

An experimental setup for the assessment of effects of carbonate rock dissolution on complex electrical conductivity spectra

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ABSTRACT

Investigating complex electrical properties of natural rocks and soils by using spectral induced polarization (SIP, i.e. low frequency impedance spectroscopy, typically measured from 1 mHz up to 100 kHz) is of high research interest for all pore space and boundary surface specific processes and properties between the matrix and the pore fluid. The deduction of hydraulic and pore space related structural properties, as well as the correlation of SIP-data with core and special core analysis data is recently in the focus of research. In the first stage of this project, a case study has been presented that investigates the complex electrical conductivity of carbonate samples using low frequency electrical impedance spectroscopy. Within the next phase, a specifically designed experimental setup for temperature controlled acidizing of carbonate rock samples has been constructed. The setup features a special core holder for saturating the samples with a retarded (i.e. temperature activated) formic acid, which is connected to adjacent fluid reservoirs by high-precision piston pumps. Fluid type can be easily switched for flushing/cleaning of the material after acidification without removing the sample from the core holder. The core analysis program includes a multi-methodical and interdisciplinary approach, combining petrophysical, mineralogical and geochemical techniques. Before and after each core acidification step, porosity, specific surface area, nuclear magnetic resonance (NMR) T_2 distributions as well as complex conductivity spectra and data from 2-D and 3-D imaging techniques have been obtained. In this manuscript, the authors would like to present the experimental setup, the workflow as well as first results of the SIP and petrophysical investigations on selected carbonate samples.

INTRODUCTION

Spectral Induced Polarization (SIP) measurements (i.e. “low frequency” impedance spectroscopy, typically conducted in a frequency range from 1 mHz up to 100 kHz) are used in many different ways to characterize natural rocks and soils. Main focus of interest is upon the enhanced characterization of the causes of polarization effects in sedimentary rocks. The interactions between the matrix-fluid-system and within the electrical double layer as well as the correlation with petrophysical parameters, such as specific surface area, permeability, and pore radii distribution as derived from mercury intrusion capillary

pressure data are investigated by SIP. A variety of polarization models, either grain based or pore based, have been developed over the past years to describe the polarization effects of sedimentary rocks [e.g.: 1, 2, 3, 4, 5]. The electric resistivity, as well as electric conductivity are both described as complex quantity values. As explained by [6], complex conductivity (σ^*) of a rock sample is determined by measuring the magnitude of conductivity ($|\sigma|$) as well as the phase shift (φ), relative to a reference resistor. The real (σ') and imaginary (σ'') part of σ^* , which represent the ohmic conduction and polarization charge transport mechanisms, respectively, are directly determined from impedance measurements. The phase shift thereby is defined as:

$$\varphi = \arctan(\sigma''/\sigma') \approx \sigma''/\sigma' \quad (\text{for } \varphi < 100 \text{ mrad}), \quad (\text{E1})$$

which is by convention defined as a positive value in conductivity space. Generally, complex conductivity models are based on two contributing conductivity terms, as denoted amongst others by [7]:

$$\sigma^* = \sigma_{\text{el}} + \sigma_{\text{surf}}^*. \quad (\text{E2})$$

The first term (σ_{el}) represents the conductivity of the electrolyte filled interconnected pore space, whereas the second term (σ_{surf}^*) reflects conduction and polarization within the Electrical Double Layer (EDL) of the interconnected pore surface. The SIP method itself has been developed from classic frequency domain IP, and takes both, electric resistivity as well as phase shift into account. This method has become a potentially good tool for the enhanced characterization of rocks and their pore structures [e.g.: 8, 9, 10]. Preliminary investigations were carried out on different carbonate rocks in a couple of systematic laboratory studies [11, 12]. Besides distinct polarization effects, a strong relationship between σ_{surf} and σ'' has been observed.

The current study aims at the controlled acidification of carbonate samples, as it has been previously investigated and reported by [13]. Furthermore, the monitoring of the according changes in petrophysical and SIP related parameters for a selection of carbonate rocks is of key interest. For this, an experimental setup has been designed for performing acidification steps systematically and under very controlled conditions, related to the needs of the accompanying SIP measurements. The measurements of the complex electrical conductivity have been performed in close combination with classical petrophysical measurements (porosity, gas-permeability, nuclear magnetic resonance, specific surface area). Additionally, state of the art 2-D and 3-D imaging techniques (environmental scanning electron microscopy - ESEM, and X-ray micro computed tomography - μ -CT) have been used to visualize and quantify subsequent changes between each acidification step. First, the authors would like to present the experimental setup, followed by the workflow (including sample preparation, sample saturation, measuring procedures and sample cleaning) as well as first results of the SIP and other petrophysical investigations on carbonate samples after a couple of acidification steps. The results are critically discussed before a brief outlook on the ongoing research is given.

