

IMPACT OF CO₂ ON THE COMPLEX ELECTRICAL CONDUCTIVITY OF CARBONATE ROCKS UNDER RESERVOIR CONDITIONS

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ABSTRACT

Carbonate rocks provide great challenges to geophysics and reservoir engineering due to their extremely heterogeneous pore space and the reactive nature of the carbonate rock matrix. The presence of a reactive gas such as CO₂ in the pore space of a carbonate rock acts on the electrical conductivity mainly through three effects: 1. the resistive gas reduces the water saturation thereby decreasing bulk conductivity; 2. the gas simultaneously dissolves in the pore water thereby changing its ion content and the pH; 3. the CO₂-rich pore water interacts with the reactive carbonate matrix, which results in mineral dissolution, precipitation, and/or pH buffering.

We systematically investigate these effects under reservoir conditions in the laboratory using the spectral induced polarization (SIP) method. This method is accompanied by measurements of the nuclear magnetic resonance (NMR) under normal conditions. Several types of carbonate rocks are investigated under normal conditions and during exposure to CO₂ aiming at temperatures up to 80°C and pressures up to 30 MPa. We use both cores and crushed samples of varying particle size. Systematic investigations of the SIP of (non-reactive) quartz sand under reservoir conditions serve as a reference.

The different carbonate types show significant variation in their SIP response (i.e., the frequency dependent complex electrical conductivity) depending on salinity, porosity, pore-space heterogeneity and – in the case of crushed samples – the organization of particles in the packing. The NMR response shows a strong difference between the amount of free and capillary bound water in the samples at the same time.

Our approach reduces the complexity of the entire system and lets us differentiate between electro-chemical interactions and pore-space controlled processes. We aim at a systematic quantification of these processes in terms of their electrical manifestation and the derivation of a model description. The combined approach of SIP and NMR allows for the assessment of monitoring options with electrical methods in carbonate reservoirs.

INTRODUCTION

Carbonate reservoirs have come into focus since they host huge resources of oil and natural gas. Consequently, they are also targets for enhanced oil recovery (EOR) and carbon dioxide sequestration techniques. Carbonates, however, provide great challenges due to their extremely heterogeneous pore space and the reactive nature of the carbonate rock matrix. Electromagnetic methods can be of great value for monitoring fluids since they are sensitive to the pore content and provide information on the electrical properties of large rock volumes. Nevertheless, the petrophysical knowledge of the electrical properties of carbonates, which is an essential basis of monitoring, is still rather poor. We therefore carry out investigations on the electrical properties of carbonate rocks with the focus on understanding the impact of chemical interaction (e.g. pH-buffering and dissolution of carbonate matrix) on the spectral complex conductivity. In order to stringently relate our observations to said chemical interaction effects, we work with crushed carbonate samples. This has several advantages: controlled destruction of the heterogeneous pore space, enlarged interfaces for interaction, increased permeability.

In a first step, we have to understand the relation between the properties of core and crushed samples so we are able to transfer our observations to the behaviour of the solid core material. We therefore systematically investigate the electrical properties of different carbonates with very low porosity, high porosity and with both vuggy and microporosity at different states of crushing. In the second step, the electrical properties of representative crushed samples are going to be measured under pressure during exposure to CO_2 .

