# Identifying Ultrafine Magnetic Particles in Rocks and Soils using Frequency-Dependent Magnetic Susceptibility and Out-Of-Phase Susceptibility

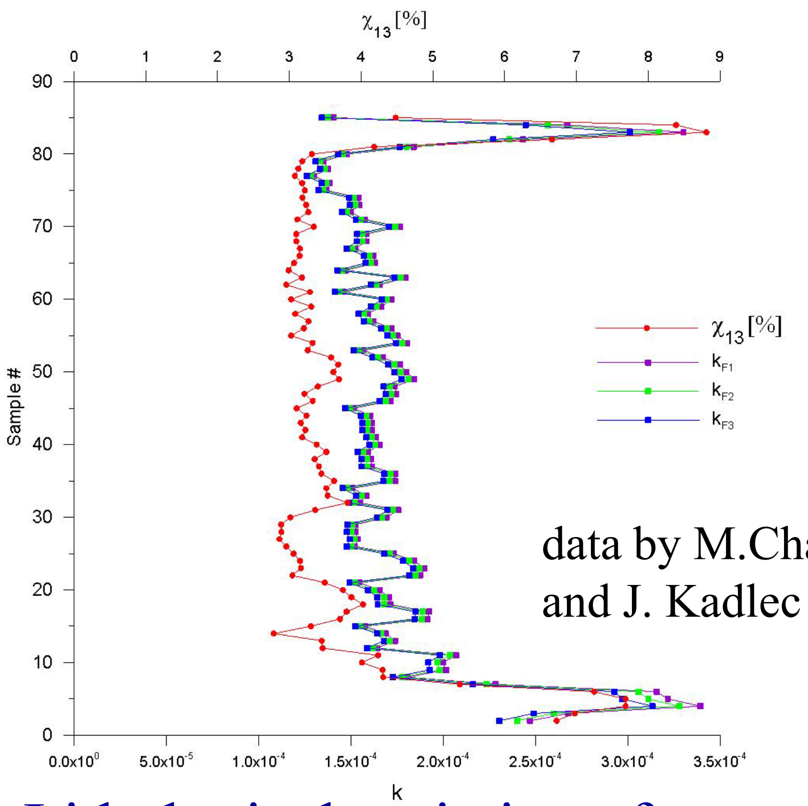
František Hrouda

AGICO Inc., Ječná 29a, Box 90, CZ-621 00 Brno, Czech Republic, E-mail: fhrouda@agico.cz

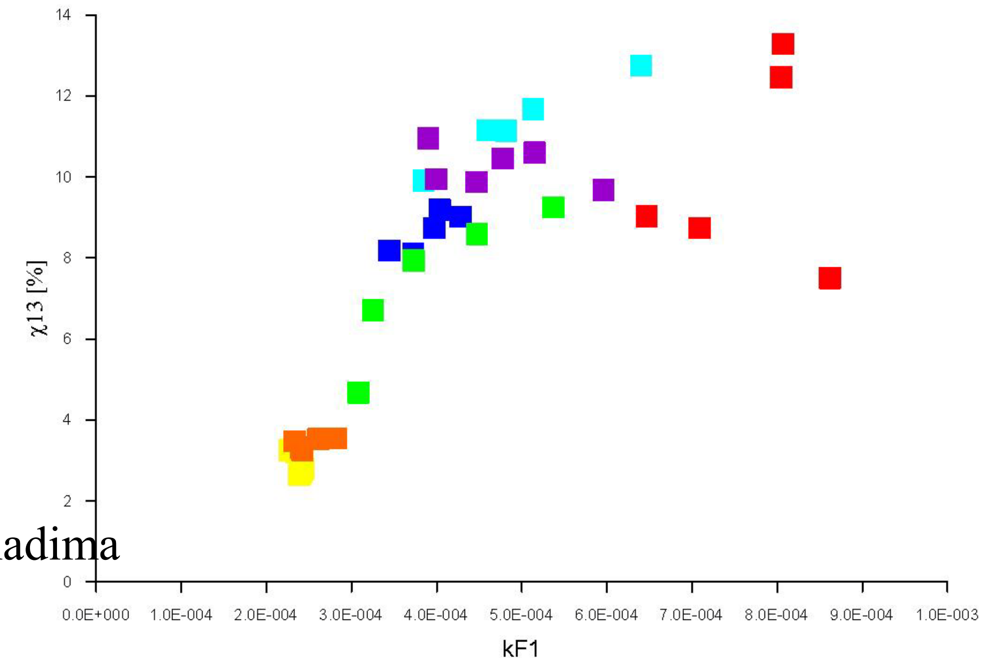
and

Institute of Petrology and Structural Geology, Charles University, Albertov 6, CZ-128 43 Praha, Czech Republic

# Interpretation of Frequency-Dependent Susceptibility




data by M.Chadima and J. Kadlec




Lithological variation of susceptibility and its frequency dependence.

Correlation between susceptibility and its frequency dependence is traditionally interpreted as due to creation of new SP particles.

All models to understand this phenomenon were originally developed for the Bartington Instrument working at two operating frequencies.

# MFK1 Multi-Function Kappabridge


***Operating Frequencies:***

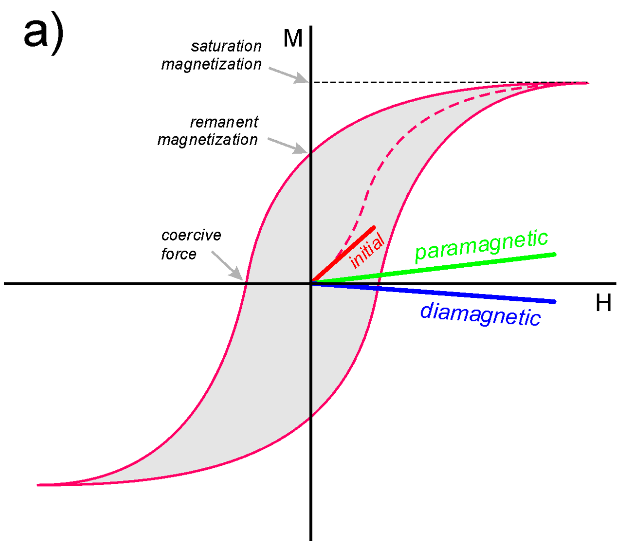
976 Hz
3 904 Hz
15 616 Hz

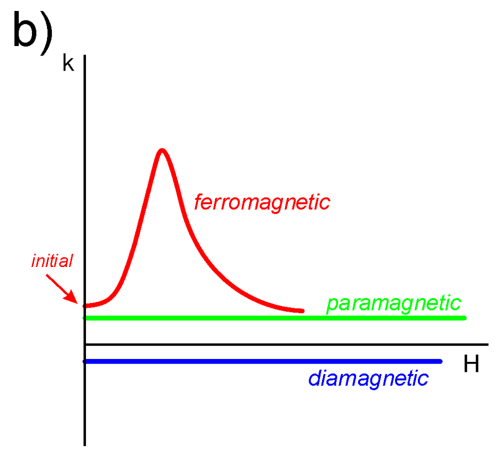
***Field Intensity Ranges:***

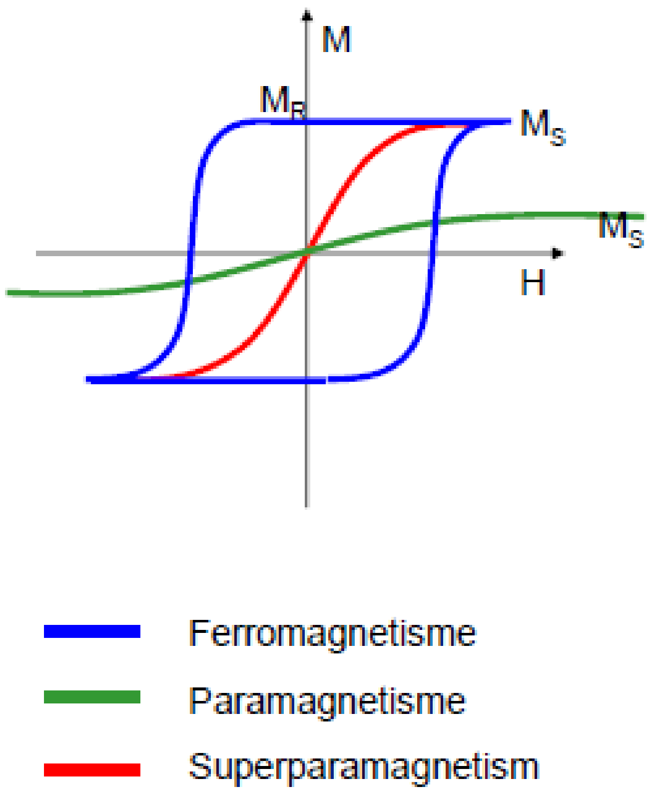
2 - 700 A/m at 976 Hz
2 - 350 A/m at 3 904 Hz
2 - 200 A/m at 15 616 Hz

Mathematical models for frequency-dependent susceptibility are re-developed for 3 frequencies of the MFK1 Kappabridge, for 2 frequencies of the Bartington instrument and for 2 very high frequencies (100 and 250 kHz) of a hypothetical instrument.

# Ferromagnetism, Paramagnetism, Superparamagnetism



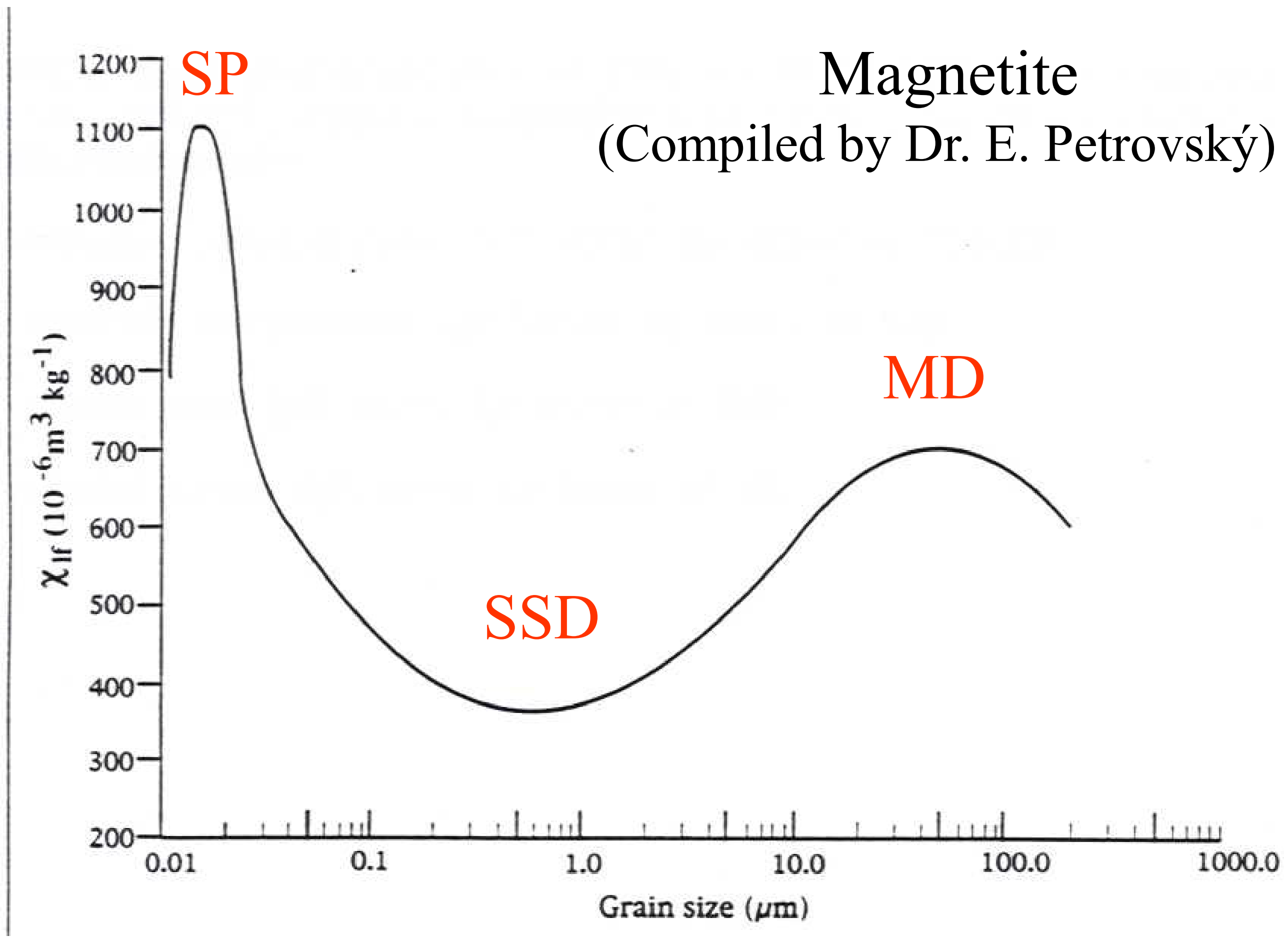

Superparamagnetism:

