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1 **Methods for analyzing the concentration and speciation of major and trace elements in** 2 **marine particles**

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19
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21
22 **Keywords:** marine particles, trace elements, GEOTRACES, particle digestion, leaching
23 methods, synchrotron X-ray fluorescence (SXRF), synchrotron X-ray absorption spectroscopy
24 (XAS)

25 26 **Abstract**

27 Particles influence trace element and isotope (TEI) cycles through both their elemental
28 composition and fate and their role on the partitioning of dissolved elements through
29 scavenging and dissolution. Because of their complex compositions, a diverse suite of
30 methods is required to analyze marine particles. Here we review some of the varied
31 approaches used to study particle composition, speciation and fate. We focus on high
32 throughput analytical methods that are useful for the international GEOTRACES program,
33 and we also describe new spectroscopic techniques that are now being applied to study the
34 spatial distribution and chemical speciation of TEIs in marine particles.

35 36 **Highlights**

- 37 • We review methods used to study marine particle composition and speciation
- 38 • Multi-element analytical methods are used in GEOTRACES for particle composition
- 39 • New X-ray spectroscopic methods are now being applied to marine particles
- 40 • Detailed spectroscopic methods are complementary to high-throughput wet chemistry
41 techniques

42 43 **1. Introduction**

44 Particulate matter in the ocean, traditionally defined as materials $> 0.2 \mu\text{m}$, is one of
45 the main reservoirs for trace elements and isotopes (TEIs), and regulates the distribution of
46 dissolved TEIs through dissolution and scavenging. There is a broad diversity of types and
47 compositions of particulate matter, including intact plankton cells, crustal aluminosilicates,
48 resuspended sediments, authigenic minerals, organic polymers or gels, biogenic detrital
49 material (e.g., fecal pellets, dead cells, empty frustules), or aggregates of a combination of
50 these. In addition, particles in the upper water column can also be generated through

51 spontaneous aggregation of Dissolved Organic Matter (DOM) into particles termed microgels
52 (Verdugo and Santschi, 2010), ranging from molecules to a typical size of 4 μm , therefore
53 becoming Particulate Organic Matter (POM, Chin et al., 1998). To understand the role of
54 particulate matter in the biogeochemical cycling of both major elements and TEIs in the ocean
55 requires knowledge about both the total composition of suspended matter and the composition
56 of individual particles.

57 Particles affect TEI cycles both through their elemental composition and through their
58 influence on the scavenging and dissolution of the dissolved elements (Goldberg, 1954;
59 Jeandel et al., this issue; Turekian, 1977). Particle mass and major element composition (such
60 as the proportions of POM, CaCO_3 , opal, and lithogenic material) may affect the efficiency of
61 the scavenging of several particle-reactive TEIs (Akagi et al., 2011; Chase et al., 2002; Roy-
62 Barman et al., 2005). A number of biopolymers, potentially produced by both phytoplankton
63 and bacteria, could also be carrier molecules for naturally occurring radioisotopes, in addition
64 to the purely inorganic surfaces generally thought to bind radioisotopes (Quigley et al., 2002;
65 Roberts et al., 2009). A greater understanding of the roles of particles often requires the
66 isolation of specific functional groups of particles and sometimes also the determination of the
67 chemical and physical speciation of different elements. For example, the accumulation of
68 TEIs by plankton is a significant control on dissolved metal distributions in the ocean, but
69 determining the TEI content of plankton in natural communities is challenging due to the
70 heterogeneous nature of the particle assemblage (Twining et al., 2008). As another example,
71 the solubility and reactivity of some particle constituents can often be related to the nature of
72 the lithogenic phase(s) that is (are) present (e.g. Si is more reactive in clays than in a grain of
73 quartz; Fe in basalts is mostly reduced and potentially more reactive than oxidized Fe in
74 granites). Thus, determining the mineralogy and speciation of TEIs in the solid phase may be
75 necessary to understand their reactivity. This additional chemical information can also
76 provide clues to the provenance of particles (Lam and Bishop, 2008; von der Heyden et al.,
77 2012).

78 The complex compositions of marine particles are reflected in their multifaceted role
79 in the cycling of TEIs. To understand these roles, a diverse suite of methods is required to
80 characterize the particles. The methods have to account for relatively dilute concentrations of
81 particles in the ocean and for the trace levels of TEIs in particulate matter. For example,
82 suspended particulate matter (SPM) is typically present at concentrations of only 2-200 $\mu\text{g}/\text{kg}$
83 (Biscaye and Eitrem, 1977; Jeandel et al., this issue). Important bioactive TEIs such as
84 cobalt may be present at ppm levels in biogenic materials, and particulate organic carbon
85 (POC) itself is often present at $<10 \mu\text{M}$ in the open ocean. Thus many particulate TEIs may
86 be present at pM (10^{-12} M) or lower levels in the ocean. While the development of *in situ*
87 optical techniques has enabled the characterization of particle abundance and size spectrum
88 and some estimates of basic particle composition such as POC and particulate inorganic
89 carbon (PIC) concentrations (Boss et al., this issue), the full chemical characterization of
90 particles is essential to understand their role in the biogeochemical cycle of TEIs. Physical
91 sampling of particles and analysis by laboratory-based techniques yield information on
92 particle mass, most major and minor element concentrations, isotopic compositions, and
93 chemical speciation. Sample collection for both major particle composition and TEI analysis
94 is discussed in McDonnell et al. (this issue), Planquette and Sherrell (Planquette and Sherrell,
95 2012), and Bishop et al. (Bishop et al., 2012).

96 Here we review some of the varied laboratory-based approaches used to study particle
97 composition. We discuss methods to measure basic particulate parameters that are necessary
98 to understand the role of particles in the cycling of TEIs. Because an understanding of the
99 role of particles in biogeochemical cycling often requires knowledge of the physical and
100 chemical speciation of particles, we also present some of the methods that have been used to

101 study particle speciation. A review of analytical methods for characterizing marine particles
102 was last published over twenty years ago (Hurd and Spencer, 1991), and many new
103 techniques are now available, particularly spectroscopic techniques.

104 A comprehensive review of all techniques that can be applied to particles is beyond
105 the scope of this paper. Instead, we aim to provide an overview of methods and touch on some
106 of the major findings that have resulted from these techniques to provide a starting point for
107 further studies. The paper begins with a description of methods to measure major particle
108 composition and suspended particle mass. These are standard techniques that are commonly
109 applied to the analysis of sediment trap material but may not be familiar to the GEOTRACES
110 community. The discussion then shifts to the main focus of this paper, i.e., to the techniques
111 used to measure TEI compositions of particulate matter. These are organized into three
112 categories: 1) analytical or “wet” chemical methods, including chemical leaches of particles,
113 followed by analysis of the solution phase, 2) nuclear techniques, and 3) spectroscopic
114 techniques, in which the interaction of radiation with matter is used to determine elemental
115 composition, mineralogy, or chemical speciation in the solid phase.

