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Chemical interaction of atmospheric mineral dust-derived nanoparticles with natural seawater – EPS and sunlight-mediated changes



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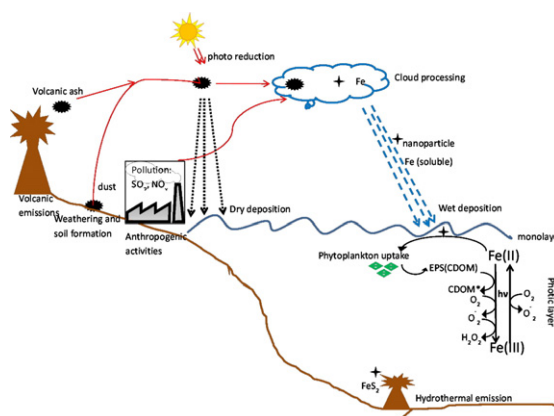
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HIGHLIGHTS

- Nanomaterials from simulated cloud processing of dusts were interacted with seawater.
- Aggregation is more polydisperse and unstable in seawater than in MQ water.
- Microalgal exopolymeric substances (EPSs) stabilises dust derived NP aggregates.
- EPS enhances Fe dissolution from NPs, and this is enhanced in the absence of light.

GRAPHICAL ABSTRACT



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ABSTRACT

Laboratory studies were conducted to investigate the interactions of nanoparticles (NPs) formed via simulated cloud processing of mineral dust with seawater under environmentally relevant conditions. The effect of sunlight and the presence of exopolymeric substances (EPS) were assessed on the: (1) colloidal stability of the nanoparticle aggregates (i.e. size distribution, zeta potential, polydispersity); (2) micromorphology and (3) Fe dissolution from particles. We have demonstrated that: (i) synthetic nano-ferrihydrate has distinct aggregation behaviour from NPs formed from mineral dusts in that the average hydrodynamic diameter remained unaltered upon dispersion in seawater (~1500 nm), whilst all dust derived NPs increased about three fold in aggregate size; (ii) relatively stable and monodisperse aggregates of NPs formed during simulated cloud processing of mineral dust become more polydisperse and unstable in contact with seawater; (iii) EPS forms stable aggregates with both the ferrihydrate and the dust derived NPs whose hydrodynamic diameter remains unchanged in seawater over 24 h; (iv) dissolved Fe concentration from NPs, measured here as <3 kDa filter-fraction, is consistently >30% higher in seawater in the presence of EPS and the effect is even more pronounced in the absence of light; (v) micromorphology of nanoparticles from mineral dusts closely resemble that of synthetic ferrihydrate in MQ water, but in seawater with EPS

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they form less compact aggregates, highly variable in size, possibly due to EPS-mediated steric and electrostatic interactions. The larger scale implications on real systems of the EPS solubilising effect on Fe and other metals with the additional enhancement of colloidal stability of the resulting aggregates are discussed.

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1. Introduction

Atmospheric chemical processes that occur in clouds generate iron rich nanoparticles (NPs) from mineral dusts (Kadar et al., 2013). Nano-iron has been suggested to be a major portion of the bioavailable fraction of the metal (Raiswell et al., 2008). However, before becoming available for biological uptake by marine phytoplankton, NPs originated from cloud mediated processes undergo rapid transformations (such as aggregation, photo-reduction, dissolution and interaction with natural organic matter) immediately in contact with seawater. These reactions are too fast to be easily monitored in the field and therefore require real time analyses and experimentation under carefully controlled laboratory conditions (Shi et al., 2010). Thus we have conducted laboratory studies to investigate how the simulated cloud-derived Fe-rich nanoparticles interact with natural oceanic seawater and how their composition, size, surface topology and chemical reactivity change under a range of environmental conditions.

Exo-polymeric substances (EPSs) secreted by phytoplankton constitute a large and dynamic pool of oceanic dissolved organic carbon (DOC) (Engel et al., 2004; Fogg, 1983) with key roles in the formation of marine biofilms and in colloid and trace element scavenging (Fogg, 1983; Myklestad, 1995). About half of the global photosynthetic activity is performed by phytoplankton (Chisholm, 2000) and ~40–60% of the resulting biomass is released as EPS suggesting its crucial importance in the global carbon cycling and potential driving force in sequestration of atmospheric CO₂. In addition, changes in the EPS assembly kinetics were recently reported to be induced by engineered NPs (Chen et al., 2011) suggesting a potential disturbance to the marine carbon cycle. This ecological impact of synthetic NPs draws attention to the importance of interactions between EPS–nanoparticles. Furthermore, our recent study (Kadar et al., 2012) revealed improved metabolic parameters in some marine microalgae cultured on synthetic nano-iron enriched media and the uptake mechanisms involved secretion of EPS. The same study showed that synthetic nano-iron was preferred over EDTA–Fe used in laboratory cultures in generic growth media suggesting that the nanoparticulate form of the metal may be more bioavailable to microalgae. Whilst originally the term EPS stands for “extracellular polysaccharides”, it is now acknowledged that these matrixes are more complex, including lipopolysaccharides, glycolipids, lipids, proteins or peptides and nucleic acids. Interaction of the atmospheric dust-derived “natural nanoparticles” with EPS could therefore be a complex key factor influencing bioavailability of iron, and although we have started to understand how marine algae might take up nano forms of the metal (Kadar et al., 2012) we do not fully understand the influence of seawater EPS on the environmental fate of (nano)particles.

