



## FERROMAGNETIC, DIA-/PARAMAGNETIC AND SUPERPARAMAGNETIC COMPONENTS OF ARAL SEA SEDIMENTS: SIGNIFICANCE FOR PALEOENVIRONMENTAL RECONSTRUCTION

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### ABSTRACT

This article presents a new method to discriminate and to quantify the contribution of dia- and paramagnetic, ferromagnetic and superparamagnetic components to the measured bulk magnetic low-field susceptibility in order to better understand and to interpret environmental changes. This new method is based on data obtained with a rotation coercivity spectrometer. Lacustrine sediments from the Aral Sea were taken to demonstrate the potential of this new method. It is shown that the terrigenous input is strongly related to changes in the paramagnetic susceptibility.

**Keywords:** magnetic susceptibility, coercivity spectrometer, ferromagnetic, dia-/paramagnetic, superparamagnetic components, lake sediments, paleoenvironmental reconstruction.

### 1. INTRODUCTION

Modern lake sediments are a unique source of information for climate changes, regionally and globally, because all environmental variations are recorded by these sediments with high resolution. Magnetic minerals are hereby of particular interest, because they occur almost in any environment, because they are susceptible tracing environmental changes, which are closely related to their formation conditions, and because magnetic mineral concentrations in the *ppm* range can be detected.

Our goal is to decipher the magnetic susceptibility signal in lake sediments by decomposing the bulk susceptibility signal of a lake sediment sequence into ferromagnetic ( $\chi_f$ ), dia-/paramagnetic ( $\chi_p$ ) and superparamagnetic ( $\chi_{sp}$ ) components. Each of these has a different origin: paramagnetic minerals are usually attributed to terrigenous sediment input, ferromagnetics are of biogenic origin, and superparamagnetic minerals may be of either biogenic or terrigenous origin. In sediments, paramagnetic components contribute most to the bulk susceptibility signal, because the ferromagnetic contributions are low. Most sediment of modern lakes contains a lot of organic material and water, which are both diamagnetic. High-field susceptibility changes reflect thus changes in terrigenous input. The latter increases with precipitation which augments the influx of terrigenous material carried by rivers into the lake, consequently the susceptibility increases sharply. However, under certain conditions, such for instance during shrinking water or withering of tributaries, the lake biota grows stronger and the bacterial activity, including magnetotactic bacteria, increases. This results in an enhanced ferromagnetic component ( $\chi_f$ ). Superparamagnetic (SP) components may also be formed, but their magnetic grain size is much smaller, i.e. in the order of about 30-40 nm.

A typical example for superparamagnetic (SP) grains formed in such an environment are hematite or

biogenically induced iron oxides or iron sulphides. SP grains have a high susceptibility at low field, but at high fields their susceptibility is low or even zero.

### 2. OBJECT OF INVESTIGATION

Since more than 50 years the Aral Sea has attracted many scientists investigating this unique environment [1-9]. The Aral Sea is a closed salt lake located at the border between Kazakhstan and Uzbekistan. The lake level began to decline dramatically in the 1960s due to water uptake for feeding the rivers Amu Darya and Syr Darya. This caused a separation of the Aral Sea in two parts - called North (or Small) Aral Sea and South (or Big) Aral Sea. The continuing decrease of the water level caused a further separation of the Big Aral into a western part (Western Aral, including the Chernyshev bay), and a northern part (Tshchebas bay) as well as other geographic changes. The central part of the Big Aral is on the verge of drying now.

Complex investigations of the Aral Sea and the surrounding region indicate multiple drying phases of the lake during the Holocene. Four main regressive phases have been distinguished during the last 2000 years: about AD 0-400, AD 900-1350, AD 1500-1650 and AD 1800 until today [1].