116

117 **2. Major particle composition and suspended particle mass**

118 The mass of total suspended matter in the ocean is the sum of its major, minor, and
119 trace components, however it depends mostly upon its major components, which include
120 particulate organic matter, biogenic silica, calcium carbonate, and often also lithogenic matter,
121 strontium and barium sulphate, and iron and manganese oxyhydroxides. The major particle
122 phases are implicated in the control of particle flux to depth (François et al., 2002; Klaas and
123 Archer, 2002) and of scavenging of particle-reactive TEIs (Akagi et al., 2011; Chase et al.,
124 2002; Roy-Barman et al., 2005). The total mass of suspended particulates is one basic
125 measurable parameter that enables greater understanding of the role that particles play in the
126 cycling of many TEIs. Gravimetric methods are the most direct way to determine the dry
127 weight of marine particulate matter, but it is critical to remove sea salt before it crystallizes
128 (e.g., Karageorgis et al., 2008), or to correct for the mass contribution of salt (Bishop, 1991).
129 The complete removal of sea salt is not always possible, however, especially with the high-
130 throughput filter types used with in-situ pumps that retain excess seawater. Because the
131 correction for sea salt is not trivial (Lam and Bishop, 2007), an alternative method is to
132 determine the “chemical dry weight” of particles (e.g., Bishop et al., 1977), which is the sum
133 of the masses of the major particle components determined separately.

134 The determination of all major particle components typically requires the collection of
135 particles onto at least two filter types (McDonnell et al., this issue), usually a pre-combusted
136 glass or quartz-fiber filter for particulate organic matter, and a carbon-based filter for biogenic
137 Si and lithogenic material. Particles collected from sampling bottles (e.g., Niskin) can be
138 filtered onto two filter types by using multiple bottles tripped at the same depth, but this may
139 reduce the volume available for each sample. In-situ filtration provides an alternative method
140 to sample significantly larger volumes. Collection of particles for major particle composition
141 by in-situ filtration is ideally accomplished using a pump that has at least two flow paths (e.g.,
142 Bishop et al., 1985; Lam and Morris, Patent pending) so that particles can be collected
143 simultaneously on two filter types.

144 Standard methods for determining each component can be used. Briefly, POC is
145 determined by combustion (e.g., <http://usjgofs.whoi.edu/eqpac-docs/proto-18.html>) and
146 converted to POM using a POM/POC ratio ranging from 1.88 g/g (Timothy et al., 2003) to 2.5
147 g/g (Bishop et al., 1977), depending on the assumed molecular formula for POM. Biogenic
148 silica is typically determined by a weak alkaline leach followed by spectrophotometric
149 detection (e.g., Mortlock and Froelich, 1989), and sometimes with correction for the
150 contribution of lithogenic Si in oceanic regions of high lithogenic Si/biogenic Si (DeMaster,

151 1981; Ragueneau et al., 2005), and then converted to opal mass assuming a hydrated form of
 152 silica (e.g., $\text{SiO}_2 \cdot (0.4 \text{ H}_2\text{O})$) (Mortlock and Froelich, 1989). CaCO_3 is determined by
 153 coulometric detection of CO_2 following addition of acid (e.g., Honjo et al., 1995), or from Ca
 154 following correction of Ca from sea salt (e.g., Lam and Bishop, 2007). Lithogenic material is
 155 determined by measuring the concentration of a lithogenic tracer such as Al or Ti, and scaling
 156 up to a crustal mass using average crustal abundances (e.g., Honjo et al., 1995). SrSO_4 is
 157 determined from salt-corrected Sr (Bishop et al., 1977). Finally Fe and Mn oxyhydroxides are
 158 estimated from Fe and Mn following a weak acid leach or from total Fe and Mn that has been
 159 corrected for lithogenic Fe and Mn (such as by using Ti as a lithogenic tracer) (Lam et al., in
 160 press; Ohnemus and Lam, in press).

161 For example, on the US GEOTRACES North Atlantic Zonal Transect (GA03), the
 162 chemical dry weight of particles was determined as (Lam et al., in press):

163
 164
$$\text{SPM (g)} = \text{POM} + \text{opal} + \text{CaCO}_3 + \text{lithogenic} + \text{Fe(OH)}_3 + \text{MnO}_2 \quad (1)$$

165 where

166
$$\text{POM} = \text{POC (g)} * 1.88 \text{ (g POM/g POC)} \quad (2)$$

167
$$\text{opal} = \text{bSi (mol)} * 67.2 \text{ (g opal/mol bSi)} \quad (3)$$

168
$$\text{CaCO}_3 = \text{Ca (mol)} * 100.08 \text{ (g CaCO}_3\text{/mol Ca)} \quad (4)$$

169
$$\text{Lithogenic} = \text{Al (g)} / 0.0804 \text{ (g Al/g crust)} \quad (5)$$

170
$$\text{Fe(OH)}_3 = (\text{Fe (mol)} - \text{Ti (mol)} * 8.7 \text{ (mol Fe/mol Ti)}) * 106.9 \text{ g Fe(OH)}_3\text{/mol Fe} \quad (6)$$

171
$$\text{MnO}_2 = (\text{Mn (mol)} - \text{Ti (mol)} * 0.13 \text{ (mol Mn/mol Ti)}) * 86.9 \text{ g MnO}_2\text{/mol Mn} \quad (7)$$

172
 173 The effect of particle composition on scavenging efficiency has so far mostly been
 174 studied using particle-reactive long-lived radionuclides such as ^{230}Th in the field (Chase et al.,
 175 2002; Roy-Barman et al., 2005), and ^{234}Th , ^{233}Pa , ^{210}Pb , ^{210}Po , and ^7Be in laboratory tracer
 176 studies with field-collected or cultured particles (Chuang et al., 2013; Chuang et al., 2014;
 177 Roberts et al., 2009). The GEOTRACES program provides the opportunity to greatly expand
 178 our understanding of the role of particle concentration and composition on the scavenging of a
 179 broader suite of particle-reactive TEIs.

