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Polystyrene foam as a source and sink of chemicals in the marine environment: An XRF study

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2   **environment: An XRF study**

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14   **Abstract**

15   Polystyrene foam (expanded and extruded polystyrene: EPS and XPS, respectively) is a ubiquitous

16   and pervasive type of marine plastic litter whose physical properties, transport and fate are distinctly

17   different to those of other common (unfoamed) types of thermoplastic litter. In this study, a range

18   of fragments of EPS and XPS retrieved from three beaches in southwest England have been

19   characterised by energy-dispersive X-ray fluorescence spectrometry in order to examine the

20   chemical makeup and potential biological and geochemical impacts and interactions of this type of

21   plastic waste. Analyses performed through sample faces and, in some cases and after dissection,

22   through the material core, revealed variable concentrations of Fe, Ti and Zn among the fragments

23   and, in some cases, within the same sample. This likely reflects the presence of reaction residues and

24   pigments arising from the manufacture of polystyrene, and, for Fe and Ti, significant and

25   heterogeneous ion and mineral acquisition from the environment during transport in suspension or

26   while beached. Acquired oxides of Fe are partly responsible for the chemical fouling observed on the

27   face of most samples and are also able to act as an adsorbent for other metals, like Pb. Detection of

28   Br in many fragments up to concentrations of 11,500 mg kg^{-1} likely results from the incorporation of

29   the flame retardant, hexabromocyclododecane, in EPS and XPS designed for (but not necessarily

30   limited to) the construction sector. These observations suggest that EPS and XPS can act as both a

31   source and sink for contaminants in the marine environment that merit further investigation.

32   **Keywords**: polystyrene foam; expanded; extruded; XRF; flame retardants; additives

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1. Introduction

Because of its low weight, high strength and excellent thermal-noise insulation and shock-absorbing properties, foamed polystyrene, encompassing expanded polystyrene (EPS) and extruded polystyrene (XPS), is widely used across a range of sectors (e.g., construction, transportation, consumer, maritime) (Wünsch, 2000; Block et al., 2017). However, many of the characteristics that make foamed polystyrene such a popular and useful commodity also ensure that it is a significant and pervasive constituent of the waste stream (Nie et al., 2015; Black et al., 2019).

In the marine environment, EPS and XPS are among of the most abundant forms of plastic litter (Hinojosa and Thiel, 2009; Davis and Murphy, 2015; Che et al., 2018; Chitaka and von Blottnitz, 2018). Sources of polystyrene foam include municipal waste, littering and loss or deterioration of polystyrene-based structures at sea (such as pontoons, floating docks, buoys and boat stands; Hansen et al., 2015; Jang et al., 2020). Unlike other common (unfoamed) thermoplastics, however, a density an order of magnitude lower than that of seawater, coupled with a closed cell structure, results in EPS and XPS waste readily fragmenting in situ and being transported on the ocean surface. Thus, at sea polystyrene foam is subject to considerable windage (Chubarenko et al., 2016), persistent exposure to chemicals resident in the sea surface microlayer (Wurl and Obbard, 2004) and colonisation by rafting organisms (Carson et al., 2013), and when beached material is widely dispersed, abraded, micronised and buried by the action of the wind (Song et al., 2017).

Despite its distinctive physical and mechanical properties, pathways and environmental and biotic interactions, however, foamed polystyrene is generally considered or quantified within the more general pool of marine plastic litter in the scientific literature (Fok et al., 2017; Nabizadeh et al., 2019; Tata et al., 2020). Significant from a geochemical and biological-toxicological perspective and that has yet to be documented is its (non-polymeric) chemical composition, including the presence of any additives and residues arising from manufacture and chemicals acquired from the environment during suspension or beaching. Accordingly, the current study reports on an energy-dispersive X-ray fluorescence (XRF) analysis of EPS and XPS fragments retrieved from various Atlantic- and English Channel-facing beaches of southwest England. XRF spectrometry affords a rapid, non-destructive means of quantifying a range of elements in solids and through a complex series of mathematical algorithms solved iteratively is suited for the analysis of materials of low-density like plastics and including foams (Piorek, 2004; Furl et al., 2012). XRF is also able to provide information on the spatial distribution of elements, including the relative significance of those incorporated into the matrix and held at the surface.