The lake level depends on two factors: the water volume of the inflowing rivers and the evaporation rate on its water surface. The rivers carry clayey material, which increases the paramagnetic contributions, while intense evaporation causes precipitation of salts, which are usually diamagnetic. Under certain average conditions, the biological productivity of the lake increases and the content of organic (diamagnetic) material increases too. Biogenic ferrimagnetic grains (magnetite, greigite) can form at the same time stable single-domain (SSD) particles, by biologically organized mineralization (BCM), and superparamagnetic particles by biologically induced



mineralization (BIM). The magnetic susceptibility of the Aral Sea sediments provides thus valuable information about water level fluctuation in the basin.

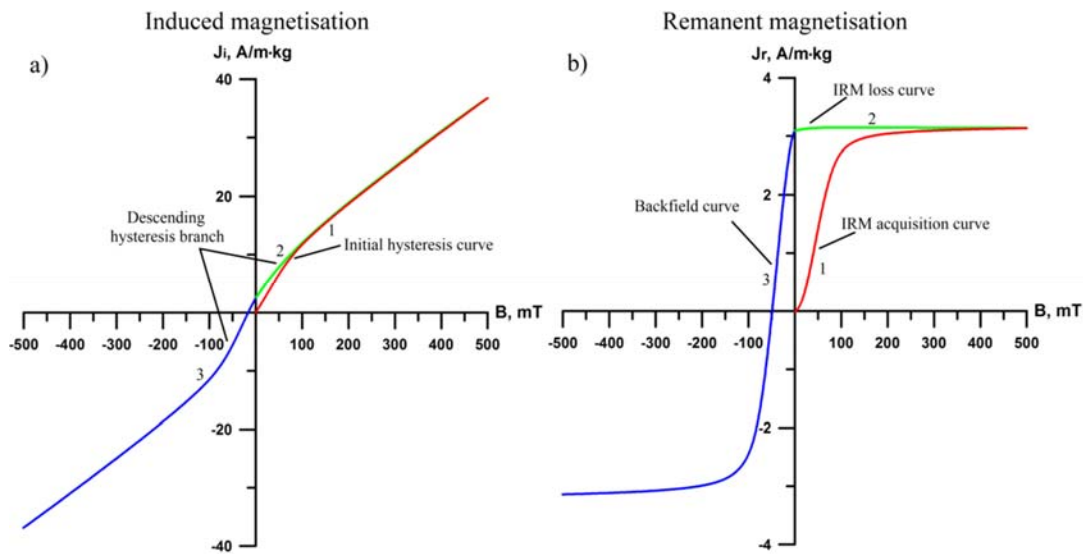
We investigated the magnetic properties of Chernyshov Bay sediments (N45°57'04.2"; E59°17'14.3") from core number 4 taken at far water depth of 9.5 m. The length of the core is 4.16 m. coring was performed with specialised equipment for lake sediments sampling that is based on Mackereth corer and which was designed and manufactured by the staff of Kazan Federal University (KFU). The core was sampled in the field camp, immediately after taking. Our technique for preparing sediment sample collections for magneto-mineralogical investigations involves stratified sampling, using a special cutting device, which is inserted into the core. The samples, 8 cm in length, were sealed and packed in marked plastic bags. A further selected collection was

placed in a permalloy shield for transportation to the laboratory. The samples remained in the nonmagnetic shield until measurement in order to minimize acquisition of viscous magnetisation.

Beside magnetic susceptibility, also remanent magnetisation curves were measured for the separate determination of the different contributions to the bulk magnetic susceptibility.

### 3. METHODS

As previously mentioned, the coercivity spectrometer measures induced and remanent magnetisation quasi simultaneously in two different induction coils. Figure-1 shows the three different sections of remanent and induced hysteresis cycle.



**Figure-1.** Example of a coercivity spectrometer measurement of a typical lake sediments sample from the Aral Sea demonstrating the three measurement cycles, *i.e.* №1 [0 ; +500] mT (red), №2 [+500 ; 0] mT (green) and №3 [0 ; -500] mT (blue). The left panel shows the induced magnetisation (without high-field slope correction) and the right panel the remanent magnetisation. Both magnetisations are measured quasi simultaneously at each field increment. The field resolution of the curves is 0.5 mT.

