

Origins of carbonates and organic matter in a 2.6 Ga palaeosol section at Schagen, Eastern Transvaal, South Africa

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Mineralogical, chemical, and isotopic characteristics of soils reflects the weathering conditions of the soil formation (e.g. surface temperature, rainfall, redox states of the atmosphere, and presence and nature of organisms) as well as the petrochemical characteristics of parental rocks. Although ancient soils (palaeosols) were subjected to various processes of water-rock interaction after their formation (e.g. diagenesis, hydrothermal alteration, and metamorphism), they have often retained some original characteristics that can be used to decipher the surface environments of the ancient Earth. For example, iron chemistry of palaeosols has been considered to be the most useful indicator for evaluating the redox state of atmosphere (Holland, 1992; Ohmoto, 1996). It has been also suggested that the $\delta^{13}\text{C}$ value of soil carbonates may indicate the proportions of CO_2 from atmospheric reservoir and CO_2 produced by decomposition of soil organisms, and that the $\delta^{18}\text{O}$ value of soil carbonates reflects the characteristics of carbonate-forming fluids, such as those of meteoric waters (Cerling, 1984)

Martini (1994) has described the palaeosols of ~2.6 Ga in age in the Eastern Transvaal district of South Africa that are unusually rich in carbonates and organic carbon. This study was carried out to investigate the origins of these carbonates and organic matter, and to put constraints on the climatic conditions and to understand the nature of terrestrial biosphere during the palaeosol formation.

Samples and methods

The palaeosols are developed on ultramafic rocks (serpentinized dunite) over a large area (> 20 km x 70 km) in the Eastern Transvaal district, South Africa, and are overlain by a 2.56 Ga quartzite formation (the Black Reef Formation) or a 2.25 shale formation (the Timeball Hill Formation). The palaeosol section at

Schagen is typically about 15 m thick and overlain by the 2.56 Ga quartzite formation. It is divisible into five lithostratigraphic zones, from top to bottom: (1) quartz and stilpnomelene-rich zone (~0.5 m), (2) calcite-rich zone (~0.8 m), (3) talc-rich zone with minor carbonate and chlorite (~3.2 m) (4) massive carbonate (dolomite) zone (~3.5 m), (5) carbonated and serpentinized dunite zone (~8.0 m) and carbonate-free serpentinized dunite zone (parental rock). We have analysed 30 samples of the palaeosol and overlying sedimentary rocks for: concentration of the major elements and 50 trace elements in bulk rocks; C/S/N/H ratios and carbon isotopic composition of the extracted organic matter; oxygen isotopic composition of quartz; and carbon and oxygen isotopic compositions of carbonates.

Results and discussion

The $\delta^{18}\text{O}$ values of quartz grains from the upper part of the palaeosol and the overlying quartzite are essentially indicated at 10.0 ± 0.1 ‰. The morphology of quartz grains and that of fluid inclusions in quartz are also identical between the two units. These observations suggest that these quartz grains had the same history (i.e. detrital grains of quartz from igneous rocks or hydrothermal veins), and that the upper part of the palaeosol was disturbed during the deposition of the overlying quartzite bed.

The carbonate content of the quartzite bed ranges from 2.4 to <0.1 wt.% with a trend of gradually decreasing upward in a 2 m section. In contrast, the carbonate content of the palaeosol varies greatly: ~15 to ~30 % in zone 1, ~80 % in zone 2, ~0 to ~20 % in zone 3, ~90 to ~100 % in zone 4, and ~10 to ~30 % in zone 5. The carbonates in the upper two zones are mostly calcite ($X_{\text{Ca}} = \sim 0.9$) but those in the lower zones are mostly dolomite ($X_{\text{Mg}} = 0.2-0.7$ and $X_{\text{Ca}} = 0.2-0.7$).