Here we used an EPS extract from a common phytoplankton species – *Nannochloropsis salina* – and added to natural oceanic seawater in order to investigate the physicochemical transformations of atmospheric dust-derived “natural Fe-rich nanoparticles” in contact with seawater so that we can better understand their environmental fate and behaviour.

This is a follow up study (part I focused on NP formation via simulated cloud processing of mineral dusts with distinct Fe-content), which investigates the possible transformations that take place when dust-derived particles come in contact with seawater. Specifically, here we have studied the composition, Fe dissolution/Fe lability, particle aggregation/size distribution, surface topology and zeta potential, i.e. colloidal stability of the dust derived NPs, both immediately and 24 h after coming in contact with seawater under a range of environmentally

realistic conditions (i.e. typical in oceanic waters, in the presence of EPS particles and under distinct photo-oxidative conditions). To the best of our knowledge, this is the first research attempting to systematically investigate the changes in physico chemical properties of Fe-rich environmental NPs upon dispersion in seawater with and without EPS, which shed new light on the environmental fate and behaviour of natural NPs derived from atmospheric aerosols.

2. Experimental

2.1. Dust samples

Three dust models including (a) Sahara desert, Morocco (30°16' N–4°55'W); (b) Libya (25°35'N–16°31'E) and (c) volcanic ash (un-weathered lapilli collected after eruption of Etna in July 2011; 37°44'N–14°59'E) were exposed to simulated cloud processing following previously reported protocol (Kadar et al., 2013).

2.2. EPS extraction from phytoplankton culture and quantification

Exopolymer particles were extracted by cross-flow ultrafiltration according to the method reported by Zhang and Santschi (2009), from a 20 L stationary culture of *N. salina* (CCAP 849/3) grown in a 450 L photo bioreactor to a density of 16×10^6 cells mL⁻¹. Culture conditions were: 20 °C; 16/8 light/dark regime; f/2 medium dissolved in Instant Ocean®. The phytoplankton culture was centrifuged at 4000 rpm for 30 min and the supernatant was collected for free dissolved EPS following the previously reported method (Zhang and Santschi, 2009). Briefly, 20 L supernatant fraction was filtered (<0.45 µm) and ultra-filtered on a 1 kDa cartridge (GE Healthcare UK) to ~300 mL retentate. The cartridge was rinsed with 200 mL MQ water, and then soaked for 6 h following washing with 200 mL MQ twice. The first retentate, the rinse and the two washing solutions were combined resulting in 1 L EPS extract which was used in subsequent experimentations as described below. The transparent exopolymeric substance (TEP) fraction of the EPS, operationally defined as Alcian Blue staining particles greater than 0.2, was quantified (Cunliffe et al., 2009) as the xanthan gum equivalents and was $4.66 \text{ mg} \cdot \text{L}^{-1} \pm 0.81$, which converted to carbon gives $2.94 \text{ mg C L}^{-1} \pm 0.51$. These are typical concentrations in very productive waters, such as estuaries and thus a 1:20 (v/v) addition of this stock EPS to oceanic, 30 kDa-filtered seawater is an environmentally realistic dose.

2.3. Nanoparticle–seawater interactions

Nanoparticles were obtained via the previously described cloud simulation protocol (Kadar et al., 2013) using 30 mg dust powder in 500 mL of 0.1 N H₂SO₄ solution (pH 1) stirred (120 rot. min⁻¹) for 96 h followed by a drop-wise neutralisation (to pH ~ 6) using concentrated NaOH solution (Sigma). Samples and standards were prepared in HDPE tubes. All equipment had been carefully acid washed prior to use. All reagents were from Sigma Aldrich and at least p.a. grade. All solutions were prepared in MQ water (Millipore). The dust suspensions at pH ~ 6 (which contain Fe-rich NPs) were then pre-filtered on 0.45 µm pore size membranes to remove insoluble material before addition to natural seawater (1:10) from the L4 station of the Western Channel Observatory of PML (50°15'N–4°13'W) with well characterised physico-chemistry (<http://www.westernchannelobservatory.org.uk/data.php>).

