Geological Survey of Canada
Commission géologique du Canada

TGI4 Ore Systems

A better method to define electrical chargeability from laboratory measurements of spectral impedance using a parallel Cole-Cole equivalent circuit

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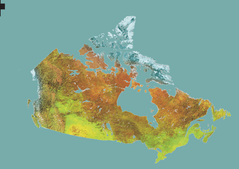
TGI4-Methodologies Activity: Optimization of Rock Physical Properties Measurements for Mineral Exploration

TGI4 Systèmes minéralisés



ABSTRACT: Induced polarization (IP) is a successful electric method to identify drill targets for mineral exploration at the property scale. The Paleomagnetism and Petrophysics Laboratory at the Geological Survey of Canada makes petrophysical measurements on cylindrical rock samples, 2.5 cm diameter and 2.2 cm long. This small size has advantages, including allowing measurement of magnetic remanence with standard paleomagnetism equipment, but it is too small to allow a 4-contact electrical impedance measurement. The samples are impregnated with distilled water under vacuum and allowed 24 hours for solutes to dissolve off pore walls, in order to approximate original groundwater ionic conductivity. We use copper-copper sulphate electrodes on the flat surfaces and measure the complex impedance at 5 frequencies per decade from 1 MHz down to 25 mHz. Typical responses on a Cole-Cole plot (i.e., real vs. imaginary components displayed parametrically as a function of frequency) look like a two or three overlapping circular arcs followed by a constant-phase diffusive response at lowest frequencies. The impedance frequency response is fit with a circuit in which the rock is modelled as a set of parallel resistor and constant-phase-element pathways, connected in series through a modified constant-phase-element representing the low frequency sample-holder response. The program "ZarcFit", written in LabView, allows the operator to tune parameters of an equivalent but far more intuitive series circuit with a set of 15 sliders, and then perform a least-squares optimization. Time domain chargeability is defined by removing the effect of the sample holder, taking the Fourier transform to convert the frequency response to its time-domain equivalent and then integrating under the resulting voltage-decay curve. Time domain measurements using two-electrode sample holders are necessarily contaminated by the low-frequency response of ionic diffusion at the electrodes. Results are compiled in the Canadian Rock Physical Properties Database. I will present examples of mineralogical/lithological sources of chargeability and a useful mineralization index from combining physical properties which can be estimated from inversion of surface geophysical surveys.

Importance of Rock Physical Properties

- The quantitative link between geology and geophysics
- Characterization of the rock property environment of ore deposits
- Characterization of the rock properties of cover
- Improved geophysical survey design, forward modeling, inversion, and interpretation

Preliminary discussion of these methods is found in:

GEOLOGICAL SURVEY OF CANADA
OPEN FILE 7227

Physical Property Measurements at the GSC Paleomagnetism and Petrophysics Laboratory, including Electric Impedance Spectrum Methodology and Analysis

R.J. Enkin, D. Cowan, J. Tigner, A. Severide, D. Gilmour, A.Tkachyk, M. Kilduff, B. Vidal, J. Baker

2012

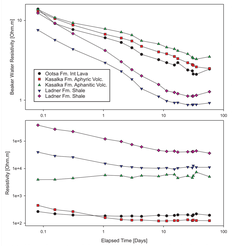
Natural Resources Canada / Ressources naturelles Canada

Canada

Sample Preparation and Impedance Measurement

Cylindrical subsamples, 2.5 cm diameter and 2.2 cm long, are collected from hand samples or core segments. The size is compatible with our paleomagnetic measurement apparatus. For coarse-grained rocks, larger samples are prepared.

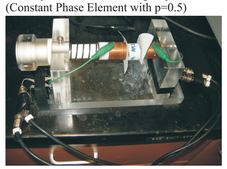
Samples are placed in labelled beakers in a vacuum chamber. After evacuation, distilled water is introduced and the chamber is vibrated on a shaker-table for 2 minutes, before they are brought back to open atmosphere.



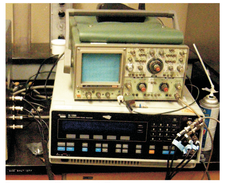
Following Archie's law, rock resistivity is proportional to the ground-water resistivity. We approximate the original ground water by allowing solutes precipitated on pore walls to dissolve over 24-36 hours. The resistivity of the beaker water reduces for days and weeks, while the sample resistivity is close to stabilized after about 24 hours. The interpretation is that the dissolution of the solutes within the pore spaces happens over hours, however, the diffusion of the solutes out of the sample is much slower.

Density is measured using the weight-in-air - weight-in-water method. For electrical properties, the porosity is determined from the difference in weight dry and water-saturated.