180

181 **3. Particulate TEI composition**

182

183 ***3.1 Analytical (“wet”) chemistry techniques to measure particulate TEIs***

184 ***3.1.1 Total chemical digests***

185 Although an extensive literature describes the chemical digestion (complete and
 186 sequential) of sediments, the digestion of marine suspended particles collected on filters
 187 presents additional challenges. Particulate TEIs were traditionally collected on polycarbonate
 188 membrane filters because of their low blanks (e.g., Cullen and Sherrell, 1999; Landing and
 189 Bruland, 1987; Sherrell and Boyle, 1992). However, because polycarbonate-membrane filters
 190 have relatively low sample throughput, and the larger diameter sizes (e.g., 142 mm or 293
 191 mm) used for in-situ filtration are difficult to handle, many GEOTRACES programs are using
 192 polyethersulfone filters (e.g., Supor) due to their low blanks, ease of handling, and high
 193 volume throughput (Bishop et al., 2012; Planquette and Sherrell, 2012). Supor filters are,
 194 however, very difficult to digest. One strategy is to employ a refluxing method in which the
 195 filter piece is not submerged in the strong acid, thus leaving it intact (Planquette and Sherrell,
 196 2012), but this method is only suitable for relatively small pieces of filter. Most heated strong
 197 acid digestions of submerged filters will break Supor filters down partially without achieving
 198 a complete dissolution. The cooled solution must often then be filtered to remove undigested
 199 filter pieces that may cause clogging of subsequent analytical steps. Complete dissolution of
 200 Supor filters can be achieved using strong oxidizing acids such as perchloric acid (Anderson

201 et al., 2012) or Piranha solution, which is a 3:1 mixture of concentrated sulfuric acid and 30%
202 hydrogen peroxide (Ohnemus et al., 2014). It may also be possible to achieve complete
203 dissolution of Supor filters using nitric acid or aqua regia at elevated temperature and pressure
204 using microwave systems (L. Robinson, pers. comm.; S. Severmann, pers. comm.) or wet
205 ashers (T. Horner, pers. comm.). Since the strong oxidizing acids that dissolve the filter do
206 not dissolve silicates, the filter dissolution step is usually followed by the digestion of the
207 collected particulate material using hydrofluoric acid in combination with nitric and (or)
208 hydrochloric acid (e.g., Anderson et al., 2012; Ohnemus et al., 2014).

209

210 3.1.2 Selective chemical leaches

211 There is a long history of applying selective chemical washes and leaches to attempt to
212 isolate specific components from the heterogeneous mixture that comprise natural particulate
213 materials (e.g., Chester and Hughes, 1967; Tessier et al., 1979), and an equally long history of
214 criticisms of these methods (e.g., Kheboian and Bauer, 1987; Nirel and Morel, 1990;
215 Sholkovitz, 1989). At the heart of the controversy is whether selective leaches are extracting
216 a scientifically meaningful fraction from a given heterogenous particulate phase, and, if they
217 are, whether the leaching of these fractions is quantitative and reproducible between research
218 laboratories. Failure to achieve quantitative recovery might occur, for example, if mobilized
219 species are re-adsorbed by refractory solid phases. Despite these controversies, leaches are
220 still actively used since they provide a quick and high-throughput method for operationally
221 assessing differences in the lability of given phases within in a sample set, which likely
222 reflects underlying chemical differences.

223 The number of leaches in existence is almost endless, and new ones are continually
224 being developed, particularly in the soil and sediment communities, that attempt to optimize
225 conditions for specific TEIs, sample types, and scientific questions. As a result, there is no
226 ideal leach that is applicable to all TEIs, and one must refer to the literature of one's specific
227 field. A few that have been used to determine the trace metal concentration in suspended
228 particles are mentioned below.

229 Collier and Edmond (1984) subjected suspended marine particles collected using
230 plankton nets to a wide range of sequential chemical leaches, focusing on the weakly adsorbed
231 and biogenic fractions. Their experiments showed that many elements were very weakly
232 associated with plankton and rapidly released into seawater. In general, however, multi-step
233 sequential leaches have not typically been applied to suspended marine particles because of
234 limitations in sample size. The phases identified by most leaches that have been applied to
235 suspended marine particles have been operationally defined. For example, "acid-leachable"
236 concentrations of particulate trace metals have been reported for particles following a 25%
237 acetic acid leach (e.g., Landing and Bruland, 1987) or a 0.6 M HCl leach (e.g., Lam and
238 Bishop, 2008) and compared to total concentrations determined by strong acid digestion
239 including HF or by other methods such as X-ray fluorescence. More recently, a modification
240 of the acetic acid leach has been developed to access a "labile-biogenic" fraction (Berger et
241 al., 2008), and washes have been developed that attempt to separate a loosely-bound,
242 extracellular fraction from an intracellular fraction (Tang and Morel, 2006; Tovar-Sanchez et
243 al., 2003), although the utility of this latter leach for heterogeneous particle samples has been
244 disputed (Twining and Baines, 2013). Despite the continuing debates about the merits of
245 individual leaches, they remain an important tool for assessing broad differences in the lability
246 and thus chemical composition of particles, as long as one acknowledges the caveats
247 associated with using them.

248

249 3.1.3 Analysis of particle leaches and digests

250 In the past, total digest solutions and leachates were typically analyzed using Atomic
251 Absorption Spectroscopy (AAS), which allows the measurement of one TEI per analysis.
252 Early results from AAS include the publication of the first particulate barite profiles, for
253 example, that allowed the understanding of the link between barite precipitation and
254 biological production and decay of organic matter in the water column (Bishop, 1988; Dehairs
255 et al., 1980). Those studies led to the development of barite in sediments as a paleo-
256 productivity proxy (Dymond et al., 1992). The first data on the trace metal composition of
257 phytoplankton collected by nets were also generated using AAS (Collier and Edmond, 1984;
258 Martin and Knauer, 1973). These showed that the carrier phase for many trace elements was
259 non-skeletal organic matter (Collier and Edmond, 1984). It was also noted that elements such
260 as Al, Fe, and Ti were found largely in the refractory phase, suggesting that terrigenous
261 (lithogenic) particles were present even in remote regions. The first full ocean-depth profiles
262 of multiple particulate trace metals were also produced with AAS (Sherrell and Boyle, 1992).
263 These authors found that the shapes of the particulate Co, Pb, Zn, Cu, and Ni profiles were
264 similar to that of particulate Mn, and postulated that Mn oxyhydroxides might play an
265 important role in scavenging trace metals. Indeed, Mn oxyhydroxides have also been
266 hypothesized to control the scavenging of long-lived radionuclides such as ²³⁰Th in the
267 Northeast Atlantic and Mediterranean Sea (Roy-Barman et al., 2005). The overall importance
268 of Mn oxyhydroxides for controlling the scavenging of particle-reactive TEIs needs to be
269 tested with more data, such as will be generated during the GEOTRACES program.

270 The development of plasma systems (producing excited atoms and ions) coupled to
271 either an optical detector (Inductively Coupled Plasma Atomic Emission Spectroscopy, ICP-
272 AES) or a mass spectrometer (ICP-MS, some including high resolution mass discrimination)
273 has considerably improved detection limits, precision, as well as analyte and sample
274 throughput for natural sample analysis (Bowie et al., 2010; Cullen et al., 2001; Ho et al.,
275 2011; Ho et al., 2010; Ho et al., 2007; Kuss and Kremling, 1999). Analytical constraints and
276 instrumental operating parameters for multi-element analysis have been described for ICP-
277 AES by Sandroni and Smith (2002), and for ICP-MS by Bowie et al. (2010), Cullen et al.
278 (2001), Feldmann et al. (1994), and Linge and Jarvis (2009).