Triplicate suspensions of each dust type were continuously stirred for 24 h and kept at 20 °C, under the following environmentally relevant conditions (total number of 48 suspensions): *i*) absence of EPS in dark; *ii*) presence of EPS in artificial sunlight (2200 Lux with Aquaglow 20 W lamp; λ 380–780 nm) equivalent to photic oceanic conditions; *iii*) presence of EPS in dark; and *iv*) absence of EPS in artificial sunlight. After 12 h the seawater reacted dust suspensions were processed for nanoparticle characterisation, i.e. total Fe content (4.5 mL subsample acidified by addition of 0.5 mL concentrated HNO₃); Fe dissolution (10 mL for centrifugal ultrafiltration using 3 kDa pore size vivaspin); colloidal stability using DLS (2 mL for particle size distribution and 2 mL for zeta potential); particle micromorphology using TEM (10 mL ultra-centrifuged onto Cu grids); and particle elemental composition using SEM–EDX (50 mL subsample filtered on 0.05 μ polycarbonate membrane) as described in details below.

2.4. Fe dissolution from (nano)particles and total Fe content

Samples (10 mL) were taken at different times and centrifuged (Beckman) for 30 min (5000 rpm and 21 °C) using vivaspin 3 kDa centrifuge tubes (Amicon Ultracel, Millipore, USA). Two aliquots of 4.5 mL of the filtrate were collected and acidified with 0.5 mL of 67% HNO₃ until analysis on Inductively Coupled Plasma Mass Spectrometry (ICP–MS, Agilent 7500cx, 3 USA) to determine the iron ion concentration. Total Fe was also determined in separate subsamples processed similarly, but without the filtration step. Operating conditions were: power = 1.4 kW; coolant gas flow = 13 L min⁻¹; auxiliary gas flow = 0.7 L min⁻¹; nebuliser gas flow = 0.80 L min⁻¹; dwell time = 10 ms; sweeps = 50; nebuliser type = concentric glass; spray chamber type = PC3; collision cell gas = 7% hydrogen in helium at a flow rate of 3.5 mL min⁻¹.

The samples were diluted by a factor of 10 (with 2% nitric acid) to overcome problems with salt clogging, the injector of the ICP torch or the sampler and skimmer cones. Matrix-matched standards were prepared using a 10-fold dilution of the certified reference material NASS 5 (National Research Council Canada). Internal standards of 10 μ g L⁻¹ In and Ir were also used for the ICP–MS analyses to compensate for any temporal instrumental drift. Detection limits for Fe = 3 nM.

Samples and standards were prepared in HDPE tubes. All equipment had been carefully acid washed prior to use. All reagents were from Sigma Aldrich and at least p.a. grade. All solutions were prepared in MQ water (Millipore).

2.5. (Nano)particle colloidal stability

Zeta potential and DLS were used to investigate the changes of zeta potential and size distribution of nanoparticles formed via cloud processing of four types of dusts subsequently dispersed in seawater under four conditions (*i–iv*). Samples were taken 24 h after dispersion in seawater and Zeta potential and size distribution/poly dispersity index (PDI) were measured using Zetasizer Nano ZS (Nano series, Malvern Instruments, UK).

2.6. (Nano)particle micromorphology and elemental composition

Particle size distribution, shape, micro-morphology and surface topology were studied by transmission electron microscopy (TEM) and SEM. TEM samples were prepared by ultracentrifugation (80,000 rpm) of 10 mL suspension onto conventional Cu grids that were coated with Holey Formvar to improve particle visualisation. At least fifteen micrographs were acquired on randomly selected grids taken from various locations of the grids, ensuring representativeness and statistical rigour. Electron micrographs were taken using a TEM at 80 keV (JEOL 1200EX), and particle size and shape parameters were evaluated using image analysis computer software (Digital Micrograph, Gatan Inc.). High-resolution micrographs of selected particle-types were thereafter acquired on a TEM operating at 200 keV (Philips Tecnai F20).

Scanning electron micrographs were also taken on the same Cu grids as those used for TEM. At least 25 typical particles along a random transect and particles were scanned for elemental composition using a Scanning Electron Microscope with Energy Dispersive X-Ray (EDX) detector.

2.7. Statistical analyses

Statistical analyses were performed using Minitab v16. All results are presented as means \pm SEM. Significant differences between groups were determined using one way ANOVA followed by Tukey's comparisons. In addition, two way ANOVA was used to determine the significance of the main effects (dust type, presence/absence of EPS, light vs. dark, fresh vs. aged). All statistical analysis used the default $p < 0.05$.