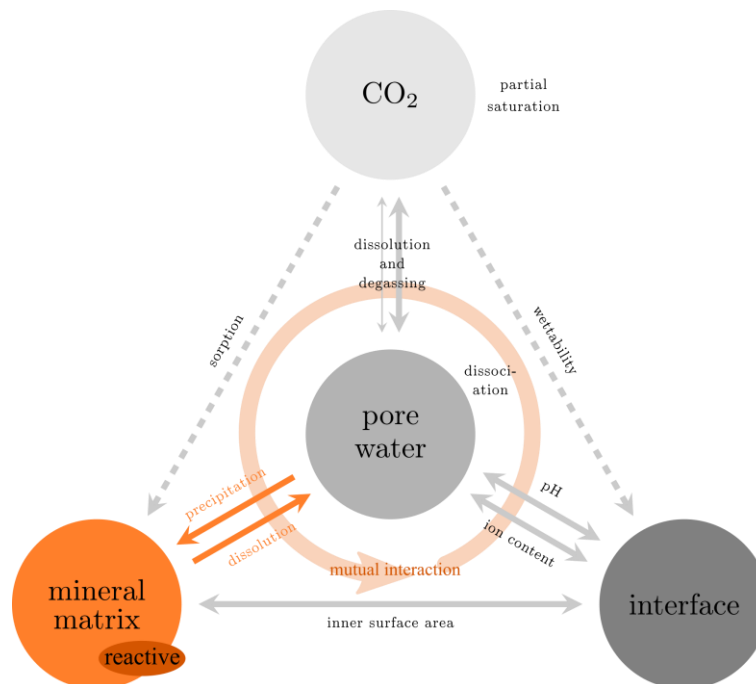


Fig. 1: Schematic representation of the phases and processes acting on the electrical rock properties during interaction between CO_2 and water-bearing rocks (after [8],[6]). Processes, which are of particular interest in the case of reactive rocks, are marked in orange.

THEORY

Electrical conductivity of water-bearing rocks

The electrical rock conductivity in general is a complex and frequency-dependent quantity and originates from both electrolytic and interface conduction mechanisms [1]:

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) \quad (1)$$

Electrolytic conductivity depends on pore space characteristics, saturation and pore water conductivity [2]. Interface conductivity depends on grain roughness (i.e. inner surface area), pH and weakly also on salinity (e.g. [3]). It depends less strongly on water saturation than the electrolytic conductivity (e.g. [4]). A decrease in pH causes a decrease in σ'' [5]. Mainly based on [2] and [4], σ^* at a fixed frequency may be described by:

$$\sigma' = S_w^n \Phi^m \sigma_w + S_w^k \sigma'_{\text{if}, S_w=1} \quad (2)$$

$$\sigma'' = S_w^k \sigma''_{\text{if}, S_w=1} \quad (3)$$

where S_w denotes water saturation, Φ is porosity, m is the cementation exponent, n and k are the real and imaginary part saturation exponent, respectively, and $\sigma'_{\text{if}, S_w=1}$ and $\sigma''_{\text{if}, S_w=1}$ denote the real and imaginary part, respectively, of interface conductivity at full saturation.

Effect of CO₂ on rock conductivity

The presence of the reactive gas carbon dioxide (CO₂) in pore space gives rise to a network of physical and chemical processes (Fig. 1, [6]). All these processes act on σ^* . First of all, CO₂ is forced into the pore space of the storage formation. A connected flowing phase is formed due to the pressure gradient. When no pressure gradient is applied, the non-wetting CO₂ forms bubbles in the pore centers. Character and efficiency of the phase replacement depend on pressure, temperature, CO₂ mass flow and pore space characteristics, such as porosity, inner surface area, pore connectivity and shape. The combination of all these parameters results in variations of capillary pressure as well as absolute and relative permeability. During flow, chemical interaction between gas and pore water take place. Also, water dissolves in the CO₂. This may lead to drying out of connate interface water. During injection, CO₂ partially replaces the pore water of the storage formation and consequently reduces rock conductivity σ^* (cf. Eqs 2, 3). The main task of electromagnetic monitoring techniques is to correctly reconstruct $S_{\text{CO}_2} = 1 - S_w$ from conductivity measurements.

CO₂ is highly soluble in water. The amount of carbon dioxide, which is dissolved in a pore water with known sodium chloride (NaCl) content at thermodynamic equilibrium, is a function of pressure, temperature and salinity. During flow the thermodynamic equilibrium is slightly disturbed. A low flow velocity and resting phases between periods of flow reduce the potential impact of this disturbance. A small portion of the dissolved CO₂ forms carbonic acid, which is unstable and dissociates into protons, hydrocarbonate and carbonate