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2. Methods

2.1. Sample collection

As part of a number of research programmes studies aimed at examining marine litter more generally (Turner and Solman, 2016) or targeting samples for experimental studies (Turner and Lau, 2016), samples of EPS and XPS had been retrieved manually during late spring or early autumn of 2015 from three beaches in southwest England. Namely, Tregantle (50.353, -4.271), a large, southwest-facing sandy beach on the south coast of Cornwall that is backed by high cliffs, Constantine Bay (50.539, -5.027), a large, southwest-facing sandy beach on the north coast of Cornwall that is backed by a dune system, and Mount Batten (50.356, -4.127), a small, sand-gravel beach in the partly-urbanised embayment of Plymouth Sound. Polystyrene fragments were usually abundant on the latest (or highest) strandline and on the back-beach near to the cliff or dune base. In the laboratory, any loosely adherent material was dislodged or brushed off under tap water before samples were dried under desiccation at room temperature for 96 h. Samples were then weighed and photographed and stored in individual polyethylene specimen bags in the dark until required for analysis.

2.2. XRF analysis

Samples were analysed by energy-dispersive portable XRF spectrometry using a Niton XL3t 950 He GOLDD+ configured in a laboratory accessory stand. The instrument was operated in a customised, standardless 'plastics' mode and because of the low density of foamed polystyrene, a thickness correction algorithm was always applied after measuring the thickness of material through the measurement surface using Allendale digital callipers (Turner and Solman, 2016). Samples were counted for periods ranging from 60 to 180 s, depending on material thickness, that were distributed in a 2:1 ratio between a low energy range (20 kV and 100 μA) and main energy range (50 kV and 40 μA). Spectra were quantified by fundamental parameter coefficients to yield concentrations on a dry weight basis (in mg kg^{-1}) and with a counting error of 2σ (95% confidence). Up to 18 elements may be analysed in the plastics mode but the focus of the present study was on those that are known to be used in various plastics (Ba, Br, Fe, Sb, Ti, Zn), act as proxies for hydrogenous and detrital phases (Fe, Ti) or are contaminants of toxicological concern (Br, Cd, Pb).

By default, the measurement face was an 8-mm diameter circular area of the central region of the largest or flattest face. For selected samples larger than about 3 cm in diameter, between four and eight measurements were made at different locations over the face to examine the distribution of elements within the matrix. Here, the small-spot facility of the instrument was employed in order to

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100   focus the X-ray beam into a 3-mm diameter circular area. For these samples, were possible, material

101   was sliced through the thickest axis with a stainless steel scalpel and the central core analysed.

102   As a performance check, polyethylene reference discs Niton PN 180-619 (Ba = 688 $\pm$ 45 mg kg^{-1}; Cd =

103   150 $\pm$ 6 mg kg^{-1}; Pb = 150 $\pm$ 12 mg kg^{-1}; Sb = 96 $\pm$ 10 mg kg^{-1}) and Niton PN 180-554 (Br = 495 $\pm$ 20 mg

104   kg^{-1}; Cd = 292 $\pm$ 20 mg kg^{-1}; Pb = 1002 $\pm$ 40 mg kg^{-1}) were analysed throughout each measurement

105   session, with the instrument returning concentrations that were consistently within 10% of certified

106   values. Detection limits varied depending on counting time, sample thickness and whether the small-

107   spot was engaged but indicative values based on the lowest counting errors returned throughout

108   the study ranged from about 10 mg kg^{-1} for Br, Pb and Ti to 100 mg kg^{-1} for Ba and Sb in EPS and

109   about 20 mg kg^{-1} for Br, Pb and Ti to 250 mg kg^{-1} for Ba and Sb in XPS. Analytical precision, defined by

110   repeat measurements (n = 5) of the same area of sample, was generally better than 10% but could

111   be as high as 25% if concentrations were close to the detection limit and determined with the small-

112   spot facility.

