

# 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  $^{87}\text{Sr}/^{86}\text{Sr}$  and similar  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions relative to previously reported Pongola carbonates from the White Mfolozi inlier.

$\delta^{13}\text{C}$  values for the Buffalo River gorge samples do not display any variation whereas  $\delta^{18}\text{O}$  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  $^{87}\text{Sr}/^{86}\text{Sr}$  values at 3 Ga of  $\sim 0.70305$  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 Nsuzi 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 Nsuzi Group have been dated at  $2985 \pm 1$  Ma (Hegner *et al.*, 1994) whilst the minimum age of the Mozaan Group is constrained by a date of  $2871 \pm 30$  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 Nsuzi succession (Figure 1).

## Sr isotopes in sea water and carbonate sediments

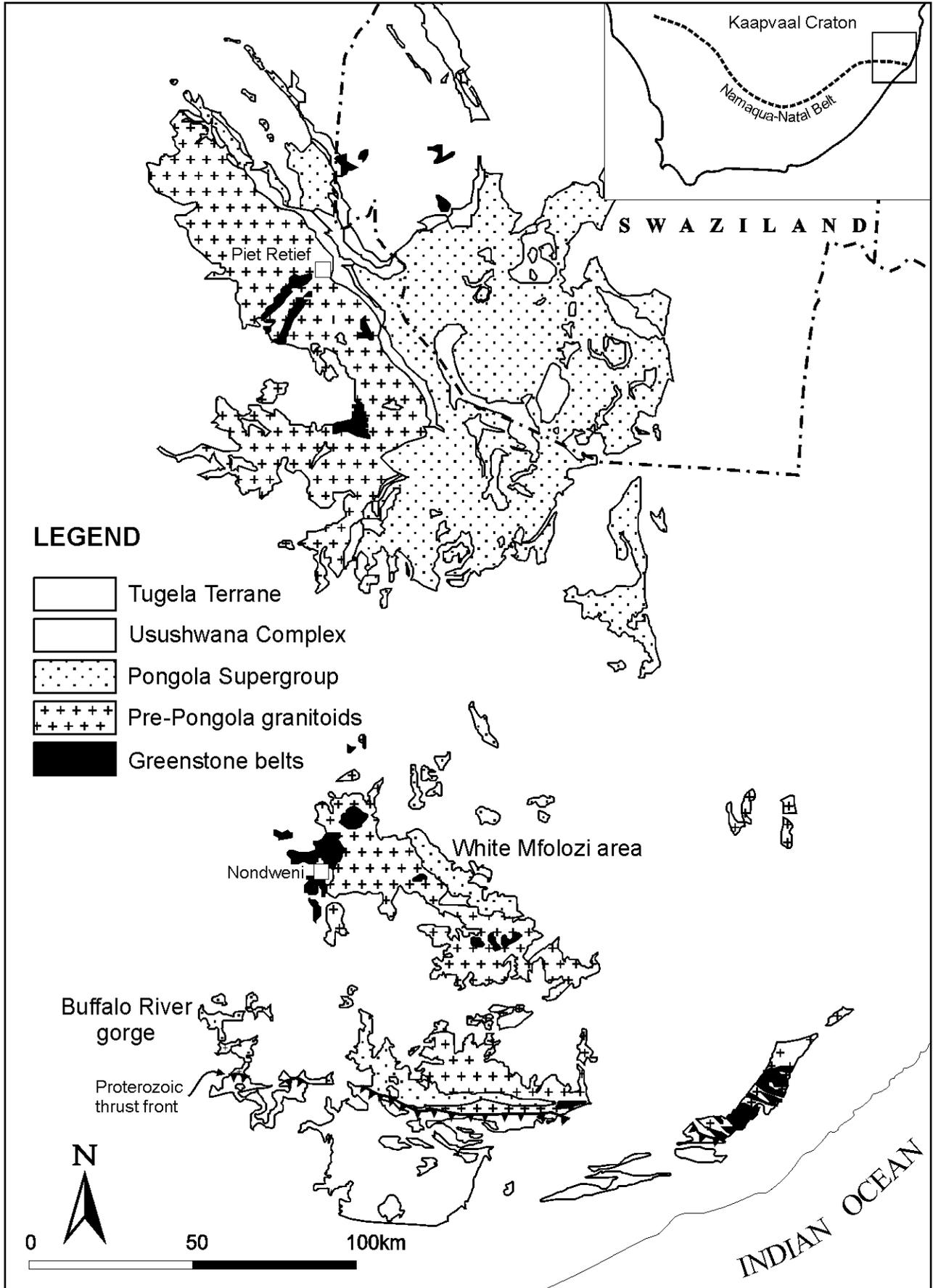
The composition of sea water is preserved in chemical and biochemical precipitates such as carbonate

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:

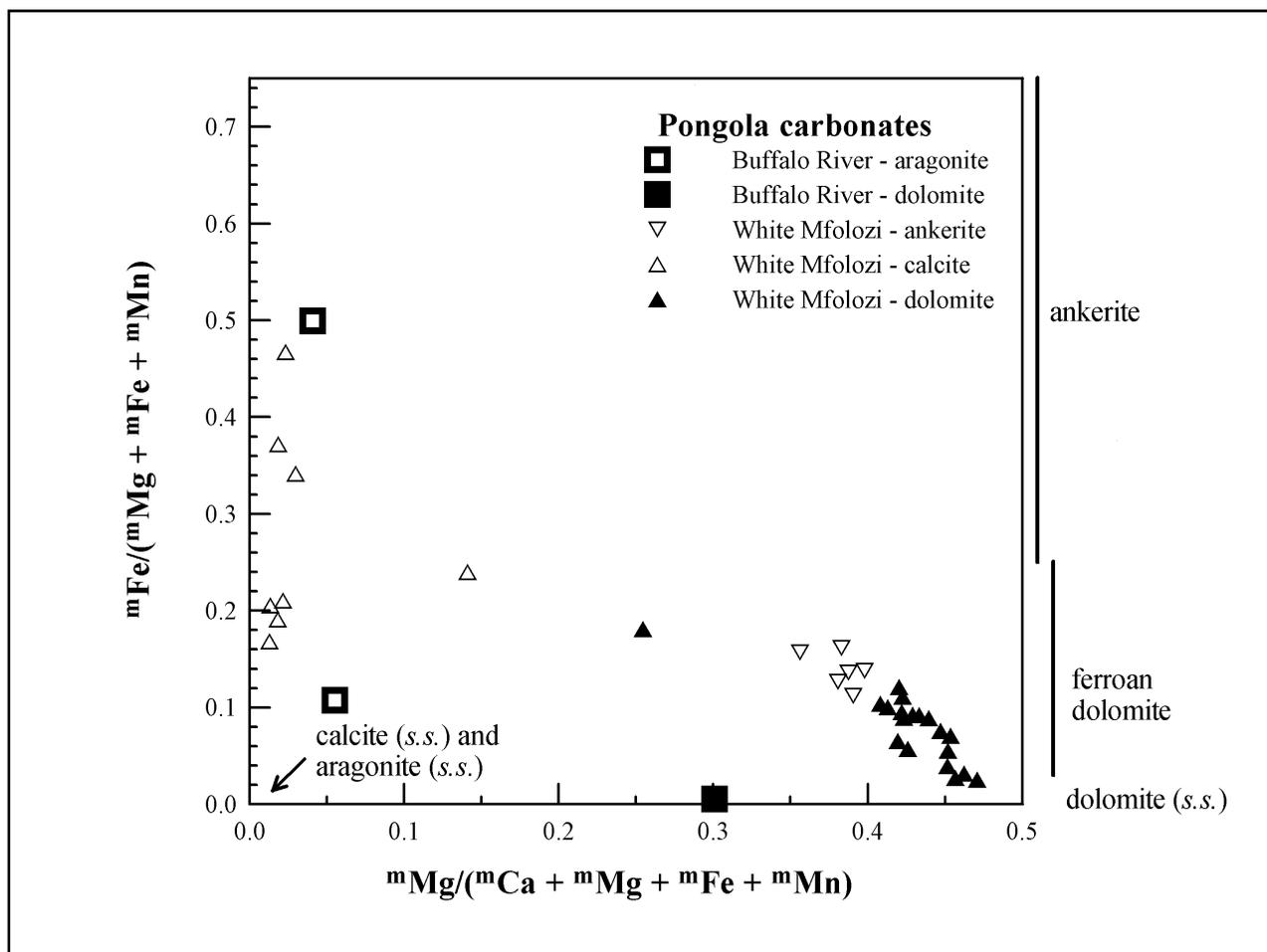
- 1) old, high  $^{87}\text{Sr}/^{86}\text{Sr}$ , continental crust; introduced to the oceans via rivers,
- 2) newly formed, low  $^{87}\text{Sr}/^{86}\text{Sr}$ , oceanic crust and fluids interacting with this crust, principally at mid-ocean ridges, and
- 3) sediments already in the basin, which interact 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 ( $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.711$ ) is more than three times greater than that from the mantle ( $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7028$ ), providing a global oceanic  $^{87}\text{Sr}/^{86}\text{Sr}$  signature of  $\sim 0.7092$  (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.



**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.

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, Nsuzze 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)

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 Hobday, 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 Chobeni 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 within the northern 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 limit 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.*, 1989b; Veizer *et al.*, 1990). 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  $\text{CO}_2$  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:

$$\delta^{18}\text{O}_{\text{SMOW}} = 1.03091 * \delta^{18}\text{O}_{\text{PDB}} + 30.91 \quad (\text{Coplen, 1988})$$

Overall accuracy of the carbon and oxygen isotope analyses is estimated to be 0.1‰ (1 $\sigma$ ).

Small pieces of rock specimen were placed in polypropylene microcentrifuge tubes. 1M HCl was added and the tubes placed in an ultrasonic bath for 10 minutes to dissolve the carbonate fraction. After centrifuging, the supernate was transferred to Savillex™ teflon beakers and spiked with enriched tracers of  $^{84}\text{Sr}$  and  $^{87}\text{Rb}$ . Rb and Sr were separated using standard cation exchange techniques on AG50Wx12 resin. Rb was analysed using double Ta filaments on a Micromass MM 30 thermal source mass-spectrometer whereas the Sr was analysed using single Ta filaments on a VG 354 thermal source mass-spectrometer using three collectors in peak-jumping mode. All Sr ratios were normalised to  $^{86}\text{Sr}/^{88}\text{Sr}=0.1194$  (Steiger and Jäger, 1977) and are quoted relative to an NIST SRM 987 value of  $0.71027 \pm 4$  (95% confidence). Analytical precision is better than 0.005% (1 sigma) for  $^{87}\text{Sr}/^{86}\text{Sr}$  and 0.5% (1 sigma) for  $^{87}\text{Rb}/^{86}\text{Sr}$ .