ions. These ions occur in addition to anions and cations of dissociated salts. Consequently, they act on the pore water conductivity σ_w . As a result of the dissociation, the pH decreases as well (computed with PHREEQC: ~ 3.0), when no buffering occurs. Static dissolution experiments on the un-buffered system demonstrated an increase in pore water conductivity with pressure due to the additional ions from dissociation for low-saline water. For solutions with > 5.8 g/l NaCl, a conductivity decrease was observed that is due to a decrease in ion mobility, which dominates the electrolyte conductivity at high salinities despite the added charge carriers (for details see [7]). The effect of CO₂ dissolution and dissociation on pore water conductivity σ_w may be predicted for all salinities based on physicochemical properties by the following model [7]:

$$\sigma_w^{\text{norm}}(p, T, c_{\text{NaCl}}) = \frac{\sigma_w}{\sigma_w^0} = \frac{1}{\sigma_w^0} \sum_{i=1}^2 [\Lambda_i \gamma_i \alpha_i c_i] \quad (4)$$

Here, σ_w denotes the electrolyte conductivity with CO₂, σ_w^0 is the initial electrolyte conductivity. Λ denotes molar conductivity, γ is the activity coefficient, α is the degree of dissociation and c is concentration. The activity coefficients γ_i of NaCl and dissociated CO₂ are exponential functions and depend on the concentrations of all dissolved components. A purely empirical formulation to describe σ_w^{norm} is also available (for details see [7]).

The impact of chemical interaction on the three-phase system of CO₂–electrolyte–sand may be deduced from the flow experiments (for experimental details see [8]). Chemical interaction may be quantified by comparing the complex conductivity under pressure to the complex conductivity after depressurization at the end of the flow experiments. For all pressures and temperatures in the case of the un-buffered system, σ' reflects the salinity regime predicted by our models (Eq. 4). At the same time σ'' increases stably. The effect may be described by a constant factor $\sigma_{\text{if}}^{\text{norm}}$ as a good approximation. These observations are due to the change in pH from acidic back to near neutral during degassing.

Besides the impact of CO₂ on the pore water, the low pH environment due to dissolution and dissociation may trigger changes of the rock matrix, which would result in an increased inner surface area, and consequently affect the imaginary part of conductivity σ'' [8]. In the special case of the inert quartz sand, the surfaces are not affected by the CO₂ or the low pH. In the case of a buffering system including carbonate rocks, we expect a different behaviour.

Summarizing, the electrical rock conductivity during interaction between rock, water and CO₂ may be described by the following model [8]:

$$\sigma^*(p, T, c_{\text{NaCl}}) = S_w^n \Phi^m \sigma_w^{\text{norm}} \sigma_w + S_w^k X \sigma_{\text{if}}^{\text{norm}} \sigma'_{\text{if}, S_w=1} + i S_w^k X \sigma_{\text{if}}^{\text{norm}} \sigma''_{\text{if}, S_w=1} \quad (5)$$

The formulation is valid for the frequency range between 0.1 Hz and 100 Hz. The quantity X covers changes in the inner surface area. Note that in case of strong mineral dissolution the porosity might change as well and parameters might influence each other.

