

C-, O- and Sr-Isotope stratigraphy of the Lower Carboniferous: high frequency fluctuations as a record of climatic changes?

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Introduction

The chemical evolution of ancient oceans is of general scientific interest. Changes in C, O, and Sr isotopic composition of seawater reflect a variety of global processes, such as glaciation, volcanic activity, plate tectonics, and fluxes in the rate of burial of organic matter. Isotopes can, therefore, serve as valuable tracers for understanding the dynamics of the Earth system. Furthermore, high resolution isotope curves can provide a tool for correlation and dating (isotope stratigraphy) that is global in scope and applicable also to non-fossiliferous sequences. For the Paleozoic, samples with the greatest utility for isotope stratigraphy are the well preserved internal 'secondary' layers of articulate brachiopod shells. This is because they (1) are relatively resistant to postdepositional diagenetic alteration (Brand and Veizer 1980), and (2) show no (Lowenstam 1961) or only a minor (< 1%, Carpenter and Lohmann 1994) biological isotope fractionation effect.

For the Carboniferous, the existing database is - particularly for $^{87}\text{Sr}/^{86}\text{Sr}$ (e.g. Veizer and Compston 1974, Popp *et al.* 1986, Brand 1990) - either sparse, or the data are concentrated to only few stratigraphic intervals, such as the Pennsylvanian (e.g. Grossman *et al.* 1993). The main objectives of this paper are twofold: (a) establishment of detailed secular $^{87}\text{Sr}/^{86}\text{Sr}$ -, $\delta^{18}\text{O}$ - and $\delta^{13}\text{C}$ - curves for the Lower Carboniferous (Dinantian), including their 4th order ($x \times 10^6\text{a}$, Veizer 1989) oscillations, and (b) delineation of causes that could have generated the observed isotopic patterns.

Methods

A total of 162 secondary layers of brachiopod shells have been analysed for their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, with 88 of these samples measured for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The samples are from (1) outcrops in the classical type region of the shallow marine Dinantian facies in Belgium and Germany, (2) three cores drilled along the northeastern

boundary of the London-Brabant Massiv (e.g. Muchez 1988), and (3) two cores drilled on the island of Rügen (Germany); a few samples are from the Sligo region of northwestern Ireland.

For isotope measurements an aliquot of 4 to 6 mg was hand picked from the calcite of secondary layer calcite under binocular microscope. Altered parts, such as micritic rims and fissure cements, were avoided. For stable isotope analyses, 3 to 5 mg of this material was reacted off-line with 100% phosphoric acid for 24 hours. P_2O_5 was added to assure the absence of free water. The distilled gas was measured on a Finnigan MAT 251 gas mass-spectrometer, calibrated against PDB and corrected to a temperature of 25°C. For $^{87}\text{Sr}/^{86}\text{Sr}$ ratios 0.5 to 1 mg was reacted with 2.5 N suprapure HCl at room temperature for about 24 h. Samples were measured on a Finnigan MAT 262 5-collector mass-spectrometer. NBS 987 was analysed with every run and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the samples were adjusted to a nominal value of 0.71024 for this standard. For the NBS 987 and EN 1 standards external precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is better than 1×10^{-5} . Tests on diagenetic alteration were carried out qualitatively on polished thin sections using a hot cathode luminescence device (e.g. Bruckschen *et al.* 1992). For quantitative geochemical tests, the Ca, Mg, Sr, Mn and Fe concentrations of the shells were examined on a Philips PU 7000 ICP-AES spectrometer, by analysis of the diluted phosphoric acid that remained after carbonate dissolution for stable isotope gas preparation. For 55 samples, trace elements were measured using the Bochum proton microprobe (PIXE, cf. Bruhn *et al.* this volume, Meijer *et al.* 1994). The construction of the isotope curves is based on well preserved samples with >600 ppm Sr and <200 ppm Mn. The stratigraphic scheme is the GTS 89.

Discussion of results

In all three isotope curves, cyclic 4th order fluctuations with periodicities of $x \times 10^6\text{a}$, superimposed on the 3rd order ($x \times 10^7\text{a}$)

trends, can be documented. The frequency of these cycles is generally higher for the post-Chadian stages, with average periodicities of 1.9, 2.4 and 2.8 million years for Sr, O and C, respectively. For the Chadian-Hastarian stages, the respective periodicities are 3.9, 3.7 and 9.1 Ma, a fact that is in line with the generally higher sedimentary cyclicity of the Visean compared to the Tournaisian (e.g. Ross and Ross 1988). For strontium and oxygen 4th order cycles, their coincidence with the 3rd order global sealevel changes is convincing. While the negative correlation between $\delta^{18}\text{O}$ and sealevel trends can be documented for the entire Dinantian (only 3 of the 18 $\delta^{18}\text{O}$ peaks do not coincide with peaks in the sealevel curve), a correlation between sealevel lowstands and high $^{87}\text{Sr}/^{86}\text{Sr}$ exists only for the Visean. Here, however, the coincidence is conspicuous, with 13 of the 14 Sr-peaks matching. In general, correlation with the Sando (1990) sealevel curve is better than with Ross and Ross (1987). The latter is superior only during the mid-Holkerian and early-Arundian for Sr and during the early- and mid-Asbian as well as early-Arundian for oxygen. Although the 3rd order sealevel fluctuations - with periods of $x \times 10^6\text{a}$, rates of $x \times 10\text{m}/10^6\text{a}$, and a maximum amplitude of 200m - can not be explained by simple orbitally driven glacial/interglacial cycles, and the causes of sealevel changes are not fully understood (Ross and Ross 1987), glacial fluctuations are presently the only known mechanism that could have produced rates of sealevel change in excess of 1cm/1000 years (Pitman and Golovchenko 1983, Ross and Ross 1987). From this perspective, the 4th order oxygen cycles can be interpreted as shifts in seawater $\delta^{18}\text{O}$ caused by waxing and waning of ice caps and by temperature dependent isotope fractionation (Epstein *et al.* 1953). A model $\delta^{18}\text{O}$ -curve is derived from the sealevel curve, assuming that the $\delta^{18}\text{O}$ ice mass effect is 0.1‰ and the temperature change 0.47°C for each 10 m sealevel change. The temperature factor was scaled from a 4C temperature and 85 m sealevel increase during the last Quaternary glacial/interglacial cycle. Two initial scenarios were modelled, one with $\delta^{18}\text{O}$ of -3 ‰ and 30C and another with $\delta^{18}\text{O}$ of -1‰ and temperature of 38°C. The modelled curves conform with the observed one. For the first, more realistic, scenario (e.g. Brand 1993), the modelled seawater $\delta^{18}\text{O}$ varied between 3.2 and -1.1‰ and the low latitude water temperatures oscillated between 31°C and 21°C during Dinantian time.

The clear correlation of sealevel lowstands with radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ peaks in the Visean can be attributed to increased continental weathering

rates of silicates during glacial periods (Raymo 1991). For the Phanerozoic, this hypothesis finds support in model calculations of François *et al.* (1992). Our data, therefore, suggest that Sr-isotopes may reflect climatic changes even on the million years time scale.

A coincidence of high $\delta^{13}\text{C}$ values with low sealevels during the Visean may indicate an increase in organic carbon burial rates, in line with enhanced silicate weathering. This may result in a decrease in atmospheric CO_2 content and possibly contribute to climatic changes.

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