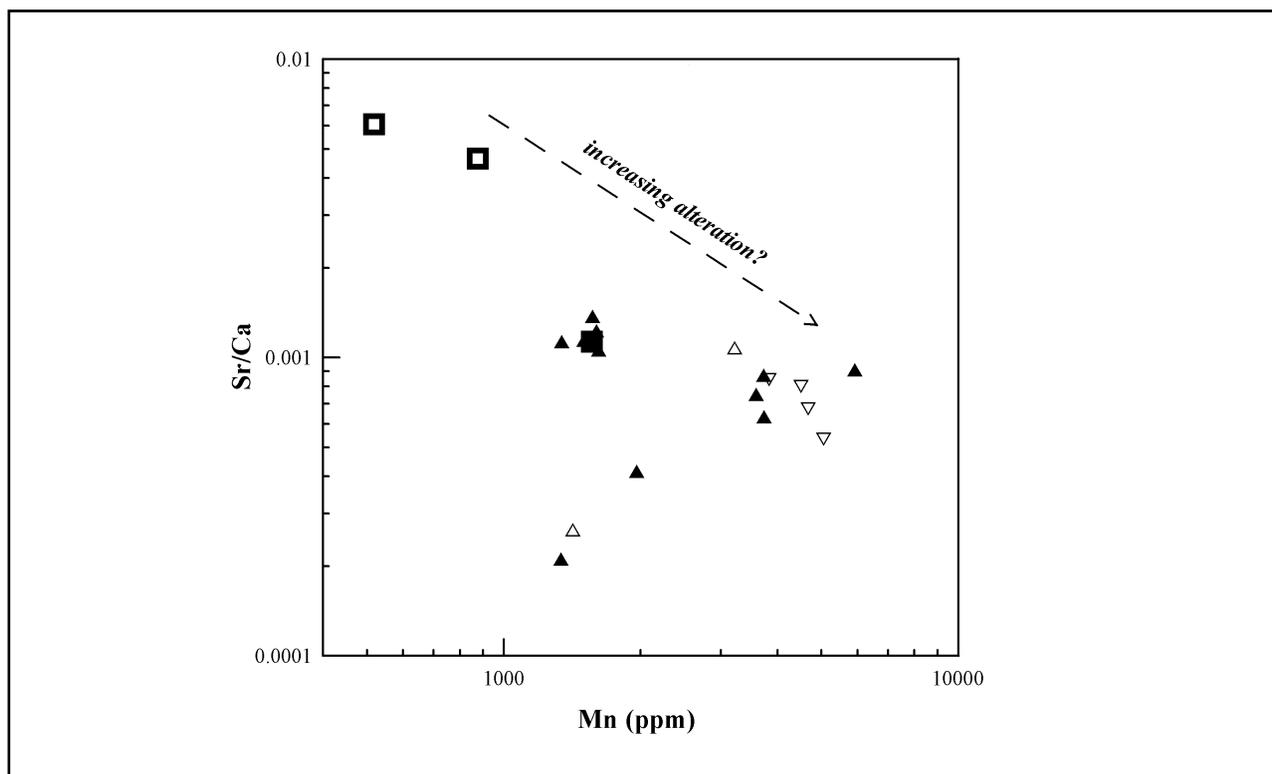
Subsequent data processing was by means of the GEODATE package of Eglinton and Harmer (1999; 2000). The decay constant used for  $^{87}\text{Rb}$  is  $1.42 \times 10^{-11} \text{ a}^{-1}$  (Steiger and Jäger, 1977). Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  has been calculated assuming that the carbonates formed at 3 Ga, slightly older than the date obtained by Hegner *et al.* (1994) for lavas near the top of the Nsuze Group in southern Swaziland.

### Results

Ca, Mg, Fe and Mn concentrations of the soluble fraction of the samples are 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 calcium 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  $+1.6 \pm 0.5$  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' ( $\sim +1$  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	27.73	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



**Figure 3.** Plot of Mn concentration versus Sr/Ca ratio, illustrating the variation amongst the Pongola carbonate samples. In general, alteration of carbonate samples leads to an increase in Mn content and decrease in Sr/Ca (Veizer *et al.*, 1990). The Buffalo River carbonate samples have markedly higher Sr/Ca and lower Mn contents than samples from the White Mfolozi inlier. Symbols as in Figure 2.

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  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  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

**Table 2.** Rb-Sr isotope results for the carbonate (1M HCl soluble) fraction of sedimentary carbonate samples from the Buffalo River gorge, northern Natal, South Africa.

