STRONTIUM ISOTOPES AS AN INDICATOR OF THE SOURCE OF CALCIUM FOR REGOLITH CARBONATES

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INTRODUCTION

Around 21% of the Australian land surface is covered by authigenic carbonate minerals, predominantly calcite and dolomite (Chen *et al.* 2002). These carbonates in Australia, referred to as "calcrete" when indurated, are mainly distributed in a broad belt that follows the Great Australian Bight and the gulfs of South Australia.

Strontium (Sr) shows a strong affinity to calcium (Ca) due to similar chemical properties and is an ideal tracer element. By measuring Sr isotope ratios it should be possible to identify the source of the Ca. Previous research in southern Australia (Quade *et al.* 1995), New Mexico (Van Der Hoven & Quade 2002) and central Spain (Chiquet *et al.* 1999) has shown the predominant source of Ca to be from aeolian processes rather than underlying bedrock. Of particular interest to this study is the work by Quade *et al.* (1995), in which they demonstrated that the Ca along coastal areas of southern Australia was predominantly derived from a marine source. Their study did not include samples from far inland Australia, but they suggested that their most inland carbonates, approximately 300 km from the coast, may have shown a trend to more bedrock Ca.

In this pilot study, a selection of carbonates collected from the southern Olary Domain, SA, have been analysed for Sr isotopes. The location of the field area is shown in Figure 1. This setting is significantly inland compared to the coastal study by Quade *et al.* (1995), and their sparse inland data suggests that we may expect to see a much stronger bedrock Ca signature in the carbonates.

STRONTIUM ISOTOPES AND CALCIUM ASSOCIATION

Sr has four naturally occurring isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. In rocks and minerals the Sr isotopic signature is conventionally represented by the ratio of ^{87}Sr/^{86}Sr. These are stable isotopes, however, ^{87}Sr is the daughter isotope of ^{87}Rb, which has a half-life of 48.8 billion years. Over time the decay of ^{87}Rb to ^{87}Sr increases the ^{87}Sr/^{86}Sr ratio in rocks and minerals because amount of ^{86}Sr remains constant (Stille & Shields 1997).

Sr and Ca have similar ionic radii and are both divalent cations. Sr will therefore substitute for Ca in minerals including plagioclase, apatite, sulphates (gypsum and anhydrite) and carbonates (calcite, dolomite and aragonite) (Capo *et al.* 1998). This makes Sr an ideal tracer element for Ca, and variations in Sr isotope ratios can be used to determine the potential source of the Ca (Hutton & Dixon 1981, Milnes & Hutton 1983, Van Der Hoven & Quade 2002).

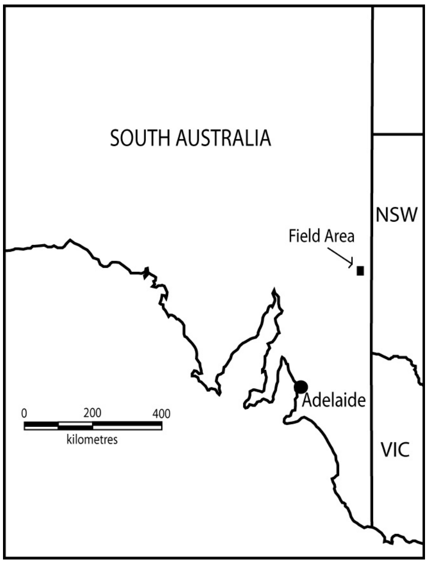

Figure 1: Location of the field area.

The Earth's crust is relatively enriched in Rb compared to the mantle, so that over time the ^{87}Sr/^{86}Sr ratio is significantly higher in old continental rocks and minerals, while young mantle-derived volcanic rocks have a lower ^{87}Sr/^{86}Sr ratio. Figure 2 illustrates the ranges of ^{87}Sr/^{86}Sr ratios from the major reservoirs (Stille & Shields 1997).

The ^{87}Sr/^{86}Sr ratio of Phanerozoic seawater reflects the combined contributions from the continental crust and mantle into the world's oceans by geological processes. Natural variations in these processes over time are reflected in the variations of the ^{87}Sr/^{86}Sr ratio. However, the value of the ^{87}Sr/^{86}Sr ratio has always ranged between the two extremes of mantle and continental crust, reflecting the main inputs (Banner 2004).