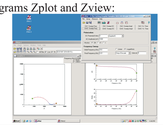
Sample contacts are with $CuSO_4$ saturated filter paper in contact with copper electrodes. We have used graphite or gold contacts, but they produce a large low-frequency charge build-up similar to a Warburg Impedance (Constant Phase Element with p=0.5)



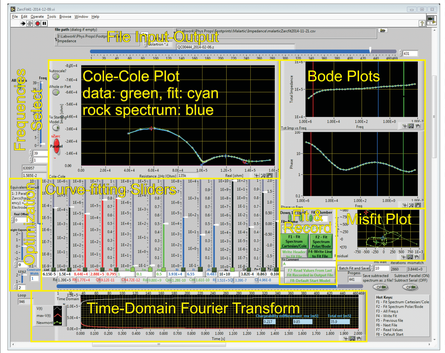
The impedance spectrum is measured using a Solartron 1260 Frequency Response Analyzer. The copper electrodes are attached to the current and voltage inputs through grounded coaxial cables. The current is driven with a 1 V sinusoidal wave, at frequencies from 1 MHz down to 0.025 Hz (40 s period) at 5 frequencies each decade. A 1000 Ω resistance is placed in series with the sample through the current circuit.



Programs Zplot and Zview:



LabView Program ZarcFit.vi



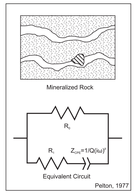
ZarcFit.vi reads in and plots frequency-domain impedance data. The operator produces an initial equivalent circuit fit by manipulating the 15 sliders, while ensuring that the parameters are realistic. There are many local minima which the optimization procedure could locate, however most are nonsensical. It takes good physics understanding and experience to produce useful fits to the electrical impedance spectra. The program then minimizes the offset between model and observation to produce a best-fit model. A Fourier transform produces the time-domain response, and Newmont standard chargeability is determined by integration from 430 to 1100 ms.

Gory details:

Parameters can be fixed (held constant) with the green buttons below each slider. In the optimization, the logarithm of the parameters are varied. For scaling, the constant-phase-element exponents (p) are left linear, but multiplied by 10. The misfit function is conditioned to disfavour p>0.2, which has the negative effect of over-spreading out the frequency spectrum of a given Zarc. The misfit function can be chosen to be in Cartesian or in Log(Polar) space. In practice, the best fits are produced by alternating between both methods. The parameters are optimized to fit the observations using a Downhill Simplex algorithm. While an L1 robust norm has been programmed, the data usually has no outliers, so the least-squares L2 norm is used. The user controls the initial step length, which can be set large if attempting to find a different optimization well, or set low if the optimization draws the solution out of the initial well. For time-series measurements, ZarcFit can automatically run through a series of files, either starting with the identical initial model, or using the final result of the previous fit. Results are output with a comma-separated-variable (.csv) format.

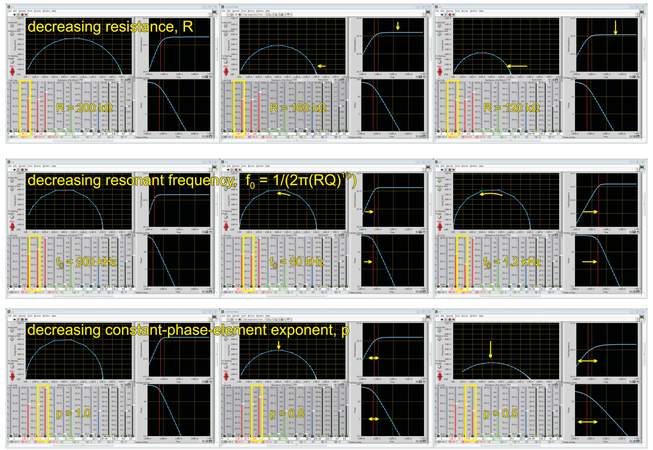
Write the author Enkin@nrcan.gc.ca to receive a copy of the program. Specialized input file formats are easily accommodated.

Zarc Parameters

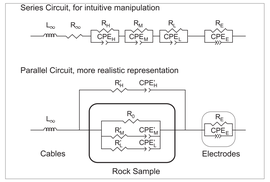


The building blocks of the electrical impedance frequency spectra are impedance arcs, or Zarcs, consisting of a parallel resistor and a constant-phase-element (CPE): $1/Z = 1/R + Q(i\omega)^p$, where Z is the total impedance, R is the resistance, Q is the CPE magnitude, $\omega=2\pi f$ is the angular frequency, and p is the CPE exponent. The resonant frequency, $f_0 = 1/(2\pi(RQ)^{1/p})$, has a physical meaning which is much more intuitive for analysis and interpretation. When p=1, the CPE is a pure capacitor, and in time domain the step-down response is a pure exponential decay. As p gets lower, the log-normal relaxation time spectra spreads out. Diffusion reactions at a surface are modelled with p=0.5 .

The screen shots below display the how to a single Zarc is controlled by the parameter sliders for resistance, R, resonant frequency f, and CPE exponent p. For each screen-picture, the graph on the left is the Cole-Cole plot of real vs negative imaginary impedance. The two right-side graphs are Bode plots of impedance magnitude and phase as a function of frequency. Since a Zarc on the Cole-Cole plot has the high frequency on the left, the Bode plots frequency axis also goes from high frequency on the left to low frequency on the right. Log(Absolute(phase)) angle is plotted, as the low phase parts of the spectrum are particularly important to fitting rock impedances.