279 Thanks to the development of ICP-related instrumentation, Kuss and Kremling (1999)
280 were the first to establish the distribution of multiple particulate TEIs on the ocean basin
281 scale. They determined 10 particulate trace elements, POC, opal, and CaCO₃ from 24 near-
282 surface samples in the North Atlantic, and showed that variability in particle composition
283 could be explained by the changing importance of biological production, different water
284 masses of the North Atlantic Current system, and atmospheric dust deposition, particularly in
285 the trade wind area off Africa. Close to the Asian continent, Ho et al. (2007) showed that
286 particulate trace metals associated with phytoplankton in the South China Sea were largely
287 derived from anthropogenic aerosols, and that these were removed from the water column via
288 the rapid sinking of biogenic particles (Ho et al., 2011; Ho et al., 2010). The increase in
289 studies reporting multi-element particulate trace metal concentrations in different ocean basins
290 is opening up many perspectives in the role of particles in the cycling of both micronutrient
291 and toxic trace metals from natural and anthropogenic sources.

292 293 **3.2 Nuclear techniques to measure particulate TEIs**

294 Although Instrumental Neutron Activation Analysis (INAA) has not been widely used
295 because it requires access to a high-flux neutron source, it was employed in the early
296 investigations of the trace element composition of marine particles because it offered multi-
297 element analysis with sufficient sensitivity to produce useful results with relatively small
298 samples (tens to hundreds of micrograms dry weight of particulate material). Neutron
299 bombardment of the sample causes element-specific radioactive emissions, which are

300 measured. INAA also offered the advantage of requiring little or no chemical preparation of
301 samples other than removing sea salt from filters before activation. The method has been
302 applied successfully to particles collected both by filtration (e.g., Fleer and Bacon, 1991;
303 Spencer et al., 1972) and by sediment traps (e.g., Brewer et al., 1980; Deuser et al., 1981;
304 Spencer et al., 1978). These early studies of the sinking flux of major and minor elements
305 showed that particle settling velocities were considerably higher than previously expected.
306 Moreover, the flux of all major and minor elements, even those not thought to be biological,
307 demonstrated seasonality that followed the annual cycle of primary production. This showed
308 that the vertical flux of biological matter was an efficient mechanism to scavenge and remove
309 many chemicals from the water column. The advent of ICP-MS for multi-element analysis of
310 marine particles has mostly eliminated analyses by INAA, although it is still finding use in
311 research on the composition of aerosols (e.g., Almeida et al., 2013; Steinnes, 2000).

312

313 ***3.3 X-Ray Diffraction (XRD)***

314 XRD is a rapid analytical technique used for phase identification of a crystalline
315 material. Monochromatic X-rays are directed at the sample and the diffracted X-rays are
316 collected. The wavelength of X-ray radiation is related to the diffraction angle and the lattice
317 spacing (d-spacing) in a crystalline sample (Bragg's law). Conversion of the diffraction peaks
318 to d-spacings allows identification of the mineral by comparison of d-spacings with standard
319 reference patterns. Both bench-top and synchrotron-based XRD techniques are used. Prior to
320 analysis by bench-top XRD, a sediment or soil sample is finely ground, homogenized, and
321 average bulk composition is determined. Particulate material has to be removed from the filter
322 (hence polycarbonate membranes recommended) and be relatively abundant, which might
323 restrict this method to coastal samples. However, XRD can now also be conducted at some
324 synchrotron beamlines (Tamura et al., 2002), which removes the requirement for sample
325 homogenization, reduces sample size requirements, and allows the targeting of micron-scale
326 areas of interest. For example, CaCO_3 in the form of the mineral ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) was
327 discovered in Antarctic sea-ice for the first time using synchrotron XRD (Dieckmann et al.,
328 2008). This abiotic precipitation of CaCO_3 in sea ice brine may have implications for carbon
329 cycling in seasonally sea ice-covered regions (Bates and Mathis, 2009). Micro-focused
330 synchrotron XRD has been used to determine the mineralogy of micron-thick Fe-rich and Mn-
331 rich layers of ferromanganese nodules (Marcus et al., 2004) and the mineralogical structure of
332 Fe-encrusted biofilms at mid-ocean ridge hydrothermal vents (Toner et al., 2009b), both of
333 which aid in the understanding of their formation conditions, as well as their roles for the
334 scavenging of other trace metals.

335

336 ***3.4 X-ray based spectroscopic techniques to measure particulate TEIs***

337 Spectroscopic techniques encompass a wide range of approaches that are all related by
338 their use of the interaction of electromagnetic radiation and matter in the solid phase. We
339 focus here on X-ray based spectroscopic techniques, and do not discuss other types of
340 spectroscopies (e.g., Infrared (FTIR) or ultra-violet (RAMAN)) that have also been useful for
341 environmental samples. There are many books and papers that review the principles of X-ray
342 theory (Bunker, 2010; Conradson, 1998; Koningsberger and Prins, 1988; Teo, 1986) and
343 applications to environmental samples (Fenter et al., 2002; Kelly et al., 2008; Parsons et al.,
344 2002). Here, we provide a brief overview and point to techniques that have applications for
345 marine particulate samples.

346 The X-ray based spectroscopic techniques involve electronic rather than nuclear
347 transitions (Section 3.2). They are united by requiring X-rays or high-energy beams of
348 charged particles to induce an electronic transition, and the detection of resultant emitted X-
349 rays or particles. X-rays are used to induce electronic transitions for X-Ray Fluorescence

350 (XRF), X-Ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS),
351 and Scanning Transmission X-ray Microscopy (STXM); an electron beam is used to induce
352 the transition for Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
353 (SEM-EDS). With the exception of XPS, in which emitted electrons are detected, the other
354 techniques measure absorbed (XAS, STXM) or emitted (XRF, SEM-EDS) X-rays to
355 determine composition. We summarize some of the essential characteristics of these X-ray
356 based spectroscopic techniques in Table 1.

357 The methods can be characterized by those that measure elemental concentrations
358 (XRF, XPS, SEM-EDS), and those that measure chemical speciation and bonding structure
359 (XPS, XAS, STXM). Collection of particles for spectroscopic analyses of TEIs should follow
360 trace-metal clean techniques (McDonnell et al., this issue). Most of the above techniques can
361 be performed in bulk mode, in which the average concentration or speciation of a particle
362 assemblage is determined over a several millimeter area, or in a micro- or nano-focused mode,
363 which allows particle-by-particle analysis and mapping of the distribution of elements and
364 chemical species at the micron or even sub-micron level. Some of these techniques, such as
365 laboratory-based XRF, have been employed in the analysis of marine suspended particles for
366 two to three decades (e.g., Feely et al., 1991a); others, such as synchrotron-based XRF and
367 XAS, have been used for the analysis of soils and sediments for several decades, but have
368 only been applied to the analysis of suspended marine particles in the last decade (e.g., Lam et
369 al., 2006; Toner et al., 2012b; Twining et al., 2003). Many of the mapping and speciation
370 techniques are relatively time-intensive, and so are best suited for detailed characterization of
371 a subset of samples to complement bulk geochemical distributions determined by higher
372 throughput wet analytical techniques (Section 3.1).

