

Carbon and oxygen isotope analyses by mid-infrared laser spectroscopy as a tool for stratigraphic classification of Upper Jurassic carbonate rocks

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Goal

- Calibrate a chemo-stratigraphic curve on a drill core representing a complete succession of Upper Jurassic carbonate rocks from Southern Germany.
- Present the method for carbonate measurements, using Isotope Ratio Infrared Spectrometry as an analytical method for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis.
- Show the ability for high throughput and good precision measurements.
- New approach for stratigraphic classification of carbonate rocks.

Introduction

Geothermal energy (GE) plays a significant role in the conversion of fossils to renewable energy sources. In the near future, deep GE will be extensively expanded in Southern Bavaria (Martens & Kühn, 2015).

Favorable geologic framework conditions are key for making this region highly promising for GE generation. These conditions are mainly attributed to the occurrence of carbonate rocks in the subsurface, belonging to the Upper Jurassic epoch.



These carbonate rocks were deposited in an epicontinental tropical sea, favoring biotic and abiotic carbonate production, depending on environmental and climatic conditions (Ruf et al., 2005). In southern Bavaria, sedimentation during the Upper Jurassic lasted for more than 18 million years and resulted in a sedimentary succession of up to 600 m of carbonate rocks (Meyer & Schmidt-Kahler, 1989). A singularity within this succession is the occurrence of sponge-algal

reefs, which can appear throughout the whole profile. Carbonate production within these reefs occurred under unique biogeochemical conditions and was later subjected to diagenetic processes like dolomitization and finally karstification after these sediments became exposed (Meyer, 1996).

Since carbonates are mainly biological sediments, their depositional environment is often complex and frequently changing. This heterogeneity is the main reason for their suitability as a reservoir rock, but also complicates their stratigraphic classification (Ruf et al., 2005).

Stable carbon and oxygen isotopes of carbonates might be a suitable tool to classify these rocks, because processes like dolomitization or shifts from inorganic to biologically driven deposition as well as global sea level changes due to climate change leave a unique isotope signal within their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope signature. For our study we used Thermo Scientific™ Delta Ray™ Isotope Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI™) Connect, which allows fast and cost-effective isotope analysis, even under field conditions. The Delta Ray IRIS is based on direct absorption spectroscopy and is used for simultaneous determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

The results from discrete samples will be used for both, data validation and stratigraphic classification within the Upper Jurassic in Southern Germany. This will allow classification of disintegrated drilling samples, such as cuttings, and help to gain more information about the structure of the Upper Jurassic in the subsurface.

Basics for application of isotopes in stratigraphic classification of carbonate rocks

Stable carbon and oxygen isotopes of carbonates are very suitable tools for classification of carbonate rocks. They preserve information about climatic, oceanographic and biological changes in the depositional system of sedimentary basins as isotopic fingerprints in the organic and inorganic constituent parts of the rocks (Weissert et al., 2004). Important features of carbonate rocks that can be identified by isotope analyses are:

1) Carbonate rock facies

The facies (i.e. structural composition) includes a vast range of different manifestations (Fluegel, 2004). Carbonate facies can range from very uniformly bedded mudstones, i.e. stratified limestones formed from very fine carbonate mud, which was precipitated inorganically from supersaturated seawater on the bottom of the seafloor, to massive reefs, build up from the skeletons of various reef-building organisms in a shallow sea. Both facies types differ in their porosity and ability to conduct fluids, like hot water or hydrocarbons.

2) Diagenesis

Carbonates can occur in different mineralogical varieties, depending on their kind of formation (e.g. biological vs. inorganic or deep vs. shallow). Most carbonates formed by bio-calcification appear as aragonite or high-Mg calcite, which is unstable and tends to dissolve or recrystallize under burial conditions, creating porosity within the rock (Ricken, 1986). Additionally, carbonates are often subjected to dolomitization, which can completely change mineralogy and structure (Fluegel, 2004). Because of recrystallization processes, dolomitization is often related to an increase in porosity and structurally linked to karstification.

3) Karstification

After exposition to meteoric weathering, carbonates start to dissolve rapidly because to their reactivity with water loaded with carbonic acid (Nowak et al., 2017). Especially if weathering occurs under tropical conditions, karstification processes can deeply affect carbonate rocks, resulting in the formation of large pores, vugs and even caves (Fluegel, 2004). These karst features represent perfect flow conduits and are a desired target in GE exploration. Karstification is not only related to dissolution processes but also to wide-ranging recrystallization processes, forming dedolomite, speleothems and tufa (Fluegel, 2004).

