the rock may change, depending on the relative amounts of the element in the carbonate sediment and meteoric water, the rock/water ratio of the system, and the degree to which they equilibrate. In general, Mn and \(^{87}\text{Sr}/^{86}\text{Sr}\) are higher and Sr lower in meteoric water than in sea water (Veizer et al., 1982) with the result that the former increases whilst the Sr content decreases. Veizer et al. (1982) therefore proposed the use of Mn concentration and the Ca/Sr ratio, together with \(^{87}\text{Sr}/^{86}\text{Sr}\) to identify the least altered of a suite of carbonate sediments. Veizer et al. (1982) included several carbonates from the Pongola Supergroup in their data set and assessed the degree to which they had suffered post-formation alteration. The samples considered in this study were from the Chobeni Formation, Nsuze Group, in the White Mfolozi inlier (Figure 1), the then only known exposures of carbonate lithologies within the Pongola Supergroup. Material considered ranges in chemical composition from dolomite to ferroan dolomite and calcite (Figure 2). Veizer et al. (1982) came to the conclusion that the samples with the lowest Mn content and \(^{87}\text{Sr}/^{86}\text{Sr}\) of \(\sim 0.712\) were “relatively well-preserved” (Veizer et al., 1982, p177). The high \(^{87}\text{Sr}/^{86}\text{Sr}\) in these samples were therefore presumed to indicate an essentially non-marine origin for the carbonate horizons from this locality. Such an interpretation would be consistent with the rift-type setting as suggested by Burke et al. (1985).

**Figure 2.** Plot of molar Mg/(Ca+Mg+Fe+Mn) versus molar Fe/(Mg+Fe+Mn) for samples from the Pongola Supergroup. White Mfolozi inlier data from Veizer et al. (1990). The range in composition of various carbonate minerals is also shown.
and Matthews (1990) although Veizer et al. (1982) noted that a non-marine origin might be difficult to reconcile with certain sedimentological criteria (Von Brunn and Hohday, 1976; Von Brunn and Mason, 1977; Beukes and Lowe, 1989), some of which suggest very large tidal fluctuations within this part of the Pongola depository.

Veizer et al. (1990) subsequently re-interpreted the various Archaean carbonate sediment data and suggested that the isotopic and chemical signatures of the Chobiens Formation samples were extensively altered during low grade regional metamorphism (Figure 2 and Figure 1). It is thus possible that the high $^{87}\text{Sr}/^{86}\text{Sr}$ (>0.711) measured for the Chobeni Formation samples are artifacts of metamorphic exchange with aluminosilicates or with meteoric water and do not reflect the original composition of the basin waters extending into the south eastern limit of Archaean cratonic exposures, Africa (Dixon, thesis in prep.) and are situated close to the south eastern part of the Mesoproterozoic Namaqua-Natal Belt (Figure 1). It is thus possible that the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Pongola samples are artifacts of metamorphic exchange with aluminosilicates or with meteoric water and do not reflect the original composition of the basin waters extending into the north eastern facies of the Pongola depository.

A number of metasedimentary carbonate horizons have recently been identified during mapping of the Buffalo River gorge in northern Kwazulu/Natal, South Africa (Dixon, thesis in prep.) and are situated close to the south eastern part of Archaean cratonic exposures, just north of the Mesoproterozoic Namaqua-Natal Belt (Figure 1). If these horizons were, indeed, deposited in an epicratonic environment and have not been extensively altered by post-depositional events, then their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ought to be substantially lower than those obtained by Veizer et al. (1982) for the White Mfolozi specimens and should be close to values expected from Archaean sea water i.e. about 0.7025 (Veizer, 1984; Veizer et al., 1989; Veizer et al., 1999). Eight samples from these horizons were selected for a combination of Rb-Sr, carbon and oxygen isotope and chemical analysis.

Analytical procedures
Ca, Mg, Fe and Mn concentrations of the carbonate fraction of the samples were determined by atomic absorption spectroscopy after dissolution in 1M HCl.

The stable carbon and oxygen isotope composition of the samples was determined by acid liberation of carbon dioxide from the carbonates using the McCrea (1950) method. This involves the reaction of 5ml 95% phosphoric acid (a large excess) with 50mg of untreated, finely crushed sample. Sample and acid are kept separate in a flask, evacuated, reacted at 25°C and left in a water bath overnight. Experience has shown that this duration of reaction will certainly cause all calcite and aragonite to react, but is not quite long enough to ensure complete reaction of dolomite. The liberated carbon dioxide is transferred in vacuum to a flask through a dry ice cold trap using liquid nitrogen. The CO$_2$ yield from the reaction may be used to calculate the carbonate content of the samples.