373

374 3.4.1 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS)

375 In this technique a scanning electron microscope (SEM) produces a focused beam of
376 high-energy electrons to generate a variety of signals at the surface of solid specimens. Re-
377 emitted electrons from the sample allow identification of the external morphology, and
378 fluorescent X-rays generated by the electrons can also be quantified by an energy dispersive
379 detector (EDS) to determine the qualitative or semi-quantitative chemical compositions of
380 materials composing the sample (Goldstein et al., 2003). Marine particles to be analyzed by
381 SEM-EDS must be collected on polycarbonate membranes and sea salt needs to be removed
382 prior to analysis. Data are collected over a selected area (typically 5 μm to 1 cm width) of the
383 surface of the sample, and a 2-dimensional image is generated. Among the re-emitted signals,
384 EDS is used to separate the characteristic X-rays of different elements into an energy
385 spectrum, which is analyzed in order to determine the abundance of specific elements and
386 allowing for the the generation of elemental composition maps (e.g., Resing et al., 2007).
387 These capabilities provide major elemental compositional information for a wide variety of
388 materials (Heldal et al., 2003). SEM-EDS coupled with automated analysis was successfully
389 applied to determine the composition of hundreds to thousands of particles from the nepheloid
390 layers from the GEOSECS Atlantic program (Bishop and Biscaye, 1982) and from the water
391 column in the Sargasso Sea (Lavoie, 1992). It has also been used to directly determine the
392 barite concentration on filtered material with satisfying comparison with chemical analysis
393 (Sternberg et al., 2008) using a method developed by Robin et al. (2003). Seasonal
394 distribution of barite in the water column of the NW Mediterranean Sea was documented with
395 this method (Sternberg et al., 2008). SEM-EDS is less sensitive to transition and heavy
396 metals due to significant background Bremsstrahlung (Heldal et al., 1996), which is radiation
397 produced by the deceleration of charged particles such as electrons.

398 *3.4.2 X-Ray Fluorescence (XRF)*

399 In laboratory- and synchrotron-based XRF, the incident X-ray is absorbed by atoms in
400 the sample, ejecting core electrons. An electron from an outer shell fills the hole, leading to
401 the emission of a fluorescent X-ray of well-defined energy (Figure 1), whose intensity is
402 measured with a detector that is placed orthogonal to the incident radiation. The energy of the
403 fluorescent X-ray is element-specific, and its intensity depends on the concentration of the
404 element. Thus, the identities and concentrations of multiple elements can be determined.
405

406 *3.4.2.1 Energy-Dispersive X-Ray Fluorescence (ED-XRF)*

407 ED-XRF is a laboratory-based XRF technique that allows for the non-destructive
408 chemical analysis of marine particles (Baker and Piper, 1976; Feely et al., 1991a). Suspended
409 particulate matter is deposited onto a polycarbonate membrane filter as a thin film. This film
410 is irradiated with X-rays, which in turn induce individual elements within the particle film to
411 fluoresce at energies characteristic of each element. This method follows principles similar to
412 that of SEM-EDS, although bench-top generated X-rays are used instead of electrons to
413 generate fluorescence X-rays. This technique is capable of quantifying most elements with
414 atomic number greater than 11, and analysis of Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Fe, Ni, Cu,
415 Zn, As, Sr, and Pb has been demonstrated for marine suspended particulate matter (Barrett et
416 al., 2012). Sample collection is usually made by passing seawater directly from a sampling
417 bottle through a filter that is supported by an in-line filter holder (see McDonnell et al., this
418 issue). Once collected, the filter membrane is rinsed with a small volume of pH 8 de-ionized
419 water and stored in a petri-dish within a desiccated environment. The dried sample is then
420 analyzed by ED-XRF. Sample films deposited onto membranes must meet two criteria. First,
421 particles must be deposited as a uniform layer or film. Second, the thickness of the film must
422 be thin relative to both the penetration depth of the primary X-ray and the depth from which
423 the fluorescent X-rays emerge (Bertin, 1975; Criss, 1976; Dzubay and Nelson, 1975). ED-
424 XRF instrumentation can be calibrated using commercially available thin-film standards
425 (Micromatter Inc.) and (or) using standards fabricated using a variation of a sodium-diethyl-
426 dithio-carbamate pre-concentration method (Hołyńska and Bisiniek, 1976).

427 The ED-XRF technique has been used successfully since the mid 1980s to document
428 the distribution and unique chemistries associated with hydrothermal venting in a variety of
429 submarine volcanic settings (Feely et al., 1991a). The chemical composition of total
430 suspended matter in hydrothermal plumes at mid-ocean ridges reveals the formation of Mn-
431 and Fe-oxhydroxides (Cowen et al., 1990) and their roles in scavenging P, V, and As from
432 seawater (e.g., Feely et al., 1998; Feely et al., 1991b), thus demonstrating that hydrothermal
433 activity results in the net removal of these species from sea water. The Fe:P and Fe:V ratios in
434 these plume samples are a function of the ambient phosphate concentration in the local ocean
435 environment, suggesting a possible paleo-indicator of oceanic phosphate concentrations.
436 More recently the technique has been applied to suspended particulate matter from the open
437 ocean (Barrett et al., 2012) and to aerosols collected in the marine atmospheric boundary layer
438 (Buck et al., 2013; Buck et al., 2010a; Buck et al., 2006; Buck et al., 2010b; Ranville et al.,
439 2010). These studies reveal the dominant impacts of aerosol deposition to the ocean on the
440 dissolved and particulate TEI chemistry in the Atlantic and Pacific Oceans.
441

442 *3.4.2.2 Synchrotron based X-Ray Fluorescence (SXRF)*

443 SXRF techniques provide the ability to quantitatively map the distribution of elements
444 at sub-micron to millimeter spatial scales. Again, fluorescence X-rays are generated, but using
445 the power and brilliance of synchrotron X-rays instead of bench-top generated X-rays (as in
446 ED-XRF or XPS) or electrons (as in SEM-EDS) to obtain adequate sensitivity when the
447 incident beam is focused to micron- and sub-micron areas.