3. Results and discussion

3.1. Colloidal stability of the model dusts in seawater and in the presence of microalgal EPS

Freshly synthesised ferrihydrite formed aggregates with hydrodynamic diameters of ~800 nm but increased three-fold in diameter within 24 h in MQ water (Fig. 1a). However, when added to seawater (30 kDa-filtered) this “ageing-associated” aggregation of ferrihydrite aggregates was less evident, i.e. the average hydrodynamic diameter did not increase significantly after 24 h, which is probably explained by the suppression of the electrical double layer and thus smaller hydrodynamic diameter in a higher conductivity media rather than a real size difference (Malvern Instruments technical book). The size match of NP aggregates in the different carrying solutions was confirmed by the TEM analysis (Fig. 1a and b). The EPS particles self-assemble into aggregates in natural seawater (Chin et al., 1998), indeed showing significant increase in their hydrodynamic diameter within 24 h of being added to seawater (Fig. 1). Curiously, synthetic ferrihydrite nanoparticle addition seemed to suppress the formation of the EPS assembly, which is contrary to previous findings on the effect of engineered polystyrene nanoparticles (Chen et al., 2011). Previous studies found that nanoparticles tend to increase EPS particle size via co-aggregation and spontaneous assembly into large flocks (Chin et al., 1998). However, in our study EPS extracted from cultured marine microalgae (*N. salina*) co-aggregated with ferrihydrite into particles with average hydrodynamic diameter of about 1000 nm, which did not increase in size over 24 h, whilst the same EPS suspension without the addition of ferrihydrite formed about 4 times larger particles (Fig. 1 and inset c). Typical TEM micrographs showed the presence of electron dense and more compact aggregates interlaced with loose aggregates when ferrihydrite was allowed to react with seawater in the presence of EPS (Fig. 1 and inset d), unlike the loose aggregates forming in the absence of EPS (Fig. 1b). It is likely that as a result of the polyanionic quality of the microalgal EPS conveyed by its functional groups that remain to be identified, the EPS–NP co-aggregation resulted in more compact aggregates in equilibrium when in suspension in seawater compared to those in the absence of EPS.

The effect of seawater and EPS on the natural nanoparticles resulted from cloud processed mineral dusts was somewhat more ambiguous and quite different from that seen with synthetic ferrihydrite, possibly due to the more heterogeneous elemental composition of the former. However, the following common trends could be distinguished for all dust types: average hydrodynamic diameter of particles decreased considerably (by over 50%) when pH was increased from 1 to 6, and this was consistent for all dust types (Fig. 2). Nevertheless, when these particles are suspended in seawater, they increase in size by approximately 50% for all NPs from dust types (as indicated by the average hydrodynamic diameters shown in Fig. 2), unlike synthetic ferrihydrite. This was corroborated by the TEM micrographs (picture insets in Fig. 2), showing that individual particles making up the aggregates have less defined edges and tend to be bigger when suspended in seawater or