All above mentioned processes are strongly linked to either chemical or biological processes, which have a strong impact on the isotopic composition of the respective carbonate.

Mudstone carbonates for example, are usually the result of CaCO_3 precipitation during mixing deep cold water with warmer shelf water (Meyer, 1996). In this case, the oxygen and carbon isotope signals are controlled by equilibrium fractionation under cold conditions. In contrast, carbonates formed on shallow carbonate platforms or reefs are formed under higher water temperatures and are either precipitated by direct biosynthesis or precipitation is triggered by high primary productivity in the seawater, causing changes in the carbon isotopic composition (McClelland et al., 2017). The same holds true for dolomitization and karstification. Since both processes can occur under different temperatures and different biogenic quota, carbonates formed under different conditions can be distinguished by their carbon and oxygen isotopic signature (O'Neil & Epstein, 1966) (Figure 1).

Stratigraphy of Upper Jurassic carbonates in Southern Germany

The Upper Jurassic of Southern Germany is characterized by up to 600 m thick limestone and dolomite succession (Meyer & Schmidt-Kahler, 1989) (Figure 2). These carbonates were deposited on the northern margin of the Tethyan Ocean on an

epi-continental sea. In the Oxfordian stage, bedded micritic mudstones and marlstones predominate, which are represented by the Dietfurt Formation (Niebuhr & Pürner, 2013). The Lower Kimmeridgian is dominated by marly limestones and marls (Arzberg Formation). At the transition to the Middle Kimmeridgian sponge algal reefs appear, forming massive carbonate rocks of the Frankenalb and Pottenstein Formation or the thick bedded Treuchtlingen Formation. Towards the Tithonian stage, sea shallowed, and reefs started to retract. These sediments are characterized by finer bedding and are mainly built up by shells of marine microorganisms. This systematic succession is characteristic for a large part of the Upper Jurassic in Europe.

Starting from very early after deposition, the reef facies got dolomitized in several stages (Reinhold, 1998).

After exposition of the succession in the Cretaceous, most of the strata and especially the reef facies were highly karstified before being covered by Upper Cretaceous marine sediments. In the Tertiary, the Upper Jurassic in Southern Bavaria was over-thrusted by alpine orogeny and covered with up to 2000 m of Tertiary sediments (Meyer, 1996).

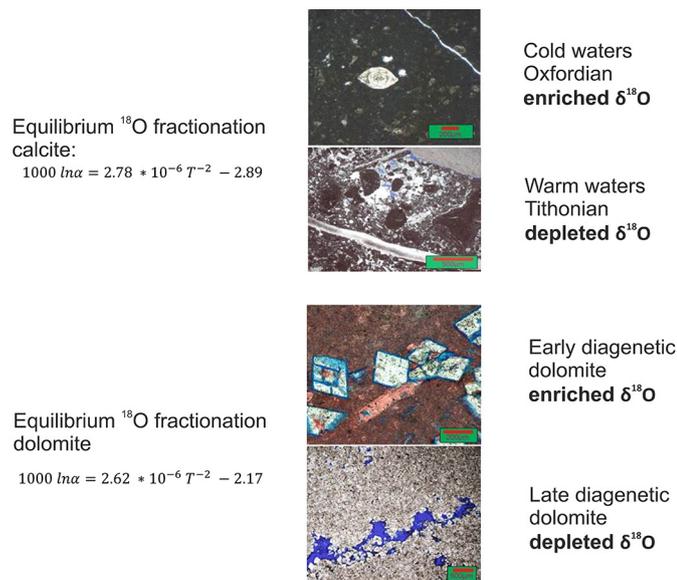


Figure 1. Facies types of Upper Jurassic rocks and related isotopes effects affecting $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures.