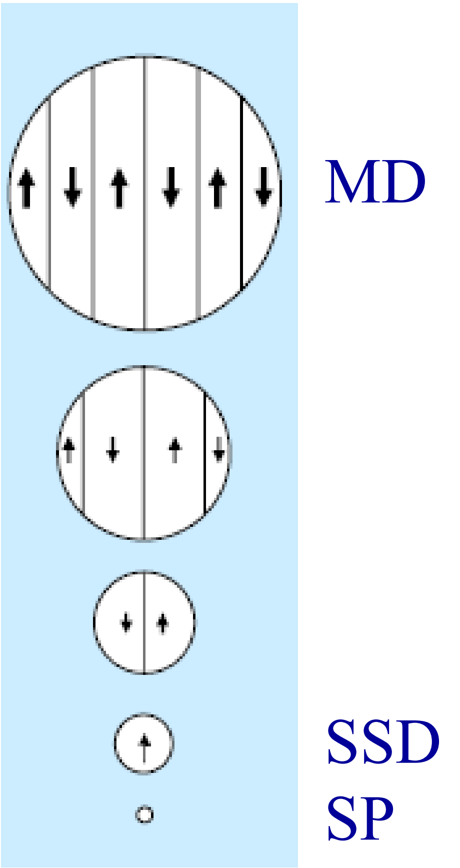
very high susceptibility

no remanence

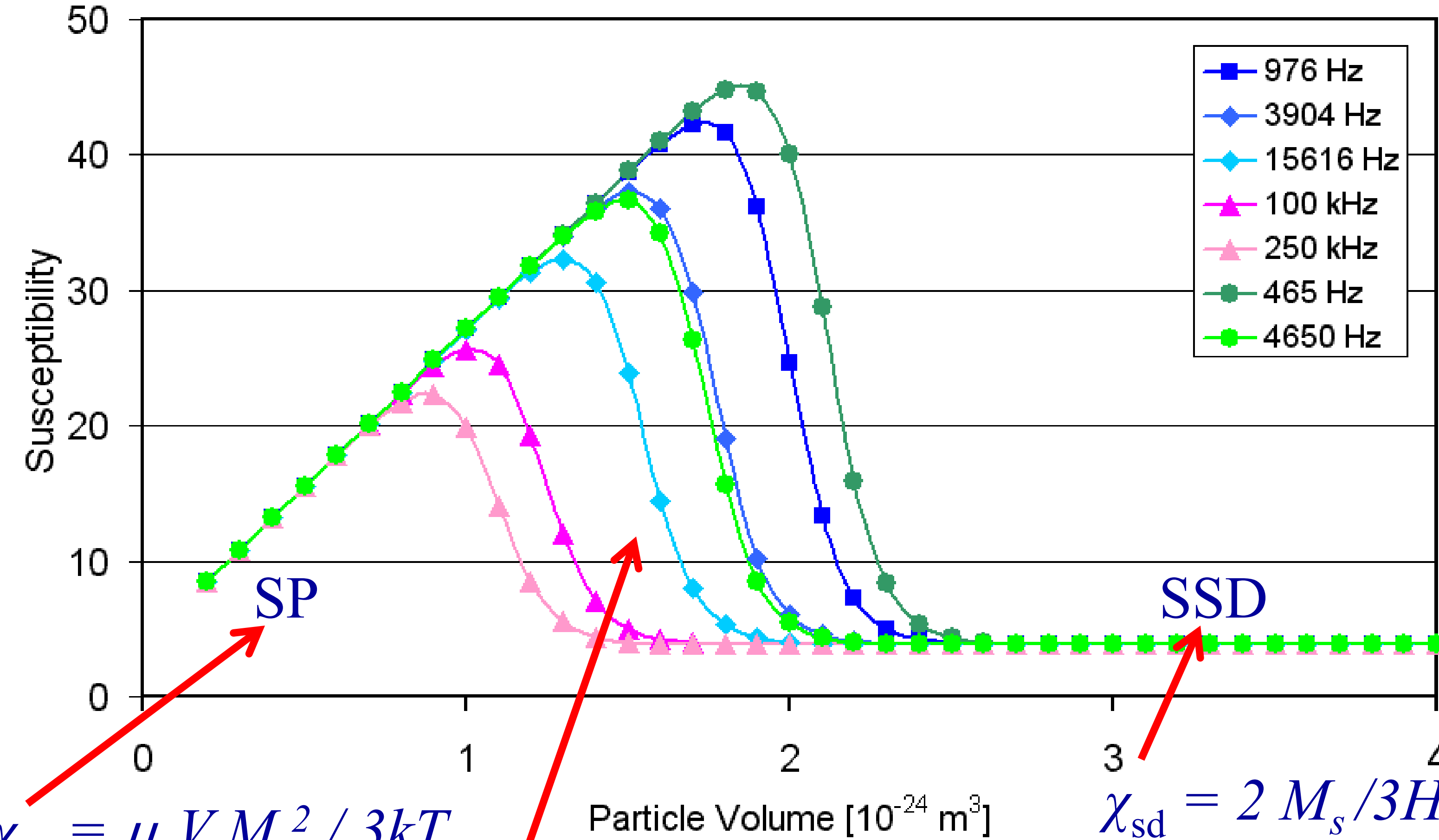
# Susceptibility and Grain Size of Magnetic Particles

multidomain (MD) magnetic particles - largest grains, medium susceptibility
stable single domain (SSD) particles - smaller grains, lowest susceptibility
superparamagnetic (SP) particles - smallest grains, highest susceptibility



# SP to SSD Transition



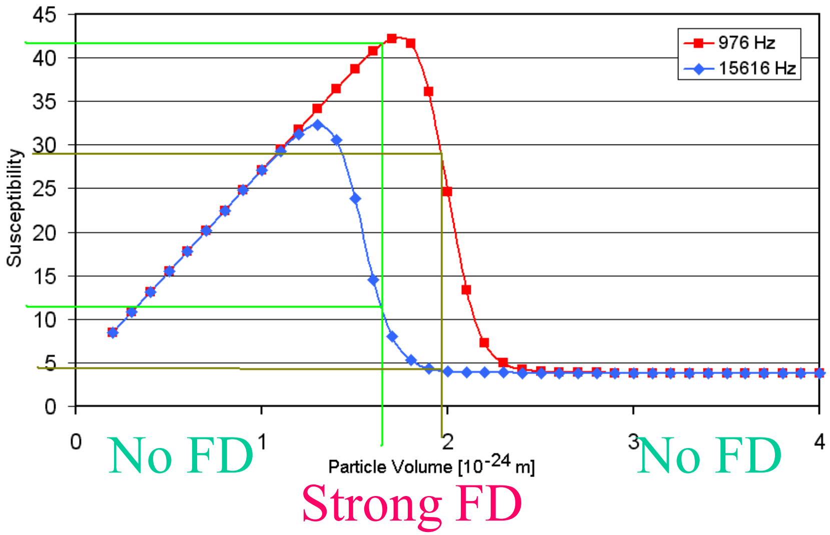

$\chi_{sp} = \mu_o V M_s^2 / 3kT$
(Dunlop and Özdemir, 1997)

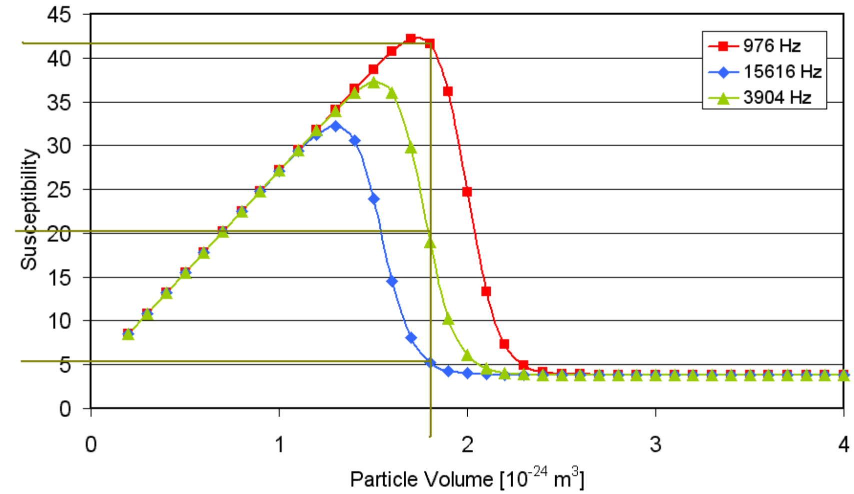
$\chi_{sd} = 2 M_s / 3H_k$
(Stoner and Wohlfart, 1948)

$\chi_{sp/sd} = \chi_{sd}[\beta/(1+i\tau_o 2\pi f e^{\beta})+1]$ (Néel, 1949)

$M_s$ saturation magnetization, $H_k$ microscopic coercivity, $\mu_o$ permeability of free space, $V$ grain volume, $f$ frequency, $\tau_o$ time constant, $\beta = KV/kT$, $K$ anisotropy constant.

# Parameters for Frequency-Dependent Susceptibility




$X_{FD} = 100\,(\chi_{LF} - \chi_{HF})/\,\chi_{LF}$ [%] (Dearing et al., 1996, GJI)

$X_{FV} = \chi_{LF} - \chi_{HF}$ [$m^3 kg^{-1}$] ← independent of para, MD, etc.

$X_{FN} = X_{FD} / (\ln f_{HF} - \ln f_{LF})$ (Hrouda, 2011, GJI)

$X_{FS} = X_{FV} / (\ln f_{HF} - \ln f_{LF})$ ← independent of frequency difference

$\chi_{LF}$ , $\chi_{HF}$ are susceptibilities at lower and higher frequencies,

$f_{LF}$ and $f_{HF}$ are respective operating frequencies.

# Construction of Models 1

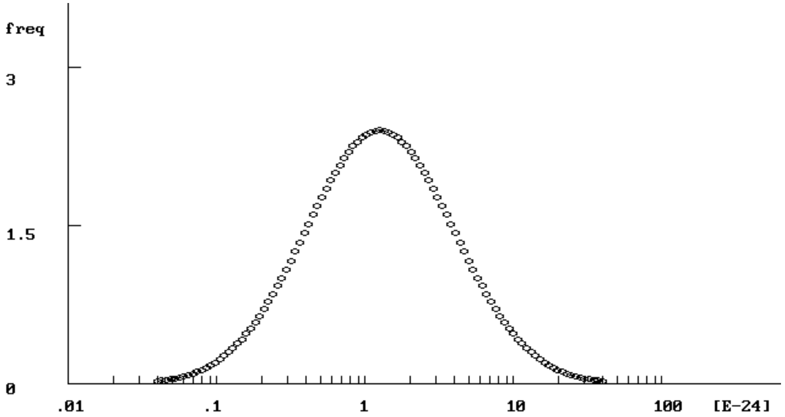
Only SP or SSD at both frequencies → no frequency dependence.

Transition SP to SSD → strong frequency dependence.

Natural rocks, soils - mixture of SP, SSD, MD distributed log-normally

$$f(V,\mu,\sigma) = \frac{1}{V\sigma\sqrt{2\pi}}\exp\left(-\frac{(\log_{10} V - \mu)^2}{2\sigma^2}\right)$$

$V$ is grain volume, $\mu$ and $\sigma$ are arithmetical mean and standard deviation of logarithms of grain volume.

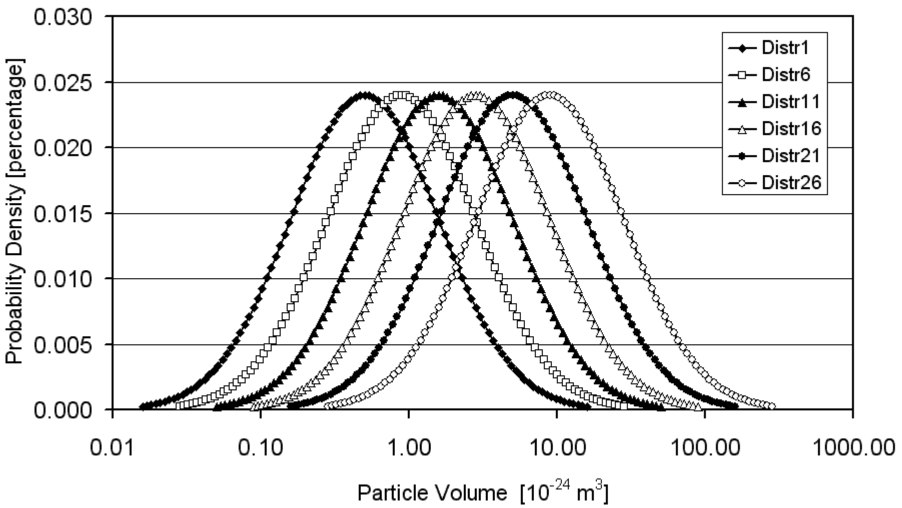


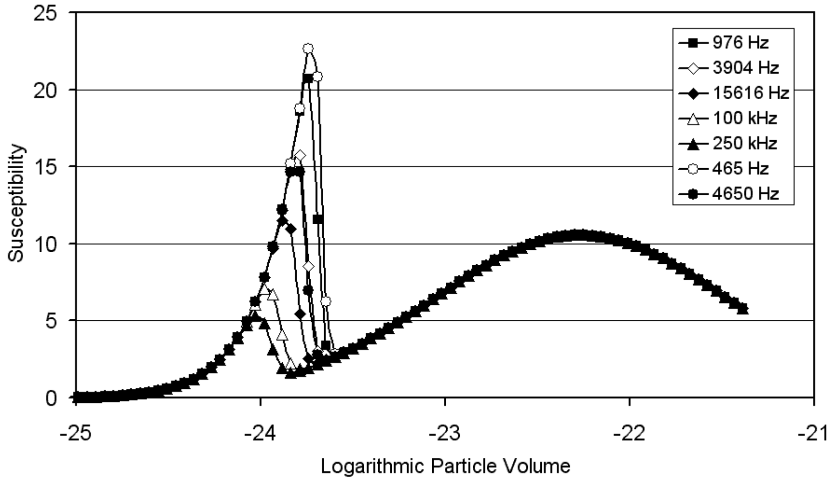

**Model Susceptibility** (for more details see Hrouda, 2011, GJI)

$$\chi_{pop}(\mu,\sigma) = \int_{-\infty}^{+\infty} f(V,\mu,\sigma) V \chi(V) d(\log_{10} V)$$

Model susceptibility is sum of all grains contributions of the distribution, comprising SP, SP-SSD, and SSD susceptibilities.