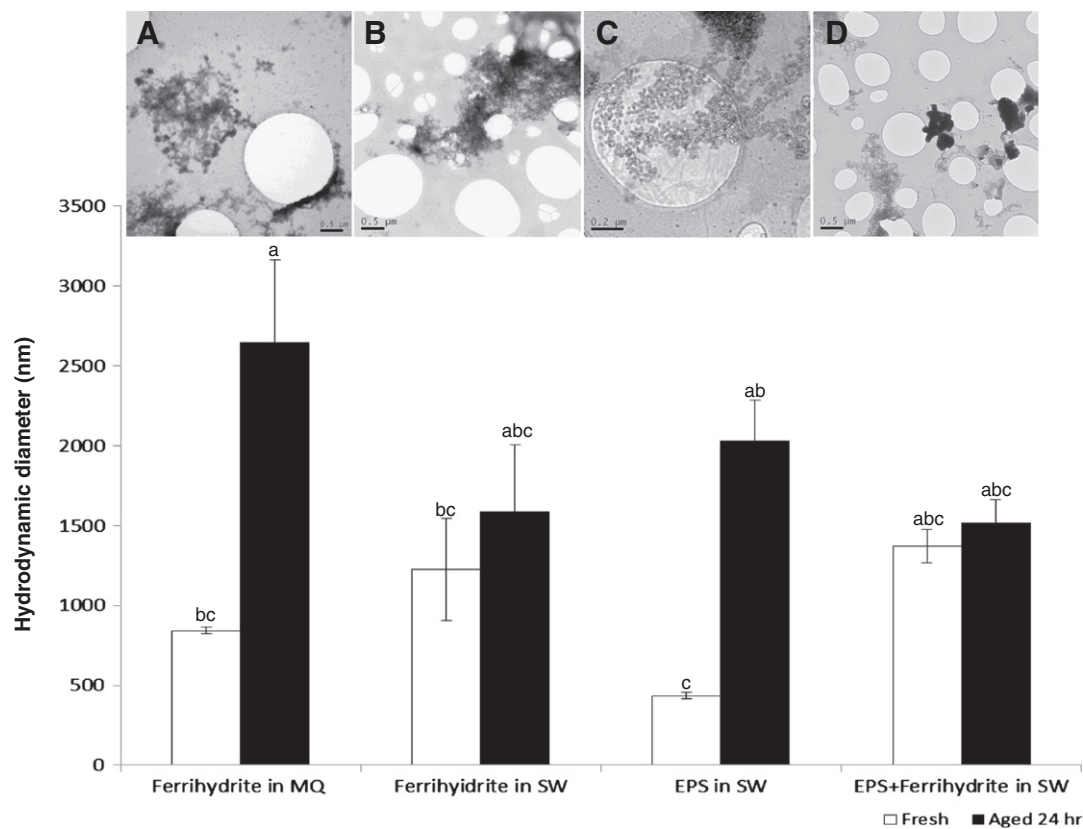


Fig. 1. Hydrodynamic diameter of ferrihydrite and EPS dispersed in experimental media with distinct composition, e.g. ultrapure water (MQ), natural seawater (SW) with and without exopolymeric substances (EPS); columns represent average hydrodynamic diameter (nm) \pm SEM, N = 5; Error bars that do not share a letter are significantly different according to one-way ANOVA followed by Tukey's comparison; The picture insets are TEM micrographs on typical aggregates in various media.

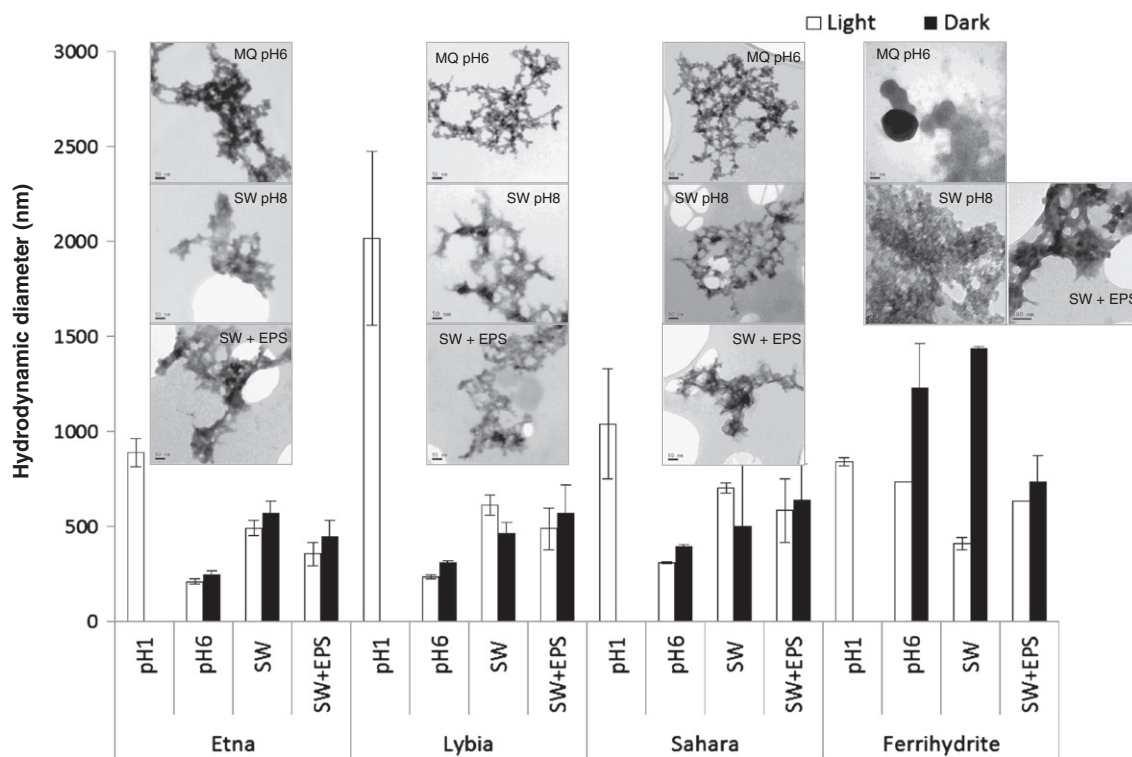


Fig. 2. Hydrodynamic diameter of nanoparticles in suspension in the alkaline phases of the simulated cloud processing of three mineral dusts (volcanic ash from Etna, dust from Sahara and from Libya and the control model ferrihydrite) followed by contact with natural seawater (SW) with and without exopolymeric substances (EPS) under artificial sunlight vs in the dark; Measurements were conducted during both the low- and the alkaline-pH steps of the cloud processing. Vertical bars represent average hydrodynamic diameters (nm) \pm SEM, N = 5. The picture insets are TEM micrographs on typical aggregates forming when nanoparticles were suspended in various experimental media.