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114   2.3. Polystyrene confirmatory analysis

115   For sixteen samples that were particularly weathered or discoloured, confirmation of the polymeric

116   matrix was achieved by attenuated total reflectance Fourier Transform Infrared (FTIR) spectrometry

117   using a Bruker Vertex 70. Here, 1-3 mm offcuts of the sample surface were clamped against the ATR

118   diamond crystal and spectra were recorded with 16 scans in the region 4000 to 600 cm^{-1} and at a

119   resolution of 4 cm^{-1}. After being smoothed, baseline-corrected and normalised via Bruker OPUS 7

120   software, spectra were matched up with spectra of polystyrene contained in various reference

121   libraries.

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123   **3. Results**

124   A total of 86 samples, exemplified in Figure 1, were returned to the laboratory for characterisation.

125   Samples ranged in size from individual foamed beads of about 4 mm in diameter and 30 mg in mass

126   to fragments of about 10 cm in length and weighing up to 10 g. EPS samples (n = 67) were identified

127   from presence of the distinctive beaded (cellular) structure while XPS samples (n = 19) were usually

128   unstructured, flatter and smoother. Where material was heavily fouled or discoloured, FTIR analysis

129   confirmed the polymeric composition of both EPS and XPS from aromatic ring stretches at 1600 cm^{-1}

130   1490 cm^{-1} and aromatic CH out-of-plane bends at 694 cm^{-1} and 537 cm^{-1} (Noda et al., 2007).

131 Most samples of EPS were well-rounded, unidentified fragments that contained surficial cracks or
132 pits, and the polystyrene itself was usually white or off-white. Dissection of samples revealed a
133 "clean" interior that was generally free of fouling or particle intrusion (Figure 1h). Samples of XPS
134 tended to be thinner and more ragged (Figures 1c and 1e), and displayed a broader range of colours
135 that that included white, beige, blue or green. Some samples of XPS had evidently been derived from
136 single-use food or drink containers that likely had a local (littering) origin. With the exception of the
137 latter type of sample, most foamed fragments were visibly discoloured at the face (and relative to
138 the core) by orange-brown chemical fouling, with some EPS soiled by fine particulates trapped in the
139 pore space between weathered beads or stained by oil.

140 Summary statistics for the concentrations of the elements in the samples as determined by XRF are
141 shown in Table 1, with the full dataset shown in Appendix A. Data in Table 1 are pooled for the three
142 locations and a direct comparison is made between the two different types of foamed polystyrene.
143 Note that measurements were made in the central region of the largest face and, because of the low
144 density of the material, values reported signify concentrations that are representative of the entire
145 depth of sample rather than the measurement face. Note also that elemental detection limits for
146 XPS were about double the corresponding detection limits for EPS because of the lower thickness of
147 the former samples. Among the elements considered, Fe and Ti were most commonly detected and
148 exhibited the highest mean, median and maximum concentrations. Bromine and Zn were detected
149 in about 60 cases each, Pb was detected in 14 samples of EPS and Ba was detected in eight samples
150 of EPS; Sb was detected in just one sample of XPS and Cd was never detected (< 25 mg kg^{-1}). A series
151 of Kruskal-Wallis tests performed in Minitab v19 revealed that median concentrations of Fe and Ti in
152 EPS were significantly greater than respective median concentrations in XPS ($H > 15$, $p < 0.01$) but
153 there was no significant difference in median concentrations of either Br or Zn between the material
154 types ($H < 1$, $p > 0.1$).

155 Table 1: Detection frequency for the different elements and summary statistics for their
156 concentrations (in mg kg^{-1}).