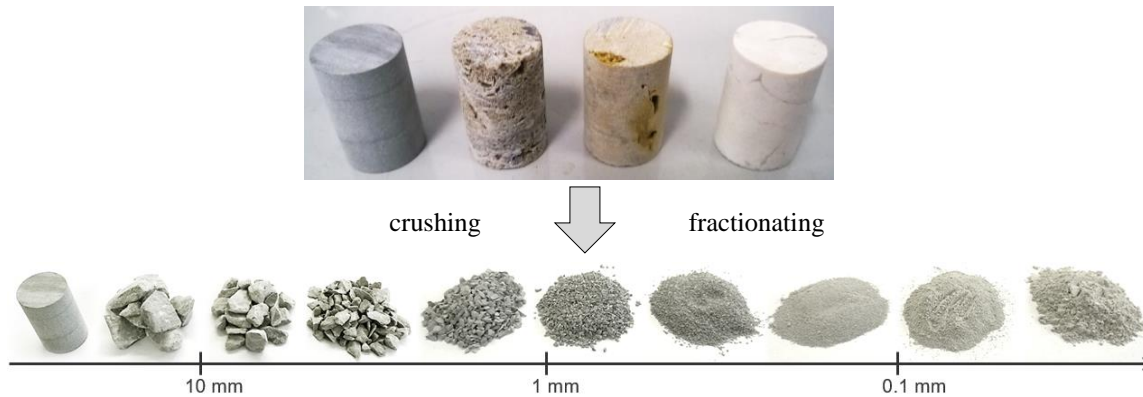


Fig. 2: Photographs of the investigated carbonate rocks. Top: cores (diameter: 2cm) of mud-dominated micritic Wellenkalk, grain-dominated oomoldic Schaumkalk, micritic Madiger Kalk with macro-pores and dense Jurakalk consisting of 99.9% pure calcite (from left to right). Bottom: crushed fractions of Wellenkalk with varying particle size.

MATERIALS AND METHODS

In order to investigate the electrical properties of carbonate rocks, four carbonates with different characteristics are considered (Fig. 2). The dense micritic Wellenkalk (top of Fig. 2, left-most core) is characterized by a crystalline, homogeneous structure and low porosity. The oomoldic Schaumkalk (second core in Fig. 2) shows high porosity and mollusc shells are macroscopically visible. The third carbonate – a micritic Madiger Kalk – is related to the Wellenkalk, but contains additional macro-pores, which increase its average porosity to almost that of the Schaumkalk. The right-most core in Fig. 2 shows a very-low porous Jurakalk, which consists of almost pure calcite and serves as a reference substance, therefore. These carbonate rocks were crushed into nine fractions of varying particle size ranging from <0.063 mm to >10 mm particle diameter (see Fig. 2, bottom).

The properties of the resulting particle-size fractions are not necessarily the same as those of a natural unconsolidated rock. All properties have to be understood as a superposition of an intra-particle (dominated by original carbonate structure) and an inter-particle (dominated by packing) response (see Fig. 3). Fig. 3 shows this for porosity and inner surface area. Depending on particle size, the considered property and the properties of the original carbonate rock, the intra- or inter-particle contribution governs the bulk property. For repeatability reasons, the high-pressure and temperature experiments under CO_2 are going to be carried out with a particle size fraction, which is dominated by the packing properties in order to eliminate the influence of the carbonate matrix heterogeneity.

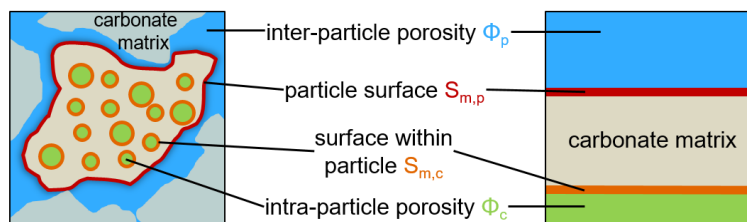


Fig. 3: Porosity and inner surface area components in a crushed sample.