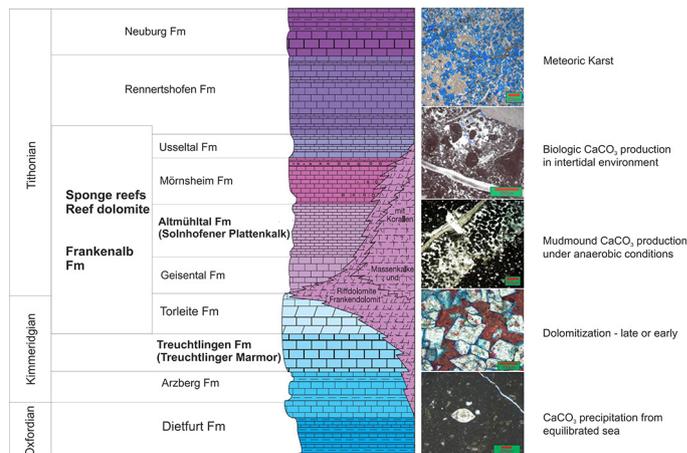


Figure 2. Stratigraphic profile and related facies types of the Upper Jurassic of Upper Bavaria.

Methods

Mid-infrared isotope ratio spectroscopy

The Delta Ray IRIS is based on direct absorption spectroscopy and uses a mid-infrared laser that operates at 4.3 μm . The laser light is generated by two tunable near-infrared diode lasers that are combined in nonlinear crystals. The laser scans over the spectral region containing four CO_2 absorption lines, and isotope ratios are calculated from the spectrum fit. Calculation of different CO_2 isotopologues and determination of stable isotope ratios from the spectrum is possible due to absorption lines that are shifted relative to each other.

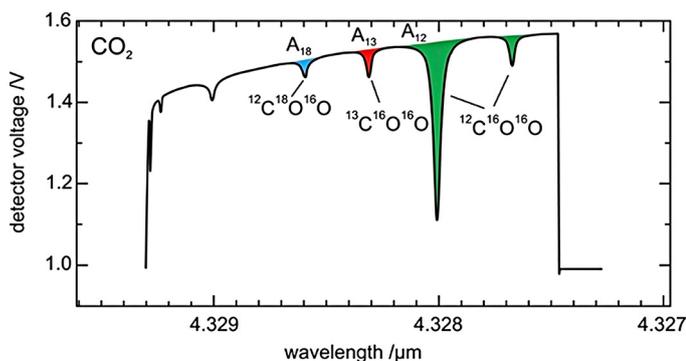


Figure 3. Mid-infrared spectral range at a wavelength of 4.2 μm . The stable isotope ratios of carbon dioxide can be calculated from the peak areas of the different isotopologues.

URI (Universal Reference Interface) Connect

With an option of continuous air measurements, URI Connect offers the possibility to measure discrete samples. It is composed of three functional units: MITCH™, Variable Volume (sample inlet), and dryer. The Variable Volume (VV) collects the sample gas, which comes from a sample port. The system automatically determines the concentration of the sample in the VV and adjusts the dilution during measurement. Dilution is done by the reference section with the MITCH valve block (gas mixing and swiTCHing device). This enables the instrument to perform the measurements at constant concentration. The referencing for isotope values is done by introduction of pure CO_2 gases diluted using a carrier gas. The change of concentration allows the determination of linearity (change of delta value with concentration), which can be used for subsequent correction of data. The concentration of the reference gas is balanced against that of the sample to improve accuracy.

Sampling

The Moosburg drill-core is a unique core representing a whole 600 m succession of Upper Jurassic rocks including all characteristic features such as massive reef facies, dolomitized sections as well as bedded limestones and Plattenkalk (Meyer, 1994). Representative samples of bulk carbonate rocks were taken approximately every 3 m, whereas important lithological transitions were sampled more densely at every 20 cm. Samples and sample meta-data (depth, stratigraphic position, lithology and geochemical analyses) were recorded for statistical analysis and were entered into the database of the Bavarian Environment Agency (Bodenatlas Bayern, BIS). Additionally, to the Moosburg core, one drilling-core from strata of Tithonian age was sampled (Kinding drilling core). This core includes parts of the Solnhofen Sub-Formation intercalated with rocks of massive facies representing a “younger reef generation” from the Southern Franconian Alb together with sponges growing on hardgrounds and corals (Meyer, 1977; Koch et al., 2010). The core is characterized by high karstification and a high degree of recrystallization. This facies in this particular stratigraphic position is a major target for geothermal exploration, because it promises high flow-rates and reduces drilling cost, due to reduced drilling depths.

Samples were milled with an agate ball mill, sieved to 63 μm and air dried at 40°C. 130 samples were taken covering 1/2 of the drilling core. Of these, 72+10 (Kinding core) were measured during one measurement session. All samples were measured in triplicates.