SAMPLES & METHODOLOGY

The samples used for this study are Edwards Brown carbonates, which are generally characterized by high porosity and reasonable Klinkenberg permeability values (average of 37.1 % and 196 mD, determined by triple weighing and steady state gas permeametry). The sample material as well as the workflow and setup of the SIP measurements has been described more in detail within the previously presented studies [12, 14]. Surface area, gas-permeability, porosity and NMR T_2 measurements have been carried out by considering the recommended practice and protocols for core analysis as recommended in [15]. The device for the acidification procedures has been specifically designed and constructed for this study (Fig. 1). It consists of two independent fluid reservoirs at the inflow and outflow side (one for fresh water, one for acid-water solution), and two independent high precision piston pumps (one for each inflow reservoir) which enable variable flow rates between 0.1 ml/h – 999 ml/h at a maximum inflow pressure of 40 bar (580 psi). Additionally, temperature, pH and conductivity of the inflowing as well as of the outflowing fluid are permanently measured during the experiment. The core holder is basically a so called Fancher-type cell, including a highly durable silica-rubber sleeve for the sample material. With this special design, creeping flow alongside the sample and sleeve is already avoided at very low overburden pressures (here: 11 bar, i.e. 160 psi).

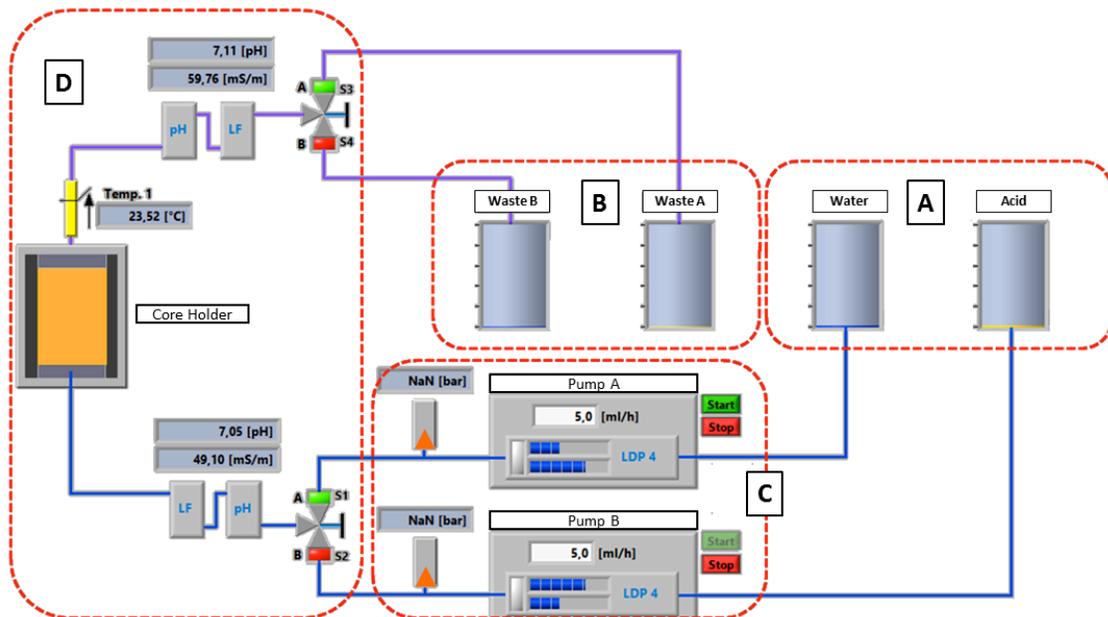


Figure 1: Schematic assembly drawing of custom built device for the acidification procedures. (A): inflow fluid reservoir tanks for water and acid; (B): outflow waste fluid reservoir tanks; (C): high precision piston pumps for each fluid, including pressure measurement at the core holder inflow; (D) core holder inside a furnace for sample saturation and cleaning, including temperature as well as pH-value and fluid conductivity monitoring at both, inflow and outflow side.