# Construction of Models 2



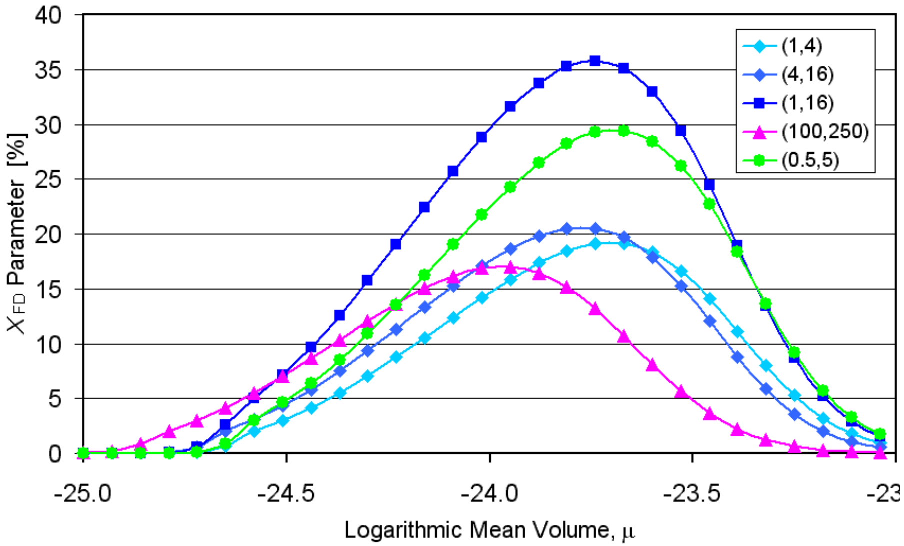



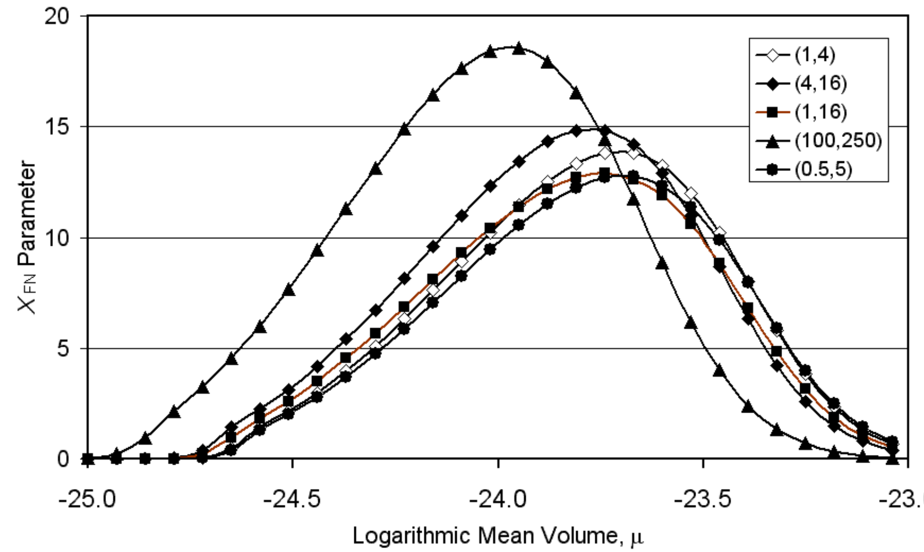

Susceptibility distribution is very different from grain size distribution.

Many lognormal distribution curves are considered for one model with different μ and σ.

In model curves, each point represents the modal value of the distribution. Each curve was considered to span from $\mu$-3$\sigma$ to $\mu$+3$\sigma$, which encompasses 99.7 % of the distribution.

# Results: Narrow Distribution (σ = 0.2)




One point represents one curve of log-normal distribution.

Peaks are shifted to small grains with increasing frequency.

Peak height according to ln $(f_{HF}/f_{LF})$

$\chi_{1,16}$ ~ 2.77 $\chi_{1,4}$ ~ 1.39

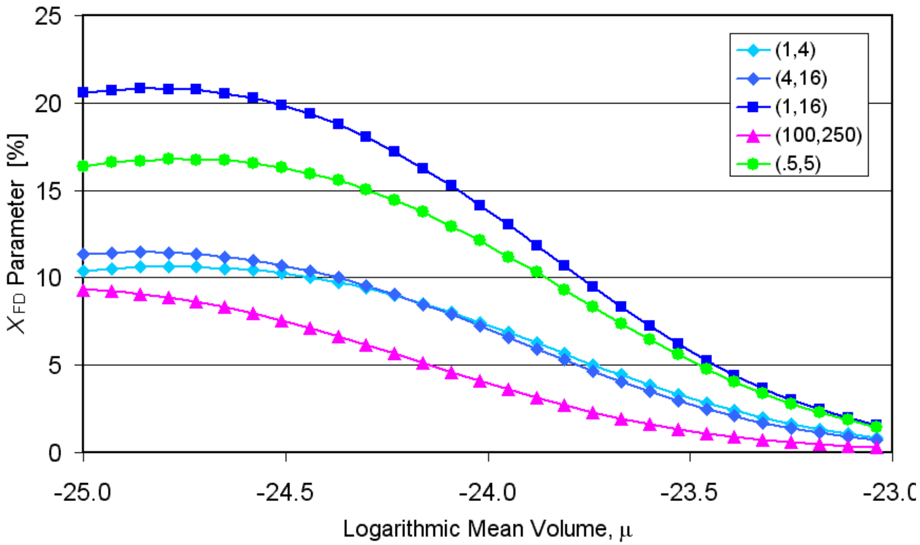
$\chi_{0.47,4.7}$ ~ 1.98 $\chi_{4,16}$ ~ 1.39

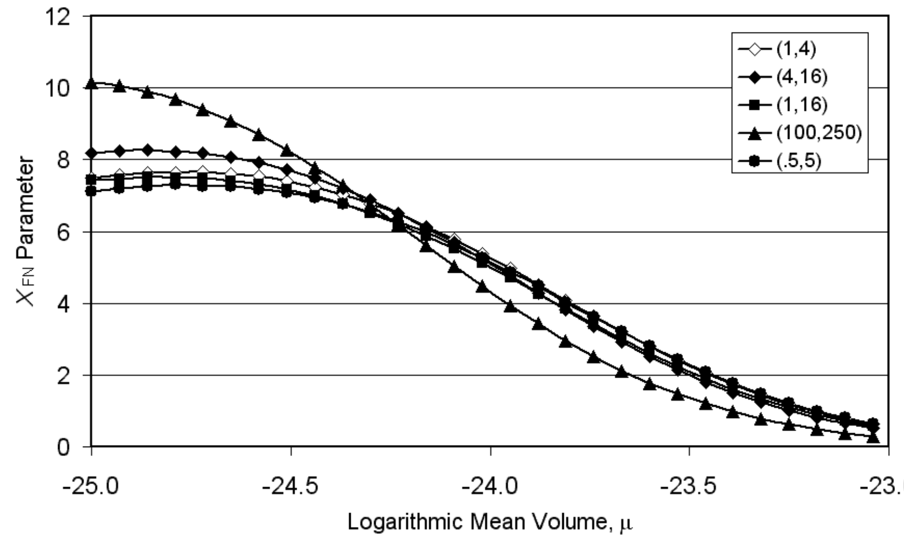
$\chi_{16,100}$ ~ 1.83 $\chi_{100,250}$ ~ 0.92

For frequencies < 100 kHz, the curves are very near one another.

Using $X_{FN}$ parameter is very advantageous, because it is almost frequency independent.

# Results: Wide Distribution ($\sigma = 0.8$)




All curves tend to decrease monotonously.

Peaks are shifted to small grains with increasing frequency.

For frequencies < 100 kHz, the curves are very near one another.

Using $X_{FN}$ parameter is again very advantageous, because it is almost frequency independent.

# Effect of Dia- and Paramagnetic Fractions on the $X_{FD}$ Parameter

Rock (soil) susceptibility ($\chi_w$) can be described by the Henry and Daly (1983, Tectonophysics) model

$$\chi_w = c_d\chi_d + c_p\chi_p + c_f\chi_f$$

where $\chi_d$, $\chi_p$, $\chi_f$ are susceptibilities of dia-, para-, and ferromagnetic fractions, $c_d$, $c_p$, $c_f$ are the respective percentages.

The whole rock (soil) $X_{wFD}$ parameter then is

$$X_{wFD} = 100\, c_{mix}\,(\chi_{mixLF} - \chi_{mixHF})/(c_d\chi_d + c_p\chi_p + c_{sp}\chi_{sp} + c_{mix}\chi_{mixLF} + c_{ssd}\chi_{ssd} + c_{md}\chi_{md})$$

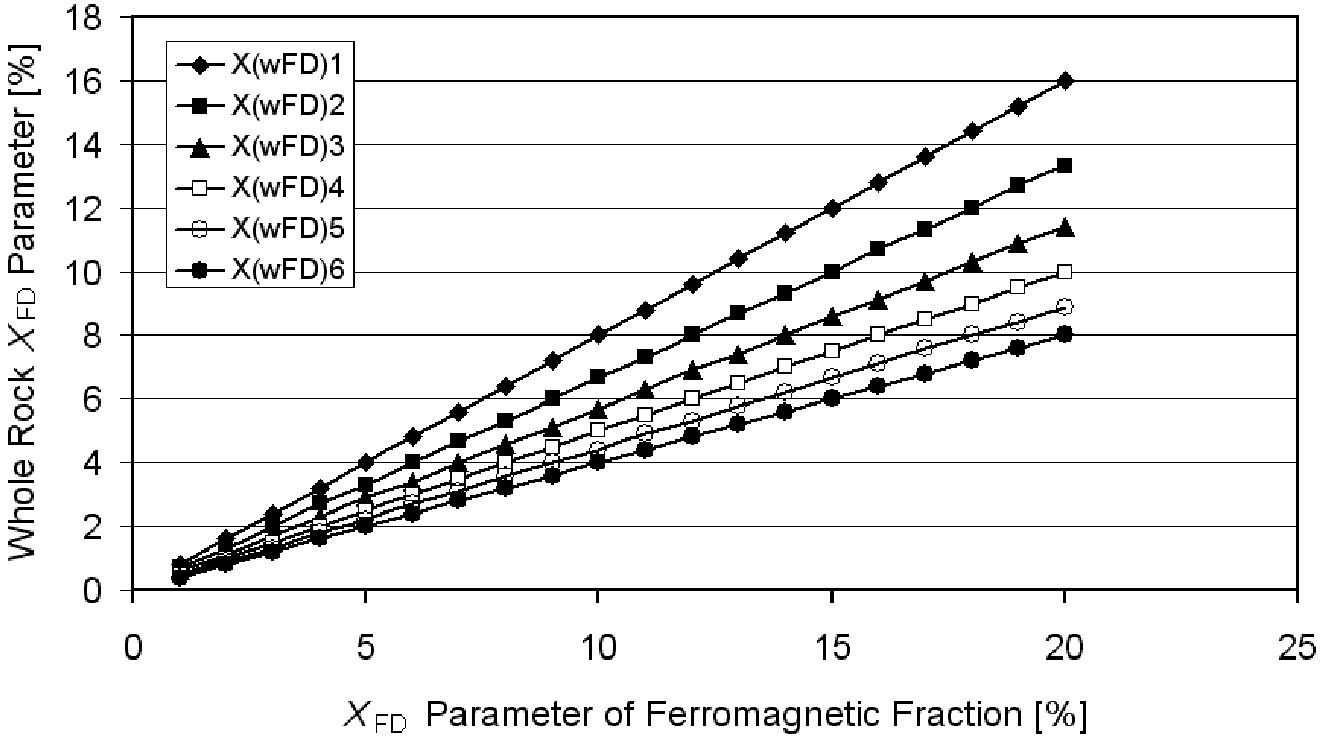
where index *mix* denotes grains on SP-SSD transition at both freq.