in seawater with EPS as compared to those in MQ (i.e. the pH 6 phase of the cloud processing). Direct size comparison of data obtained from DLS and TEM however, have to be interpreted with caution as: 1) aggregate size/morphology is affected by TEM sample processing (i.e. vacuum exposure of grids under observation); 2) particle diameter calculated from DLS refers to how a particle diffuses within a fluid, and it depends not only on the particle “core” but also on any surface structure, as well as the concentration and the types of ions in the medium. Further rheological studies are required to better understand the colloidal transformations taking place when nanoparticles interact with seawater and EPS. Our results however indicate that in irradiated samples EPS addition has a “stabilising” effect in that the average hydrodynamic diameter of the aggregates in suspension decreases whilst zeta potential shifts slightly towards but without reaching the stability value of -30 eV (Malvern Instruments technical note on Zeta Potential theory). However, this “stabilising effect” was only observed in the absence of light for synthetic ferrihydrite.

In general, with few exceptions the aggregates formed in the absence of light are slightly larger than those illuminated, but the high size variability prevented detection of statistical significance at 95% level. Aggregate size inhomogeneity was also corroborated by the high polydispersity index (>0.8) indicating the presence of particles with large size variations in all samples except those at the alkaline phase of cloud processing (Fig. S1). Similarly, zeta potentials were highly variable (Fig. S2); the lowest values were about -10 eV that indicate colloidal instability. The main factor that statistically significantly influenced colloidal stability of dust derived nanoparticles was media of dispersion (i.e. MQ water, seawater and seawater with EPS) (Table S1).

3.2. Particle dissolution in seawater – the effect of EPS and light

Soluble Fe release from cloud processed particles, measured as the <3 kDa filter fraction, in seawater was quite similar for all dust-types, but there were both light- and EPS-related differences (Fig. 3). Fe dissolution increased considerably in the presence of EPS and the relative increase was more prominent in the dark. This EPS-mediated increased dissolution was consistent for all three dust types (Fig. 3) and was also reported previously in the presence of a bacterial EPS extract (Hassler et al., 2011a, 2011b). A possible reason is that EPS acted as a chelator via surface complexation and solution coordination, sustaining dissolution (Chang and Matijevic, 1983). Surface complexation by chelate binding to the

metal ions on the NP surface weakens the lattice bond between the metal ion and the other components of the particle, and then the metal complexes dissociate from the particle. Solution coordination is liberation of the metal ion from the particle surface, which then reacts with the chelate or the hydroxide in solution causing a further metal ion release from particles. The strongly metal-binding sulfhydryl group of EPS could have accelerated dissolution (Miao et al., 2010) at the concentrations applied here. However, a more detailed examination of the exact composition of the *Nannochloropsis* EPS extract is needed to elucidate which interaction mechanisms between NPs and the biopolymer functional group may be responsible for induction of Fe dissolution. Our present understanding of dissolution is that rates are controlled by the diffusion coefficient of the solute molecule, particle surface area, and diffusive sublayer thickness, when solution volume and other environmental conditions such as pH and temperature are fixed. High dissolution rates could therefore be expected for NPs as a result of their extremely high specific surface area, even when they are aggregated. It has been previously shown with other metal oxide NPs (Miao et al., 2010) that despite rapid aggregation into micro metre size particles the dissolution rate of free ions from aggregates remains at a similar level with that of primary NPs until they become more compact with time and thus their specific surface area is reduced concurrently with the dissolution rate. It is possible that in our study the EPS–NP co-aggregation in seawater resulted in more loosely bound aggregates than those in the absence of EPS, which were inferred from both the TEM micrographs (inserts in Figs. 1 and 2) and the polydispersity index values.

Another possible reason for more Fe dissolution in the presence of EPS could be the photo reactive formation of H_2O_2 via the superoxide intermediate which is capable of reducing Fe(III), thus aiding dissolution, as suggested by other laboratory experiments (Steigenberger et al., 2010) focussed on the redox cycling of Fe in the presence of both artificial and natural polysaccharide extracts from diatoms detecting light-produced superoxide that reduced Fe(III) maintaining elevated Fe(II) concentrations and thus positively affecting Fe bioavailability. However, such photo reductive processes cannot explain our results on augmented Fe dissolution in the absence of light. It is therefore more likely that Fe is stabilised within the <3 kDa fraction as a result of the polyanionic quality of the microalgal EPS conveyed by its functional groups that remain to be identified. The mechanisms involved may include environmentally important processes like the photolysis, reduction and thermal reduction of Fe(III) complexes in all of which EPS can act as electron donor. The