448 Comparisons of SXRF with standard bulk techniques have shown this approach to
449 produce comparable results for biogenic TEIs (Mn, Fe, Ni, Zn) and biomass elements P and Si
450 (Núñez-Milland et al., 2010; Twining et al., 2004b; Twining et al., 2003) in identical samples.
451 However, application of SXRF to measure cellular metal quotas alongside ICP-MS
452 measurements of bulk particulate element concentrations in natural systems has shown that
453 these approaches provide different information. Bulk particulate Fe concentrations
454 (normalized to the biomass proxy P) are typically higher than co-occurring cellular Fe:P ratios
455 due to the inclusion of lithogenic and detrital particles that are relatively rich in Fe (King et
456 al., 2012; Twining et al., 2011; Twining et al., 2004b). In certain cases analyses can be
457 expanded to include minor trace metal constituents such as Co and V (Nuester et al., 2012).
458 Using this approach, significant spatial, temporal and taxonomic variations in the TEI content
459 of naturally-occurring phytoplankton have been measured (Twining and Baines, 2013;
460 Twining et al., 2011; Twining et al., 2004a; Twining et al., 2010). For example, Fe, Ni and
461 Zn contents of cyanobacteria from neighboring mesoscale eddies in the Sargasso Sea can vary
462 by more than an order of magnitude as a result of different nutrient inputs (Twining et al.,
463 2010), while in the equatorial Pacific Ocean metal quotas of eukaryotic phytoplankton vary
464 across and along the equator, due to both upwelling and the passage of tropical instability
465 waves (Twining et al., 2011). SXRF-produced maps of sub-cellular TEI distributions are also
466 valuable, suggesting physiological uses for metals (Nuester et al., 2014) as well as the internal
467 and external associations of metals with cells in some cases (Núñez-Milland et al., 2010;
468 Twining et al., 2004b; Twining et al., 2003).

469 Coarser-scale SXRF mapping of size-fractionated suspended particulate or sediment
470 trap samples on filters can reveal the larger-scale systematic behaviors of different TEIs. For
471 example, the often-dominant lithogenic and authigenic components of elements such as Fe
472 and Mn are manifested as intense micron-sized Fe and Mn hotspots (pixels with very high
473 count rates) above the much lower biogenic background. Indeed, abundant micron-sized Fe-
474 rich particles detected by SXRF in subsurface marine particles were the primary indication of
475 the importance of lateral transport of Fe from the continental margin to the open Subarctic
476 Pacific (Lam et al., 2006). In contrast to particulate Fe and Mn distributions in hotspots, TEIs
477 such as Zn that have a much larger biogenic component are distributed evenly with biogenic
478 matter (Lamborg et al., 2008). The spatial distribution of trace elements in single particles
479 and particle aggregates that can be inferred by SXRF adds a new perspective to previous bulk
480 determinations of particulate trace metal concentrations.

481

482 3.4.3 X-ray Absorption Spectroscopy (XAS)

483 For measurements of chemical speciation, the absorption of X-rays by a sample is
484 measured as a function of incident energy. XAS techniques differ to XRD in that they are
485 element-specific and do not require chemical structural order. This makes XAS suitable for
486 characterizing trace elements that are poorly (or not) crystalline. X-ray absorption is a
487 function of sample thickness and the X-ray absorption coefficient (μ), which is the probability
488 for an X-ray to be absorbed by a sample (Kelly et al., 2008).

489 The probability of X-ray absorption depends strongly on atomic number and incident
490 energy, as well as the local bonding environment of the target atom, providing information
491 about the chemical speciation of the sample (Kelly et al., 2008; Sham and Rivers, 2002). All
492 XAS techniques include collection of data at the absorption “edge”, which is a term used to
493 describe the rapid increase in the absorption of X-ray photons at the energy just above the
494 binding energy of the electrons associated with the atoms being probed by the incident X-rays
495 (Figure 2). At energies above the absorption edge, core electrons are ejected from the atom,
496 where they are called photoelectrons.

497 Electrons are contained within shells corresponding to the principle quantum numbers
498 (e.g., 1, 2, 3...). By convention in X-ray physics, the shells are labelled with letters: K (1st
499 shell), L (2nd shell), M (3rd shell). The K-edge therefore corresponds to the absorption of X-
500 rays by electrons in the 1s sub-shell, and the L₂L₃ edge corresponds to the absorption of X-
501 rays by electrons in the 2p_{1/2} and 2p_{3/2} sub-shells, where the subscripts denote the total angular
502 momentum quantum number. The energies of the absorption edges are unique to each
503 element and each sub-shell. The K-edge is always at higher energy than the L-edge for a
504 particular element, and the energies of K- and L-edges increase as a function of atomic
505 number. For example, the carbon K-edge for elemental carbon occurs at 284 eV, while the K,
506 L₂, and L₃ edges for elemental iron occur at 7112 eV, 720 eV, and 707 eV, respectively.
507 Example absorption spectra for iron at the L₃- and K-edges are shown in Figure 2. Because
508 each absorption edge is the result of different electronic transitions, the information gained
509 also differs slightly, but the principle remains the same.

510 When the incident radiation is in the soft X-ray energy range (< 2 keV) or for
511 particularly concentrated samples in the hard X-ray energy range (> 5 keV), the absorption of
512 incident radiation can be directly measured using a detector that is placed behind the sample
513 in the X-ray path. The X-ray absorption coefficient is derived from the measured X-ray
514 intensities in front of and behind the sample (Kelly et al., 2008). Since X-ray fluorescence
515 results from and is proportional to the absorption of X-rays (Section 3.4.2), measuring the
516 emitted X-ray fluorescence is an alternative and more sensitive method for detecting X-ray
517 absorption for dilute samples. When using fluorescence, the fluorescence detector is placed at
518 right angles to the incident radiation to minimize the intensity of scattered X-rays from the
519 incident beam (Kelly et al., 2008; Parsons et al., 2002).

520 521 *3.4.3.1 XANES, NEXAFS, and EXAFS*

522 The region of the X-ray absorption spectrum around the absorption edge is referred to
523 as the X-ray Absorption Near Edge Structure (XANES) region, also called the Near Edge X-
524 ray Absorption Fine Structure (NEXAFS) (Figure 2). The position (energy) of the edge is a
525 function of the oxidation state of the element of interest. At incident X-ray energies above the
526 absorption edge, the absorption of X-rays leads to the ejection of a photoelectron that is then
527 backscattered from surrounding atoms, modulating the absorption probability of incident X-
528 rays. This is because the absorption of X-rays by a core election is only possible if there is an
529 available state for the photo-electron to transition to. The presence of a backscattered photo-
530 electron wave alters the probability of this, thus modulating the absorption coefficient
531 (Newville, 2004). The resulting oscillations in the absorption coefficient in the higher energy
532 Extended X-ray Absorption Fine Structure (EXAFS) region are measured, and are related to
533 the average distances, identity, and number of coordinating atoms.