Isotope analysis was performed on a SIRA 24 mass spectrometer using dual inlet and multi-collector technology. Calibration was effected by laboratory standards traceable to IAEA NBS 19. Conversion of the VPDB values to VSMOW was done using the equation:

$$\delta^{18}\text{O}_{\text{SMOW}} = 1.03091 \times \delta^{18}\text{O}_{\text{VPDB}} + 30.91$$  \hspace{1cm} (Coplen, 1988)

The stable carbon and oxygen isotope composition of the samples is presented in Table 1 whereas Rb-Sr isotope analyses of the samples are presented in Table 2. Oxygen and carbon isotope data, together with $^{87}\text{Sr}/^{86}\text{Sr}$ (recalculated to the assumed age of the sediments) are presented in Table 3. Sample compositions range from high-Mg calcite to low Fe and high Fe carbonate (Figure 2). Sr/Ca varies from 0.006 to 0.001 with Mn ranging from 518 to 1562 ppm, respectively (Figure 3). The $\delta^{13}\text{C}$ values are constant at +1.6 + 0.5 per mil (PDB) and $\delta^{18}\text{O}$ ranges from 11.3 to 15.3 per mil (SMOW). The carbon isotope values are similar to the ‘best Archaean estimate’ (+1 to +1 per mil PDB) of Veizer et al. (1990) whilst the oxygen isotope ratios of the carbonate fractions of the samples are significantly

| Table 1. Chemical composition of the carbonate fraction for three of the Pongola samples. Analyses by AAS after dissolution in 1M HCl. The average Archaean marine shelf carbonate composition of Veizer et al. (1990) is provided for comparison. |
|---------------------------------|-----|-----|-----|--------------------------|
| **D1** | **D6** | **D10** | **Average shelf carbonate** |
| Ca (wt %) | 24.91 | 27.75 | 24.07 | 22.18 |
| Mg (wt %) | 6.54 | 0.99 | 0.65 | 8.80 |
| Fe (wt %) | 0.08 | 0.28 | 1.58 | 1.15 |
| Mn (ppm) | 1562 | 518 | 875 | 5140 |
lower (~10 to 14 per mil lower than the ‘best estimate’ of ~25 per mil SMOW; Table 3, Figure 4).

**Discussion**

Sr/Ca values in two samples from the Buffalo River gorge are substantially higher than in the carbonates from the White Mfolozi inlier whilst that of dolomite from the former is similar to values obtained at the latter locality (Figure 3). The high Sr concentrations and Sr/Ca ratios in some of the samples analysed suggests original formation as aragonite. Mn concentrations are lower in the aragonite samples and comparable in the dolomite samples (Figure 3).

Carbon and oxygen isotope signatures of carbonate from the Buffalo River gorge samples are similar to those reported by Veizer et al. (1990) for the White Mfolozi inlier (Figure 4). In both cases, the oxygen isotope compositions of the carbonates are substantially lower (by ~7 to 15 per mil) than expected for carbonates precipitated from Archaean sea water (Veizer et al., 1990). Pongola Supergroup carbonate samples from the Buffalo River gorge have more restricted $\delta^{13}C$ and $\delta^{18}O$ isotope signatures than carbonate metasediments from the White Mfolozi inlier but plot on the same trend, suggesting that similar processes may have acted in changing the carbon and oxygen isotope compositions of the carbonate in these samples.

Some estimate of metamorphic temperatures of the Archaean lithologies (including the Pongola Supergroup) from the south-eastern Kaapvaal Craton.
may be obtained from the metamorphic petrology of lithologies and from the Rb-Sr isotope history of mica in various pre-Pongola granitoids (Elworthy et al., 2000). Mineral assemblages generally reflect regional greenschist to lower amphibolite grade metamorphic conditions (Hunter and Wilson, 1988). Biotite Rb-Sr dates indicate that the Archaean rocks within ~25km of the current northern limit of the obducted Proterozoic Namaqua-Natal Belt were heated to temperatures in excess of ~350°C at ~1 Ga but that those further north cooled below this temperature at ~2.6 Ga and were not subsequently substantially reheated (Elworthy et al., 2000). The Buffalo River gorge area falls within the region overprinted at ~1 Ga whereas the White Mfolozi inlier site falls to the north. Since both sets of data have similar oxygen and carbon isotope signatures, variations due to differing metamorphic grade or age of metamorphism do not appear to be a factor.