The relationship between $X_{wFD}$ and $X_{fFD}$ (ferro) parameters is

$$X_{fFD} = X_{wFD}\,\chi_{wLF}/\chi_{fLF},$$

where $\chi_{fLF} = c_{ssd}\chi_{ssd} + c_{md}\chi_{md} + c_{mix}\chi_{mixLF}.$

# Effect of Paramagnetic Fraction on $X_{FD}$ Parameter




$\chi_{wLF}/\chi_{fLF}$

1 – 0.8

2 – 0.7

3 – 0.6

4 – 0.5

5 – 0.4

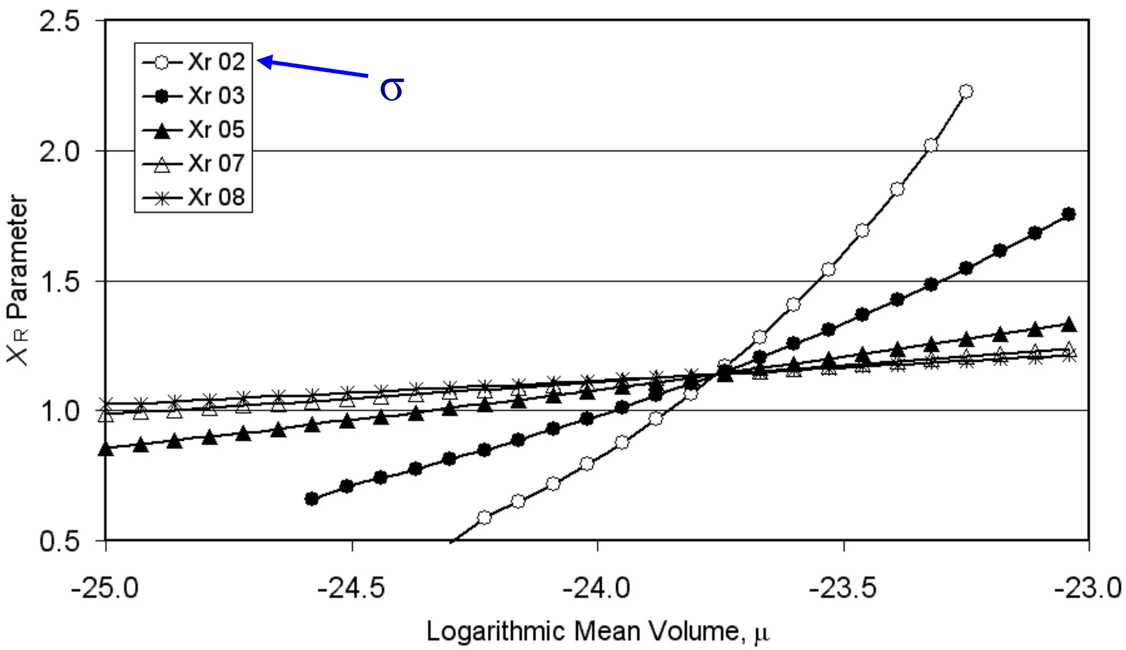
6 – 0.3

The paramagnetic fractions decrease the $X_{w(FD)}$ parameter value. Consequently, low value of $X_{w(FD)}$ does not necessarily mean low amount of SP-SSD particles.

# New Parameter $X_R$

$X_R = (\chi_1 - \chi_4)/(\chi_4 - \chi_{16})$

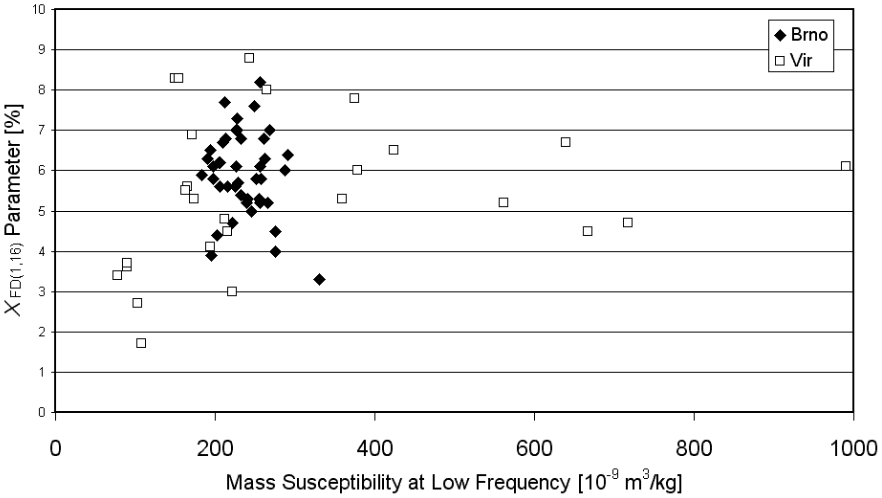
where $\chi_1, \chi_4, \chi_{16}$ are susceptibilities at 976, 3904 and 15616 Hz, is not affected by the dia- and paramagnetic fractions.

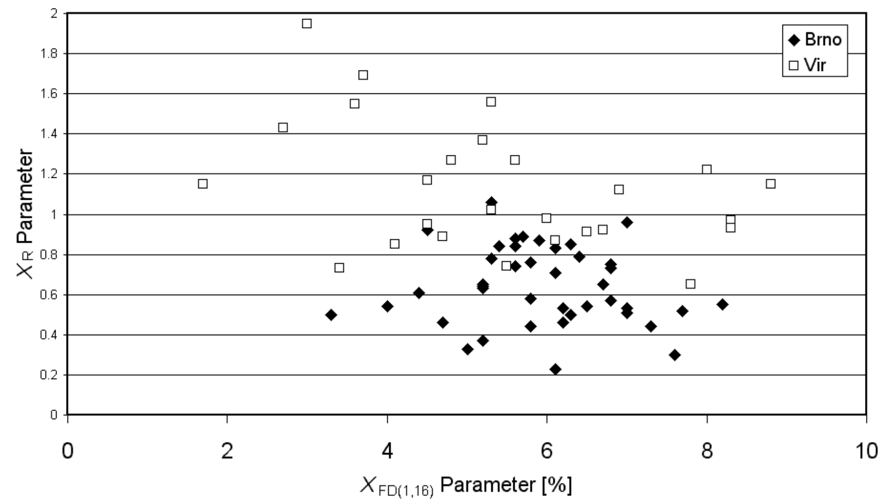



Wide distributions show low $X_R \sim 1$, while narrow distributions may show very variable values (high in general).

# Dam Sediments

Investigated are sediments of the Brno Dam located on Svratka river and soils in the vicinity of Vír Dam also located on Svratka river.




Similar spans of $X_{1,16}$ parameter indicate similar proportions of SP-SSD grains in sediments of both areas.

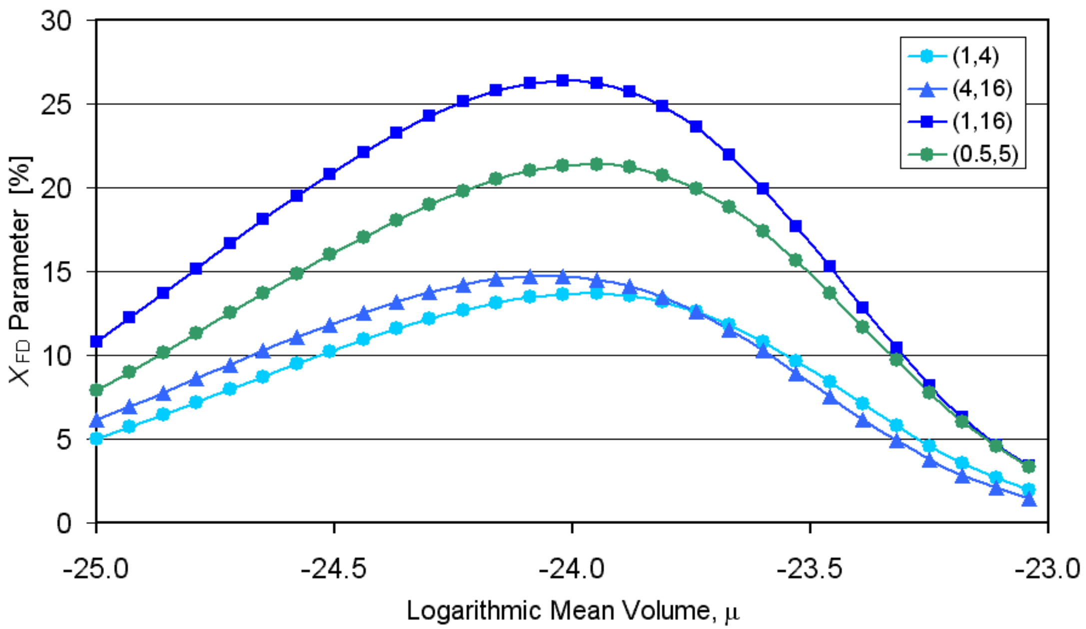
In Brno Dam sediments, $X_R$ <1.

In Vír soils, $X_R$ varies about 1 being often higher.

Different values of $X_R$ parameter indicate differences in grain size distributions of SP-SSD grains in both areas.

# Comparison of MS-2 (Bartington) and MFK1 (Agico) Instruments

The MFK1and MS-2 instruments use different operating frequencies for determining the $X_{FD}$ parameters.




MFK1 Kappabridge

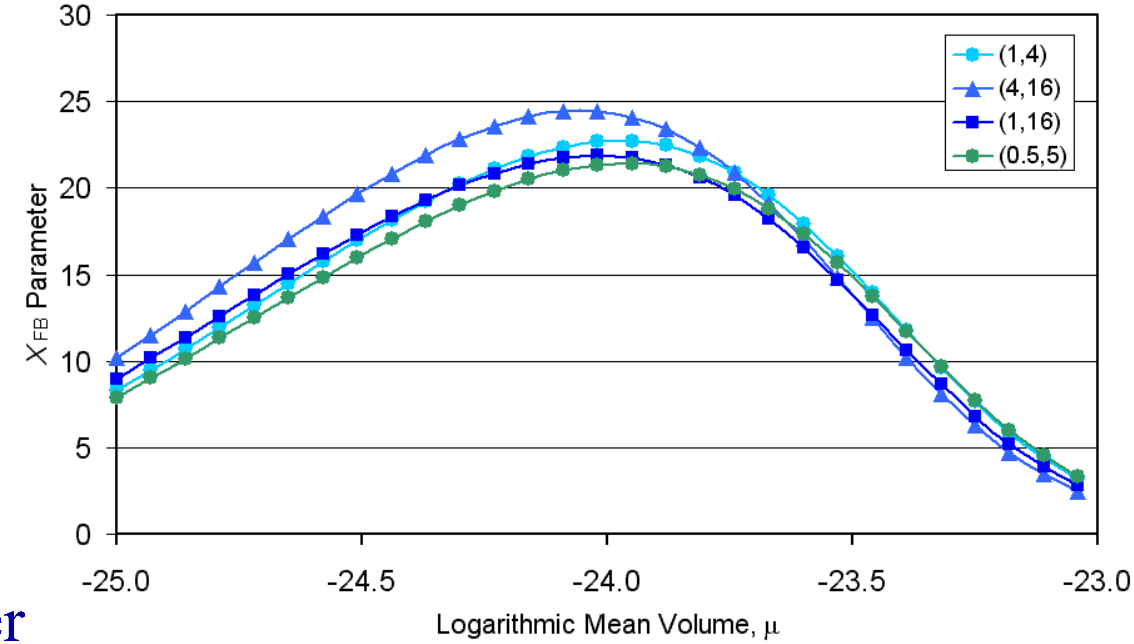
MS-2 Bartington

Large differences exist between individual curves,
$X_{FD}$ depends on instrument, some normalizing is needed !!!

# Suggesting Normalization

The problem can be overcome, if $X_{FN}$ instead of $X_{FD}$ parameter is used. In addition, MFK1 $X_{FD}$ parameter can be re-calculated to MS-2 $X_{FB}$ parameter as follows

$$X_{FB} = \frac{\ln 10}{\ln f_{HF} - \ln f_{LF}} X_{FD}$$




Differences are very small now.

In Bartington, $X_{FB} = X_{FD}$.

In Kappabridge, $X_{FB}$ differ according to frequencies.

The Kappabridge and Bartington parameters are interrelated in only approximate way because of different segments of distribution.