Dia- or paramagnetic components of the bulk susceptibility ( $\chi_p$ ) are determined by fitting a slope through the descending branch of the hysteresis loop in the interval [+430; +500] mT, Figure-2(a). Errors may be caused by single domain grains of haematite or iron oxide-hydroxides, which have high coercive forces. Such samples can easily be identified because their initial hysteresis curve does not overlap the descending branch of the hysteresis loop in that field range. However, most of our samples do not contain high coercivity minerals.

The ferromagnetic component of the susceptibility ( $\chi_f$ ) is difficult to determine directly. However, a proposed substitute is the slope of the initial hysteresis curve  $\chi_f'$  (Figure-2b) at low fields between 0

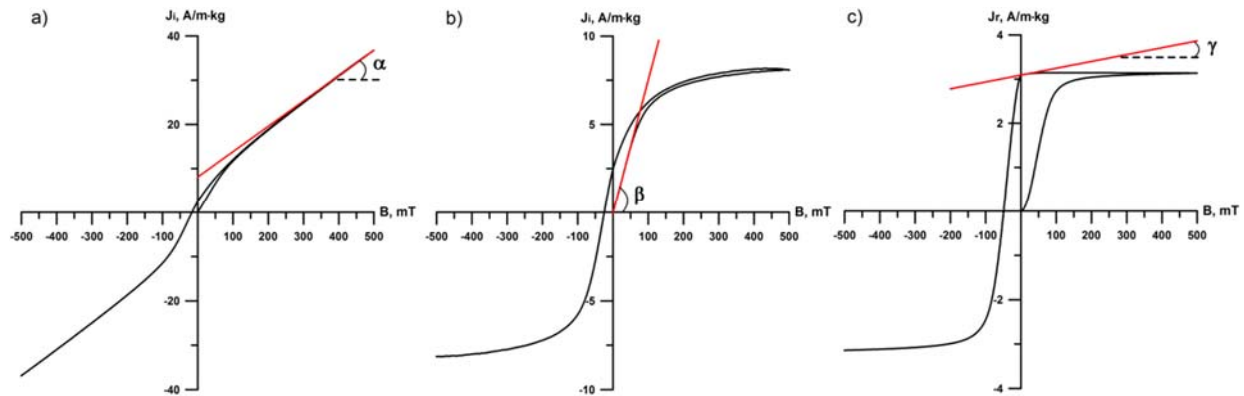
and 10 mT, after applying a high-field slope correction, that corrects the hysteresis for possible dia- and paramagnetic contributions.

The parameter  $\chi_f'$  accounts for ferrimagnetic and super paramagnetic (SP) contributions. The contribution of the latter can be deduced from the loss curve of isothermal remanent magnetisation (IRM). In Figure-1b, one sees that the IRM loss curve (green) remains almost constant, but at low field it decreases. If SP or magnetically viscous grains are absent, this curve should be horizontal until the zero field is reached. A remanence decrease at low fields is due to magnetically viscous grains with relaxation times of 0.1 s or less. This time results from rotation speed of the disk which is about 14.5 Hz. Remanent magnetisation is measured 0.051 s after the



induced magnetisation. The superparamagnetic component of the susceptibility ( $\chi_{sp}'$ ) is the slope of the IRM loss

curve at low fields between 10 and 0 mT (Figure-2c).



**Figure-2.** a) Determination of  $\chi_p$  on the descending branch of the hysteresis loop, b) Determination of  $\chi_f'$  on the initial hysteresis curve after subtraction of the paramagnetic component, c) Determination of  $\chi_{sp}'$  on the IRM loss curve  $J_r$ .

#### 4. RESULTS

Figure-3 compares susceptibility measurements of MS2-Bartington susceptometer (Figure-3a) with those estimated with the coercivity spectrometer (Figure-3b-e). Concerning the latter, the bulk susceptibility  $\kappa_\Sigma$  (Figure-3b) is estimated as the sum of ferrimagnetic (Figure-3c), dia-/paramagnetic (Figure-3d) and superparamagnetic (Figure-3e) contributions.