	Ba	Br	Cd	Fe	Pb	Sb	Ti	Zn
EPS (*n* = 19)								
detection, %	9.0	79.1	0	100	20.9	0	98.5	65.7
mean	536	1610		9620	50		2670	392
median	438	224		8170	20		1620	173
min	350	12		282	11		68	42
max	1060	11500		29100	175		50900	3560
XPS (*n* = 19)								
detection, %	0	31.6	0	89.5	0	5.3	94.7	89.5
mean		890		2300		373	579	193
median		120		1150			518	135
min		27		85			25	36
max		4710		7120			1740	674

Figure 2 shows the spatial distribution of Br, Fe, Ti and Zn in five samples of EPS (samples of XPS were generally too thin to perform this characterisation (see Figure 1) and Pb was never detected in the core of EPS). Specifically, the variation in concentrations measured on the largest or flattest face, []$_{face}$, are shown against single or replicate measurements of concentration of the core, []$_{core}$, once the sample had been dissected. For Br, relative standard deviations (rsds) of concentrations are < 30% except for the face of one sample (rsd ~ 65%). Overall, however, mean concentrations lie close to unit slope, indicating that concentrations determined through the face and in the core are similar. The distributions of Fe and Ti are are rather scattered on the charts, and especially in the *y*-axis where rsds of up to 50% are observed, and concentrations of both elements measured on the face are similar to (*n* = 2), greater than (*n* = 2) or lower than (*n* = 1) corresponding concentrations measured in the core. Regarding Zn, with the exception of one sample lying well above unit slope, concentrations measured on the face and core are similar and exhibit relatively little variation among replicate measurements. Note that Ba, not plotted, was detected on the face and core of one sample and returned concentrations that were similar (676 $\pm$ 47 mg kg^{-1} and 672 $\pm$ 25mg kg^{-1}, respectively).

4. Discussion

The results of this study are consistent with the reaction residues and functional additives known to be present in foamed polystyrene or in thermoplastics more generally but are significant in providing an insight into the concentration ranges of these chemicals in EPS and XPS fragments encountered in the marine environment. Thus, the detection of Fe in most samples may be attributed to the use of Fe$_2$O$_3$ as a catalyst in the production of styrene (Wünsch, 2000) while the presence of Zn in many cases, and at least in EPS, may be attributed to residual Zn stearate that is often used to ensure

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181   uniform cell nucleation in the production of the expanded material (European Union, 2008). The

182   detection of Ti in most cases reflects the common usage of TiO_2, and principally rutile, as a pigment

183   that is blended or moulded into the material to provide a high refractive index and chemical stability

184   (Murphy, 2001), while the lack of Ba is due to the avoidance of fillers of high specific gravity, like

185    $BaSO_4$, in products specifically designed to be lightweight (Turner and Filella, 2020).

186   Detectable Br in a high proportion of EPS samples and about a third of XPS samples is attributed to

187   the presence of brominated flame retardants (Gallen et al., 2014). XRF is unable to discriminate

188   different brominated compounds but the most commonly used in foamed PS, and in particular that

189   destined for the construction sector, was 1,2,5,6,9,10-hexabromocyclododecane (HBCD). Production

190   of HBCD began in the 1980s until it was added to Annex A of persistent organic pollutants in the

191   Stockholm Convention that require elimination (United Nations, 2013) and effectively banned

192   (Schlummer et al., 2017). HBCD was added to foamed polystyrene at concentrations that are low

193   relative to concentrations of other halogenated compounds used to flame-retard plastics (about 0.7

194   to 2.5% by weight; Alaee et al., 2003). Moreover, and unlike flame-retarded plastics more generally,

195   foamed PS impregnated with HBCD did not require the addition of antimony trioxide (Sb_2O_3) as a

196   synergist to meet various building code specifications (Papazoglou, 2004), thereby accounting for

197   the lack of detection of Sb in the current samples (Table 1).