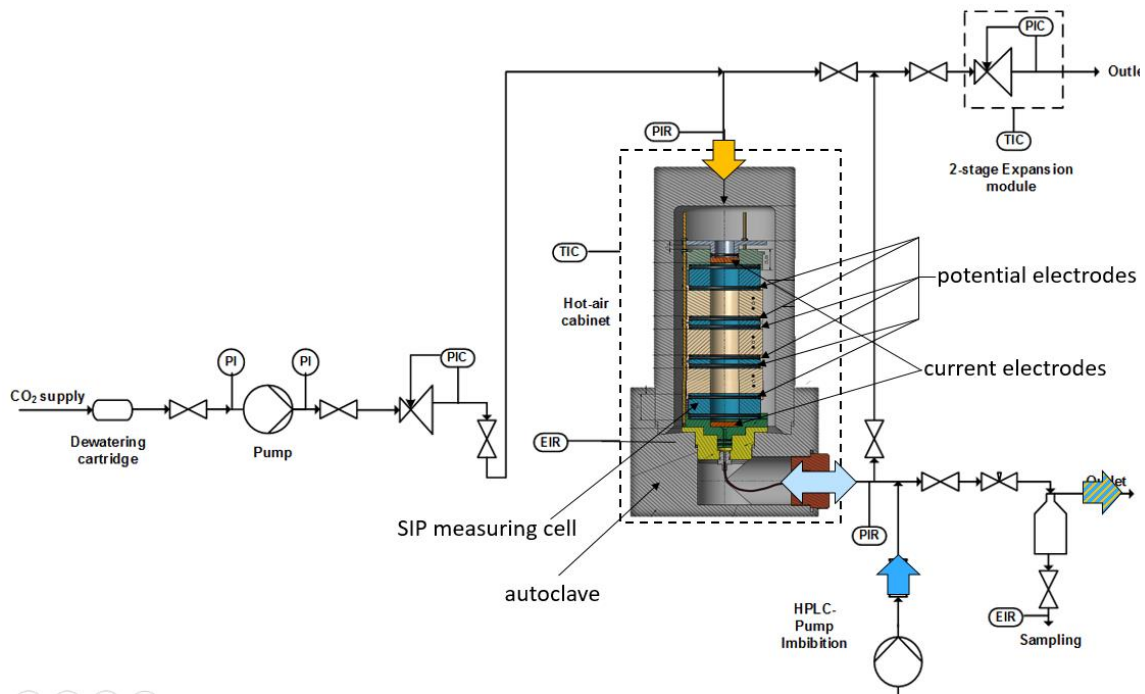


Fig. 4: Laboratory set-up for SIP-measurements at elevated pressure and temperature (based on [7,8]).

The laboratory set-up for measuring the spectral complex conductivity in a time-lapse manner during exposure to and flow-through by CO_2 at elevated pressure and temperature is shown in Fig. 4. It is based on the apparatus described in [7,8] and is now equipped with a new SIP measuring cell and the possibility to both drain and flush the sample. Systematic investigations of the electrical properties of the crushed samples were carried out at normal conditions.

NMR measurements were carried out at ambient pressure with a standard CPMG sequence at a constant temperature of 19°C . In a well-established processing procedure, the envelope of the decaying signal was transformed into a T_2 relaxation time distribution, which allows for evaluating the water and surface properties of the samples. Both fully water saturated and gravitatively drained samples were investigated.

RESULTS

The NMR results for all fractions of crushed Wellenkalk are shown in Fig. 5. Qualitatively speaking, all investigated carbonates exhibit the same behaviour. At large particle diameters, a T_2 peak representing the free water between the particles dominates the NMR response. As the particles get smaller, their specific inner surface ($S_{m,p}$ in Fig. 3) increases and the amount of capillary bound water increases as well. This results in a decreasing magnitude of the free-water peak and the evolving of a peak at shorter T_2 times, which finally dominates the whole response at very small particle sizes. This interpretation is supported by the measurements on drained samples (lower left panel): the free-water peak vanishes whereas the capillary-bound water peak for small particles remains stable.