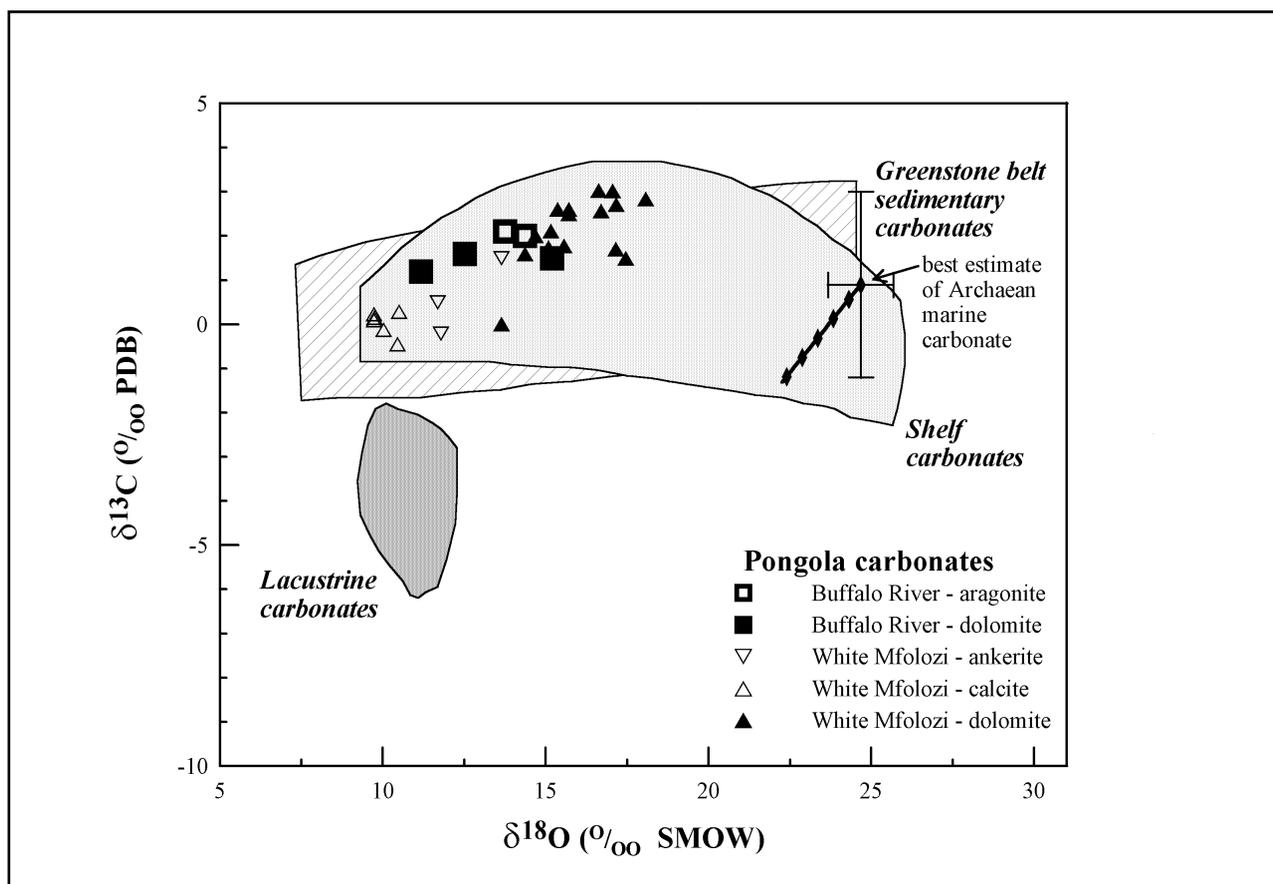
Sample	Rb	Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2 \text{ s.e.m.}$	% insoluble residue
D1.5.10	0.154	297.8	0.0015	0.724748 + 10	33
D6.18.4	0.011	1018	0.00003	0.703053 + 11	27
D10.6.9	0.332	913.0	0.0011	0.704590 + 12	51
D1.7.91	0.213	243.0	0.0025	0.718584 $\pm$ 10	29
D2.7.91	0.074	399.3	0.0005	0.714731 $\pm$ 12	30
D1	0.150	282.1	0.0015	0.731482 $\pm$ 21	39
D6	0.012	1680	0.00002	0.703274 $\pm$ 16	26
D10	0.340	1118	0.0009	0.704496 $\pm$ 15	45

**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.  $^{87}\text{Sr}/^{86}\text{Sr}$  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  $\text{CO}_2$  released during stable isotope analysis or the percentage insoluble residue (after dilute HCl dissolution) in cases where stable isotope analyses were not performed.