198   Assuming that Br concentrations result from only HBCD and given that the fractional mass

199   contribution of Br to HBCD is 0.75, the maximum concentration of the flame retardant reported in

200   Table 1 is about 15,300 mg kg^{-1} (or 1.5% of HBCD by weight). This value is in good agreement with

201   the maximum concentration of HBCD measured directly in EPS and XPS fragments retrieved from the

202   north Pacific Ocean (Jang et al., 2017) and is within the content range required for flame-retardancy

203   of construction material (Alaee et al., 2003). This observation, coupled with Br being undetected in

204   samples of XPS that were evidently related to single-use food-drink containment (such as take-out

205   trays and Styrofoam cups) suggests that the majority of samples collected herein originate from the

206   construction industry. However, this may not necessarily be the case because a single grade of HBCD

207   often appears to have been used for wider production (for use in both construction and packaging,

208   for example) (Lassen et al., 2019) and there is evidence for the uncontrolled use or recycling of the

209   flame retardant (Rani et al., 2014; Abdullah et al., 2018). The latter pathway would account for the

210   high variability of Br concentrations among the samples and the occurrence of concentrations well

211   below those required for flame-retardancy in many cases.

212   From a regulatory perspective, the EU has recently introduced a low concentration limit of 0.1%

213   (1000 mg kg^{-1}) by weight for certain brominated compounds, including HBCD, above which items

214   may not be recycled, and a limit of 0.01% (100 mg kg^{-1}) above which products are not permitted for

215   sale in the EU (European Commission, 2016). Converting the Br measurements summarised in Table

216   1 into HBCD concentrations reveals that 18 samples of EPS and one sample of XPS would be non-

217   compliant for recycling and that 43 samples of EPS and three samples of XPS would be non-

218   compliant for resale.

219   Another factor to consider that has a potentially significant impact on elemental concentrations

220   measured in the EPS and XPS samples is the acquisition of chemicals from or their loss to the

221   environment while at sea or once beached. Since the additives and residues identified above are not

222   covalently bonded to the polymeric matrix, there is scope for migration from foamed polystyrene

223   into seawater. Predicted or measured diffusion rates for ions and compounds in virgin plastics vary

224   considerably but are generally very small (Town et al., 2018), with estimates of diffusion half-lives

225   for various brominated flame retardants on the order of tens of thousands of year or more (Sun et

226   al., 2019). That said, physical and chemical processes acting on plastics in the marine environment,

227   including digestion by animals, may considerably accelerate leaching (Tanaka et al., 2015; Smith and

228   Turner, 2020) and result in a more heterogeneous distribution of chemicals in the weathered matrix

229   (Turner et al., 2020).

230   With a specific surface area of about 2 m^2 g^{-1} and a point of zero charge of about 4.7, the inherent

231   surface properties of foamed polystyrene are more favourable for the adsorption of metal ions than

232   many other polymers (Zhang et al., 2018). Moreover, the low density of EPS and XPS ensures that

233   material is exposed to elevated concentrations of metals and other contaminants in the sea surface

234   microlayer (Wurl and Obbard, 2004). On aging, the surfaces of EPS and XPS become discoloured and

235   fouled by organic and inorganic precipitates, a process that is visibly and chemically heterogeneous

236   (see Figure 1 and the *y*-axis distributions of Fe and Ti in Figure 2) and that likely further enhances the

237   adsorption of contaminant metals like Pb. In theory, the degree of metal enrichment at the face may

238   be related to the age of sample or the time spent in suspension in seawater. However, it is

239   important to bear in mind that metal enrichment at or near the polymer surface may also arise from

240   the entrapment of fine detrital particulates within the surficial interstices of the material that evade

241   removal during sample cleaning. Moreover, because of the low density of foamed polystyrene,

242   measurements undertaken through the face are, strictly, more representative of concentrations

243   through the entire sample (and not the measurement face alone).

244   Amongst the elements analysed, there was a strong association between Fe and Ti once two

245   samples with exceptionally high Ti concentrations (> 10,000 mg kg^{-1}) had been excluded (Figure 3a).

246   Results of regression analyses of all data and individual data sets defining the faces of XPS and EPS

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247   samples and the central core of EPS samples are shown in Table 2. Thus, concentrations of Fe and Ti

248   are significantly related in each case, with relatively small intercepts (*c*) and slopes (*m*) that range

249   from 3.90 for XPS faces to 6.72 for EPS cores. A value of *m* that is greater in EPS than XPS suggests

250   that residual, catalytic Fe relative to pigmented Ti is higher in EPS, while the greatest value of *m* that

251   defines the cores of EPS suggests that the ratio of authigenic Fe to Ti acquired from the environment

252   is lower than the elemental ratio arising from manufacture.