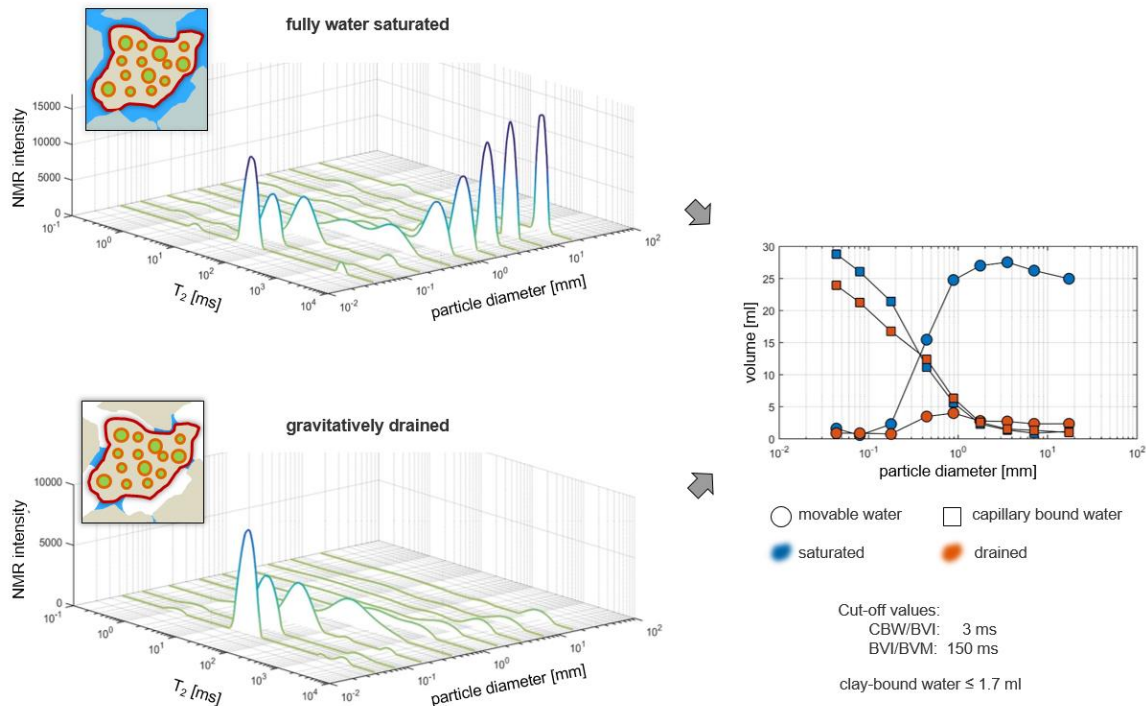


Fig. 5: NMR results for all fractions of crushed Wellenkalk. T_2 relaxation time distributions vs. particle size for the fully water-saturated samples (top left panel) and the gravitatively drained samples (bottom left panel)

The SIP response for all four carbonates is plotted in Fig. 6. Measurements on core samples (left column) demonstrate the variability of carbonate rocks. Although all cores have been saturated with similar salinities (appr. 0.07 S/m; variations in salinity only originate from the natural equilibrium of the rocks with their pore-filling fluid) the real part conductivity varies significantly, which is due to the differences in porosity. The imaginary conductivity also shows strong variations. Especially, the dense and clean Jurakalk (violet markers) shows very low imaginary conductivity. Stronger polarization in the other carbonates might also be due to the existence of minor clay content.

The right-hand side column in Fig. 6 gives the SIP response of one fraction of crushed carbonates for all four rocks. It is obvious that at this particle size (0.63 – 1.25 mm) the behavior of the carbonates in terms of real conductivity is already homogenized. However, the imaginary conductivity is still very different between the rock types, even new features appear in the frequency response (c.f. Wellenkalk, blue markers). The clean Jurakalk still is the carbonate with the lowest imaginary conductivity.

These first results show that the crushing has to be handled carefully and the carbonates need to be crushed to a sufficient extend to show a homogeneous frequency response. Comparisons between the SIP responses from all fractions for one carbonate reveal systematic changes in the electrical properties.