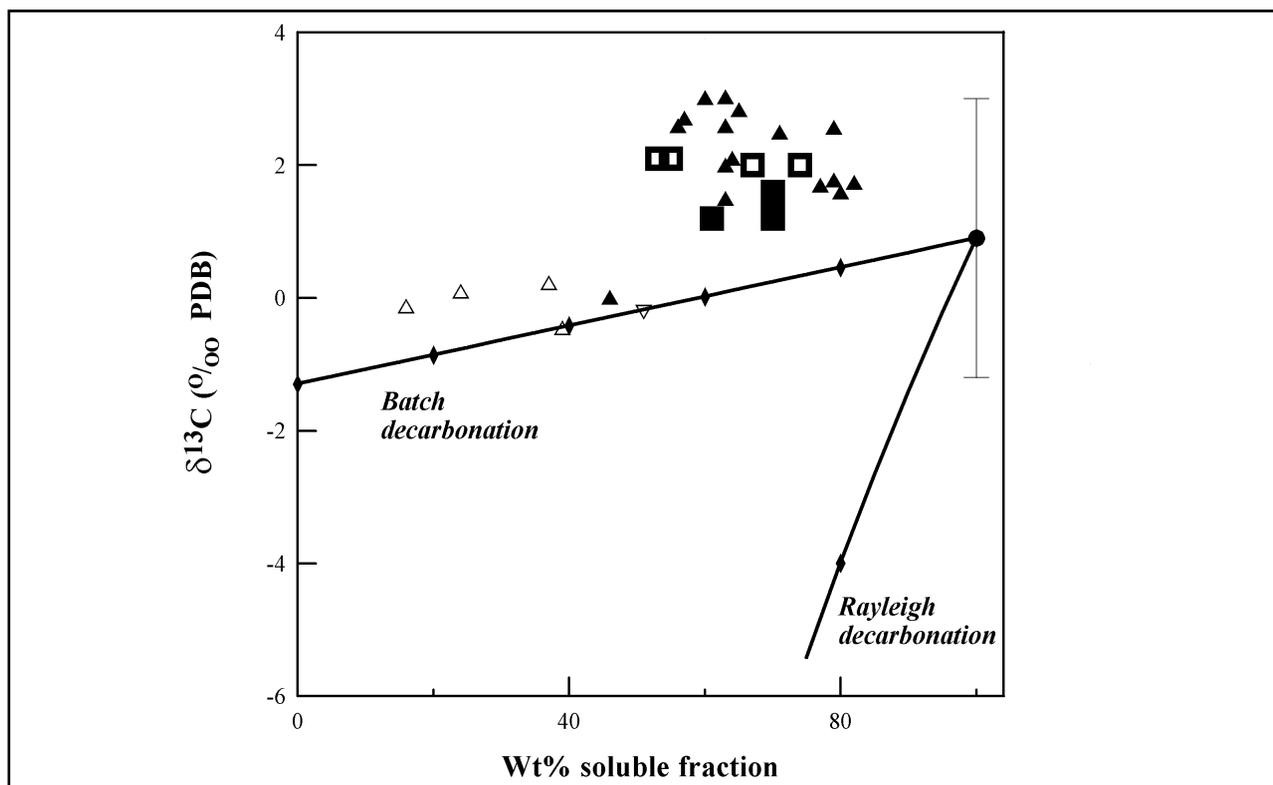
	% carbonate	$\delta^{13}\text{C}$ (per mil PDB)	$\delta^{18}\text{O}$ (per mil SMOW)	$^{87}\text{Sr}/^{86}\text{Sr}_{3000\text{Ma}}$ ( $\pm 95\%$ )
D1.5.10	70	+1.2	11.3	$0.72468 \pm 7$
D6.18.4	67	+2.0	14.5	$0.70305 \pm 7$
D10.6.9	53	+2.1	13.8	$0.70454 \pm 7$
D1.7.91	70	+1.5	15.3	$0.71847 \pm 7$
D2.7.91	70	+1.6	12.6	$0.71471 \pm 7$
D1	61			$0.73142 \pm 7$
D6	74			$0.70327 \pm 7$
D10	55			$0.70446 \pm 7$
Best Archaean		$\pm 0.9 \pm 2.1$	$24.7 \pm 1$	$< 0.7033$
NBS 19		1.95	28.6	

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.

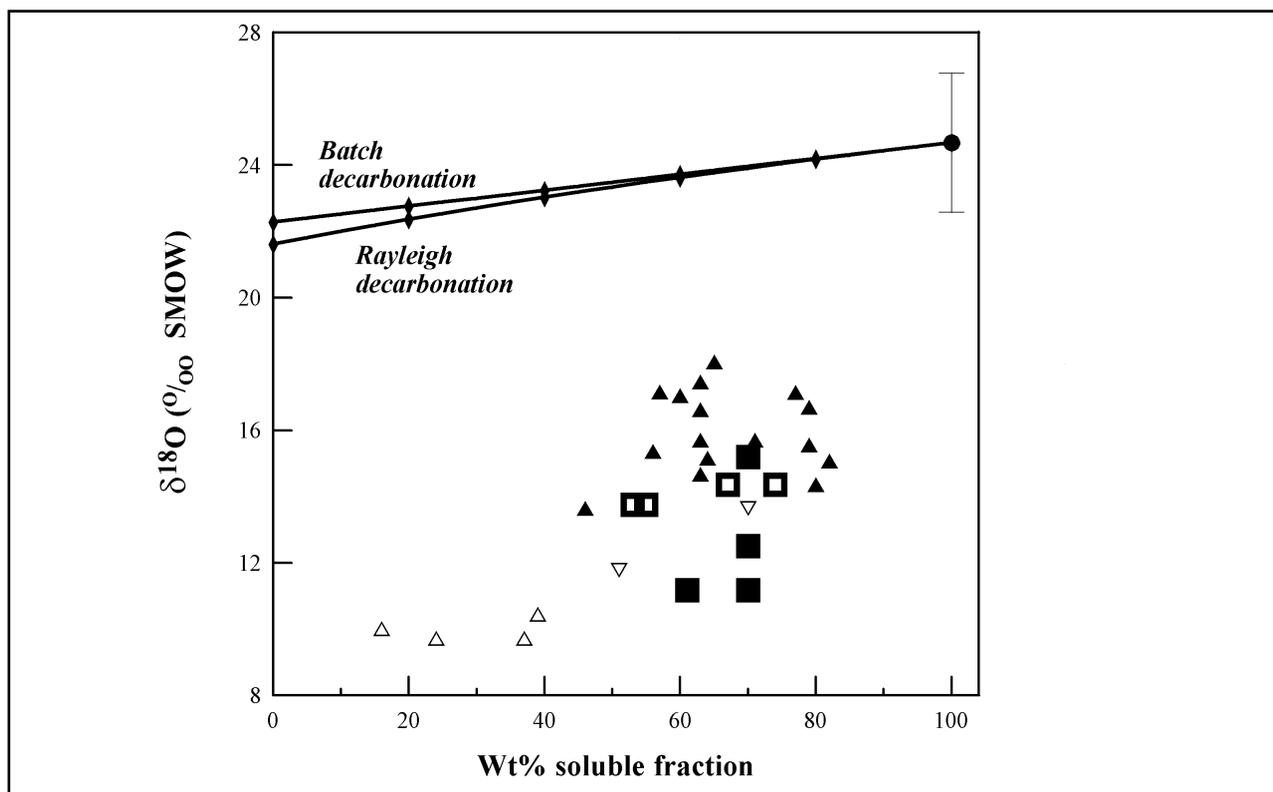
Figure 5 illustrates the expected variation in  $\delta^{13}\text{C}$  relative to carbonate content of the samples and of theoretical modelling of decarbonation reactions which follow batch and Rayleigh processes (Valley, 1986). Whilst the variation in  $\delta^{13}\text{C}$  is reasonably consistent with a decarbonation process, there is a far greater change in  $\delta^{18}\text{O}$  (Figure 6) than can be explained by decarbonation



