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C-isotope geochemistry – tool for chemostratigraphy and carbon cycle history

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Summary

Chemostratigraphy uses chemical fingerprints stored in sediments and sedimentary rocks for stratigraphic correlation. Stable carbon isotope signatures fixed in sedimentary inorganic and organic matter are among the most powerful proxies used in chemostratigraphy. Carbon isotope records provide information on both stratigraphy and on the history of the global carbon cycle, as documented in early studies which were focusing on Cretaceous C-isotope records 8e.g. (Scholle & Arthur, 1980). The Mesozoic C-isotope record is punctuated by repeated negative and positive carbon isotope anomalies with amplitudes reaching several permil.

Globally identified negative carbon isotope spikes in the carbonate and organic carbon isotope records at the Permo-Triassic Boundary (e.g. Oberhänsli *et al*., 1989), at the Triassic-Jurassic boundary (e.g. Galli *et al*., 2005), in the Toarcian (e.g. Hesselbo *et al*., 2000) and Aptian (e.g. Menegatti *et al*., 1998) and at the Paleocene –Eocene Boundary (e.g. Röhl *et al*., 2007) correspond to major perturbations of the carbon cycle, possibly triggered by sudden release of carbon dioxide and/or methane from volcanic or gas hydrate sources. These negative spikes in the carbon isotope record serves as excellent stratigraphic marker.

Positive carbon isotope excursions with a duration of up to millions of years record the response of the biosphere to carbon cycle perturbation. Increased organic carbon burial rates contribute to climate stabilization after times of rapid injection of carbon dioxide into the atmosphere (negative spikes). Positive excursions provide stratigraphic information, which can be used for establishment of accurate age models in earth history.

***Keywords*:** Carbon isotopes, chemostratigraphy, carbon cycle, Mesozoic

Carbon isotope stratigraphy and the carbon cycle

Carbon isotope records provide information on both stratigraphy and on the history of the global carbon cycle. The use of C-isotope geochemistry as a proxy of the global carbon cycle through time started in the late 1970ties. A first high-resolution C-isotope record, established by Scholle & Arthur (1980) demonstrated that the global carbon cycle was repeatedly perturbed and that these perturbations are recorded in major positive C-isotope excursions. Changes in the C-isotope signature of marine carbonate are best explained by changes in organic carbon versus carbonate carbon burial rates. Times of increased burial rates of organic carbon are registered in positive carbon isotope excursions. Therefore, it is not surprising that many of the documented C-isotope excursions in the Cretaceous coincide with Oceanic Anoxic Events. This indicates that Oceanic Anoxic Events were triggered by perturbations of the global carbon cycle. Negative C-isotope anomalies are often described as spikes because of the short duration of thousands of years in comparison with the positive carbon isotope excursions lasting up to millions of years. The importance of negative spikes in the Mesozoic C-isotope record was recognized in early studies of the Cretaceous –Tertiary boundary (e.g. Hsü & McKenzie, 1990) and of the Permo-Triassic boundary. Menegatti *et al* (1998) identified a negative C-isotope spike at the base of OAE1a. This discovery provided supporting evidence for a volcanic trigger of Oceanic Anoxic Events, possibly amplified by clathrate derived methane bursts. Negative spikes with a duration of a few 10^3 to 10^5 years serve as proxy for sudden changes in the marine carbon pool. Rapid addition of volcanic CO_2 and/or of clathrate derived methane triggered the observed changes in the carbonate and organic carbon isotope records. The negative C-isotope spike marking the base of Oceanic Anoxic Event 1a records how the perturbation of the global carbon cycle triggered major changes in oceanography. Comparable negative spikes in the C-isotope record spanning the last 250 million years today are documented from the PETM (e.g. Röhl *et al*., 2007), the Toarcian (e.g. Hesselbo *et al*., 2000), the Cretaceous-Paleogene boundary (e.g. Hsü & McKenzie, 1990), the Triassic-Jurassic boundary (Galli *et al*., 2005) and from the Permo-Triassic boundary.

Negative spikes sometimes coincide with major extinction events as at the Permo-Triassic, Triassic-Jurassic and Cretaceous-Paleogene boundaries. At other times, they can be related to global changes in oceanography but not to major extinction events as in the Toarcian, Aptian and at the PETM. This suggests, that global perturbations of the carbon cycle recorded in the C-isotope data have variable impact on biota, on chemical and physical oceanography and probably also on climate. Negative spikes in the carbon isotope record are of short time duration and, therefore, serve as an excellent stratigraphic marker levels providing a time line across the globe.

The carbonate carbon isotope record – platform to basin correlation

High amplitude fluctuations of the carbon isotope record have first been documented in pelagic limestone successions. Informal reference sections have been introduced to the literature, but so far no formal definition of "reference sections" for carbon isotope stratigraphy do exist. For the Lower Cretaceous, magnetostratigraphically dated pelagic limestone successions from the Southern Alps in Northern Italy are proposed to serve as most reliable reference sections. The Valanginian carbon isotope excursion documented in sedimentary successions from the Southern Alps (Italy, see Channell *et al*., 1993) provides convincing evidence that the isotope curves were not affected by possible addition of isotopically heavier aragonitic carbonate mud form a nearby platform (Swart & Eberli, 2005). Correlations with platform successions are often possible despite more "difficult" neritic archives. Variable amounts of aragonite present in neritic sediments will be reflected in C-isotope composition of bulk sediment (see Swart & Eberli, 2005). Meteoric diagenesis of shallow water carbonates may alter primary marine carbonate carbon isotope signatures. A comparative approach in platform-basin correlations is suggested using pelagic sections for comparison and integrating chemostratigraphic data with available biostratigraphic information. Amplitude of change in the isotope records should be used as an additional parameter when isotope anomalies are compared between sections. Data available indicate that shallow-water limestones record higher amplitude changes than pelagic limestone records.

Amplitudes of carbon isotope excursions show a decreasing trend within the Phanerozoic. Paleozoic carbon isotope curves are punctuated by excursions reaching up to 6 permil (e.g. Joachimski *in* Weissert *et al*., 2008), while excursions in the Mesozoic carbon isotope records have amplitudes rarely exceeding 3 to 4 permil with higher amplitude changes recorded in neritic carbonate successions. Even lower are carbon isotope fluctuations in the Cenozoic, with the exception of the negative spike at the Paleocene-Eocene boundary. If interpreted as a record of carbon cycle, these data suggest that buffering capacity of carbon system improved through geological time, as suggested by Zeebe & Westbroek (2003).

If combined with organic carbon isotope data, carbonate poor successions can be correlated with informal "reference successions". Expanded coastal and deltaic successions preserve carbon isotope curves, which facilitate the correlation of basinal with shelf and coastal carbonate successions (e.g. Hermann *et al*., 2010).

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