# Precision in Determination of $X_{FD}$ Parameter

(Hrouda and Pokorný, 2011, SGG)

The error of the entity $Q$, which is not measured directly, but which is a function of the other entities ($Q = f(x,y,z,..)$), can be calculated from

$$\Delta Q = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 (\Delta x)^2 + \left(\frac{\partial f}{\partial y}\right)^2 (\Delta y)^2 + \left(\frac{\partial f}{\partial z}\right)^2 (\Delta z)^2 + \ldots\ldots\ldots}$$

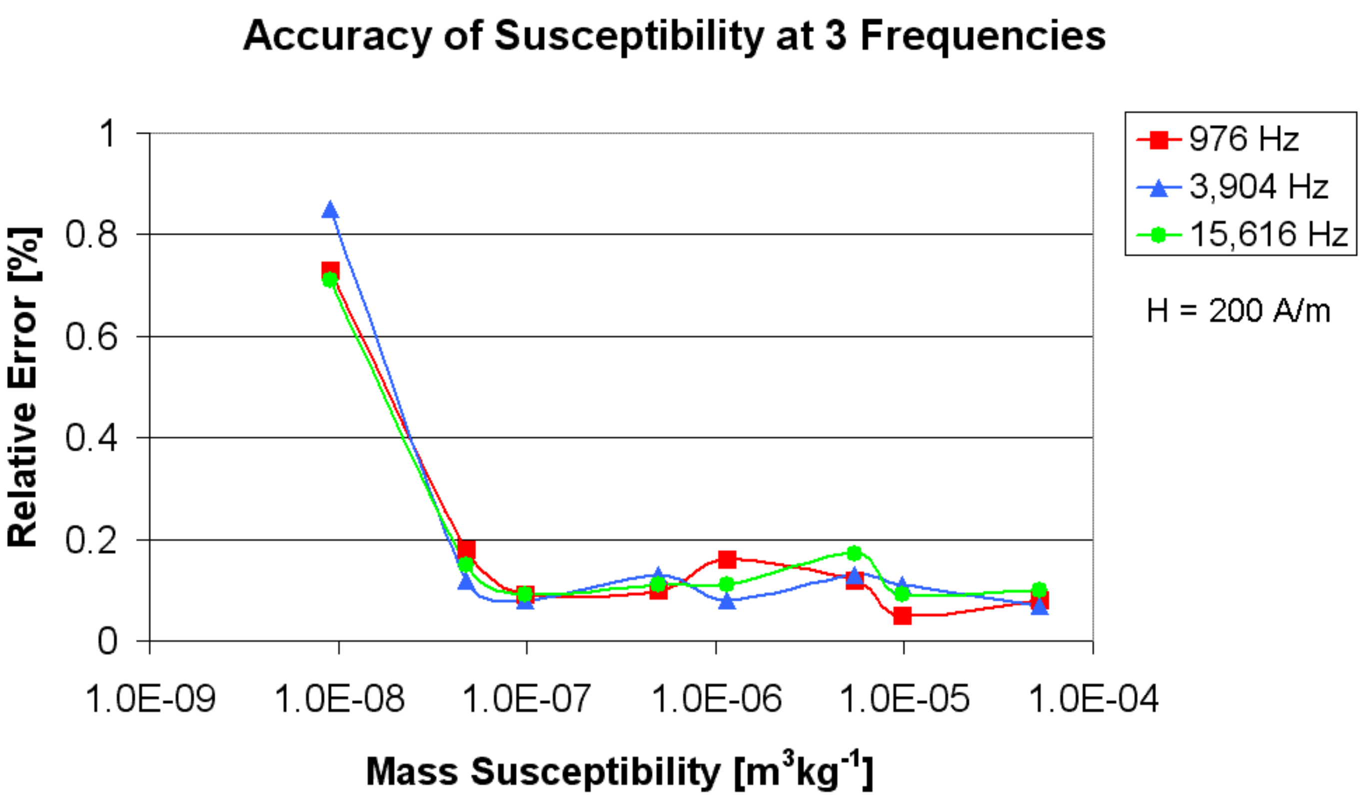
Substituting $X_{FD}$ for $Q$ and executing yields

$$\Delta X_{FD} = (100 - X_{FD})\sqrt{(\vartheta\chi_{LF})^2 + (\vartheta\chi_{HF})^2}$$

where $\vartheta\chi_{LF}$ and $\vartheta\chi_{HF}$ are relative errors.

This formula calculates the expected absolute error in the $X_{FD}$ parameter according to the relative errors of the susceptibilities at two frequencies and the value of the $X_{FD}$ parameter.

# Measurement Accuracy in MFK1 Kappabridge




artificial specs., magnetite in plaster of Paris

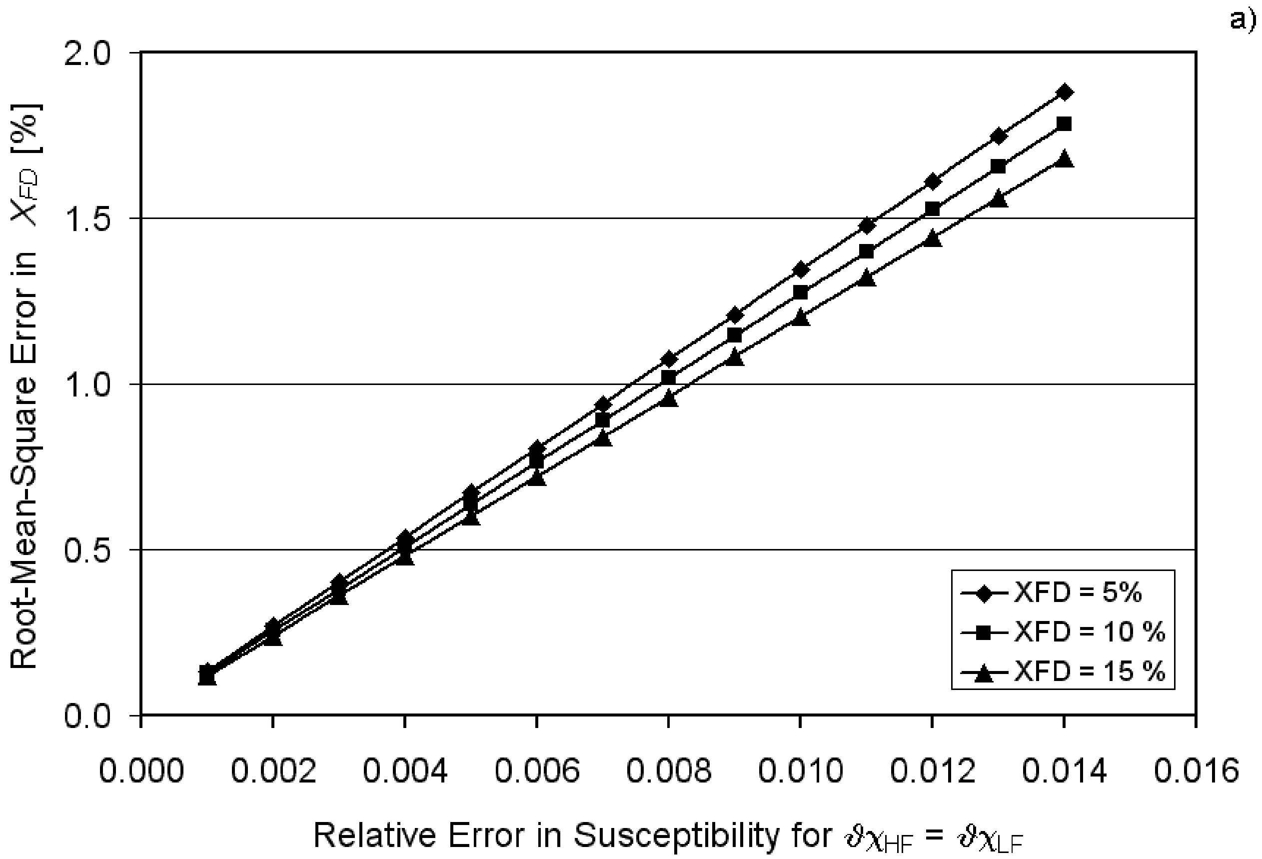
repeated (10x) measurement

**calibration before each collection measurement**

In specimens with mass susceptibility higher than $3x10^{-8}$ $m^3kg^{-1}$, the relative error is better than 0.2 % at all three frequencies.

# Error Modelling 1

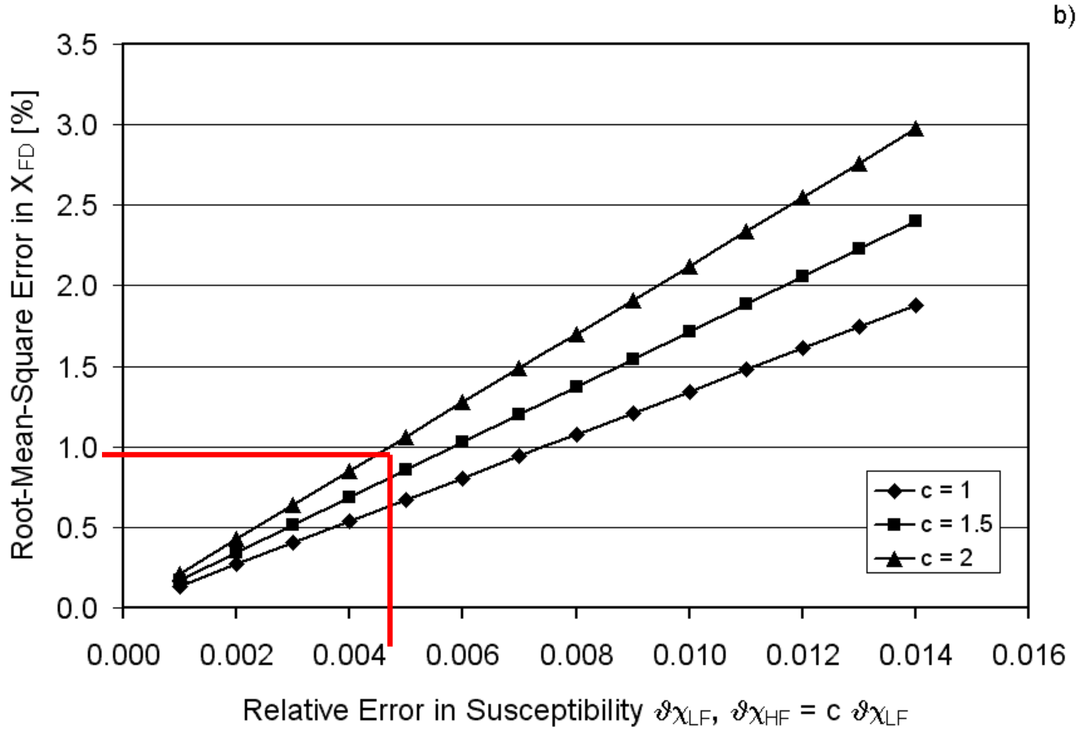
The $X_{\mathrm{FD}}$ values (5%, 10%, 15%) and relative errors $\vartheta\chi_{LF} = \vartheta\chi_{HF}$ were considered




The resultant root-mean-square error in determining the $X_{\mathrm{FD}}$ parameter varies only weakly according to the $X_{\mathrm{FD}}$ parameter.

# Error Modelling 2

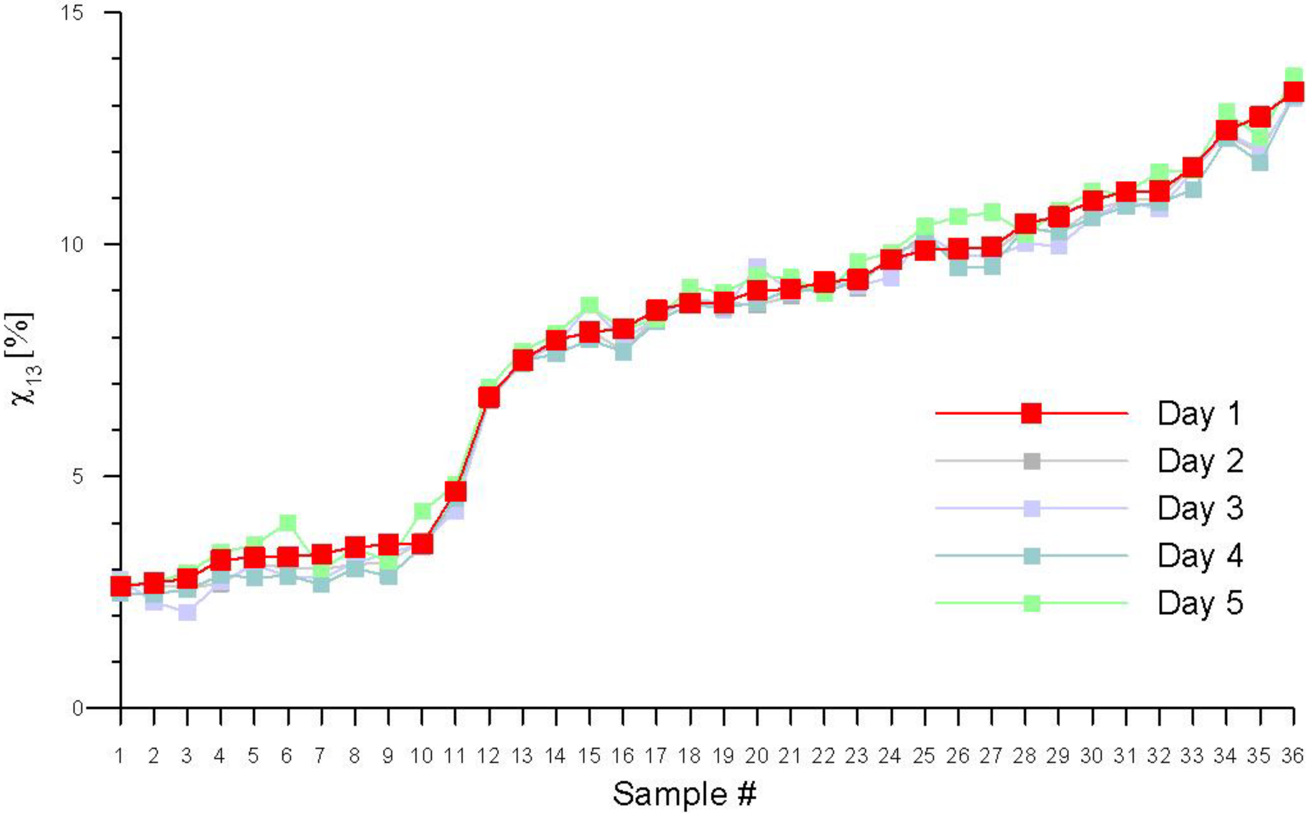
The $X_{FD}$ values (5%, 10%, 15%) and relative errors $\vartheta\chi_{LF} < \vartheta\chi_{HF}$ were considered




If the root-mean-square error in determining the $X_{FD}$ parameter should be less than 1%, the relative error in determining the $\chi_{LF}$ susceptibility must be less than 0.005. This is relatively severe requirement.