253   In contrast, a lack of association was observed between the concentrations of Fe and Br (Figure 3b).

254   Here, concentrations of HBCD and residual Fe appear to be unrelated during the manufacturing

255   process, perhaps because of the uncontrolled use and recycling of the former (Rani et al., 2014).

256   Moreover, while Fe is readily acquired from the environment, HBCD and other forms of Br are not

257   taken up appreciably and may be more subject to heterogeneous leaching from the matrix (Tanaka

258   et al., 2015).

259

260   Table 2: Statistical parameters defining relationships between concentrations of Fe and Ti shown in

261   Figure 3a.

	n	m	c	r^2	p
all data*	85	5.85	370	0.674	<0.0001
XPS	16	3.90	298	0.752	<0.0001
EPS	64	5.53	1140	0.576	<0.0001
EPS-core	5	6.72	-412	0.989	0.0005

263   *After exclusion of two samples where [Ti] > 10,000 mg kg^{-1}.

264

265   **5. Conclusions**

266   The findings of this study reveal that waste EPS and XPS can act as both a source and sink of

267   contaminants in the marine environment. Reaction residues and additives in the matrix detected by

268   XRF include Fe_2O_3, TiO_2 and brominated compounds (presumably dominated by the flame retardant,

269   HBCD), with the latter of greatest environmental concern. Accumulations of Fe- and Ti-based ions

270   and minerals on the surface of polystyrene foam reflect the propensity of the material to acquire

271   chemicals from the environment, with evidence that these phases can also act as adsorbents of

272   more harmful metals like Pb. Given the ability of EPS and XPS to undergo long-range transport and

273   ready fragmentation, it is recommended that future research focuses on the geochemical reactivity

274   and biological interactions of this type of plastic litter.