534 While both XANES and EXAFS analyses provide information about the local bonding
535 environment of the central absorbing atom, there are some key theoretical and practical
536 differences between the two. The most important practical difference is that collection of
537 XANES data typically takes minutes for environmental samples, whereas collection of
538 EXAFS data typically takes hours. XANES data are excellent for determining the oxidation
539 state of the element of interest (e.g., Wilke et al., 2001), and are often sufficient for
540 distinguishing between major groups of minerals (e.g., oxyhydroxides versus sulfides) (e.g.,
541 Lam et al., 2012; Toner et al., 2014), but may not be able to distinguish between more closely
542 related species (e.g., different forms of oxyhydroxides), for which EXAFS may be required
543 (e.g., Manceau and Drits, 1993; Toner et al., 2009b).

544 A variety of empirical methods have been developed to extract oxidation state and
545 crude mineralogical information from the position and size of the features at the L-edge (e.g.,
546 von der Heyden et al., 2014; von der Heyden et al., 2012) and K-edge (e.g., Marcus et al.,

2008; Wilke et al., 2001). Extending the collection of XANES data several hundred eV above the main edge additionally facilitates the quantitative analysis of unknown XANES spectra by linear combination fitting using a library of reference materials (Kelly et al., 2008). The theoretical basis of oscillations in the EXAFS range is well understood, so the equation describing EXAFS oscillations can be solved from first principles for the number and identity of neighboring atoms, the distance to the neighboring atom, and the disorder in the neighbor distance (Bunker, 2010; Koningsberger and Prins, 1988). Alternatively, EXAFS spectra can also be quantitatively analyzed by linear combination fitting. There are several freely available software packages to analyze XANES and EXAFS data (e.g., Marcus, 2011; Ravel and Newville, 2005; Webb, 2005). The details of XAS data analysis are beyond the scope of this paper, but we refer the reader to the many excellent online tutorials (e.g., <http://xafs.org/Tutorials>), papers (e.g., Conradson, 1998; Kelly et al., 2008; Parsons et al., 2002), and books (e.g., Bunker, 2010; Fenter et al., 2002; Koningsberger and Prins, 1988; Teo, 1986) that exist on EXAFS theory and applications.

3.4.3.2 Scanning Transmission X-ray Microscopy (STXM)

STXM is a spectromicroscopy technique that combines the high resolution of an X-ray microscope with some of the spectroscopic information of NEXAFS (Bluhm et al., 2006). It operates in the soft (lower energy) X-ray range (~100-2000 eV), which has lower penetration than a hard X-ray microprobe and so can only be applied to very thin samples. One of its primary advantages is that it can produce maps detailing elemental associations and chemical speciation at very high spatial resolution (tens of nanometers), provided the elements of interest have an appropriate absorption edge in the STXM energy range. The STXM energy range encompasses both the carbon K-edge and the iron L-edge, permitting the determination of organic matter functional groups (e.g., Brandes et al., 2004; Lehmann et al., 2009), some of which may be binding Fe (Toner et al., 2009a; von der Heyden et al., 2014). For STXM, particles must be removed from the filter on which they were collected, washed of sea salt, and placed onto an X-ray transparent substrate.

3.4.3.3 Applications of XAS to marine particle cycling

Particulate iron has thus far received the most attention by XAS techniques in the marine community because of its relatively high concentration in suspended particulate matter, particularly near continental margins and hydrothermal vents, but particulate C and S speciation in suspended marine particles have also been reported using these techniques (Breier et al., 2012; Lam and Bishop, 2008; Lam et al., 2006; Lam et al., 2012; Toner et al., 2009a; Toner et al., 2012b; von der Heyden et al., 2012).

Iron is typically analyzed either at the K- or L₃-edge (see Figure 2). XANES and EXAFS at the K-edge have been applied for the determination of the local coordination environment at the iron site in metalloproteins such as cyanobacterial ferritin (e.g., Castruita et al., 2006), model complexes (e.g., Duckworth et al., 2008), and minerals (Lam and Bishop, 2008; Lam et al., 2012; Toner et al., 2012a; Toner et al., 2009b; Waychunas et al., 1986). A hard X-ray microprobe performing microfocused XANES (μ XANES) and EXAFS (μ EXAFS) spectroscopy can provide detailed mineralogical information of individual particles at the micron-scale (e.g., Ingall et al., 2013; Lam et al., 2006). The related chemical species mapping technique allows rapid identification of minor species that would never be identified by bulk techniques (Lam et al., 2012; Toner et al., 2012b; Toner et al., 2014). These studies have shown the high heterogeneity in the speciation of marine particulate iron, including poorly crystalline Fe(III) compounds such as oxyhydroxides and clays, Fe sulfides, and Fe(II) silicate minerals, and have implications for the solubility and bioavailability of different forms of particulate iron.

597 The Fe L-edge has been less utilized, although it can provide more detailed electronic
598 information (Wasinger et al., 2003). Because it is typically conducted on STXM beamlines
599 that have much higher spatial resolution, this allows smaller, colloidal particles to be probed
600 (e.g., Toner et al., 2009a; von der Heyden et al., 2014; von der Heyden et al., 2012). Using
601 STXM, persistent particulate Fe(II) has been found associated with particulate organic carbon
602 in both hydrothermal plumes (Toner et al., 2009a) and oxygenated euphotic zones (von der
603 Heyden et al., 2012), raising questions about our understanding about the presumed stability
604 of reduced forms of iron in oxygenated seawater.

605 The speciation of mineral Fe can also be used as a tracer for the provenance of Fe to
606 iron limited open ocean regions (Lam and Bishop, 2008; Lam et al., 2006; Lam et al., 2012;
607 von der Heyden et al., 2012). For example, the abundance of crystalline Fe(II) minerals in
608 subsurface waters of the Western Subarctic Pacific suggested a source from the surrounding
609 volcanic margin, demonstrating the importance of lateral transport of Fe over many hundreds
610 of kilometres (Lam and Bishop, 2008).

611

612 3.4.4 X-ray Photoelectron Spectroscopy (XPS)

613 X-ray Photoelectron Spectroscopy (XPS) follows the same physical principles as XAS
614 (Behra et al., 2001; Brown Jr and Calas, 2012), and can use a bench-top or synchrotron X-ray
615 source to illuminate the sample. The energy difference between the incidental beam and the
616 kinetic energy of the electron beam ejected by the sample allows the description of the
617 elemental concentration (in parts per thousand range) and the speciation within the first 10 nm
618 of the solid surface. Unlike XAS, which can be used on liquid and colloidal samples, XPS
619 analysis is restricted to samples in the solid form and under high vacuum, but is well adapted
620 to the study of surface physico-chemistry.

621

622

623 **4. Conclusions**

624 In this paper, we have reviewed techniques that are used to study the composition and
625 speciation of marine particles. The analytical « wet » chemistry techniques described here are
626 being used in a high-throughput fashion to measure the first full ocean depth, basin-wide
627 sections of marine particulate distribution and composition as part of the international
628 GEOTRACES program (Lam et al., in press; Ohnemus and Lam, in press; Twining et al., in
629 press). We also described the physical principles behind spectroscopic techniques that may
630 not be as familiar to the oceanographic community. Some of these spectroscopic techniques
631 are already being used on select samples in GEOTRACES to complement high-throughput
632 analytical techniques, such as the speciation of particulate iron in oxygen minimum zones and
633 hydrothermal vents using XAS, and the trace metal quotas of phytoplankton using SXRF.
634 This pairing has enormous potential to unveil new discoveries about particles and their role in
635 the cycling of TEIs.