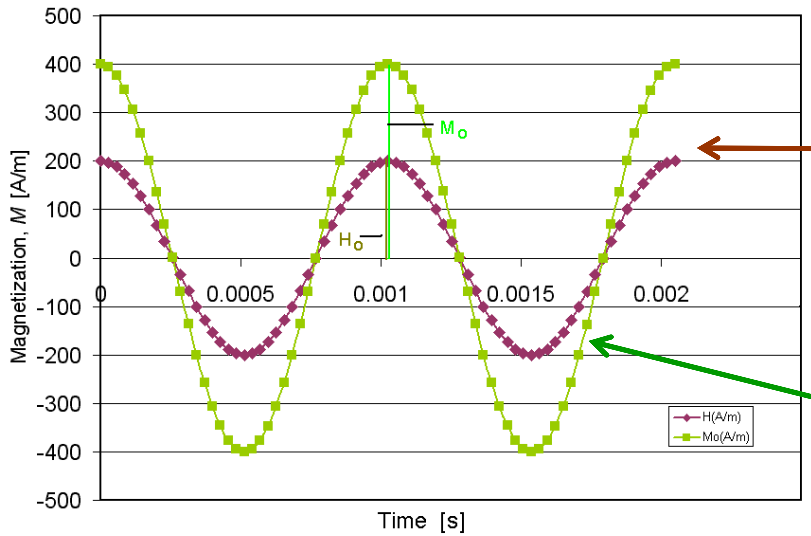
# Experimental Accuracy Investigation

A collection of cave sediments was measured 5 times in different days. Data of the first day were ordered increasingly, data of the other days were ordered in the order of the first day.




Variation in the $X_{FD}$ parameter in the order of 1% is well reproducible.

# What is Out-Of-Phase Susceptibility?




(after Jackson, 2003-4, IRM Quarterly)

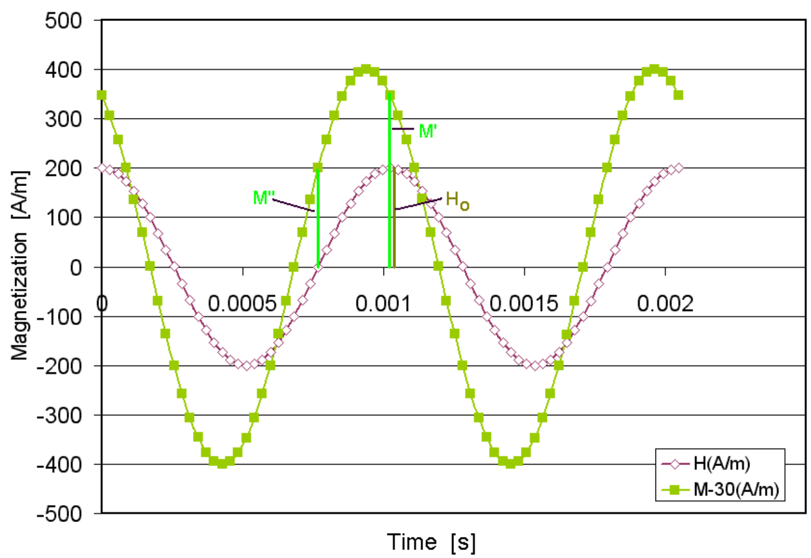
*Magnetizing Field* $H(t)=H_o\cos(\omega t)$

($H_o$ is amplitude, $\omega$ is angular frequency)

In dia, para, MD ferro materials

*In-phase response* $M(t)=M_o\cos(\omega t)$

*Susceptibility* $\chi = M_o/H_o$




In SP to SSD grains, the r*esponse* is

$M(t)=M_o cos[\omega(t\text{-}\Delta t)]= M_o cos(\omega t\text{-}\delta)$

($\Delta t$ is time lag, $\delta$ is phase)

*Susceptibility* resolves into *in-phase* ($\chi' = M'/H_o$) and *out-of-phase* ($\chi''$) components, related as $\tan\delta = \chi''/\chi'$

# Physical Mechanisms of Out-Of-Phase Response

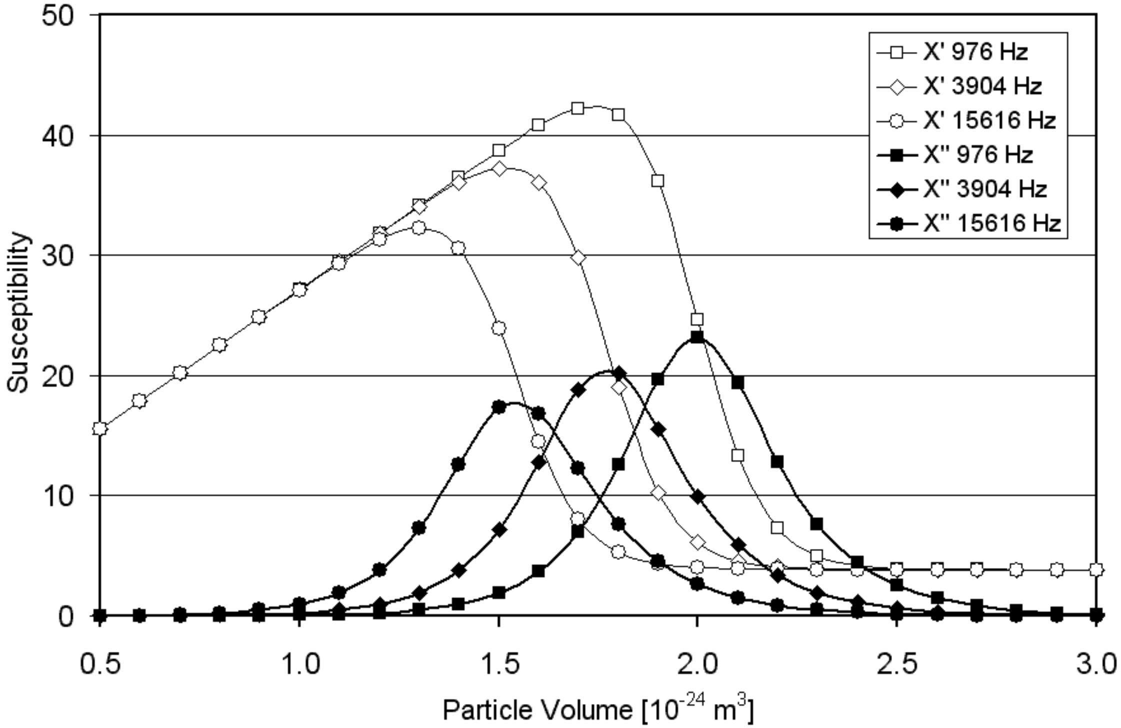
(Jackson, 2003-4, IRM Quarterly)

(1) viscous relaxation,
(2) electrical eddy currents
(induced by AC field in conductive materials)
(3) weak field hysteresis
(non-linear and irreversible dependence of $M$ on $H$)

The mechanisms (1), (2) result in frequency dependence of both in-phase and out-of-phase responses, the mechanism (3) yields signal that is frequency independent, but amplitude dependent.

In environmental magnetism, we have to avoid rocks with mechanisms (2) and (3).

# Out-Of-Phase Susceptibility vs. Particle Volume




General Equation for SP-SSD transition (Néel, 1949)

$$\chi_{\mathrm{sp/sd}} = \chi_{\mathrm{sd}}\left[\frac{\beta}{1+\mathrm{i}\tau_o\omega \mathrm{e}^{\beta}}+1\right]$$

*In-Phase Susceptibility*

$$\chi' = \chi_{\mathrm{sd}}\left[\frac{\beta}{1+(\tau_o\omega \mathrm{e}^{\beta})^2}+1\right]$$

*Out-Of-Phase Susceptibility*

$$\chi'' = -\chi_{\mathrm{sd}}\frac{\beta\tau_o\omega \mathrm{e}^{\beta}}{1+(\tau_o\omega \mathrm{e}^{\beta})^2}$$

($\omega = 2\pi f$)

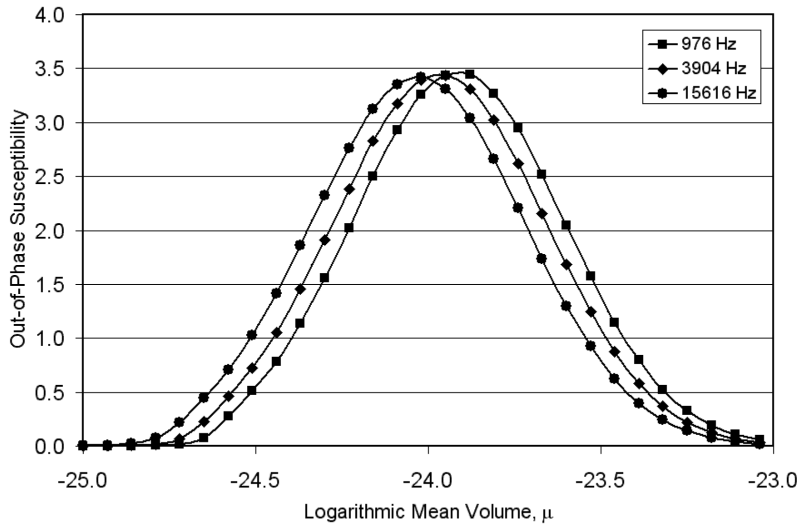
In pure SP and SSD particles $\chi'' = 0$

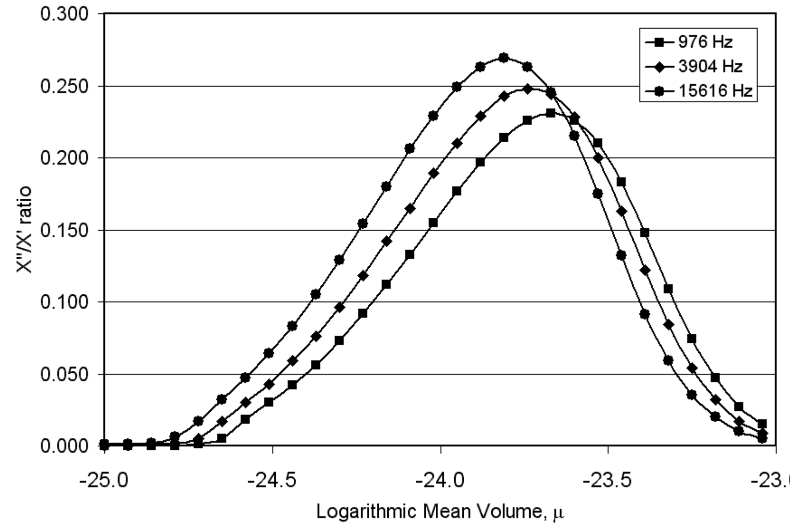
π /2 Law

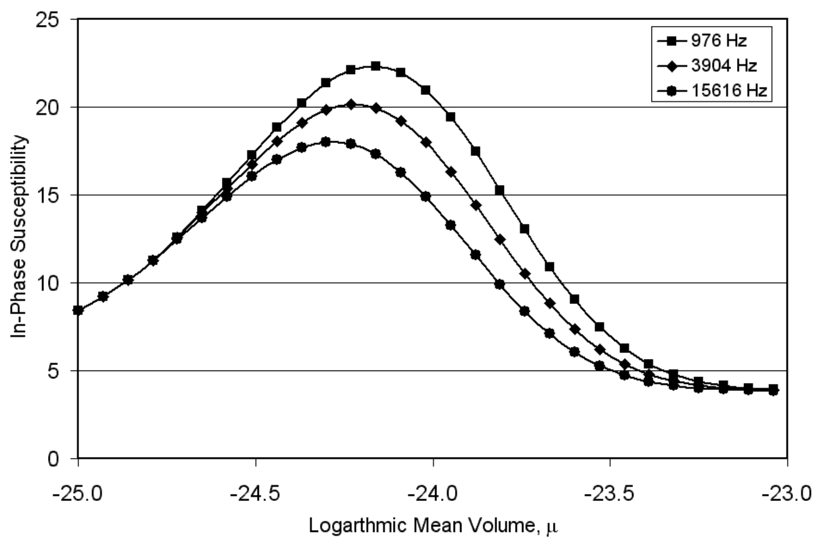
$$\frac{\partial \chi'}{\partial \ln f_m} = -\frac{2}{\pi}\chi''$$

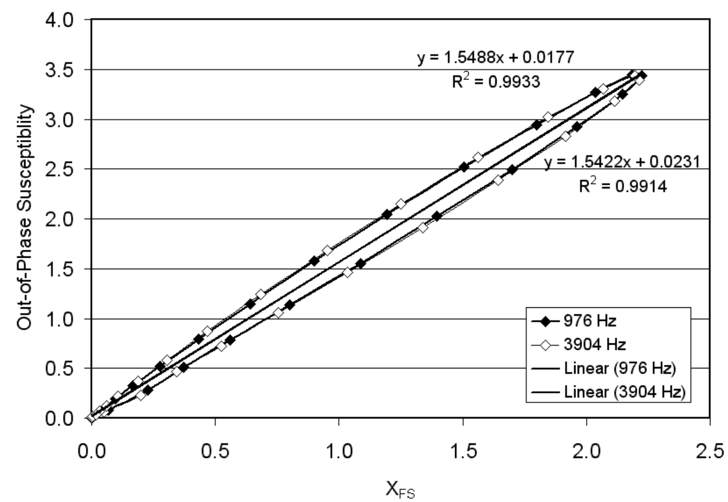
(Details in Hrouda, Pokorny and Chadima, 2011, in prep.)