For acidification, the samples were treated with a 2.5 vol.-% solution of Acidgen™ FG3, resulting in a pH-value of the solution of approximately 3.7. It has been showcased within an earlier study that this type of acid is very capable of providing a homogeneous acidification of carbonate samples under quite easy to handle laboratory conditions [13]. The general chemical reactions for the creation of the water-acid mixture (stage 1) as well as for the acidification procedure after saturating of the sample with the solution (stage 2) can be described as follows:

Stage 1 (water-acid solution): $\text{Acidgen}^{\text{TM}} \text{FG3} + \text{H}_2\text{O} \rightarrow 2\text{HCOOH}$;

Stage 2 (acidification): $2\text{HCOOH} + \text{CaCO}_3 \leftrightarrow \text{Ca}(\text{HCOO})_2 + \text{CO}_2 + \text{H}_2\text{O}$.

Within stage 1, the combination of acid and water forms a formic acid solution. The products after reaction with the carbonate phase (stage 2) are water, gaseous CO_2 and calcium-formate, which is totally dissolved within the water due to its high solubility (around 160 g/l). The final, i.e. optimized workflow used in this study as illustrated within Figure 2 has been created during extensive (more than 2 ½ months) testing and measuring procedures. First, a general core analysis program has been conducted, including surface area (N_2 adsorption), porosity (triple weighing), permeability (Klinkenberg corrected, steady state), NMR T_2 , μ -CT, ESEM) measurements. This program was followed by a SIP measurement for each sample (for SIP, CaCl_2 brine conductivity is around 100 mS/m, i.e. concentration of 0.52 g/l), before the plugs were saturated with the acid solution. The initially water saturated sample (fluid conductivity 50 mS/m) is flushed with 10 pore volumes (PV) of the acid solution (5 PV in each direction in order to prevent trapping effects) at flowrates of 40-50 ml/h. Sample saturation with acid solution is assumed to be completed, once the electrical conductivity at the outflow reaches steady state. This procedure is followed by triggering the chemical reaction inside the material by increasing the sample temperature to 40°C for a shut-in period of 24 hours. Afterwards, the sample is flushed with at least 20 PV of fresh water (again, 10 PV in each direction) until the fluid conductivity at the outflow reaches same level as measured at the inflow. SIP and core analysis measurements follow these steps in order to quantify the effects of the acid treatment, before the overall workflow is repeated as previously described.

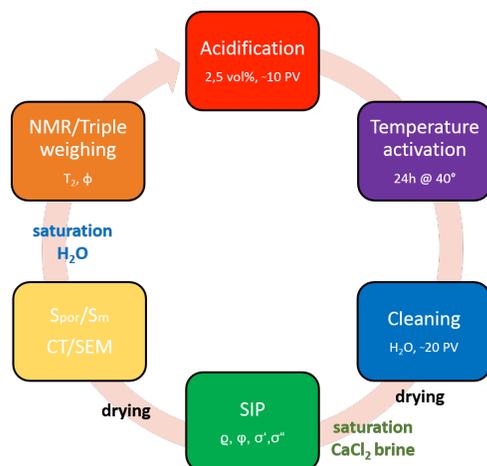


Figure 2: Principle drawing of the final workflow that has been used for the laboratory measurements and acidification procedures on the Edwards Brown carbonate samples.

RESULTS & DISCUSSION

The homogeneity of the acidification process throughout the internal structure (surface) of the carbonate samples has been widely confirmed especially by ESEM-imaging before and after each step (Fig. 3). The acidification takes place at two different locations within the samples: first, carbonatic cement in between the idiomorphic crystals is widely and preferably dissolved by the acid solution (Fig. 3, indicated by red arrows). Second, at the surface of the idiomorphic crystals, which is widely affected by a continuous, but also slower dissolution process (Fig. 3, indicated by blue arrows). Additional geochemical analyses have shown that the idiomorphic crystals consist of Ankerite (Fe-bearing carbonate, $\text{CaFe}[\text{CO}_3]_2$) whereas the cement consists of very pure calcite (CaCO_3), which results in a higher solubility against the acid solution for the cement as for the crystals itself. ESEM imaging qualitatively confirms this finding, since it is not possible to quantify, i.e. to investigate these processes by geochemical analysis separately and in detail.