Sample preparation

Borosilicate Exetainer® vials were washed twice in de-ionized water and dried before use. After adding 400–500 μg of sample, vials were sealed with new septa and residual air was removed from the vials by an automated autosampler-assisted flushing procedure. The flushing procedure is carried out at a flow of 30 mL/min for 3 min. Further, samples were manually acidified using three droplets of 104% phosphoric acid (anhydrous phosphoric acid; 104% of $\text{H}_3\text{PO}_4 = 0.25 \text{ mol H}_2\text{O/L H}_3\text{PO}_4$) and placed into a heated rack at a constant temperature of 80°C. After one hour at 80°C, the measurement was started. The Principle of Identical Treatment was applied in sample and standard preparation, in the measurement procedure, as well as in the evaluation of the results. The international reference

materials NBS 18 and IAEA-603 were used to perform a two-point calibration, while NBS 19 was used as quality control sample. The normalized carbon isotope ratios of the samples were reported in per mill (‰) relative to VPDB. Fractionation factors for correcting $\delta^{18}\text{O}$ values of dolomites for acid fractionation were obtained from Rosenbaum and Sheppard (1988) and are normalized for fractionation at 25°C.

Measurement setup

The sampling and measurement procedures were driven automatically from the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS™). The built-in sample processing method “Transfer Sample” was chosen for sample measurement. This method executes sample collection from the autosampler, sample concentration determination prior to measurement, and optimization of the measurement conditions. Each sample measurement was followed by a measurement of a working standard gas to correct for instrument drift. To gain maximum precision, both samples and working standards were measured for 180 s. Prior to each sample transfer, the Variable Volume and plumbing was flushed with carrier by means of an action script.

With this measurement setup the full sample rack with 60 samples was measured within 20 hours.

Statistical analysis

For determining trends in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ changes with depth, locally weighted regression (LWR) was used to fit a polynomial surface determined by one or more numerical predictors with R package “stats” (R Core Team, 2013).

Principal component analysis (PCA) was used to examine the variation of both isotope ratios in one plot. PCA allows identifying main independent directions of variation (i.e. principal components) in a dataset of interrelated variables (Hotelling, 1933). Source and process variation is represented more clearly when projected onto new principal component axes (Craddock et al., 2018).

Analysis was done with R-statistics software using the “stats” package (R Core Team, 2013). In a PCA biplot, ray angles show an approximate measure of correlation: low angle rays are likely positively correlated, rays that plot in opposite directions are likely negatively correlated and rays that are perpendicular are likely uncorrelated. A ray that plots close to a principal axis is highly correlated with that principal component.

Results and discussion

Two-point data calibration – correction

For correction, data from Qtegra Software were exported to a Microsoft™ Excel™ file. The obtained isotope ratios for NBS 18 and IAEA-603 were averaged and used to generate two-point calibration curves for the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios. The calibration functions were then applied to the measured isotope ratios of the samples.

Accuracy of the method was confirmed by quality control sample measurements (NBS 19: $\delta^{13}\text{C} = 1.95\text{‰}$ VPDB; $\delta^{18}\text{O} = -2.20\text{‰}$ VPDB;), (Figure 4).

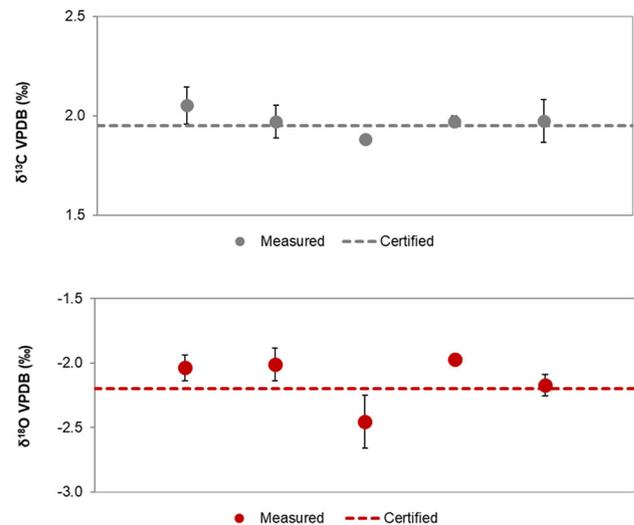


Figure 4. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of NBS 19 measured as “unknown” sample.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of carbonate rocks

Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show characteristic changes with depth. At the Callovian/Oxfordian transition (Sengenthal Formation, bSt), $\delta^{13}\text{C}$ shifts from around -0.7 to 1.8‰ (Figure 5). The shift in $\delta^{13}\text{C}$ coincides with a shift in $\delta^{18}\text{O}$ from -5 to -1.8‰ (Figure 6). Both isotopes exhibit a constant trend towards more negative delta values to -4‰ throughout the Oxfordian (Dietfurt Formation, wD) up to Lower Kimmeridgian strata (Arzberg-Formation). The appearance of dolomitized sponge-algal reefs in the Middle Kimmeridgian (Frankenalb Formation, wFr) is characterized by scattering $\delta^{13}\text{C}$ as well as $\delta^{18}\text{O}$ signatures at the base (between app. 1.1 and 2.7‰ in $\delta^{13}\text{C}$ and -6.8 and -2.4‰ in $\delta^{18}\text{O}$). In the upper section $\delta^{18}\text{O}$ remains scattered between -3.1 and -4.6‰, whereas $\delta^{13}\text{C}$ shifts towards more positive values with lower scattering between 2.3 and 2.8‰. Up to now, no samples were measured from Upper Kimmeridgian

and Tithonian strata. However, first measured samples from the Upper Jurassic/Cretaceous transition (Purbeck Facies, Pur) show a trend towards more negative values in $\delta^{13}\text{C}$ as well as varying $\delta^{18}\text{O}$ values, most probably due to intertidal depositional conditions (Figure 5 and 6). $\delta^{18}\text{O}$ values of the karstified Kinding core range between -4.0 and -4.5‰. However, $\delta^{13}\text{C}$ signatures are far more depleted than values from the Moosburg core, with values between -7.6 and -8.3‰.

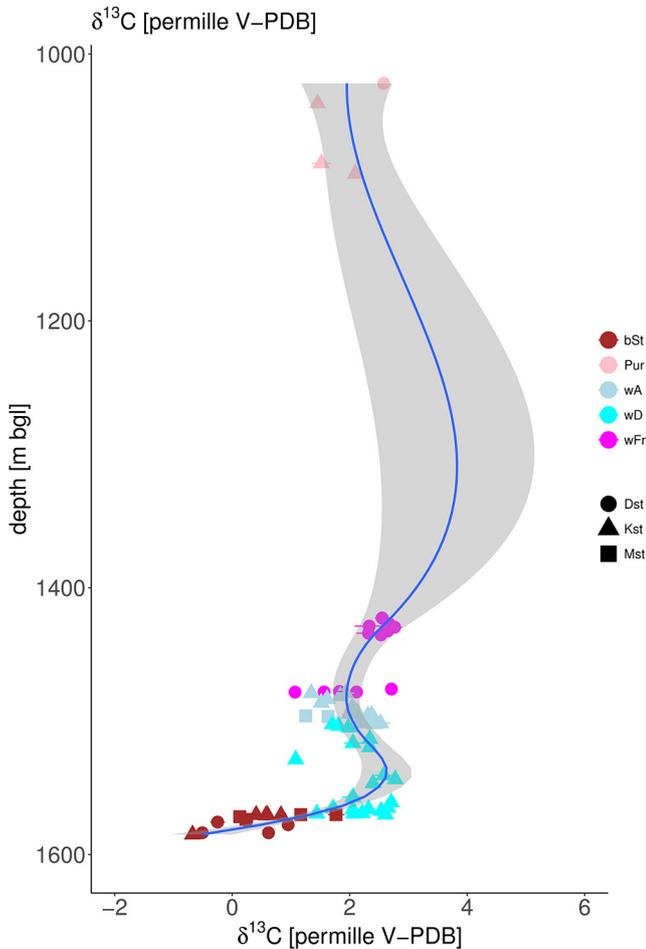


Figure 5. $\delta^{13}\text{C}$ depth profile. $\delta^{13}\text{C}$ values show a characteristic trend with depth. Circle, triangle and square represent different lithologies. The blue line represents the LWR model and grey bands its 95% confidence interval. Error bars represent standard deviation of three replicate samples.