TABLE 1. Concentrations of carbonate and organic C and their isotopic compositions

Formation	Depth (m)	Zone (lithology)	Bulk rock		Carbonate		Kerogen	
			carb.C (wt.%)	org.C (wt.%)	$\delta^{13}\text{C}$ (‰, PDB)	$\delta^{18}\text{O}$ (‰, PDB)	$\delta^{13}\text{C}$ (‰, PDB)	H/C (atomic)
Monte Christo		dolomite	~10	~0	~-0.4	-5.5	-	-
Oaktree		dolomite	~10	~0	~-1.2	-6	-	-
Black Reef		shale	0.1-0.5	1-2	-	-	-32.8 ± 2.3	0.1-0.3
Black Reef	+0.1 to +2.0	quartzite	<0.1-2.4	<0.1-0.2	0.2 ± 0.9	-15.1 ± 7.2	-16.3 ± 0.9	~0.05
palaeosol	-0.5 to -0.1	1	2-3	0.1-0.2	-4.7 ± 6.7	-18.3 ± 0.9	-15.8 ± 0.4	~0.05
palaeosol	-1.3 to -0.9	2	8.4-9.9	0.3	-1.5 ± 0.1	-20.2 ± 0.2	-15.2 ± 0.2	~0.05
palaeosol	-4.3 to -1.7	3	0-3	0.1-0.3	-1.9 ± 0.5	-20.3 ± 0.2	-15.0 ± 0.4	~0.05
palaeosol	-7.6 to -4.8	4	10.6-11.5	0-0.3	0.3 ± 2.6	-16.6 ± 5.1	-14.8 ± 0.4	-
palaeosol	-14.5 to -8.4	5	3.2	0.13	-0.3 ± 4.1	-16.8 ± 2.6	-	-

The $\delta^{13}\text{C}$ values of the carbonates range from -12.5 to +2.3 ‰ (PDB) with a complicated trend: decreasing from -12.5 to -2.3 ‰ downward through zones 1, 2 and 3, but increasing from -2.9 to 2.4 ‰ downward through zones 4 and 5 (Table 1). A carbonate from the uppermost part of zone 1 shows the lightest $\delta^{13}\text{C}$ value of -12.5 ‰. These carbon isotope data can be interpreted by a model postulating two sources of CO_2 (and/or HCO_3^-) for the carbonates: one was the atmospheric CO_2 with $\delta^{13}\text{C}$ value around -10 ‰ (or HCO_3^- of around -2 ‰); and the other was the HCO_3^- with the $\delta^{13}\text{C}$ value less than -13 ‰ which was probably produced by the decay (oxidation) of organic matter. The former HCO_3^- was probably responsible for the formation of carbonates with $\delta^{13}\text{C}$ value around -2 ‰, and the latter for carbonates of about -13 ‰.

The $\delta^{18}\text{O}$ values of the carbonates range from -20.7 to -9.9 ‰ (PDB): carbonates in zones 1, 2 and 3 have similarly low $\delta^{18}\text{O}$ values (~-20 ‰) but those in zone 4 have much higher $\delta^{18}\text{O}$ values (-12.4 and -9.9 ‰; PDB). The low $\delta^{18}\text{O}$ carbonates (~-20 ‰ PDB) were probably formed by meteoric water of about -18 ‰ (SMOW), and the high $\delta^{18}\text{O}$ carbonates (~-10 ‰ PDB) by evaporate soil water.

The organic carbon content of the palaeosols ranges from 0.1 to 0.4 wt.% in zone 1 through 3, and between 0 and 0.1 wt.% in zone 4 and 5. The TOC contents of the overlying quartzite bed are less than 0.2 wt.%. In contrast, the upper shale unit of the

2.56 Ga quartzite formation contains from 1.0 to 2.0 wt.% TOC. The kerogens extracted from the palaeosols are all low in the H/C ratios (less than 0.1), indicating that they are highly matured. Therefore, it is unlikely that the organic matter in the palaeosol is modern contamination.

The $\delta^{13}\text{C}$ values of kerogens in the palaeosols (-16.2 to -14.3 ‰) are distinctly different from those in the overlying marine shale unit (-35 to -30 ‰). This suggests that the organic carbon in the palaeosols was indigenous of the palaeosols, and the $\delta^{13}\text{C}$ values of around -15 ‰ represent those of 2.6 Ga terrestrial organisms. These $\delta^{13}\text{C}$ values are similar to those of the organisms lived in evaporating, hyper saline, and low sulphate lacustrine environment during the period between 2.8 and 2.1 Ga (Watanabe *et al.*, 1997).

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