



# Carbon and oxygen isotope analysis of hydrate-associated Oligocene authigenic carbonates using NanoSIMS and IRMS



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## ABSTRACT

Petrography and stable C and O isotope compositions of methane-derived carbonates from the Polish Outer Carpathians were analyzed. Two methods were employed in isotopic determinations. Conventional IRMS measurements on powdered bulk samples were performed with high precision (errors ~0.06‰ for  $\delta^{13}\text{C}$  and ~0.08‰ for  $\delta^{18}\text{O}$ ,  $1\sigma$ ), whilst in situ measurements were made using NanoSIMS with a high spatial resolution (5  $\mu\text{m}$ ), but with low precision (errors ~3.0‰ for  $\delta^{13}\text{C}$  and ~2.3‰ for  $\delta^{18}\text{O}$ ,  $2\sigma$ ). The NanoSIMS study proved very useful in identifying the sources of the fluids precipitating the carbonates. They were formed predominantly by the anaerobic oxidation of biogenic methane (AOM). The very fine spatial resolution of the analyses revealed highly variable  $\delta^{13}\text{C}$  values, even in individual crystals, from extremely negative related to AOM to positive related to methanogenesis (Me). Other methods, including laser ablation and standard SIMS, would fail to detect this variability and would not indicate the true sources of the fluids, because they would show average values. Therefore, any straightforward interpretation of the sources of authigenic carbonates based on these methods may be attempted only if the  $\delta^{13}\text{C}$  values are extreme, i.e. resulting either from AOM or Me.

Unusual clast-like druses from the carbonates were analyzed in detail with NanoSIMS. They are filled with strongly  $^{13}\text{C}$ -depleted (down to -54‰) and  $^{18}\text{O}$ -enriched (up to 6‰) fringe calcite which precipitated on the walls of the druses from heavy-oxygen-containing water, released from the dissociation of gas hydrates. The rocks can thus be termed clathrites. The bulk rock isotope analyses of powdered samples of these druses show no evidence of hydrates and alone would not point to the true origin of these rocks. Precipitation of the carbonate cements started when hydrates were still present, so they are a type of melt-and-seal fabric. The recognition of such features may be crucial evidence of the former occurrence of hydrates in fossil methane-derived carbonates. The isotopic results have demonstrated that NanoSIMS can be very useful in reconstructing the diagenetic evolution of pore water by analyzing the stable isotope compositions of even microcrystalline cements. This provides a basis for the application of NanoSIMS to tracing diagenetic pathways from various, even complexly formed, authigenic precipitates.

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## 1. Introduction

Stable carbon and oxygen isotope analysis has for several decades been a widely used method in the study of carbonate materials of various origins. The vast majority of studies have been based on isotope measurements of powdered bulk samples, using carbonate preparation devices connected to mass spectrometers. This conventional isotope ratio mass spectrometry (IRMS) allows for very precise measurements of isotope ratios in carbonate samples as small

as 20  $\mu\text{g}$ . The most important restriction of this method is that it shows average isotope ratios for the entire carbonate material enclosed in the samples. Therefore, the results may be useful only if the carbonate fraction is composed entirely of, or strongly dominated by, one kind of carbonate material with uniform isotopic composition. For instance, paleoecological and chemostratigraphical interpretations are based on bulk rock  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of pelagic limestones (e.g. chalk) which are normally composed almost exclusively of coccoliths (e.g. Schönfeld et al., 1991; Jenkyns et al., 1994; Jarvis et al., 2002). However, the most unequivocal results are obtained when analyses are performed on all the carbonate grain types separately. The isotopic compositions of belemnites, coccoliths, planktonic and benthic foraminifers, or cement, which are commonly present in chalk, can give much more precise information, as they represent

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nectonic, planktonic, benthic and diagenetic signals, respectively. One way to achieve this is to collect powder samples of all the carbonate grain types independently and perform IRMS.

Some larger grains can be sampled using dental microdrills of ~0.5–3 mm diameter (Rosales et al., 2004; Spötl and Matthey, 2006; Gorzelak et al., 2011) or microsampling devices (micromills), allowing for sampling with a resolution down to a few tenths of a millimeter (e.g. Steuber et al., 2005; Spötl and Matthey, 2006; Natalicchio et al., 2012). However, some carbonate constituents are too small for these methods and they must be separated mechanically (e.g. Minoletti et al., 2005; Beltran et al., 2009). The main limitation of this approach is that it requires meticulous work to separate the minute carbonate forms, such as coccolith plates or microspar cement crystals, and that it does not guarantee perfect separation. Another possibility is to analyze individual carbonate constituents in situ. The most widely used methods are laser ablation IRMS (LA-IRMS) which allows for stable C and O isotope measurements in spots as small as 30  $\mu\text{m}$  in diameter (Sharp and Cerling, 1996; Moran et al., 2011) and standard secondary ion mass spectrometry (SIMS), such as CAMECA IMS 1270, enabling measurements in smaller spots, usually about 10–15  $\mu\text{m}$  large (Rollion-Bard et al., 2008; Cox et al., 2010). SHRIMP II or SHRIMP SI have not been fully tested yet for such purposes and first reports present results of O isotope analyses in 25  $\mu\text{m}$  large spots (Aubert et al., 2012). Therefore, these methods cannot also be applied to the study of minute carbonate cements. Instead, high resolution SIMS such as IMS 1280-HR or NanoSIMS can be powerful tools for stable C and O isotope analyses of even very small sedimentary carbonate constituents, as they allow for in situ measurements with a spatial resolution down to several micrometers. The IMS 1280-HR has been used for measuring isotopic composition of carbonates and it is known to enable analyses in 5–15  $\mu\text{m}$  large spots with errors ( $2\sigma$ ) between 0.4 and 1.7‰ (Kozdon et al., 2011; Vetter et al., 2014), but measurements in ~3  $\mu\text{m}$  spots should be possible soon (Kita et al., 2015). Here, we report on the NanoSIMS performance, which has not been that precisely tested.