The concentrations of Sr and Rb in natural materials are extremely variable. Average exposed upper crust Rb and Sr concentrations are 95 ppm and 337 ppm, respectively. However, Rb concentrations vary from < 1 ppm in carbonates to ca. 200 ppm in some granites, while Sr concentrations range from about 1 ppm in ultramafic rocks to over 2,000 ppm in deep-sea carbonates. In soils the range of Sr concentrations is also variable, but averages 240 ppm. In carbonates the concentration of Sr is around 610 ppm (Capo *et al.* 1998).

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The $^{87}Sr/^{86}Sr$ ratio of locally derived dust will reflect the ratio of the exposed soil, sediments and bedrock. The $^{87}Sr/^{86}Sr$ ratio of this dust may be significantly higher than modern seawater (Capo *et al.* 1998).

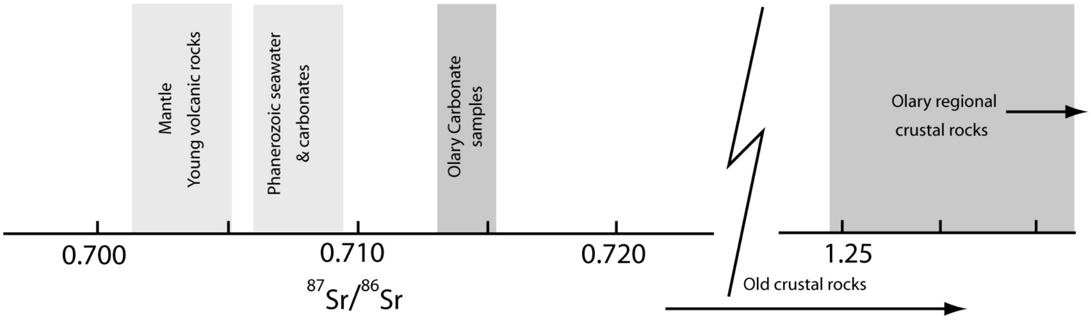

Figure 2: The range of $^{87}Sr/^{86}Sr$ ratio values for the major reservoirs and those recorded from the Olary area. Adapted from Stille & Shields (1997).

SOURCES OF CALCIUM

The sources of Ca required for a carbonate to form are varied. Goudie (1983) lists the following: bedrock; vegetation litter; shells; volcanic emissions; atmospheric dust; rainfall; lakes; surface runoff; and groundwater. In many areas Ca is leached from the soils by rainwater, but in semi-arid regions, where precipitation is less than the evapotranspiration, carbonates can accumulate (Goudie 1983). Lintern (2004) supports this view and explains that the reason for such a widespread occurrence of calcrete in South Australia is due to the aridity of the area, with an average annual rainfall in most areas of less than 250 mm per year. An atmospheric source of Ca, either marine or dust, has been demonstrated through the use of Sr isotopes by several authors to be the predominant source of Ca in pedogenic carbonates, with the input of Ca from the weathering of underlying bedrock being described as minimal (Quade *et al.* 1995, Chiquet *et al.* 1999, Naiman *et al.* 2000, Van Der Hoven & Quade 2002). The source of the dust is discussed by Naiman *et al.* (2000), who state that the source of carbonate dust must ultimately be derived from carbonate bedrock and/or soil carbonate. They conclude that the primary source of carbonate dust is from the recycling of pre-existing soil carbonate horizons through erosion, fluvial transport and aeolian processes.

In South Australia, workers have suggested that during low eustatic sea levels exposed calcareous beach deposits on the continental shelf were transported inland by aeolian processes (Crocker 1946, Firman 1963, Wetherby 1980, Phillips & Milnes 1988). Milnes & Ludbrook (1986) analysed microfossils in calcarenites and calcretes in South Australia and determined them to be of Miocene age, deposited following regression after the Middle Miocene. Reworking (possibly during multiple episodes) of these sediments by wind action in the Pleistocene would account for the distribution of the carbonates in Pleistocene dunes and the complex carbonates of the inland regions. Hutton & Dixon (1981) state that differences in chemical composition and accessory clay minerals over wide areas do not support this view. Instead they state that the clay mineralogy reflects the nature of the underlying rocks. They claim that if the carbonates were from a single source then they would be uniform in chemical composition and accessory clay minerals over wide areas.