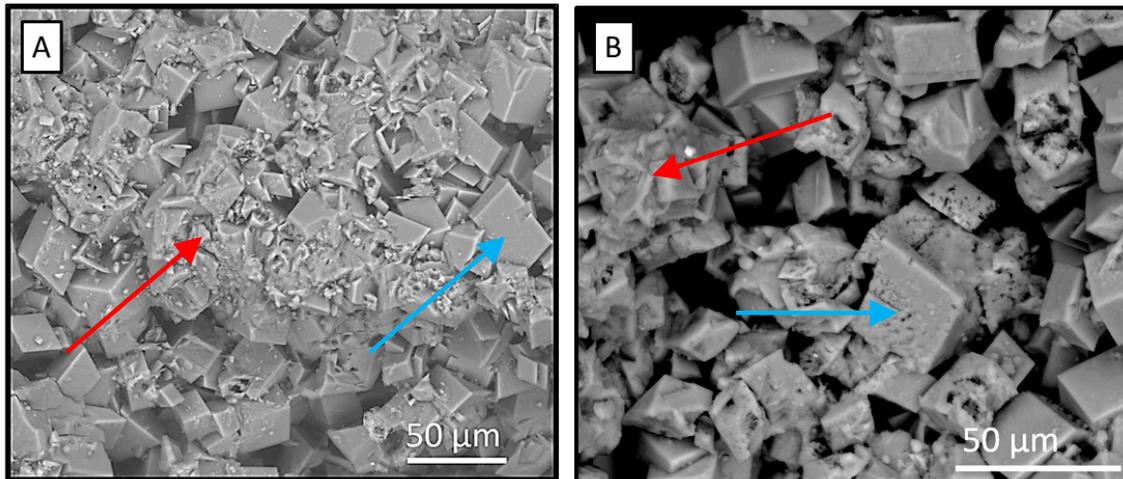


Figure 3: ESEM images of a representative Edwards Brown carbonate sample before (A) and after (B) acidification by using Acidigen™ FG3.

Consequently, porosity and specific surface area feature the highest sensibility throughout the classical petrophysical core analysis data set (Fig. 4). Porosity increases in average by 12.6 % (from 0.37 to 0.41) during the first two acidification steps. Specific surface area increases in average by 22.8 % (from $21.1 \mu\text{m}^{-1}$ to $25.8 \mu\text{m}^{-1}$). This result is in good accordance to the ESEM observations, showing the ongoing dissolution of the idiomorphic crystal surfaces (Fig. 3), which greatly increases the surface roughness. The changes of the pore structures have been investigated more in detail by X-ray μ -CT and NMR T_2 measurements for specifically selected (i.e. partially broken and hence not anymore usable) samples (Fig. 5). The results of the NMR T_2 measurements widely confirm the assumptions about the dissolution process as pointed out earlier.

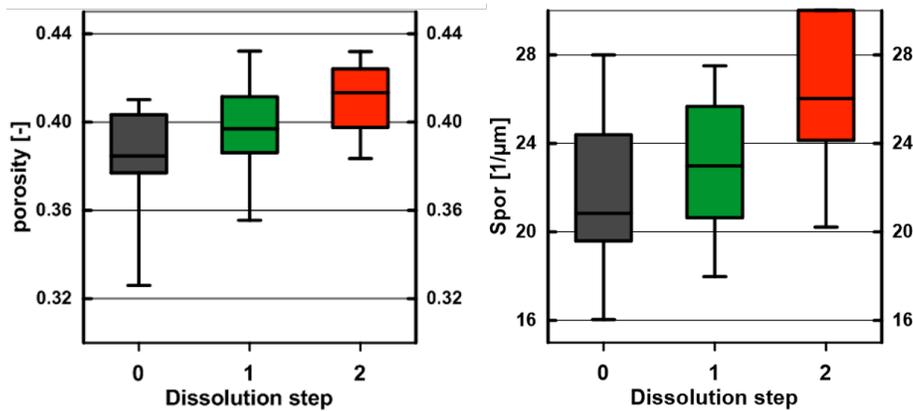


Figure 4: Box-Whiskers plots of porosity (left) and specific surface area related to pore volume (right) versus acidification steps for the entire Edwards Brown sample set (27 samples; please note: so far only few samples have been investigated with distinctively more than two acidification steps, hence we showcase less steps but with a significantly better statistical basis for all samples).