277

278 **Appendix A: Supplementary material**

279 Supplementary data to this article can be found online at…

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Figure 1: Examples of the EPS (a,b,d,f,g,h) and XPS (c,e) samples retrieved from beaches of southwest England. Annotated bars are approximately 1 cm.
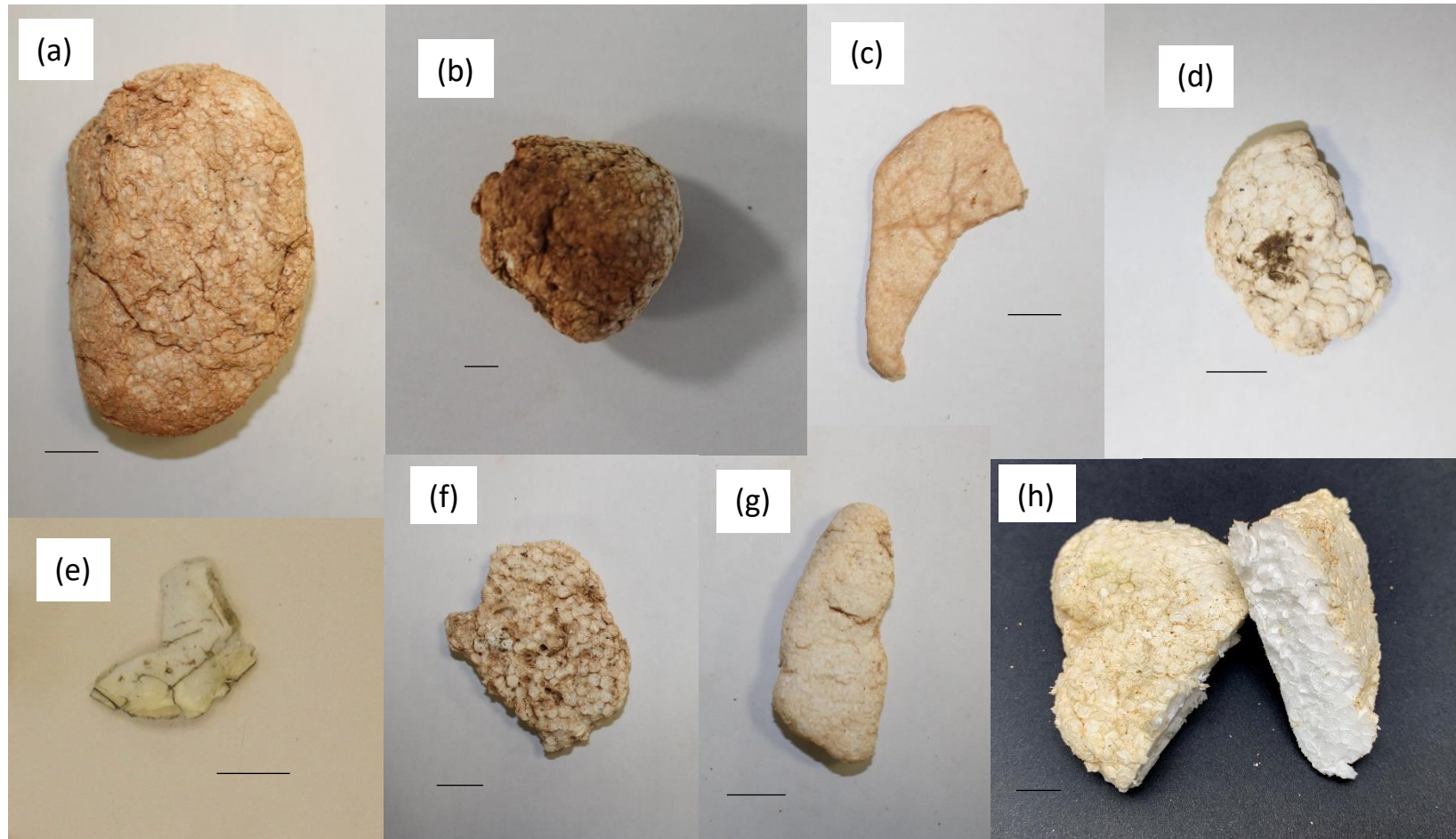
Figure 2: Elemental concentrations measured at various locations on the face versus concentrations measured in the core of five samples of