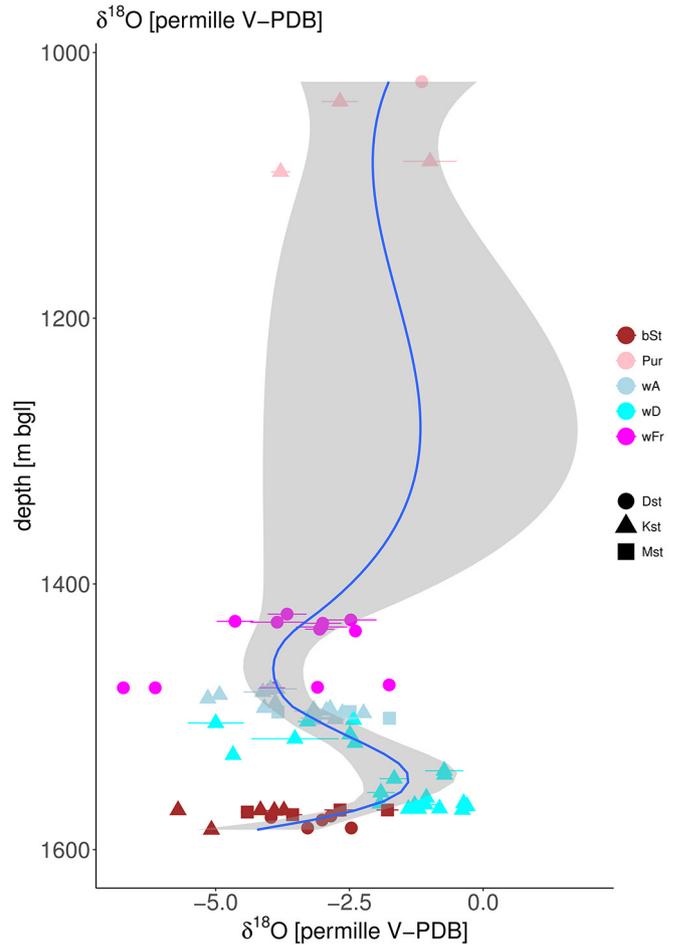


Figure 6. $\delta^{18}\text{O}$ depth profile. $\delta^{18}\text{O}$ values show a characteristic trend with depth. The blue line represents the LWR model and grey bands its 95% confidence interval. Error bars represent standard deviation of three replicate samples.

Statistical analysis

Figure 7a shows a biplot representing the two principal components of the dataset that explain 87%. Data is represented as dots, whereas arrows represent variables. The bottom and left axis show the loadings of each variable for PC1 and PC2, respectively. Variables include depth, lithology and stratigraphic position, whereas stratigraphic position and depth were transformed to a numeric code of consecutive values. The data was additionally Log transformed in order to account for differences in scale. PC1 explains 54% and PC2 33% of the variability in the dataset (Figure 7b). $\delta^{13}\text{C}$ and stratigraphic position (Formation) are positively related to PC1 and inversely to PC2, whereas $\delta^{18}\text{O}$ and lithology (Lithology) are inversely related to PC2 as well as PC1. $\delta^{18}\text{O}$ shows a strong positive correlation with lithology along PC1 but little correlation with stratigraphic position. $\delta^{13}\text{C}$ is positively correlated with stratigraphic position along PC2 and negatively correlated with depth.