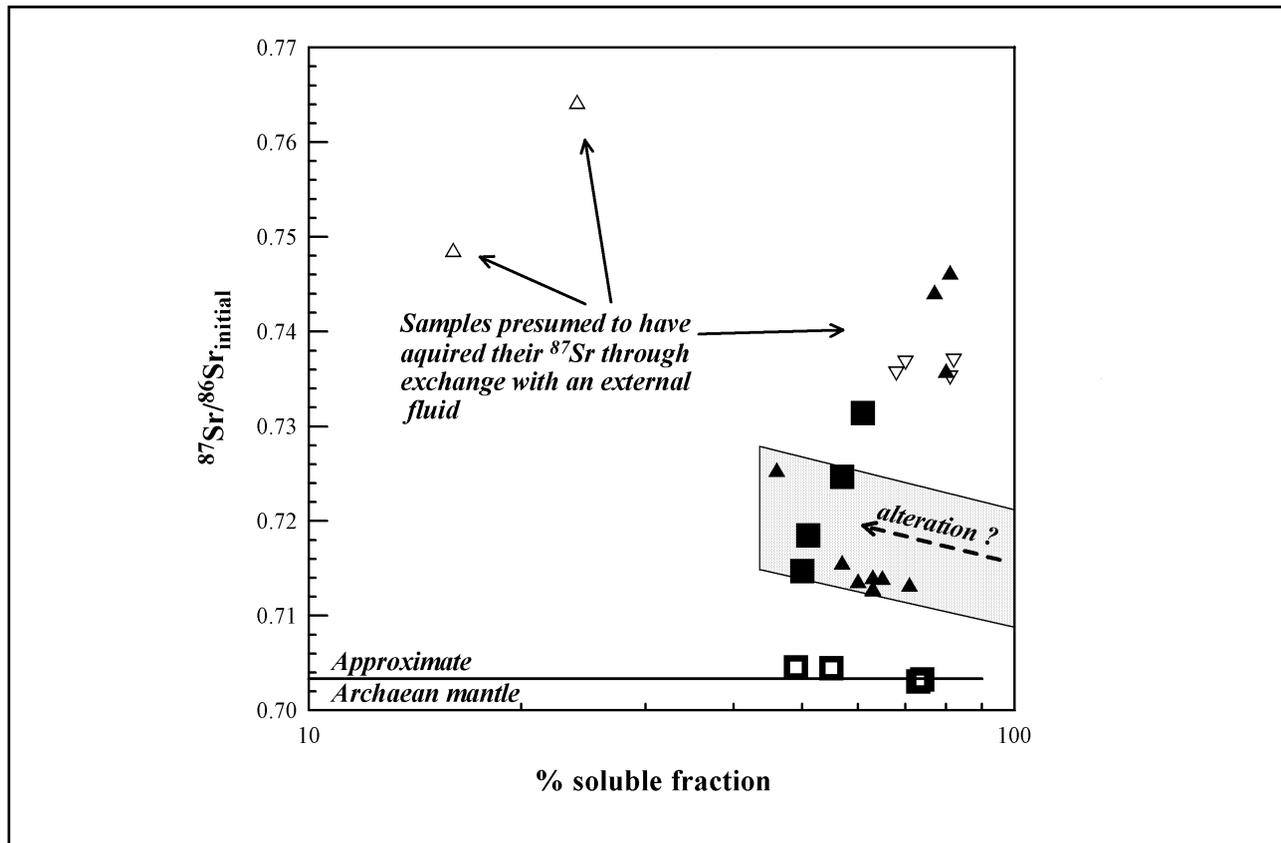
**Figure 4.** Variation of  $\delta^{18}\text{O}$  relative to  $\delta^{13}\text{C}$  for Pongola carbonates. Data from White Mfolozi inlier and labeled fields are from Veizer *et al.* (1990). Large plus symbol denotes the 'best estimate' of pristine Archaean marine carbonate compositions (Veizer *et al.*, 1990). Thick 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  $\delta^{13}\text{C}$  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  $\delta^{18}\text{O}$  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.