EPS. (a) Br, (b) Fe, (c) Ti, (d) Zn; errors are one standard deviation about the mean (n = 3 to 7) and the red line signifies unit slope.
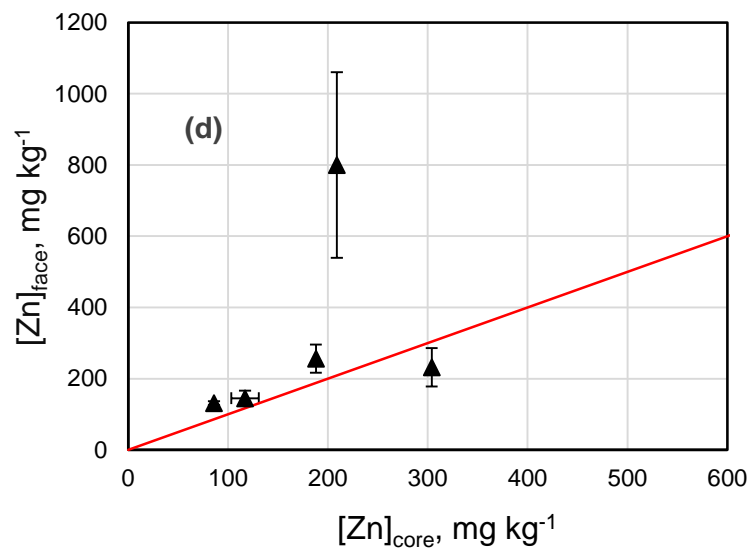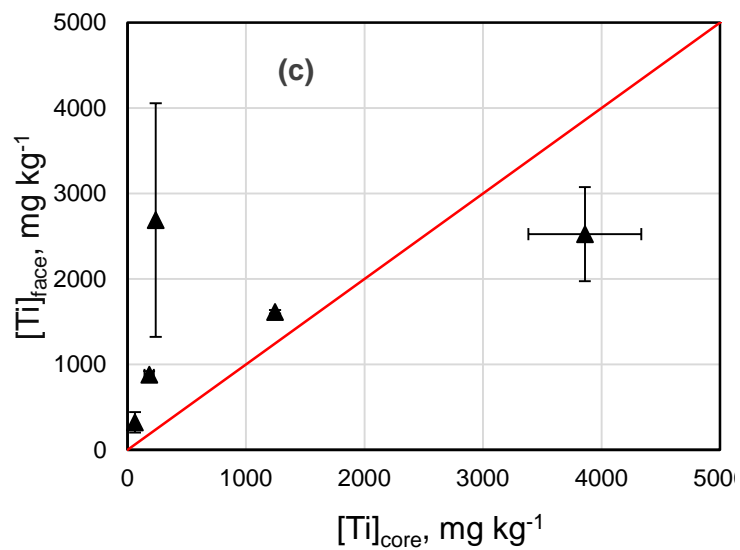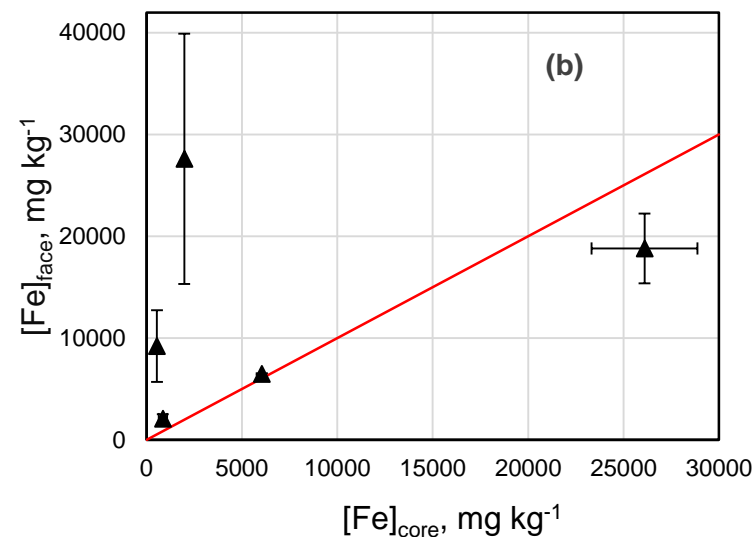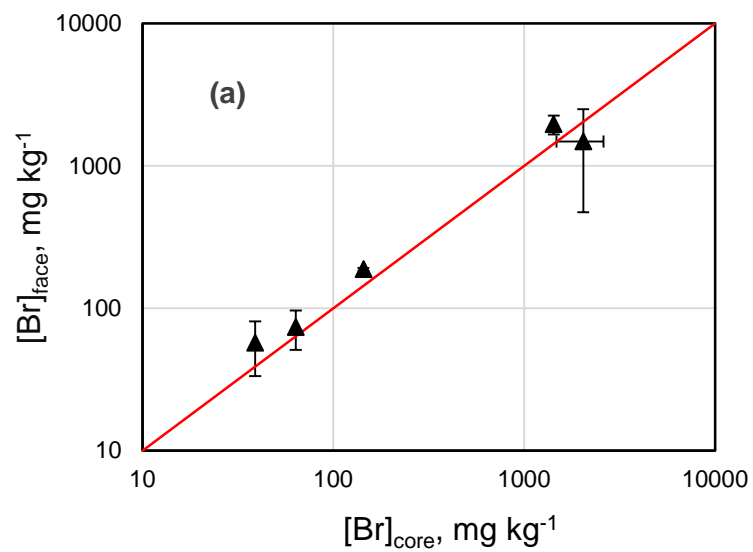
Figure 3: Concentrations of (a) Fe versus Ti and (b) Fe versus Br measured on the central face of XPS and EPS samples and in the core of selected EPS fragments. Parameters defining Fe versus Ti are shown in Table 2.