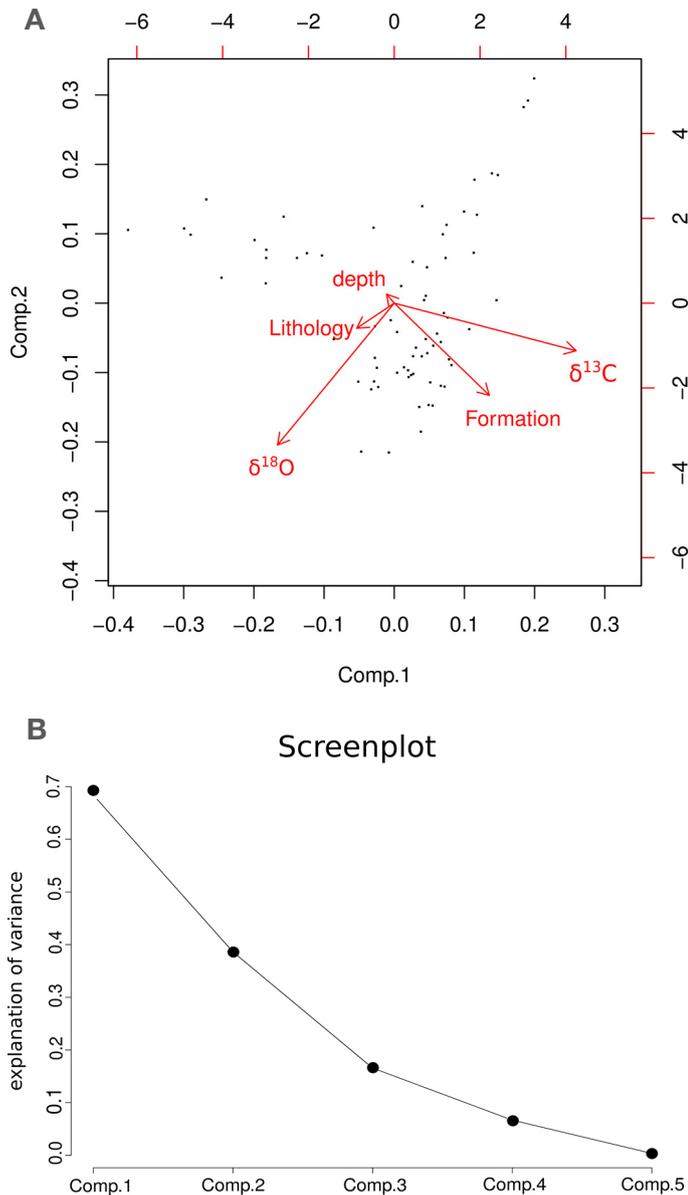


Figure 7. Biplot (A) and variogram (B) of the data set. $\delta^{18}\text{O}$ and lithology correlate along PC 2, whereas $\delta^{13}\text{C}$ and formation correlate along PC 1.

Figure 8 represents a plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ for limestones and dolostones, respectively. Drawn ellipses represent 68% confidence intervals. Based on the current data, formations of Callovian, Oxfordian and Lower Kimmeridgian age (bSt, wD, wA) are significantly distinct from each other. Because of low sample number at the current project state, no conclusions can be drawn for limestones of Tithonian age. They scatter across a wider range and cannot be distinguished significantly from wD and wT data. Limestones from the Kinding core cluster in a very distinct region compared to the Mossburg samples due to their more negative $\delta^{13}\text{C}$ values.

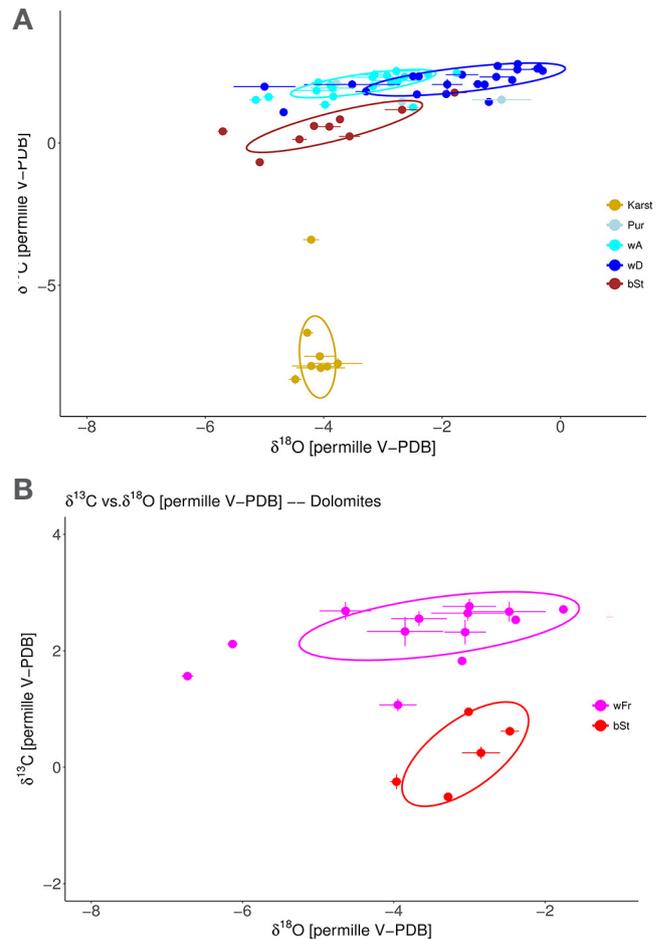


Figure 8. 3D scatter plot of $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ values with 68% confidence ellipses. All lithological formations can be separated according to their lithology and stable isotopic values. Error bars represent standard deviation of three replicate samples.