In general, a distinct shift towards smaller T_2 -times as well as an increase of the NMR amplitude could be observed (Fig. 5, left, indicated by dashed lines for visualization purposes only), which implies an increase of the amount of small pores and also leads to an increase of the pore volume that is created during the dissolution process. Additionally, an increase of the NMR amplitude at larger relaxation times is observed (Fig. 5, left, marked by purple circle) and could be explained by the dissolution of the cement, which does not lead to the creation of “new” pores but to a distinct growth of existing and larger pore areas within the material. This assumption is substantiated by digital image analysis of the μ -CT data sets (Fig. 5, right), from which the equivalent diameter of the segmented pores is derived as described by [16].

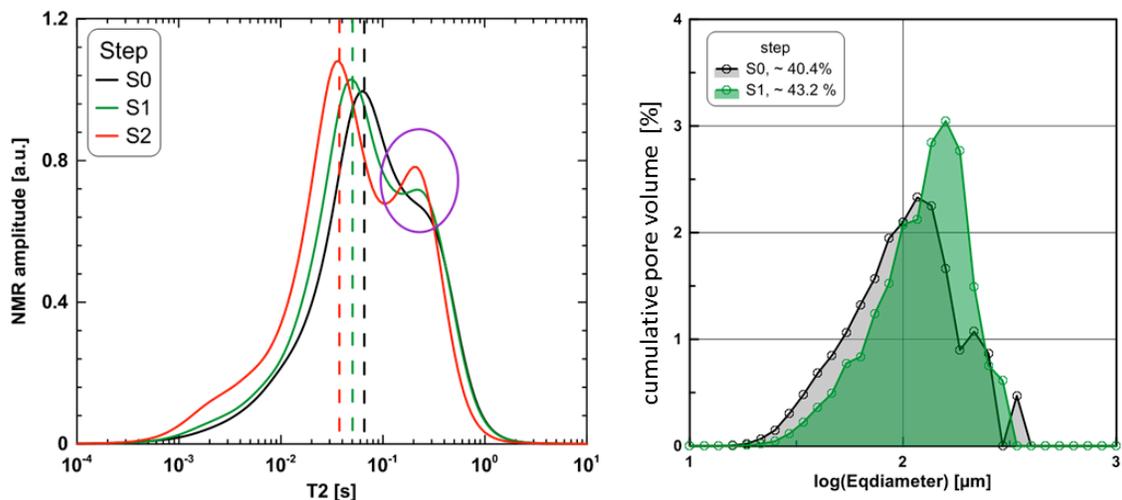


Figure 5: Results of selected NMR T_2 measurements (left) and μ -CT based pore size analyses after a couple of acidification steps for representative Edwards Brown carbonate samples.

The derived distribution curve is moderately shifted towards larger equivalent diameters after acidification of the carbonate sample, but the overall volume increases considerably, which is again consistent with the observed changes of the pore structures. Due to resolution limits, it was not possible to detect the increase in the number of small pores. Figure 6 shows representative results of an SIP measurement before and after different acidification steps. Phase and resistivity amplitude spectra as well as the imaginary (i.e. out-of-phase part, σ'') and real (i.e. in-phase part, σ') part of the complex conductivity are presented. The resistivity and accordingly σ' , changes more randomly after different dissolution steps than expected. Due to the overall high conductivity of the sample material, absolute measurement accuracy may be lower than needed for a reliable detection. The same behavior is observed within the phase shift and σ'' spectra, hence only a slight shift could be measured without any noticeable change in frequency. Though this might point towards a reduction in the polarizability of the material, measuring accuracy needs to be significantly improved.