# Narrow Distribution

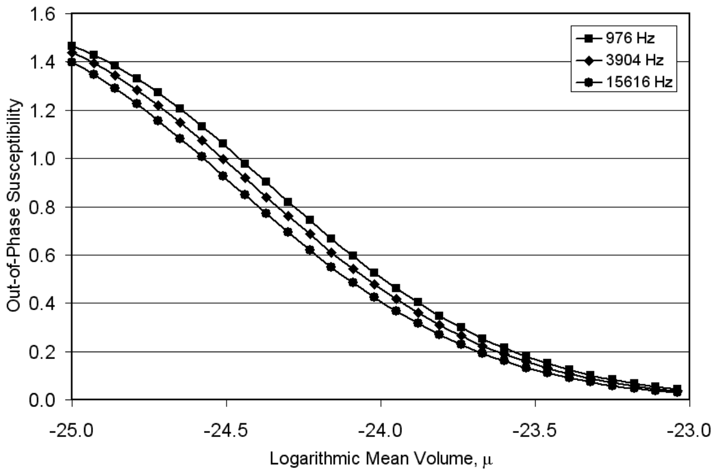


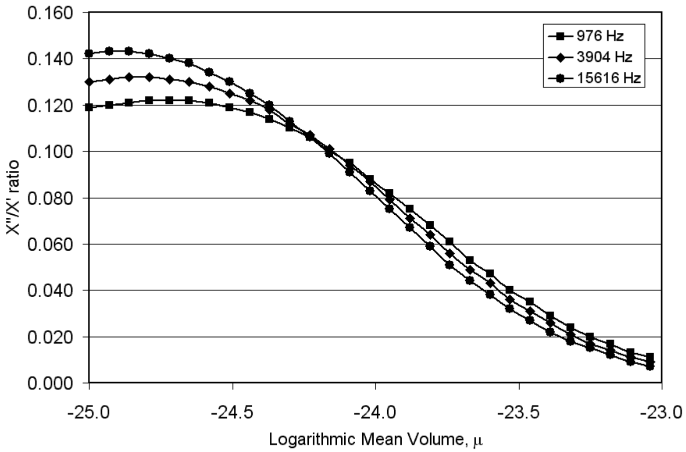



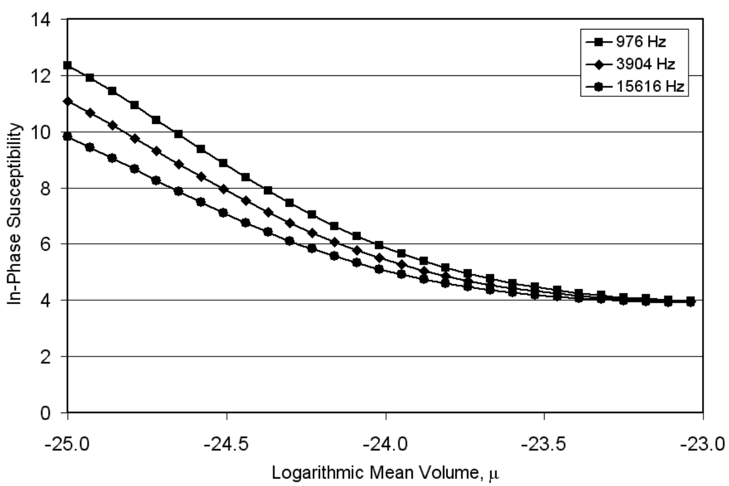



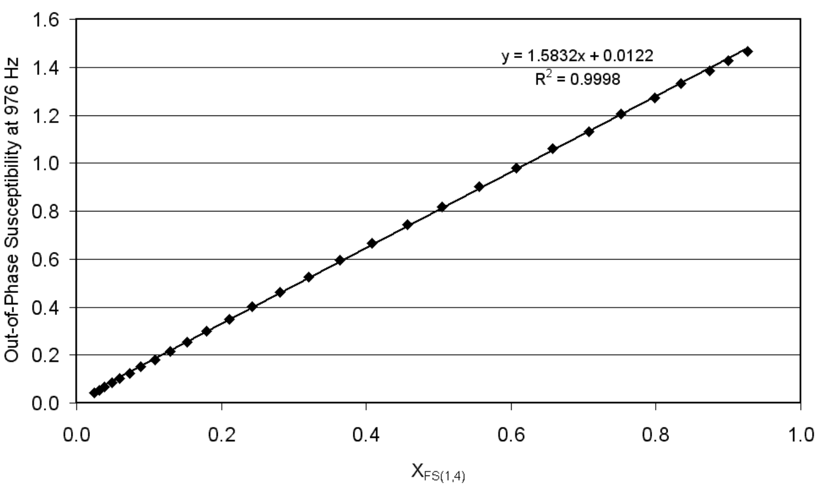



# Wide Distribution



# Effect of Para, etc., on Phase Angle

Whole Rock Susceptibilities

$$\chi'_{\mathrm{w}} = c_{\mathrm{d}}\chi_{\mathrm{d}} + c_{\mathrm{p}}\chi_{\mathrm{p}} + c_{\mathrm{sp}}\chi_{\mathrm{sp}} + c_{\mathrm{ssd}}\chi_{\mathrm{ssd}} + c_{\mathrm{md}}\chi_{\mathrm{md}} + c_{\mathrm{mix}}\chi'_{\mathrm{mix}}$$

$$\chi''_{\mathrm{w}} = c_{\mathrm{mix}}\chi''_{\mathrm{mix}}$$

$$\tan \delta_{\mathrm{w}} = \chi''_{\mathrm{w}} / \chi'_{\mathrm{w}}$$

$$\tan \delta_{\mathrm{w}} = c_{\mathrm{mix}}\chi''_{\mathrm{mix}} / (c_{\mathrm{d}}\chi_{\mathrm{d}} + c_{\mathrm{p}}\chi_{\mathrm{p}} + c_{\mathrm{sp}}\chi_{\mathrm{sp}} + c_{\mathrm{ssd}}\chi_{\mathrm{ssd}} + c_{\mathrm{md}}\chi_{\mathrm{md}} + c_{\mathrm{mix}}\chi'_{\mathrm{mix}})$$

**The frequency-independent components affect (generally decrease) the phase angle, even though they themselves show no phase shift !!!**

# Relationship between Out-Of-Phase and Frequency-Dependent In-Phase Susceptibilities

π/2 Law

$$\frac{\partial \chi'}{\partial \ln f_{\mathrm{m}}} = -\frac{2}{\pi}\chi''$$

$X_{\mathrm{FS}}$ parameter can be considered as macroscopic equivalent of $\partial \chi' / \partial \ln f_m$ member. Then,

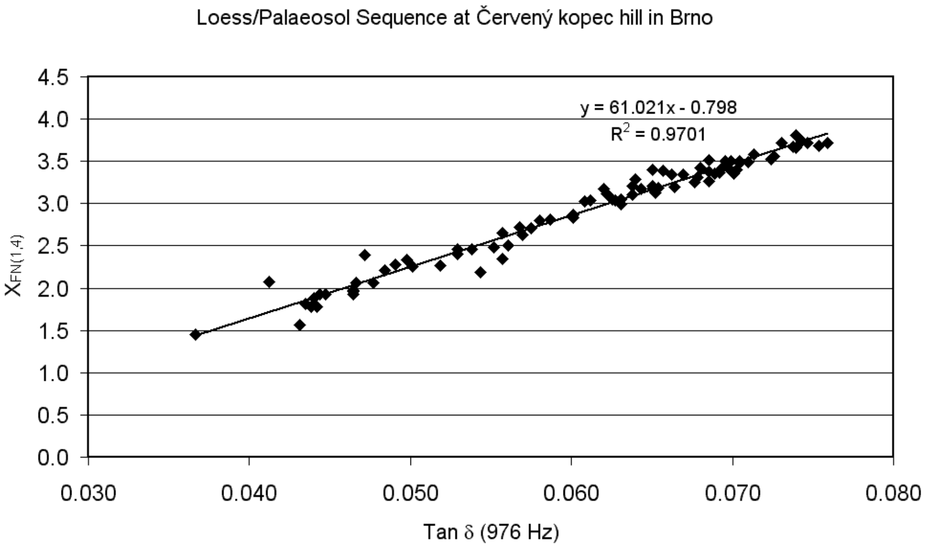
$$X_{\mathrm{FS}} = \frac{\chi'_{\mathrm{LF}} - \chi'_{\mathrm{HF}}}{\ln f_{\mathrm{mHF}} - \ln f_{\mathrm{mLF}}} = -\frac{2}{\pi}\chi''$$

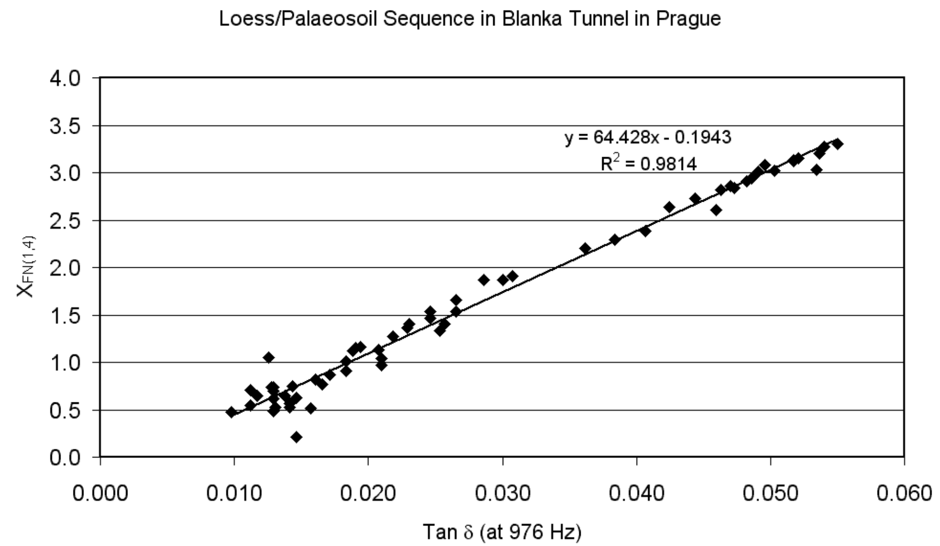
Substituting for $\chi''$ from $\tan\delta = \chi''/\chi'$ and rearranging the terms yields

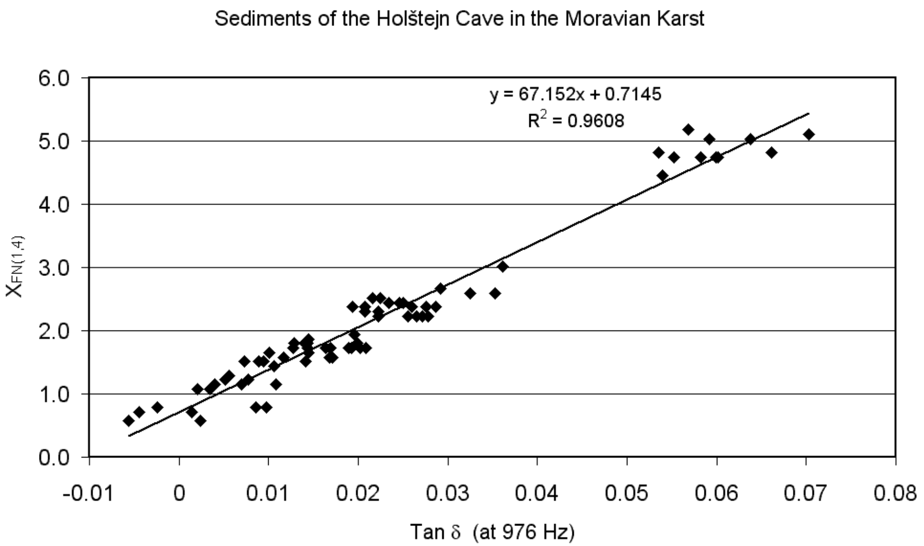
$$X_{\mathrm{FN}} = -\frac{200}{\pi}\tan\delta = -63.7\tan\delta$$