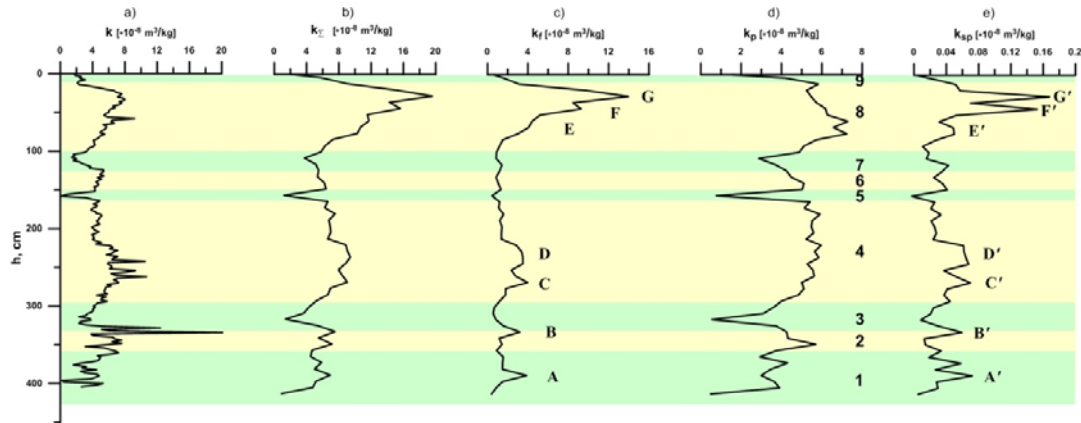
The bulk susceptibility values  $\kappa_\Sigma$  are in the same order of magnitude as the Bartington values ( $\kappa$ ). However the latter are slightly lower (*cf.* Figure-3a, b), because different specimens were used for the measurements. Moreover, specimens measured with the Bartington susceptometer contained a high volume percent of water. Because of its strong diamagnetism it lowers the susceptibility values. Nevertheless, the rather close values of Bartington and coercivity spectrometer bulk susceptibility determinations prove the reliability of our newly introduced susceptibility estimation based on isothermal magnetisation curves. The bulk magnetic susceptibility is dominated by ferromagnetic and dia-/paramagnetic contributions, while superparamagnetic contributions play a subordinate role.

In order to better interpret the susceptibility signal, the data is represented in a Day-Dunlop diagram [18, 19] in Figure-4. The data fits fairly well the theoretical mixing line of single domain (SD) greigite and multidomain (MD) magnetite. Specimens with enhanced ferrimagnetic susceptibility contributions plot in upper left part of the data cluster, which indicates that the enhanced ferrimagnetic susceptibility contributions are associated with SD grains.