Reconstructions of diagenetic pathways are based on  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of authigenic carbonates which are normally composed of a single kind of precipitate. However, apart from cements filling veins and nodules, authigenic carbonates such as concretions, beds, and crusts are usually composed of multi-stage microcrystalline cements and may contain sedimentary carbonate grains. Pore water evolution based on stable C and O isotope ratios can be evaluated from these rocks only if the measurements are performed on the successive cement generations separately. For instance, pore water evolution can be traced in concretions by analyzing isotope compositions in successive zones from the center to the edge of a concretion (see Curtis et al., 1986; Dix and Mullins, 1987; Morad and Eshete, 1990), but only if the growth mechanism was concentric. Nevertheless, such a simple growth of authigenic carbonates seems to occur rather infrequently and concretions, beds or crusts may commonly be formed with a more complex pattern, e.g. pervasively (Mozley, 1996; Raiswell and Fisher, 2000; Bojanowski and Clarkson, 2012). This growth mechanism is associated with cementation taking place within the entire space of a rock by simultaneous nucleation of crystals. Later generations of cement do not contribute to enlargement of the rock, but to a gradual sealing of the residual porosity by the growth of individual crystals. Such pervasively formed authigenic rocks are composed of microcrystalline cements which commonly exhibit elemental or mineral zoning. Therefore, microcrystalline authigenic carbonates which exhibit complex internal structures should ideally undergo in situ isotopic analyses in order to obtain the isotope compositions of individual cements, not mixtures. The use of microprobe isotope measurements for the interpretation of the sources of such rocks has already been suggested by Raiswell and Fisher (2000), but as far as we know, has not yet been performed.

Following that suggestion, this research has been undertaken primarily to evaluate the applicability of NanoSIMS to obtaining reliable

stable C and O isotope measurements in authigenic carbonates. The rocks are Oligocene cold seep precipitates from the Outer Carpathians, composed of morphologically and genetically different carbonate cements of various sizes. Stable C isotope analyses performed on powdered samples showed that they were formed due to the anaerobic oxidation of methane (AOM) and due to the sulfate reduction (SR) (Bojanowski, 2007a, 2012). Some observations and simple modeling of stable O isotopes suggested that these rocks may have been related to the decomposition of methane hydrates. Hydrates are commonly found in association with seep carbonates in present-day marine sediments (e.g. Bohrmann et al., 1998; Greinert et al., 2001; Sassen et al., 2004; Teichert et al., 2005). These hydrate-associated authigenic carbonates are called clathrites and they provide evidence of processes related to methane hydrate formation and destabilization. Because hydrates dissociate during burial, they are not preserved in the sedimentary rock record. Clathrites should, however, be preserved. Yet, reports of fossil hydrate-associated carbonates are extremely rare (cf. Krause, 2001; Pierre and Rouchy, 2004; Martire et al., 2010) and their recognition is clearly underestimated. Thus, the second objective of this work is to present in detail the isotopic composition and fabric of one of the very few examples of fossil clathrites. Such contributions are essential for the recognition of fossil hydrate-associated settings in the future, because they provide the reference data and the criteria for the documentation and characterization of hydrate-associated features in a rock record.

## 2. Regional setting

The Outer Carpathians are a Miocene thrust-and-fold orogenic belt, stretching from Romania through Ukraine and Poland to Slovakia. The belt is composed of a thick, mainly turbiditic succession. The Polish part is in the northernmost part of the Carpathian range. It is composed of several main nappes. Magura, the uppermost nappe, is thrust over the Obidowa-Słopnice, the Grybów, the Dukla and the Silesian nappes. The Obidowa-Słopnice and the Grybów nappes emerge only in tectonic windows. The rocks examined here are exposed in the Świątkowa Wielka tectonic window (Fig. 1) (e.g. Koszarski, 1985; Oszczytko-Clowes and Oszczytko, 2011). They are hosted by dark, calcareous mudstones of the Oligocene Krosno Formation, which is between 80 and 110 m thick in the locality examined. This succession was deposited on a bypass slope in relatively stable conditions: turbiditic sediments were laid down episodically, whereas the background hemipelagic sedimentation was continuous throughout (Bojanowski, 2007b). The Krosno Formation was deposited in the upper bathyal zone in a basin a few hundred meters deep (Książkiewicz, 1975; Olszewska, 1984).

The succession is full of various authigenic carbonates, dispersed throughout the profile. Those in the uppermost part of the profile are calcitic and were formed as a result of methane oxidation (Bojanowski, 2007a). These seep-carbonates (GPS position: between 49°31.620' and 49°31.690' N, between 21°24.150' and 21°24.650' E) comprise concretions, a laminated limestone bed and a carbonate build-up. The build-up is a mound-shaped carbonate body (10 m high and 50 m wide) composed of intraformational carbonate breccia. Unique features related to the hydrocarbon seepage or venting have been documented in the breccia, e.g. characteristic calcite-filled druses (likely pseudomorphs of gas-hydrate particles), calcified microbial biofilms and fossils of giant sulfur bacteria (Bojanowski, 2007a). The exact age of the methane-derived carbonates is between 31.2 and 30.2 Ma (Barski and Bojanowski, 2010). The Outer Carpathian basin was at that time isolated from Parathetys and experienced anoxicity, low-salinity and cool-water conditions (Melinte, 2005; Švábenická et al., 2007).

## 3. Methods

Standard petrographic microscopy was performed on thin sections using a NIKON Eclipse E600POL polarizing microscope. Detailed

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