**Figure 7.** Variation in initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (calculated at 3000 Ma) relative to the proportion of soluble carbonate in the samples. Approximate Archaean mantle curve, field for alteration and White Mfolozi samples (stippled) from Veizer *et al.* (1990). Symbols as in Figure 2.

alone (Valley, 1986). Figure 4 also illustrates the substantial shift in  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  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:

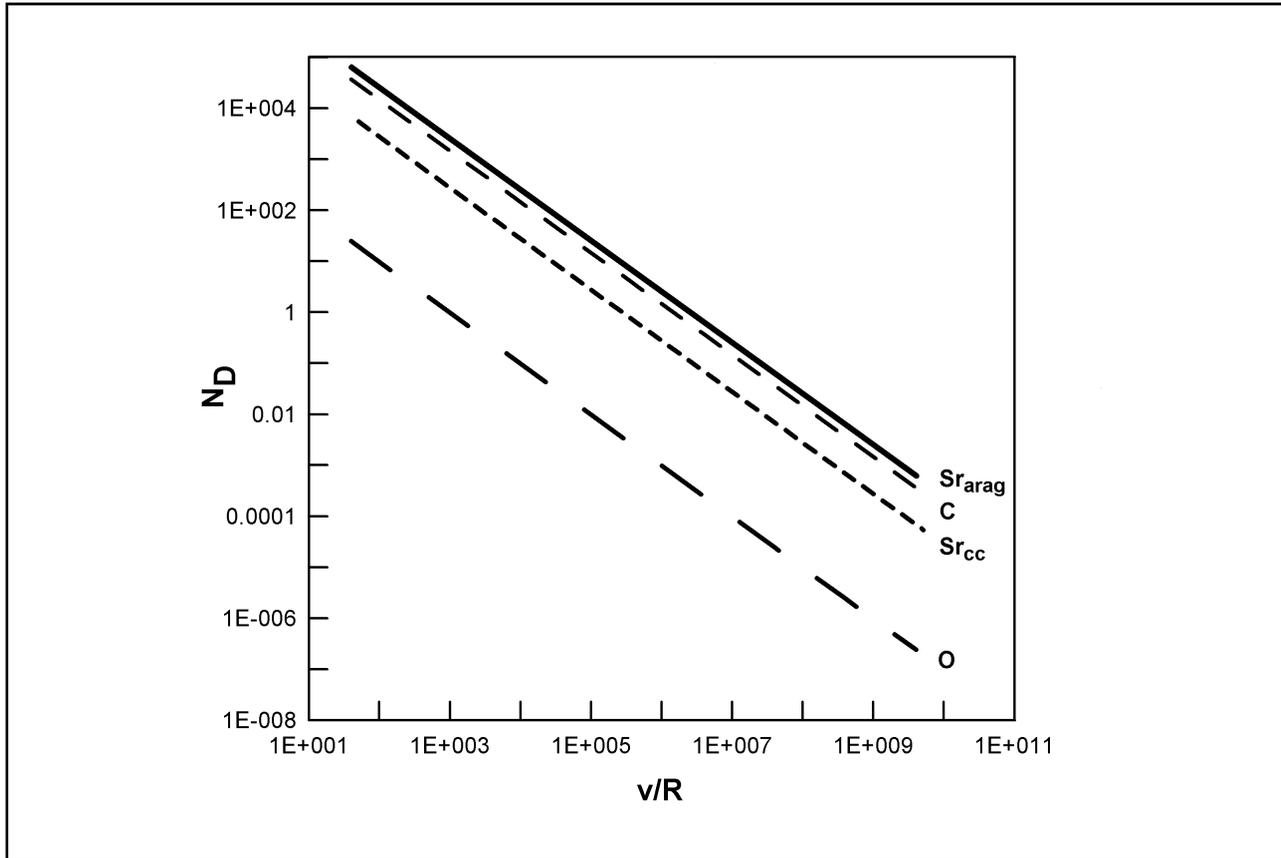
$$N_D = \frac{l M R_d c_s}{v c_f}$$

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,



**Figure 8.** Variation in Damköhler number relative to velocity/reaction rate for O, C and Sr (aragonite and calcite) assuming typical values for carbonate metasediments such as those in the Pongola Supergroup. Modeling is based on water – rock exchange in dynamic, advective-dispersive systems (Johnson and DePaolo, 1994). Lithologies with higher Damköhler numbers require a greater fluid flux to alter their isotope compositions, hence the order of isotope disturbance in carbonate rocks should be  $O > Sr_{cc} > C > Sr_{aragonite}$ .

Values used for the modelling are:

- Oxygen:  $\delta^{18}O$  in rock = +25.0, in fluid = +0.1; O in rock = 48%, in fluid = 88.9%
- Carbon:  $\delta^{13}C$  in rock = +0.9, in fluid = -1.0; C in rock = 12%, in fluid = 80mg/l
- Strontium:  $^{87}Sr/^{86}Sr$  in calcite = 0.70305, in fluid = 0.76000; Sr in calcite = 100ppm, in fluid = 600 $\mu$ g/l
- Strontium:  $^{87}Sr/^{86}Sr$  in aragonite = 0.70305, in fluid = 0.76000; Sr in aragonite = 1500ppm, in fluid = 600 $\mu$ g/l

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  $^{87}Sr/^{86}Sr$  values (calculated at 3 Ga) of  $0.70305 \pm 7$  to  $0.70327 \pm 7$ . These samples are also amongst those with the highest Sr contents (Table 2). Neither Sr concentration, nor  $^{87}Sr/^{86}Sr$  show any correlation with the proportion of insoluble residue (Figure 7). As previously noted, the effects of alteration will typically raise the  $^{87}Sr/^{86}Sr$  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  $^{87}Sr/^{86}Sr_{present} = 0.703053 \pm 11$ , the latter being significantly lower than for carbonates from the White Mfolozi inlier ( $^{87}Sr/^{86}Sr \sim 0.712$ ; Veizer *et al.*, 1982). The low  $^{87}Sr/^{86}Sr$  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  $^{87}Sr/^{86}Sr$  of  $0.70305 \pm 7$  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