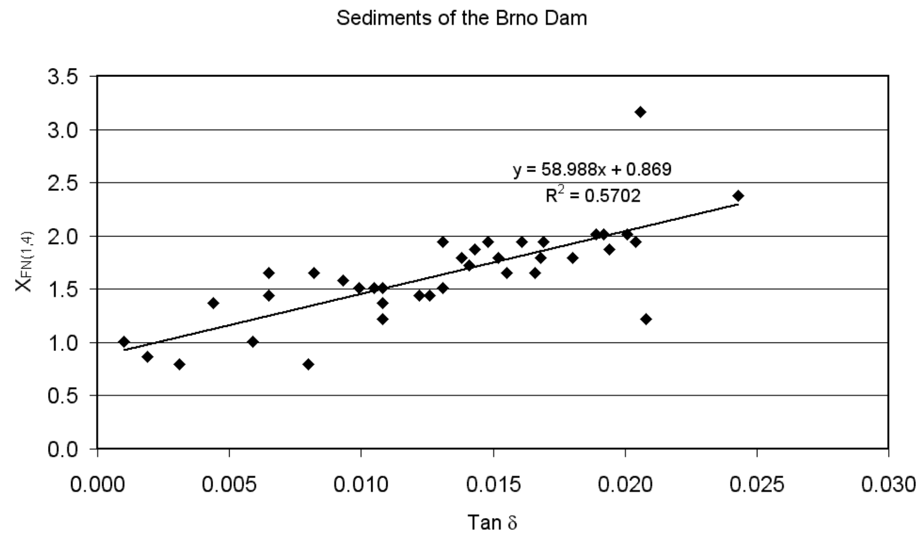
$$X_{\mathrm{FD}} = -\frac{200(\ln f_{\mathrm{mHF}} - \ln f_{\mathrm{mLF}})}{\pi}\tan\delta$$

# Examples of Correlation between $\chi''$ and $X_{FN}$

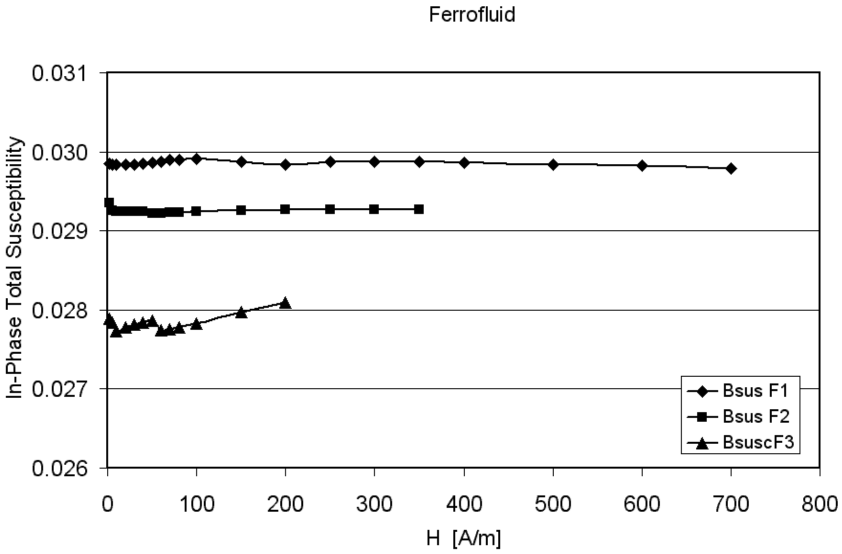


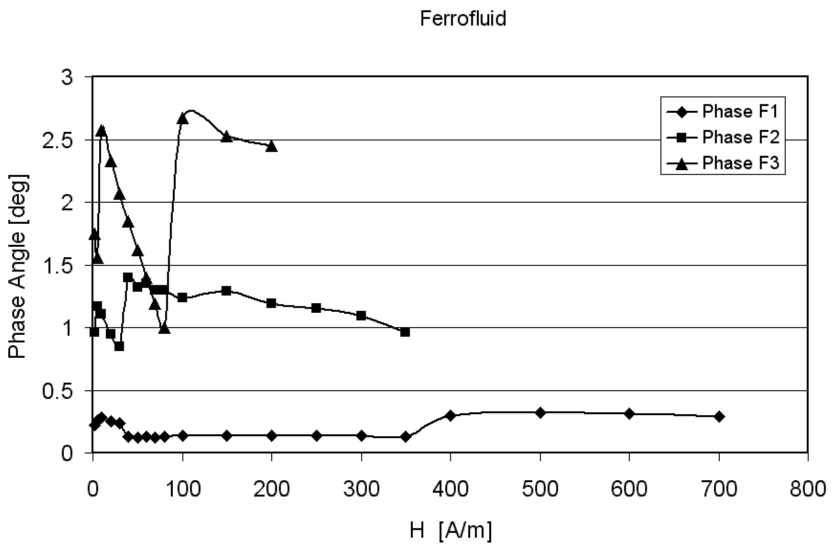



# Ferrofluid - $\chi''$ due to viscous relaxation




Suspension of very small to ultrafine magnetite particles in mineral oil.

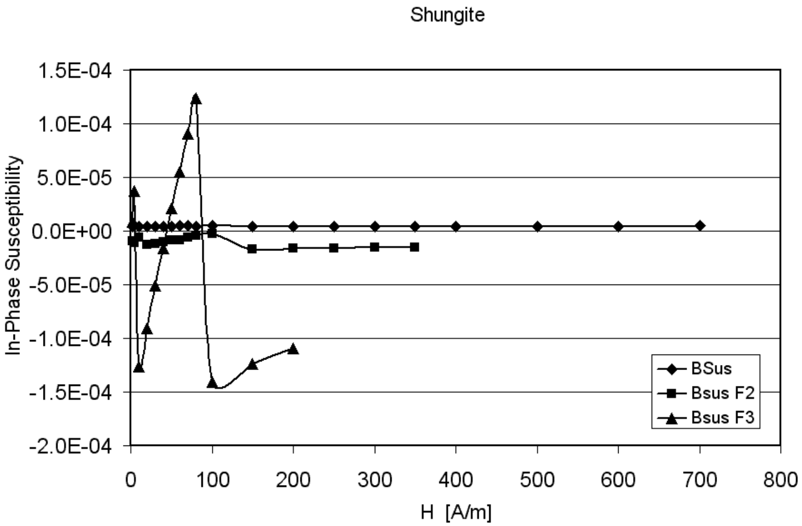
No field variation and strong frequency dependence in $\chi'$.

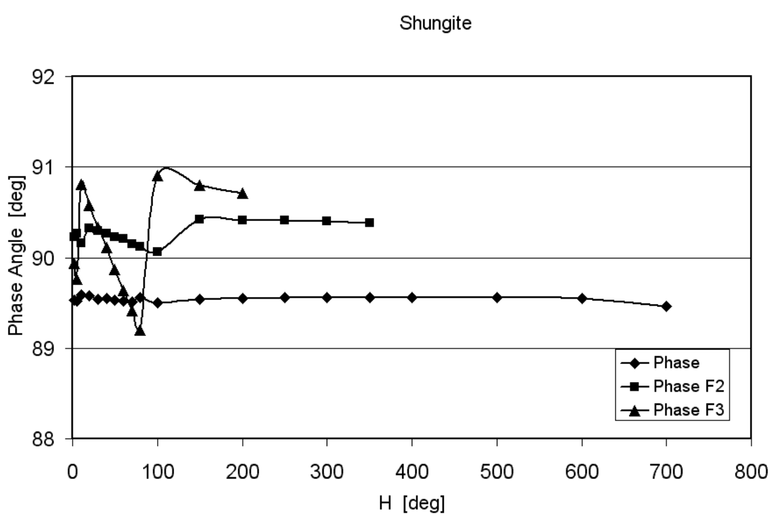



No field variation and very weak $\chi''$ resulting in low phase angle.

$\chi''$ in ferrofluid is evidently due to viscous relaxation.

# Shungite - $\chi''$ due to electrical eddy currents



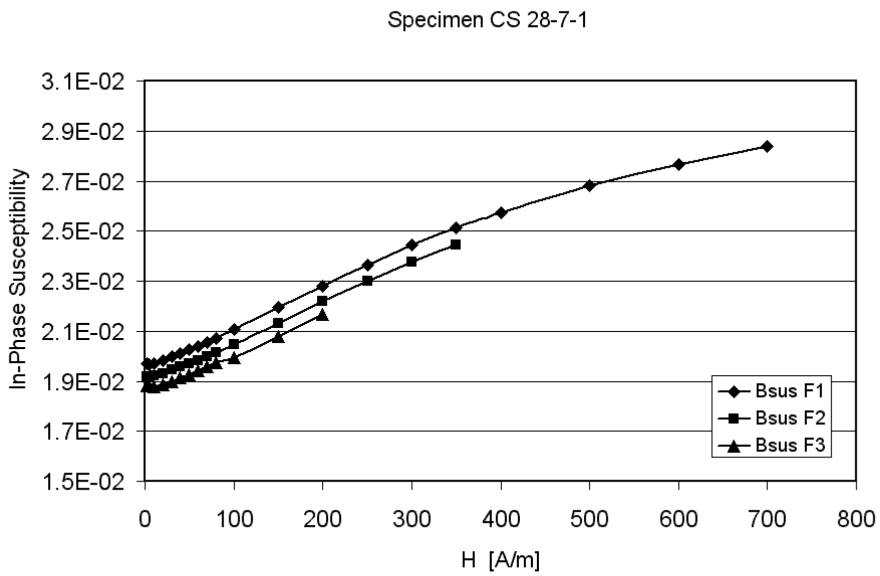

***Shungite*** is highly conductive metamorphic rock from Karelia containing elementary noncrystalline carbon with a metastable structure incapable of graphitization.

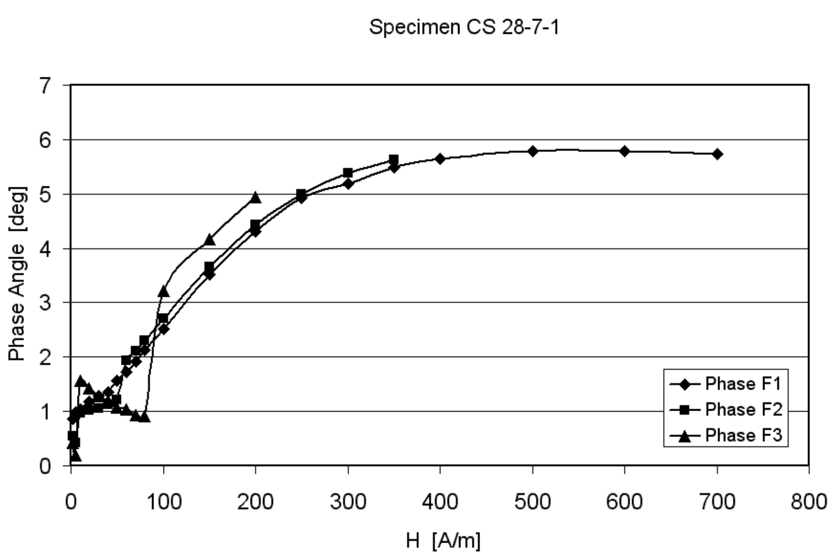
Very low and field independent $\chi'$.

Strong $\chi''$ resulting in phase angle about 90°, which is virtually field independent.

$\chi''$ in shungite is evidently due to electrical eddy currents. No interpretation in terms of ultrafine particles is possible.

# Basalt - $\chi''$ due to weak field hysteresis




Strongly Field dependent
Very weakly Frequency dependent In-Phase component.

Strongly Field dependent and virtually Frequency independent phase angle.

$\chi''$ in this basalt specimen is evidently due to weak field hysteresis.

# Conclusions 1

1. Frequency-dependent magnetic susceptibility results from **interplay** between SP and SSD or even MD magnetic particles
2. Peaks in models with log-normally distributed grain volumes are shifted towards small grains with increasing frequency.
3. New parameter $X_R$ helps us to differentiate between wide and narrow distributions. It is independent of paramagnetic fraction.
4. Paramagnetic fraction tends to decrease frequency dependence. Low whole rock $X_{FD}$ does not necessarily indicate low amount of SP-SSD particles, but can also be indicative of paramagnetic and/or MD fraction.
5. New parameter $X_{FB}$ helps us to compare Bartington and Kappabridge measurements.
6. MFK1 Kappabridge reliably measures $X_{FD}$ values of about 1%.

# Conclusions 2

1. Out-of-phase susceptibility is a good and rapid tool for investigating magnetic particles on SP-SSD transition provided that it is solely due to the viscous phenomena. Simple test was proposed for checking validity of this assumption in each particular case.

2. Main advantage of χ''compared to $X_{FD}$ is that it does not require measurement at two or more frequencies.

3. Formulas were proposed for approximate conversion of χ'' to $X_{FD}$. Correlations found in natural specimens seem to be acceptable from the practical point of view.

4. Paramagnetic and MD ferromagnetic fractions tend to decrease the phase ($\delta$).

# Thanks to:

Drs. Marta Chlupáčová, Jiří Pokorný, Martin Chadima, Jaromír Hanák, Jaroslav Kadlec, Pavel Müller, Daniel Nývlt, Zdeňka Petáková, Eduard Petrovský, Václav Procházka

Concerning the frequency models, an extended explanation can also be found in

Hrouda, F., 2011. Models of frequency-dependent susceptibility of rocks and soils revisited and broadened. *Geophysical Journal International*. doi: 10.1111/j.1365-246X.2011.05227.x ,

and a more extended paper on the out-of-phase MS signals will be available soon.