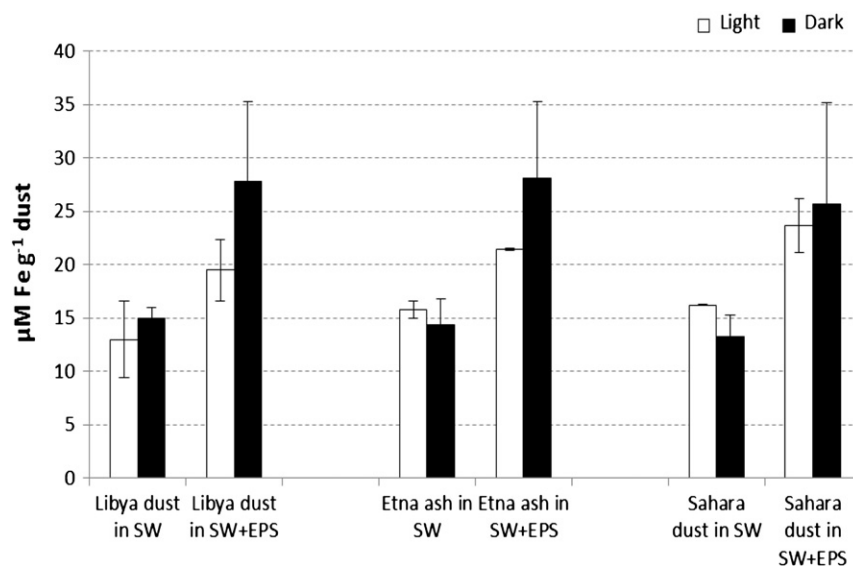


Fig. 3. Dissolution of Fe measured as <3 kDa filter fraction from nanoparticles formed via simulated cloud processing of the three model mineral dusts (volcanic ash from Etna, dust from Sahara and from Libya and the control model ferrihydrite) following suspension in natural seawater (SW) with and without exopolymeric substances (EPS), under artificial sunlight vs in the dark; Vertical bars represent average concentrations \pm SEM, $N = 3$.

ecological significance and scale of EPS–nanoparticle interactions in real aquatic environments are consequent of its ubiquitous nature, i.e. about ~40–60% of the planktonic photosynthetic product is released as EPS, and its key role in biofilm formation, colloid and trace element scavenging, and ultimately in the global carbon cycling.

3.3. Typical (nano)particles in seawater from geochemically distinct mineral dusts

Elemental composition of the nanoparticles formed via SCPMD was analysed using EDX–SEM performed on the TEM grids allowing for additional higher resolution micromorphology observations (Fig. 4). The Cu peaks are due to background from the grid and need to be disregarded here. SEM micrographs of the dust derived material (Fig. 4 A, D, G, J and M) showed the presence of large aggregates of nano-sized particles loosely held together. Freshly synthesised ferrihydrite, mainly composed by Fe and O (Fig. 4B), when suspended in seawater containing EPS aggregated into more compact heterogeneous particles (Fig. 4C). The EPS extract contained assemblages in which individual particles had diameter below 50 nm (Fig. 4D), and showed large peaks for C, O, S and Si (Fig. 4E), which is consistent with the polysaccharide composition. When added to seawater EPS assembles in large particles with filamentous texture (Fig. 4F). Nanoparticles formed from Libyan dust (Fig. 4 G–

I), although showing a very similar morphology with ferrihydrite, are more heterogeneous in composition, i.e. show large peaks for Al, Si, Ca and Fe. Following the 24 h in contact with seawater containing EPS, some of the resulting large aggregates seemed to interweave closely with the EPS (Fig. 4I), which needs further investigations.

Volcanic ash derived particles seem to amass in slightly smaller aggregates than those from Libyan dust (Fig. 4J), show large peaks for Al, Ti, Si, S, Cl, Ca and Fe (Fig. 4K), and when suspended in seawater, the resulting aggregates tend to become less compact (Fig. 4L). SEM micrographs of the cloud processed Saharan dust particles were very similar to those from Libyan dust and EDX spectra similarly showed high Al, Si and Fe peaks (Fig. 4M and N) and the TEM micrographs showed slackened aggregates when suspended in seawater with EPS. These EDX-spectra (Fig. 4B, E, H, K and N), although not able to exactly quantify the amount of iron in individual nanoparticles (this method only gives semi-quantitative information about element composition when the element makes more than about 0.1–1.0% of the total mass of specific particles on the selected area) (Utsumomiya and Ewing, 2003), and the presence of Fe peaks confirm that typical nanoparticles that form when mineral dusts are cloud processed are Fe-rich. This has also been shown in previous studies (Kadar et al., 2013).