Equivalent Circuit



Rocks naturally provide parallel conduction mechanisms, however the parameters which control a parallel circuit produce non-intuitive variations on the frequency-domain spectrum plots. Parallel impedances add by their reciprocals, while series impedances add linearly. Thus the ZarcFit sliders are designed to control the parameters for an equivalent series circuit. The more realistic parallel circuit is used internally for the parameter optimization and for the interpretation of the petrophysical properties.

The rock's impedance is mostly modelled by R_w (Archie's Law ionic conduction) and the low-frequency Zarc (dry sliders), and occasionally the intermediate frequency Zarc (green sliders) when there is a third conduction pathway. The red and black sliders model the apparatus response.

More gory details:

The following equations are used to transform the intuitive series circuit parameters (un-primed) to the more realistic parallel circuit parameters (with primes). The equations are approximate and are accurate only when there is no significant overlap in the relaxation time ranges between the parallel conduction mechanisms:

$R'_1 = R_w + R_1 + R_{s1} + R_s$

$R'_2 = R_2 (R_2 / R_w)^2 / R_w$

$Q'_2 = Q_2 (R_2 / (R_w = R_w))^{-1}$

$R'_3 = (R_w + R_w) (R_w = R_w + R_w) / R_w$

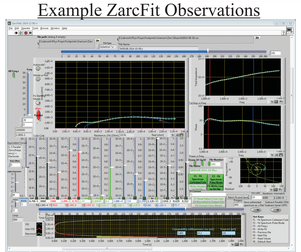
$Q'_3 = Q_3 (R_3 / (R_w = R_w + R_w))^{-1}$

$R'_1 = (R_w + R_w + R_1)(R_w + R_w + R_w) / R_w$

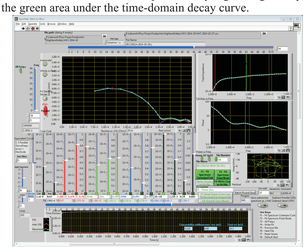
$Q'_1 = Q_1 (R_1 / (R_w + R_w + R_w))^{-1}$

Empirically, it appears the lowest frequency electrode response (<0.1 Hz) is best fit with a modified Constant Phase Element ($Z_s = 1 / (Q_s i^{\omega p})$), where ps and pf are separate exponents for the phase angle and the frequency.

Example ZarcFit Observations



An altered graphitic pelite from the basement of the Athabasca Basin, Saskatchewan, Canada. This sample has very high chargeability, as seen by the green area under the time-domain decay curve.

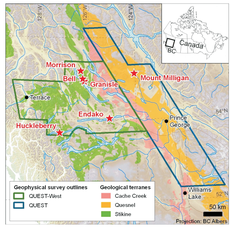


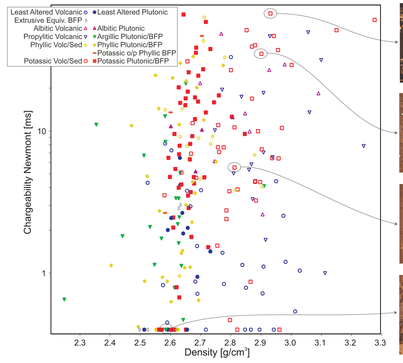
Altered porphyritic granite from Highland Valley copper deposit, British Columbia, Canada. Triple Zarc from sericite and bornite chargeability.

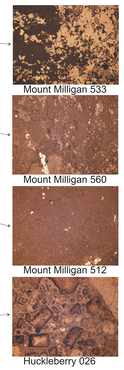
Example Application: BC Porphyry Deposits

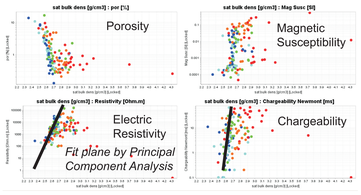
"Linking Porphyry Deposit Geology to Geophysics via Physical Properties: Adding Value to Geoscience BC Geophysical Data", D.E. Mitchinson, R.J. Enkin, and C.J.R. Hart, Geoscience BC Report 2013#14.

Semi-quantitative mineralogy determined by X-Ray Diffraction on powders from neighbouring samples to samples for petrophysical study. Rock physical properties include density and porosity, magnetic susceptibility and remanence, electric resistivity and chargeability.

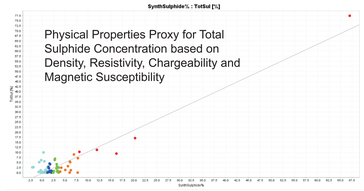








Coloured by Sulphide + Oxide Concentration
Low Density-Resistivity-Chargeability define surface



Coloured by Synthetic Sulphide Proxy

No single rock physical property provides a useful proxy for mineralization (sulphide concentration) in this geological environment. The low-mineralized rocks (<40 percentile) fall on a plane in density-resistivity-chargeability space, which is defined through Principal Component Analysis. The perpendicular to that plane provides a useful proxy for total sulphide + oxide content. After calibrating magnetic susceptibility as a proxy for oxide content, a proxy for total sulphide content is derived.

This proxy for mineralization is based on physical properties that can be derived from magnetic, gravity and DC-IP electric surveys on the surface.