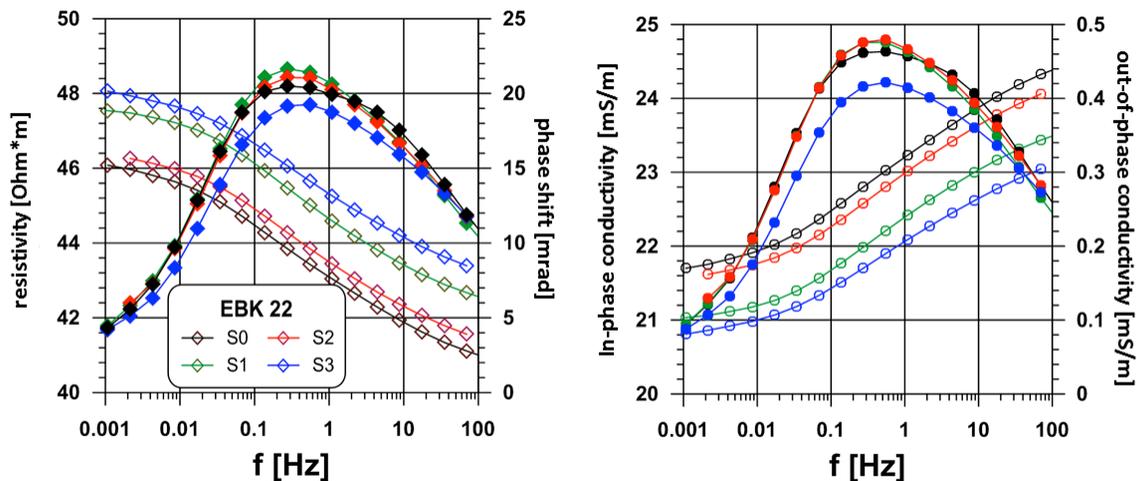


Figure 6: Representative results from SIP measurements after different acidification steps of the Edwards Brown carbonate samples. Changes for resistivity amplitude (blank diamonds) and phase shift (solid diamonds) are shown on the left hand side. Changes for the in-phase (blank circles) and out-of-phase conductivity (solid circles) are shown on the right hand side.

This leads to the result that φ and σ'' are more sensitive towards the pore structure and surface changes than resistivity amplitude and σ' . The decrease in the phase shift and σ'' amplitude is however quite remarkable, especially if the large increase of the surface area is considered. As shown by [4], an increase of the surface area should result in an increase of σ'' . The ratio σ''/S_{por} is called “specific polarizability”, which - by trend - seems to be different for carbonate samples, as shown in Figure 7, since an increase in surface area leads to a decrease in σ'' . Geochemical and ESEM analysis have shown, that the Edwards samples are very “pure”, i.e. around 90 vol.-% Ankerite / Calcite, around 7-9 vol.-% Quartz and less than 1 vol.-% of clay (Illite). Additionally, the samples are especially homogeneous, without any lamination or bedding planes. Hence it seems legit to assume that the measured signals directly correlate with the acidification of the carbonate phase.

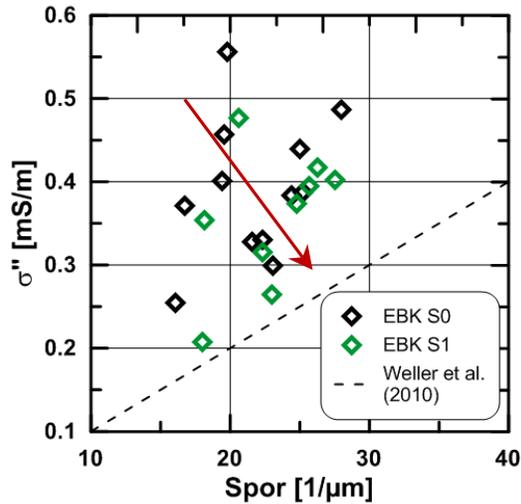


Figure 7: Specific surface area versus imaginary part of conductivity for a sub-set of Edwards Brown carbonate samples before (black diamonds) and after (green diamonds) acidification. The dashed black line indicates the correlation as observed for a large variety of sandstones by [4]: increasing S_{por} , increasing σ'' . The red arrow indicates the observed trend for the carbonates: increasing S_{por} , decreasing σ'' .

SUMMARY & CONCLUSIONS

For this paper, the authors have showcased the motivation as well as the development of a specifically designed device and the development of a joint methodical workflow for carbonate acidification experiments. With this approach, the impact of acidification procedures upon both, mineral and pore structures can be investigated systematically and under controlled and favorable laboratory conditions. The induced dissolution processes impact several petrophysical parameters with different sensitivity. The changes within the material can be partially resolved by SIP measurements and point towards an impact upon the specific polarizability of the rock material. Nevertheless, more systematic investigations, as well as distinct improvements for the SIP measurement accuracy are substantial to derive clear correlations in the future.

OUTLOOK

The ongoing development and improvement of this device, as well as the combination of acidification procedures and spectral induced polarization measurements is part of the ongoing research at our working group. The data set will be consequently increased and others types of carbonates will be investigated as showcased here within the future.

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