636

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644 **Tables**

645 Table 1. A summary of X-ray based spectroscopic techniques for the analysis of marine particles

Technique	Sample preparation	Mode of excitation	Measured parameter	Notes	Information obtained
Scanning Electron Microscopy—Energy-Dispersive Spectrometry (SEM-EDS)	Particles on membrane filter	Benchtop-generated electrons	Elemental X-ray fluorescence	Incident electron beam probes surface (few μm)	Surface morphology and elemental concentration maps ($\sim 5 \mu\text{m}$ spatial resolution)
Energy Dispersive X-Ray Fluorescence (EDXRF)	Particles on membrane filter	Benchtop-generated X-rays	Elemental X-ray fluorescence	Incident (hard) X-rays penetrate entire sample	Elemental concentration (bulk)
Synchrotron X-Ray Fluorescence (SXRF)	Particles on C-coated EM grid Or particles on membrane filter for coarser mapping	Synchrotron-generated X-rays (Hard X-rays)	Elemental X-ray fluorescence map	Incident (hard) X-rays penetrate entire sample	Elemental concentration maps (submicron to micron spatial resolution)
X-ray Absorption Near-Edge Structure (XANES)	Particles on membrane filter	Synchrotron-generated X-rays	X-ray absorption spectrum	Fast (<20 minutes/sample), but not very detailed	Chemical bonding environment of target element and oxidation state, broad groups of chemical species (bulk or microfocused)
Extended X-ray Absorption Fine Structure (EXAFS)	Particles on membrane filter	Synchrotron-generated X-rays	X-ray absorption spectrum	Detailed information, but very long analysis time (~ 8 hrs/sample)	Detailed chemical bonding environment of target element (bulk or microfocused)
Scanning Transmission X-ray Microscopy (STXM)	Particles on X-ray transparent substrate such as C-coated EM grid or Si-Ni window	Synchrotron-generated X-rays (soft X-rays only: <2 keV)	Elemental X-ray absorption and X-ray absorption spectrum	Samples must be very thin (transparent to soft X-rays)	Elemental concentration and speciation maps (tens of nm spatial resolution)
X-ray Photoelectron Spectroscopy (XPS)	Solids	Benchtop-generated X-rays Synchrotron generated X-rays	Number and kinetic energy of ejected photoelectrons	Surface (10 nm) technique ; detection limit of 0.1% atom number	Elemental concentration and speciation of particle surfaces

646

648 **Figure Captions**

649 Figure 1. Principles of X-ray fluorescence (XRF). Incident X-ray radiation ($h\nu$, green squiggly
650 arrow) is absorbed by the target atom, ejecting a (photo)electron (black circle) from the
651 innermost orbital, or shell (short horizontal lines). An electron from an outer shell fills the
652 hole (open circle), emitting fluorescent radiation ($h\nu'$, red squiggly arrow) at a lower energy,
653 which is detected by a fluorescence detector. The energy of the emitted fluorescent X-ray is
654 element-specific, and is the basis of XRF techniques to determine elemental concentrations
655 (EDXRF, SXRF). SEM-EDS follows the same principles, except that an incident electron
656 beam is used instead of X-rays to excite a core electron. Figure taken from Wikimedia
657 Commons.

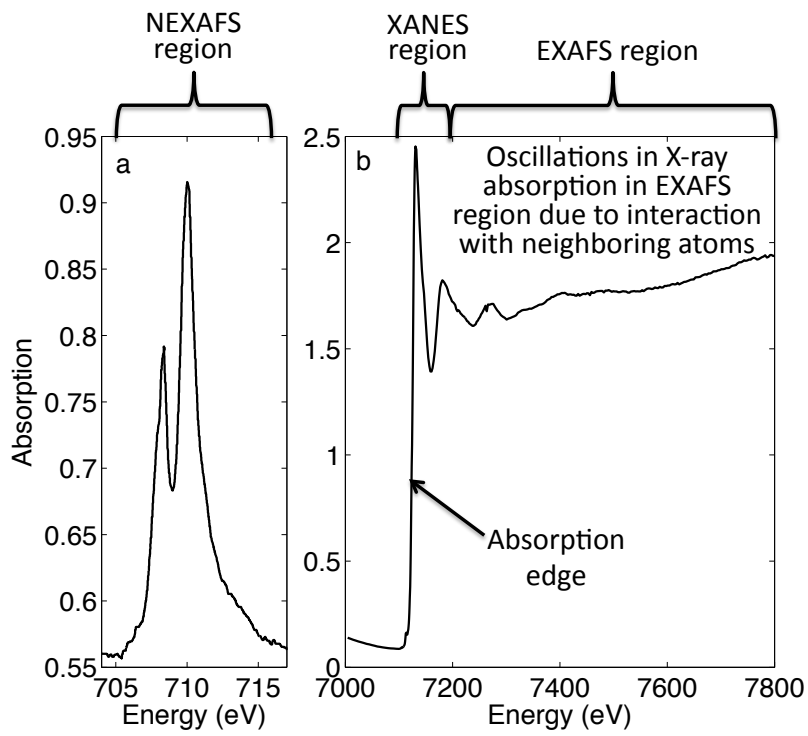
658
659 Figure 2. Example X-ray absorption spectra for marine particulate iron at a) the L_3 -edge and
660 b) the K-edge, showing the absorption of X-rays by iron in the sample as a function of
661 incident X-ray energy. The highest absorption (the “absorption edge”) occurs when the
662 incident energy equals the binding energies of core electrons, which is around 710 eV for $2p_{3/2}$
663 electrons (L_3 -edge) and around 7125 eV for $1s$ electrons (K-edge). The exact position
664 (energy) of the absorption edge is a function of the oxidation state of the element in the
665 sample (higher energy for more oxidized elements). The edge region is often referred to as the
666 NEXAFS region for soft (lower energy) X-rays, and the XANES region for hard (higher
667 energy) X-rays, but the two terms are equivalent. At energies above the main edge (the
668 EXAFS region), the ejected photoelectron wave is backscattered from surrounding atoms,
669 modulating the absorption probability of incident X-rays. The resulting oscillations in
670 absorption are used to determine the local bonding structure of the central absorber atom.
671 Iron L-edge and K-edge XAS data were collected at beamlines 11.0.2 and 10.3.2,
672 respectively, at the Advanced Light Source, Lawrence Berkeley National Laboratory.

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676 **Figures**
677 Figure 1.



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682 Figure 2.
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