**Table 3.** Carbon, oxygen and Sr isotopic composition of the carbonate fraction for Pongola samples. C and O analyses were performed by the Quaternary Dating Research Unit at the CSIR and are quoted relative to PDB and SMOW, respectively. \(^{87}\)Sr/\(^{86}\)Sr calculated from data in Table 2 assuming an age of 3000 Ma. The ‘best estimates’ of Veizer et al. (1990) for Archaean marine carbonate compositions are provided for comparison. Percentage carbonate is based on the amount of CO\(_2\) released during stable isotope analysis or the percentage insoluble residue (after dilute HCl dissolution) in cases where stable isotope analyses were not performed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Carbonate</th>
<th>(\delta^{13}C) (per mil PDB)</th>
<th>(\delta^{18}O) (per mil SMOW)</th>
<th>(^{87})Sr/(^{86})Sr (best estimate) (±95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1.5.10</td>
<td>70</td>
<td>+1.2</td>
<td>11.3</td>
<td>0.72468 ± 7</td>
</tr>
<tr>
<td>D6.18.4</td>
<td>67</td>
<td>+2.0</td>
<td>14.5</td>
<td>0.70305 ± 7</td>
</tr>
<tr>
<td>D10.6.9</td>
<td>53</td>
<td>+2.1</td>
<td>13.8</td>
<td>0.70454 ± 7</td>
</tr>
<tr>
<td>D1.7.91</td>
<td>70</td>
<td>+1.5</td>
<td>15.3</td>
<td>0.71847 ± 7</td>
</tr>
<tr>
<td>D2.7.91</td>
<td>70</td>
<td>+1.6</td>
<td>12.6</td>
<td>0.71471 ± 7</td>
</tr>
<tr>
<td>D1</td>
<td>61</td>
<td></td>
<td>0.73142 ± 7</td>
<td></td>
</tr>
<tr>
<td>D6</td>
<td>74</td>
<td></td>
<td>0.70327 ± 7</td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>55</td>
<td></td>
<td>0.70446 ± 7</td>
<td></td>
</tr>
<tr>
<td>Best Archaean</td>
<td>±0.9 ± 2.1</td>
<td>24.7 ± 1</td>
<td>&lt; 0.7033</td>
<td></td>
</tr>
<tr>
<td>NBS 19</td>
<td>1.95</td>
<td>28.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.** Variation of \(\delta^{18}O\) relative to \(\delta^{13}C\) for Pongola carbonates. Data from White Mfolozi inlier and labeled fields are from Veizer et al. (1990). Large plus symbol denotes the ‘best estimate’ of pristine Archaean marine carbonate compositions (Veizer et al., 1990). Tick line illustrates the anticipated decrease in carbon and oxygen isotope composition of carbonate material associated with batch decarbonation (Valley, 1986). Tick marks on this curve are at 20% increments of weight percent carbonate.
Figure 5. Variation of $\delta^{13}$C relative to weight percent carbonate in Pongola carbonates. Data from White Mfolozi inlier are from Veizer et al. (1990). Sample symbols as in Figure 2. Black dot with error bars denotes the ‘best Archaean estimate’ of Veizer et al. (1990). Thick lines illustrate the anticipated decrease in carbon isotope composition of carbonate material associated with batch and Rayleigh decarbonation (Valley, 1986). Tick marks on these curves are at 20% increments.

Figure 6. Variation of $\delta^{18}$O relative to weight percent carbonate in Pongola carbonates. Data from White Mfolozi inlier are from Veizer et al. (1990). Sample symbols as in Figure 2. Black dot with error bars denotes the ‘best Archaean estimate’ of Veizer et al. (1990) for marine carbonate. Thick lines illustrate the anticipated decrease in oxygen isotope composition of carbonate material associated with batch and Rayleigh decarbonation (Valley, 1986). Tick marks on these curves are at 20% increments of weight percent carbonate.
alone (Valley, 1986). Figure 4 also illustrates the substantial shift in $\delta^{18}O$ relative to that expected for batch-style decarbonation of a calc-silicate lithology.

The mineralogy of the samples is also inconsistent with metamorphic decarbonation of the samples. In all cases where silicate minerals occur, these are dominated by quartz and minerals such as forsterite and diopside, expected products of decarbonation reactions, are rare. It would seem therefore that, in addition to minor decarbonation reactions due to metamorphism, there has also been modification of the isotope composition of the carbonates due to fluid flow. The processes involved appear to have influenced the oxygen isotope signature more than that of carbon whilst the extent of Sr isotope change seems variable. Whilst this might simply be a case that the isotope signatures of rock and fluid were very dissimilar for oxygen and quite similar for carbon, the variation noted in $\delta^{13}C$ appears to be typical of many regionally metamorphosed terranes in which substantial fluid-rock exchange has occurred (Valley, 1986). Modelling of fluid-rock exchange for carbonate lithologies using techniques developed for advective-dispersive systems (Bowman and Willett, 1991; Bowman et al., 1994; Johnson and DePaolo, 1994b) indicates that the oxygen isotope signature is likely to change before that of carbon and that, of the three isotope systems measured in the present study, strontium will be the most resistant to change. Carbonate rocks dominated by calcite will be less resistant to Sr isotope exchange than those containing aragonite. These relationships are illustrated in Figure 8 which is a plot of (fluid velocity)/(reaction rate) versus Damköhler number. The latter variable is a dimensionless quantity which is characteristic of a specific fluid-rock exchange system. Johnson and DePaolo (1994b) define it as:

$$N_D = \frac{1}{M} \frac{R_d}{v \cdot R_s}$$

where

- $l$ is the characteristic scaling distance for a system
- $M$ is a function of the rock porosity and degree of pore space saturation
- $v$ is the average fluid velocity
- $R_d$ is the average reaction rate for rock-fluid interaction for the isotope of interest
- $c_s$ is the concentration of the isotope in the reacting solid
- $c_f$ is the concentration of the isotope in the fluid

Differences in Damköhler number are dominated by the relative concentrations of the element of interest in the solid to that in the fluid i.e. by $c_s / c_f$.

As noted earlier, Mn concentrations are lower in the ‘aragonite’ samples than in those comprising calcite and dolomite, consistent with a lower degree of alteration of the former. Together, these features indicate that,
although fluid flux through the Buffalo River gorge succession has been sufficient to alter both the oxygen and carbon isotope signature, it has been insufficient to reset the Sr isotope composition of the high Sr, ‘aragonite’ samples i.e. those with high Damköhler numbers. Dolomitic and calcitic samples, which originally had lower Sr contents and thus lower Damköhler numbers, have, however, been altered. Two of the Buffalo River gorge samples preserve 87Sr/86Sr values (calculated at 3 Ga) of 0.70305±7 to 0.70327±7. These samples are also amongst those with the highest Sr contents (Table 2). Neither Sr concentration, nor 87Sr/86Sr show any correlation with the proportion of insoluble residue (Figure 7). As previously noted, the effects of alteration will typically raise the 87Sr/86Sr of the carbonate whilst lowering the Sr concentration. The least radiogenic, highest Sr concentration composition of a suite of samples will thus provide the closest approximation to the original sea water composition. In the case of the carbonate specimens analysed from the Buffalo River gorge, the relevant values are thus 1680 ppm Sr and 87Sr/86Sr=0.70305±11, the latter being significantly lower than for carbonates from the White Mfolozi inlier (Veizer et al., 1982). The low 87Sr/86Sr and high Sr concentrations in two of the samples analysed suggest original formation as aragonite with extensive contributions of ‘mantle-derived’ Sr to the water of the depository. The 87Sr/86Sr of 0.70305 ± 7 at 3 Ga is slightly raised relative to the estimates of Veizer et al. (1989b) for Archaean sea water, based on carbonates from greenstone belts and is somewhat higher than a value of 0.70128 obtained for high Sr marble from the late Archaean Ramagiri schist belt in the Dharwar craton of south India (Zachariah, 1998). It is, as far as we are aware, the lowest value yet recorded for Archaean shelf carbonates, albeit only slightly lower than that reported by Veizer et al. (1990) for shelf carbonates from the ~2.5 Ga Hammersley Group in Australia.
Conclusions

High $^{87}\text{Sr}^{86}\text{Sr}$ signatures of the carbonate sediments from the Chobeni Formation exposures in the White Mfolozi inlier may be due to deposition within an intracratonic, non-marine environment as inferred by Veizer et al. (1982), which is consistent with the intracratonic, rift-type setting model of Matthews (1990). Alternatively, the high $^{87}\text{Sr}^{86}\text{Sr}$ in these samples could be due to extensive alteration during low grade metamorphism as suggested by Veizer et al. (1990). In contrast, carbonate samples from the Buffalo River gorge provide clear evidence for a marine origin with $^{87}\text{Sr}^{86}\text{Sr}$ values and Sr concentrations similar to those expected for Archaean carbonate sediments with a large component of mantle strontium. Oxygen and carbon isotope signatures of ‘aragonite’, calcite and dolomite in these carbonate metasediments display a greater range in composition than can be explained by decarbonation processes and the mineralogy of the silicate component of the samples is also not consistent with extensive decarbonation. Variation in these two isotope systems is best explained by fluid-rock exchange. The extent of fluid flux through the various carbonate metasediments of the Pongola Supergroup has been sufficient to modify the oxygen and carbon isotope signature of all samples as well as the Sr isotope ratio of samples dominated by dolomite or calcite but not those which are thought to have originated as aragonite.

References