Quade *et al.* (1995) investigated Sr isotopic variation in the soil carbonates of coastal South Australia and Victoria. They concluded that the ocean was the principal source of calcium for nearly all soils near the coast with contributions from bedrock generally very small. One exception was the area around Mt Gambier where the weathered volcanic ash, rich in calcium, provided about 40% of the Sr. They also showed that the $^{87}Sr/^{86}Sr$ ratio of the carbonates gradually increased inland, reflecting up to 8% non-marine Sr input, parallel with the prevailing winds towards the east and reflecting the mixing of marine Sr with inland dust from exposed bedrock and soil. In other words, the proportion of marine Sr is slowly diminishing as it is transported further inland.

METHODS

Powdered samples were leached in dilute acetic acid to selectively dissolve the carbonate. Care must be taken to avoid extracting Sr from any residual detrital phases, which would render the results meaningless. The leachate is collected and dried before taking up in 6M hydrochloric acid (HCl) and dried once more to convert it to a chloride. The Sr is concentrated on cation exchange columns, and $^{87}Sr/^{86}Sr$ ratios measured using the University of Adelaide's Thermal Ionisation Mass Spectrometer (TIMS).

As well as reporting the results as a direct $^{87}Sr/^{86}Sr$ ratio, Capo *et al.* (1998) suggest that the ratios be normalized to allow comparison of data from different laboratories. They suggest the use of $\delta^{87}Sr$, which is calculated in the following equation and is analogous to normalizations for stable isotopes such as oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$):

$$\delta^{87}Sr = 10^3\left[\frac{^{87}Sr/^{86}Sr_{SAMPLE}}{^{87}Sr/^{86}Sr_{SEAWATER}} - 1\right]$$

RESULTS AND DISCUSSION

$^{87}Sr/^{86}Sr$ ratios of the soil carbonate samples are illustrated in Figure 2. Samples have yielded relatively uniform $^{87}Sr/^{86}Sr$ ratios, from 0.71336 to 0.71554 with an average value of 0.71446.

The small variation between the measured $^{87}Sr/^{86}Sr$ ratios of the samples is indicative of a single Ca source. This is significant given that the samples are approximately 10 km apart. The underlying bedrock in the area consists of metasediments of the Palaeoproterozoic Willyama Supergroup and Mesoproterozoic granitoids (Flint & Parker 1993). Samples from these rocks were analysed by Benton (1994) who reported present-day $^{87}Sr/^{86}Sr$ ratios from 1.225 to 1.783 for granites and 1.264 for a metasediment. These high values are as expected for old upper crustal rocks. The large difference between the Sr isotopic composition of the carbonate compared to the underlying bedrock indicates that Ca is not being sourced from these rocks.

Modern seawater has a $^{87}Sr/^{86}Sr$ ratio of 0.709 (Burke *et al.* 1982). Using the lowest measured bedrock Sr isotope composition (1.225), measured Sr isotopic ratios for the carbonates lie within 1% of the seawater value. This result suggests that the Ca source is predominantly from an atmospheric (dry or wet) origin. Considering that the location is approximately 400 km from the coast, it is surprising that the proportion of bedrock Ca appears to be so small.

CONCLUSION

The use of Sr isotopes as a tracer for Ca can assist in determining the source areas of the Ca found in Australian carbonates. Initial results show that the main source of Ca in the regolith carbonates of the Olary region, South Australia, is almost entirely derived from marine and/or reworked inland dust sources.

No attempts have yet been made in this analysis to investigate the $^{87}Sr/^{86}Sr$ ratios of dust and rainfall in the area. These are the expected sources of the Ca and should be measured to enable a direct comparison with the regolith carbonates.

The samples were collected from rabbit warrens for convenience. In this situation the rabbits have mixed and exposed the carbonates, so that the samples should be relatively homogenous. However this process may also be viewed as contamination of the samples. A direct comparison of these samples with a nearby fresh sample would indicate if this were the case.

These preliminary results have some interesting implications for transport processes and distribution of Au in calcrete. Even from an inland setting such as the Olary Domain, the Ca source in calcretes is nearly exclusively atmospheric. Although Ca and Au have been shown to be associated in soil profiles in a number of studies, there may be no commonality to the controls on their distribution in soil carbonates. In other words, the processes that are transporting Au from bedrock to carbonate are not transporting Ca from bedrock to carbonate.

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