- Beukes, N.J. and Lowe, D.R. (1989). Environmental control on diverse stromatolite morphologies in the 3000 Myr Pongola Supergroup, South Africa. *Sedimentology*, **36**, 383-397.
- Bowman, J.R. and Willett, S.D. (1991). Spatial patterns of oxygen isotope exchange during one-dimensional fluid infiltration. *Geophysical Research Letters*, **18**, 971-974.
- Bowman, J.R., Willett, S.D. and Cook, S.J. (1994). Oxygen isotopic transport and exchange during fluid flow: one-dimensional models and applications. *American Journal of Science*, **294**, 1-55.
- Burke, K., Kidd, W.S.F. and Kusky, T.M. (1985). The Pongola structure of southeastern Africa: the world's oldest preserved rift? *Journal of Geodynamics*, **2**, 35-49.
- Coplen, T.B. (1988). Normalization of oxygen and hydrogen isotope data. *Chemical Geology*, **72**, 293-297.
- Eglington, B.M. and Harmer, R.E. (1999). GEODATE for Windows version 1: Isotope regression and modeling software. *Council for Geoscience Open File Report*, **1999-0206-O**, 1-51.
- Eglington, B.M. and Harmer, R.E. (2000). GEODATE for Windows isotope-regression and modelling software. *Journal of African Earth Science*, **31**, 20-21.
- Elworthy, T., Eglington, B.M., Armstrong, R.A. and Moyes, A.B. (2000). Rb-Sr isotope constraints on the timing of late- to post-Archaean tectono-metamorphism affecting the south eastern Kaapvaal Craton. *Journal of African Earth Science*, **30**, 641-650.
- Hegner, E., Kröner, A. and Hofmann, A.W. (1984). Age and isotope geochemistry of the Archaean Pongola and Usushwana suites in Swaziland, southern Africa: a case for crustal contamination of mantle-derived magma. *Earth and Planetary Science Letters*, **70**, 267-279.
- Hegner, E., Kröner, A. and Hunt, P. (1994). A precise U-Pb zircon age for the Archaean Pongola Supergroup volcanics in Swaziland. *Journal of African Earth Science*, **18**, 339-341.
- Hunter, D.R. and Wilson, A.H. (1988). A continuous record of Archaean evolution from 3.5 Ga to 2.6 Ga in Swaziland and northern Natal. *South African Journal of Geology*, **91**, 57-74.
- Johnson, T.M. and DePaolo, D.J. (1994). Interpretation of isotopic data in groundwater-rock systems: model development and application to Sr isotope data from Yucca Mountain. *Water Resource Research*, **30**, 1571-1587.
- Matthews, P.E. (1990). A plate tectonic model for the late Archaean Pongola SuperGroup in southeastern Africa., In: S. P. H. Sychanthavong (Editor), *Crustal Evolution and Orogeny.*, Oxford Publications, New Delhi, India, 41-73.
- McCrea, J.M. (1950). On the isotopic chemistry of carbonates and a paleotemperature scale. *Journal of Chemistry and Physics*, **18**, 849.
- Steiger, R.H. and Jäger, E. (1977). Subcommittee on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth and Planetary Science Letters*, **36**, 359-362.
- Valley, J.W. (1986). Stable isotope geochemistry of metamorphic rocks, 445-489. In: J.W. Valley, H.P. Taylor and J.R. O'Neil (Editors), *Stable Isotopes In High Temperature Geological Processes*, Mineralogical Society of America, 445-489.
- Veizer, J. (1984). The evolving earth: water tales. *Precambrian Research*, **25**, 5-12.
- Veizer, J., Clayton, R.N., Hinton, R.W., Von Brunn, V., Mason, T.R., Buck, S.G. and Hoefs, J. (1990). Geochemistry of Precambrian carbonates: 3-shelf seas and non-marine environments of the Archean. *Geochimica et Cosmochimica Acta*, **54**, 2717-2729.
- Veizer, J., Compston, W., Hoefs, J. and Nielsen, H. (1982). Mantle buffering of the early oceans. *Naturwissenschaften*, **69**, 173-180.
- Veizer, J., Hoefs, J., Lowe, D.R. and Thurston, P.C. (1989b). Geochemistry of Precambrian carbonates: II. Archean greenstone belts and Archean sea water. *Geochimica et Cosmochimica Acta*, **53**, 859-871.
- Veizer, J., Hoefs, J., Ridler, R.H., Jensen, L.S. and Lowe, D.R. (1989a). Geochemistry of Precambrian carbonates: I. Archean hydrothermal systems. *Geochimica et Cosmochimica Acta*, **53**, 845-857.
- Von Brunn, V. and Hobday, D.K. (1976). Early precambrian tidal sedimentation in the Pongola supergroup of South Africa. *Journal of Sedimentary Petrology*, **46**, 670-679.
- Von Brunn, V. and Mason, T.R. (1977). Siliciclastic-carbonate tidal deposits from the 3000 m.y. Pongola Supergroup, South Africa. *Sedimentary Geology*, **18**, 245-255.
- Zachariah, J.K. (1998). A 3.1 billion year old marble and the  $^{87}\text{Sr}/^{86}\text{Sr}$  of late-Archaean seawater. *Terra Nova*, **10**, 312-316.

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