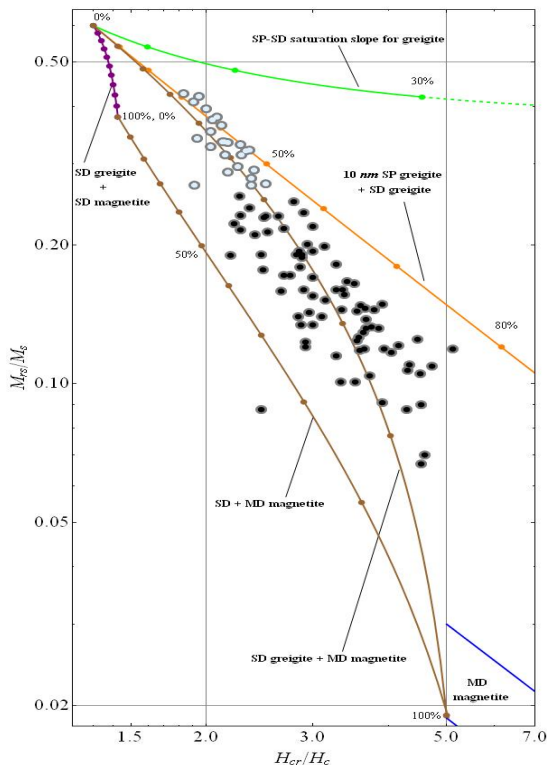
#### 5. DISCUSSIONS

In general, minima in bulk susceptibility correspond to decreases in lake water level, according to previous studies [0, 0, 0]. Fluctuations of the dia-/paramagnetic component are associated with the influx of allocthenic minerals and are proportional to the volume of water brought into the basin. Stages 1, 3, 5, 7, 9 in Figure-3 d are therefore interpreted as low water level marks, while stages 2, 4, 6 and 8 correspond to the high water level. Particularly, the sharp decreases (stages 1, 3, 5 in Figure-3d) are associated with the occurrence of salt in the sediment, indicating thus a high evaporation rate.

In addition, the ferromagnetic and superparamagnetic components allow distinguishing stages of high biological activity in the lake. The ferromagnetic component  $\chi_f$  can be enhanced for two reasons: 1 due to increased influx of detrital magnetic materials from the tributaries of the Aral sea, and 2. due to *in situ* biological formation of magnetic minerals. The first option can rather be excluded because the paramagnetic susceptibility  $\chi_p$  does not correlate significantly with  $\chi_f$  (*cf.* compare peaks A-G in Figure-3). The increase in  $\chi_f$  is therefore interpreted as of biological origin. This occurs by bacterial formation via biologically controlled mineralization (BCM) and / or biologically induced mineralization (BIM) resulting in single domain / superparamagnetic magnetite or greigite *e.g.* [14, 15]. Both have been identified also in lake sediments [15, 16, 17].



**Figure-3.** Magnetic susceptibility profiles of Aral Sea core 4 (a) Magnetic low-field susceptibility measured with a MS2-Bartington susceptometer (b-e) Low field susceptibilities obtained with the coercivity spectrometer (b) Bulk susceptibility as sum of ferromagnetic (c) dia-/paramagnetic (d) and superparamagnetic (e) contributions. The numbers indicate different stages lake water level. The letter in (c) mark peaks in the ferromagnetic component  $\chi_f$ , while primed letter mark corresponding changes of superparamagnetic component ( $\chi_{sp}$ ).



**Figure-4.** Day-Dunlop diagram [18, 19] for the samples plotted in Figure-3(b-e) including theoretical mixing lines (following [19]) of greigite and magnetite mixtures of different grain sizes. Specimens with enhanced ferrimagnetic susceptibility contributions (*cf.* letters A-G in Figure-3c) are highlighted in light-blue. Numerical values for mixing line calculations were taken from [19] and [20], [21] for magnetite and greigite, respectively.

## 6. CONCLUSIONS

**a)** A new method is proposed for the separation and quantification of dia-/paramagnetic, superparamagnetic and ferrimagnetic contributions to the bulk magnetic susceptibility signal coercivity spectrometer measurements.

**b)** The magnetic susceptibility signal of the Chernyshov Bay sediments from the Aral Sea is related to terrigenous gains of clay particles and nanometric iron oxides and sulfides. The susceptibility signal is mainly carried by dia-/paramagnetic minerals. The decrease of this component is related to the terrigenous gain which is bringing by steam supply consequently it means rivers bring the smaller volume of water to the lake. According to different volume of supplement water can be studied the geological balance of lake. Also, decrease of dia-/paramagnetic component can be concerned with authigenic salt deposition.

**c)** The ferrimagnetic component is associated with biogenic authigenic material (magnetite, greigite) formed in sediments.

**d)** It is possible to separate the superparamagnetic signal from the bulk magnetic susceptibility. However, the studied sediments have rather low superparamagnetic contribution to the bulk susceptibility. Further studies are therefore required for confirming the proposed method.

## ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University also by RFBR research projects No. 14-05-31376 - a, 14-05-00785- a.





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