The TEM micrographs taken after reaction with seawater do not have the resolution to show individual particles and thus no clear distinction in

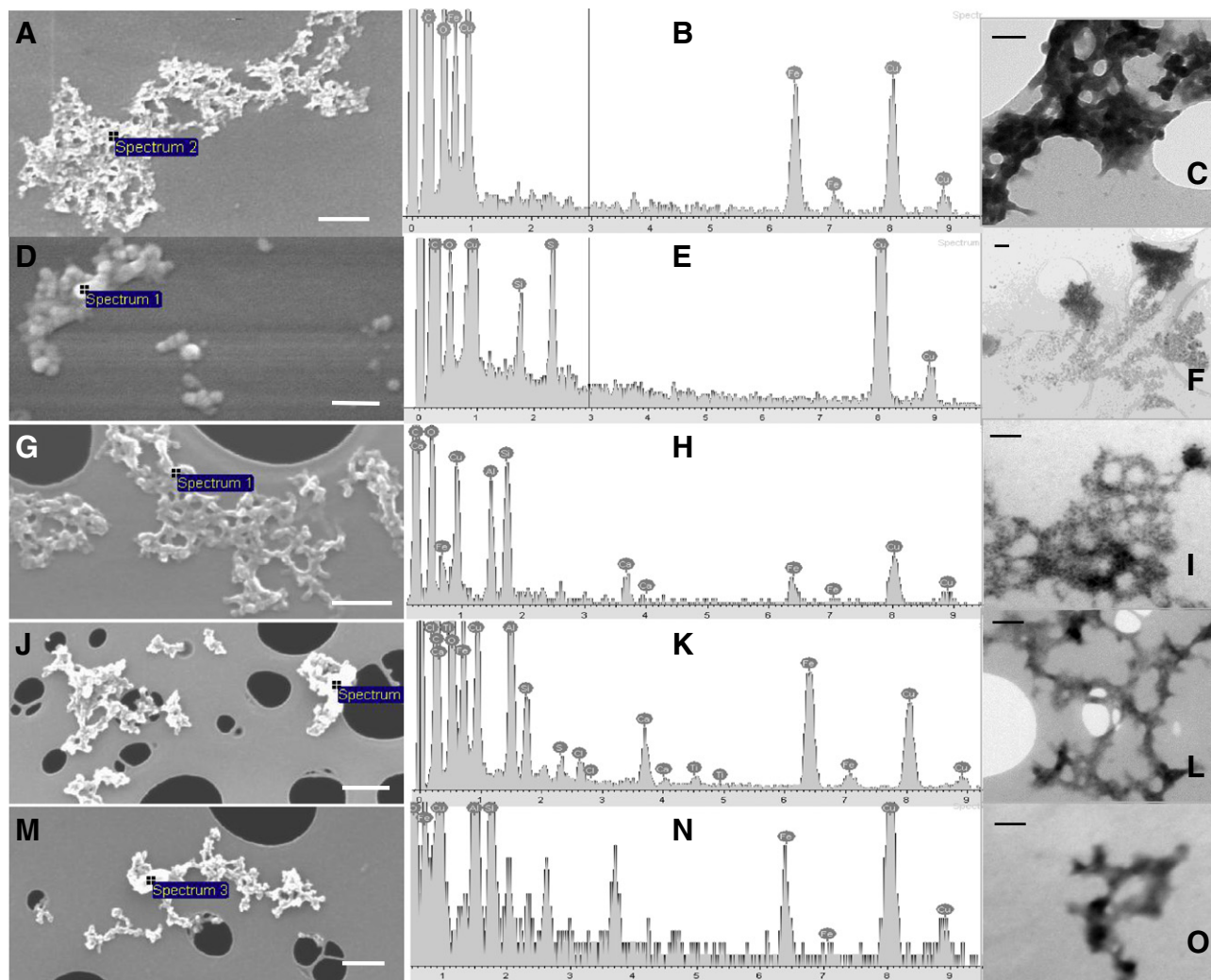


Fig. 4. Micromorphology and elemental composition of nanoparticles from simulated cloud processing of three geochemically distinct mineral dusts including control nano-ferrhydrite particles before and after interaction with seawater and EPS; (A–C); Ferrhydrite; (D–F); EPS; (G–I) Libyan dust; (J–L) volcanic ash from Etna and (M–O) Saharan dust. Selected SEM micrographs of particles prior to suspension in seawater (A, D, G, J and M; Scale bars denote 250 nm) and corresponding EDX spectra (B, E, H, K and N) with TEM micrographs taken after 24 hour interaction of nanoparticles with seawater and EPS (C, F, I, L, and O; Scale bars denote 100 nm).

micromorphology of particles making up the aggregates of different dusts was possible. However, many of the NP aggregates have less distinct boundaries, which might suggest some dissolution in seawater. A common trend was the loosening in aggregate compactness, which was also confirmed by augmented hydrodynamic diameters when particles were dispersed in seawater. To conclude, nanoparticles derived from cloud processing of mineral dusts are Fe rich and release free Fe when in contact with seawater. EPS that is produced by most marine microorganisms seems to enhance dissolution and colloidal stability of the resulting aggregates and thus may significantly improve Fe bioavailability and play a significant role in Fe biogeochemistry in the ocean.

Conflict of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.08.059>.

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