

Scanning Electron Microscopy Point Counting (SEMPC) and Digital Image Analysis Microscopy (DIAM) for Determination and Quantification of Iron and Other Phases in Ancient Marine Sediments

Jesper Kresten Nielsen (jkncolnago@hotmail.com)

Geological Institute, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark

This contribution examines the potential of the Scanning Electron Microscopy Point Counting (SEMPC) and Digital Image Analysis Microscopy (DIAM) techniques to analyze and quantify small-sized mineral phases in geological materials, specifically the composition and optical quantification of pyrite in ancient marine sediments. Quantifiable phases (SEMPC) are recognized and categorized by two different classification schemes using mineral-specific stoichiometric compositions and relative element ratios and concentrations. It is argued that the combined use of the two techniques can support and characterize the paleoenvironmental indicators (e.g. Degree Of Pyritization, DOP) that involve extractable Fe species.

Samples and techniques Fourteen samples were analysed from the shallow drill GGU core 303102 representing the Upper Permian Ravnefjeld Formation, Triaselv in central East Greenland. The samples comprise organic-rich laminated shales and organic-lean bioturbated siltstones deposited under euxinic to normal marine conditions (Nielsen et al., in prep).

SEMPC was set to ten matrices, each containing 10x10 microanalysis points (in total 1000 point per sample), within a representative sample frame for quantitative chemical compositions by ZAF-corrected EDX spectrums (Laursen, 1997). Chemical data comprise the concentrations for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Zr, Mo, Ba, and Pb. Two classification schemes place each analysis point, counting one, in different "mineral" and "element" categories (Table 1) reducing the data to few tens numbers.

DIAM confirms that Cr-reducible sulfur (Canfield et al., 1986) represents the pyrite sulfur (and iron) content. Measurements of color-selected features, such as pyrites in reflected light, were obtained with the area representing the amount of pyrite. The image processing was held to a minimum with minor corrections for three-dimensional aspects. Iron systematics viewed through the SEMPC and DIAM measurements Iron in the marine sediments of the Upper Permian Ravnefjeld Formation is mainly confined to pyrite (up to 2.12% Fe) with the sulphide generated by bacterial sulphate reduction (Nielsen et al., 1999). Pyrites are disseminated throughout the laminated sediments, but are restricted to assemblages in

burrows in the bioturbated sediments. This is reflected in the DIAM data, where measurements of fewer features (equal to pyrites) and a larger area per color-selected feature may characterize the bioturbated sediments. The pyrite counts (SEMPC) follow the DIAM data with the count being below 20 for the bioturbated sediments and above 20 for finely laminated sediments (except the upper laminated unit L2). In addition, the pyrite sulfur (and iron) contents determined by chromous reduction (Nielsen et al., in prep) agree with those found by the DIAM technique. This confirms that the main extractable sulfur comes from pyrite and not from alternative sulfur phases.

Otherwise, iron sites coincide with Fe-rich clay minerals such as chlorite. These iron sites were intensively sulfidized during diagenesis (Nielsen and Pedersen 1998) in the lower laminated unit L1 of the Ravnefjeld Formation. Counts of non-pyritized Fe silicates with iron contents above 2% (Table 1) range above those in the L1 and increase proportionally in the upper part of the Ravnefjeld Formation (unit L2). Also the Fe extractable Fe by HCl (FeH) and by dithionite (FeD), which are used to derive paleoenvironmental indicators such as DOP ($= \text{Fepyrite}/(\text{Fepyrite}+\text{FeH})$) and IA ($= (\text{Fepyrite}+\text{FeD})/\text{Fetotal}$) (Raiswell et al., in press), increases. The resulting low DOP and IA values may be explained by the effects of exposure time rather than accessibility to sulphide, since the same phases are more pyritized in the L1 unit. Consistency between the SEMPC and extractable iron data suggest that pyritization was here limited by relatively high sedimentation rates. In contrast, lower sedimentation rates allowed time for reactive silicate Fe to participate in the pyrite forming processes. Variable frequency of pyritized silicates support the existence of sulfidic pore waters with the sulphide reacting towards iron-rich silicates on a scale of few thousand years.

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Mineral categories	Formulas
Pyrite	$S/Fe < 1.5; S/Fe > 0.8; S > 2; Fe > 2$
Element categories	
Highly Fe-rich silicates *	$FeO > 10; (SiO_2 + Al_2O_3) > 10; S < 2$
Less Fe-rich silicates *	$10 > FeO > 2; (SiO_2 + Al_2O_3) > 10; S < 2$
Fe-lean silicates *	$FeO < 2; (SiO_2 + Al_2O_3) > 10; S < 2$

* Sulfur-lean.

Table 1. Fractions of the two classification schemes used for the SEMPC

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