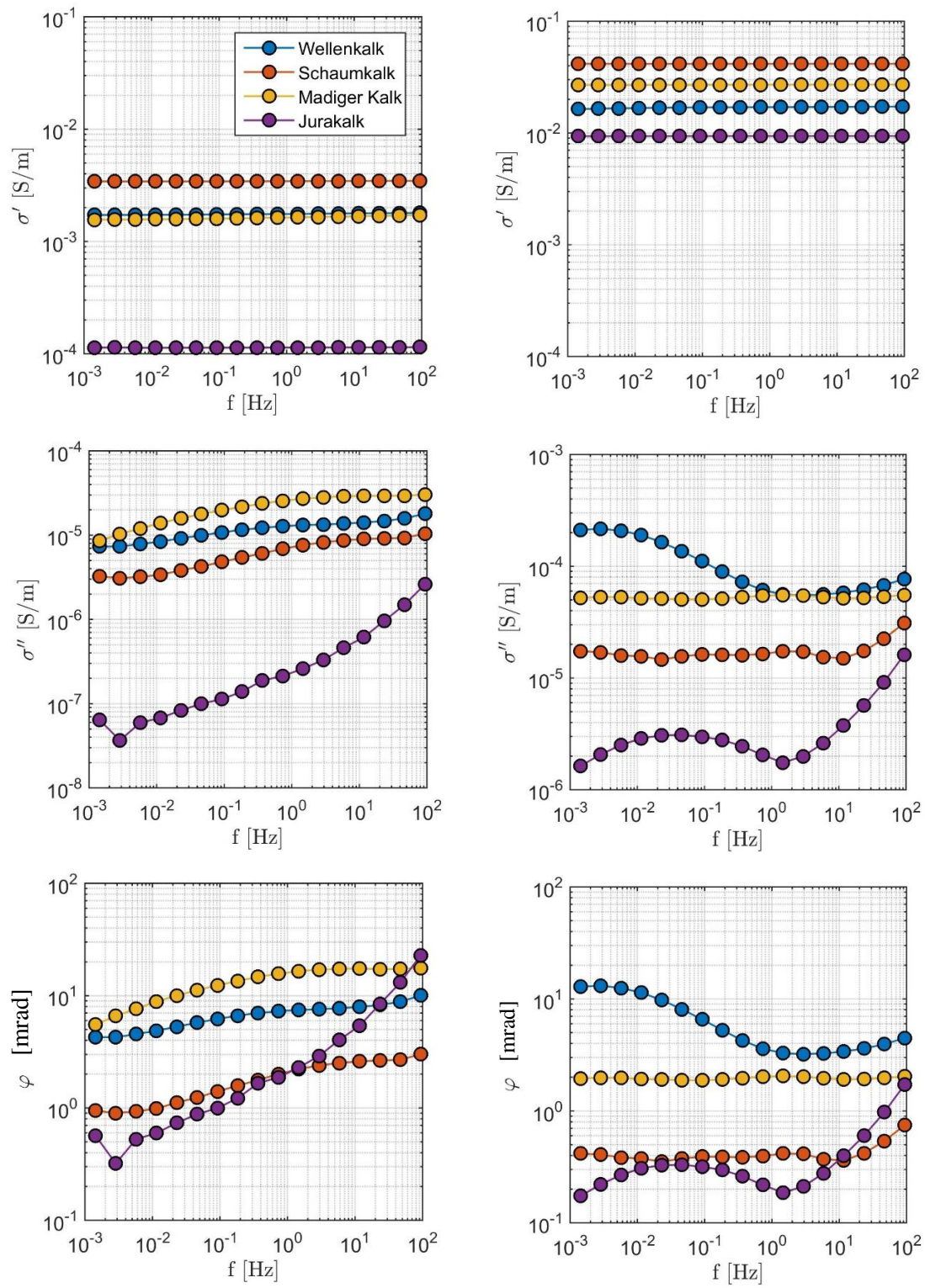


Fig. 6: Complex conductivity of the cores (left column) and a crushed sample (right column, particle size 0.63 – 1.25 mm) in terms of real and imaginary conductivity and phase shift (from top to bottom).

CONCLUSIONS

Carbonate rocks provide great challenges to petrophysics due to their heterogeneous pore space and the reactive nature of the carbonate matrix. Using measurements on both cores and crushed carbonate samples, we investigate the complex electrical properties of carbonate rocks at both normal and reservoir conditions. First results of this work in progress demonstrate the variability of carbonate rocks and the effects of crushing on carbonate properties. Systematic crushing of the solid materials allows for controlling porosity (demonstrated by SIP) and inner surface area (demonstrated by NMR).

Next steps are the completion of the SIP measurements and accompanying mineralogical analyses at normal conditions to gain a full understanding of the properties of crushed samples. In the near future, time-lapse measurements at elevated pressure and temperature during interaction between carbonate matrix, CO₂-rich saline pore water and free CO₂ phase are going to be carried out. This work will contribute to our general understanding of carbonate reservoirs and to the development of a laboratory approach to study the impact of chemical interaction on electrical rock properties.

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