Dolomites cluster in two regions depending on their stratigraphic position. Dolomites from massive facies of Middle Kimmeridgian age (wFr) are characterized by more positive values compared to dolomites from Callovian strata (bSt). However, data points from the lower position of wFr plot outside the confidence ellipse, indicating different dolomitization processes in this section.

Discussion

Controls of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonate rocks

Measured data show that stable isotope ratios of bulk carbonate samples are a powerful tool to stratigraphically classify Upper Jurassic carbonate rocks. 82 samples, which were measured during one measuring campaign, were sufficient to calibrate a chemo-stratigraphic curve for almost 250 m of the Upper Jurassic in Southern Bavaria. The course of the regression model represents both, changes in depositional environment and carbonate production as well as diagenetic processes like dolomitization and karstification. The trend towards

more positive $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ at the transition bSt and wD (Callovian/Oxfordian age) represents the transgression of the Tethyan sea and the stream of cold water on the northern Tethyan shelf (Ruf et al, 2005). The shift towards more positive values along wD and wA indicates a gradual warming from Oxfordian to Kimmeridgian.

Perturbations at the bottom of the dolomitized massive facies represents most probably different stages of dolomitization. Reinhold (1998) identified 4 stages of dolomitization in dolomites from the eastern Swabian Alb. Progressive dolomitization is characterized by both, depletion in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The general isotopic composition indicates that dolomites in the Moosburg core were formed in a later dolomitization phase under slightly elevated temperatures during shallow burial diagenesis. The variations at the bottom of wFr might indicate the influence of meteoric waters during later dolomitization processes, which would explain vugs appearing in this section (Meyer, 1994), whereas the uniform $\delta^{13}\text{C}$ and lower $\delta^{18}\text{O}$ variability of upper dolomite samples indicate more uniform formation conditions under closed system conditions. The correlation between isotopic composition and poro-perm parameters has to be further investigated, in order to use isotopic values for prediction of potential flow-rates triggered by dolomite matrix porosity.

Applicability of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope ratios for classification of lithological formations

PC1 and PC2 explain more than 87% of the variability in the dataset. The strong correlation of $\delta^{18}\text{O}$ and lithology along PC2 indicates that it represents mainly the influence of lithology, especially dolomitization on the $\delta^{18}\text{O}$ signature in the samples. By contrast, PC1 is dominated by variation of the $\delta^{13}\text{C}$ ratio and represents differences between the different litho-stratigraphic units. Thus, PCA analysis suggests that $\delta^{13}\text{C}$ as well as $\delta^{18}\text{O}$ are suitable parameters to differentiate between different lithologies as well as different stratigraphic units. This is also illustrated in Figure 8. All limestone formations from

Callovian to Kimmeridgian age can be distinguished according to their $\delta^{13}\text{C}/\delta^{18}\text{O}$ ratio. A great potential in the application of stable isotope stratigraphy lies in the identification of highly karstified areas, as proved by samples from the Kinding drilling core. $\delta^{13}\text{C}$ values are strongly influenced by recrystallization of calcite or dolomite by meteoric water DIC. Recrystallization driven by dissolution/precipitation processes triggered by soil CO_2 , which has a $\delta^{13}\text{C}$ values of around -23‰ (Gillon et al., 2012, Nowak et al., 2017). Dissolution of carbonate rock by dissolved CO_2 creates DIC which can be described by following equation:



whereas half of the produced DIC is derived from soil CO_2 (-23‰) and half of the DIC from carbonates (1‰), resulting in an $\delta^{13}\text{C}$ value of usually -9 to -12‰ VPDB, which can be further increased by isotopic exchange (Nowak et al., 2017).

Thus, karstified sections, which are the main target for geothermal exploration in Upper Jurassic rocks in Southern Bavaria can be easily identified by stable carbon isotopes.

Conclusions

Based on detailed sampling and precise determination of stable carbon and oxygen isotope analyses of bulk carbonate rocks, we were able to calibrate a chemo-stratigraphic curve of almost the half section of the Upper Jurassic in Southern Bavaria. Both isotopes show a distinct pattern with depth, representing both changes in depositional environment and lithology. With the aid of both isotopes all formations as well as distinct dolomite types could be significantly distinguished. Especially highly karstified areas can be certainly identified.

In addition, we confirmed that mid-infrared laser spectroscopy is a great tool for high throughput and high precision measurements of carbonate material.

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