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1 **Major and Trace Element Geochemistry of the European Kupferschiefer – An Evaluation of**
2 **Analytical Techniques**

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10

11 **Abstract**

12 Simple and rapid techniques are needed for routine quantitative chemical bulk-rock analyses of
13 Kupferschiefer, a black shale containing variable amounts of silicates, base metal sulphides,
14 carbonates and an organic content of up to 30 weight percent. In this study, WD-XRF, TXRF, and
15 ICP-OES of acid- as well as peroxide-digested samples were tested as potential techniques based
16 on their availability and adaptability to analyse major (Si, Ti, Al, Mg, Ca, Fe, K, but also Cu, Zn,
17 Pb) and selected trace (Ag, As, Ba, Co, Mo, Ni, V) element concentrations. Because of the
18 absence of a suitable reference material, a comparative study was undertaken using
19 instrumental neutron activation analysis to ascertain the accuracy of different approaches. Our
20 results suggest that data from ICP-OES were much higher in accuracy compared to INAA than
21 those from WD-XRF and TXRF, independent of the digestion procedure. The choice of digestion
22 procedure is reflected in low detection limits but an underestimation of Cu, Ag, Co, and V

23 concentrations reported by ICP-OES relative to those obtained by INAA in the case of acid
24 digestion and increased detection limits coupled with a loss of over 25 % Ag relative to INAA for
25 peroxide digestion.

26

27 **Supplementary material:** Geochemical data, List of irradiation times and measured isotopes

28

29 **Introduction**

30 Whilst a suite of suitable analytical methods is available for quantitative chemical analyses of
31 common silicate rocks (Heinrich and Hermann, 1990), many ores and mineral raw materials
32 impose significant challenges for geochemical analysis. This is especially valid, if a sample
33 consists of complex or refractory minerals with high metal concentrations in combination with
34 silicates and an abundance of organic material. All these attributes are characteristics of the
35 European Kupferschiefer and render quantitative bulk geochemical analyses challenging.

36 In the strictest sense, the term Kupferschiefer ('copper shale') describes a highly carbonaceous
37 and carbonate-bearing shale that forms the base of the Zechstein sequence developed across
38 Central Europe in an intracontinental sedimentary basin of Permian age (Wedepohl, 1964; Paul,
39 2006; Borg et al., 2012). Though several lithotypes (carbonaceous shale, sandstone, limestone)
40 host stratabound polymetallic base metal mineralization, it is the Kupferschiefer itself that
41 forms the center of the mineral system (Vaughan et al., 1989; Speczik, 1995; Bechtel et al.,
42 2000; Borg et al., 2012). Today, large-scale industrial exploitation of the Kupferschiefer-type ore
43 deposits takes place in Poland, making the Kupferschiefer-type deposits Europe's largest source
44 of Cu and Ag (KGHM Polska Miedź, 2015; Thomson Reuters, 2015).

45 The highly carbonaceous Kupferschiefer shale contains up to 30 wt% C_{org} (Matlakowska and
46 Sklodowska, 2011). The organic matter is composed primarily of marine kerogen type II with the
47 addition of minor amounts of type III (Sun and Püttmann, 2004), i.e., a mixture of aliphatic and
48 aromatic compounds with a poor reactivity to solvents. The Kupferschiefer also contains very
49 variable concentrations of inorganic carbonate - most commonly represented by the minerals
50 dolomite and calcite – and of clay minerals. The latter are represented by illitic mica, and
51 varying amounts of kaolinite and chlorite (Wedepohl, 1964; Bechtel et al., 2000). The sulfide
52 mineralogy is consistent in its complexity. Whilst Kupferschiefer mineralization comprises
53 predominantly of bornite, chalcocite, digenite, chalcopyrite, non-stoichiometric Cu-sulfides,
54 pyrite, sphalerite, galena, covellite, cobaltite and minerals of the tennantite-tetrahedrite series
55 (Vaughan et al., 1989; Matlakowska et al., 2012) there are more than 80 ore minerals that have
56 been reported to occur in minor and trace amounts (Piestrzynski and Pieczonka, 2012).

57 The combination of organic carbon, silicates, and sulfides present in mineralized Kupferschiefer
58 poses significant difficulties in quantitative chemical bulk analysis. Geochemical studies on
59 carbonaceous shales (Quinby-Hunt et al., 1989; Henrique-Pinto et al., 2017) have obtained
60 accurate results by a combination of instrumental neutron activation analysis (INAA) and
61 multiple-step digestion procedures with ICP-MS. However, this approach is impractical in daily
62 routine analysis. It is thus little surprising that there is very limited bulk geochemical data
63 available for the Kupferschiefer in the published literature. The little geochemical data that is
64 available for the Kupferschiefer has often been collected by stationary or portable XRF for major
65 element and base metal concentrations (Tab. 1). Trace element analysis, excluding Au, Pt, Pd,
66 Re, were commonly obtained by ICP-OES/MS with HF-based digestion procedures (Bechtel et

67 al., 2001a; Müller et al., 2008). Little is known regarding the errors associated with these
68 analyses, due to the absence of an appropriate reference material.

69 *Table 1: Techniques used in recent studies of base metal concentrations in mineralized*
70 *Kupferschiefer*¹

INAA	ICP-OES/MS	Portable/stationary XRF	XRF Fusion
Wennrich et al., 1988	Bechtel et al., 2001a; Borg et al., 2005; Müller et al., 2008; Kamradt et al., 2012	Bechtel et al., 2001a, 2001b, 2002; Schubert et al., 2003; Borg et al., 2005; Müller et al., 2008; Oszczepalski et al., 2011; Kamradt et al., 2012	none

¹ Portable and stationary XRF analysis were based on pressed powder tablets

71
72 The present study was carried out within the framework of the international EcoMetals
73 research project (Kutschke et al., 2015) with the goal to identify an efficient and robust
74 approach to quantitative chemical analysis of well-mineralized Kupferschiefer. Two types of
75 digestion procedures were tested. Peroxide digestion within an HCl-solution was chosen, based
76 on its recommendation for sulfide and organic-rich materials (Halicz and Russell, 1986;
77 Balcerzak, 2002; Twyman, 2005). The well-established HNO₃-HF-based acid digestion procedure
78 (Hill, 2007) was tested as an alternative. It was decided to use ICP-OES instead of MS due to the
79 fact that the concentration of copper was expected to be in most samples well above 10,000
80 ppm. In addition, most trace elements of interest (Ag, As, Co, Mo, Ni, V) range well above 100
81 ppm and do not require a method with detection limits as low as those of ICP-MS. Pressed
82 powder tablets were used for XRF analysis. A preparation of glass beads by fusion was
83 prohibited by standard procedures, owing mainly to the high concentration of sulfide and
84 copper (more detail in the discussion).

85 Comparative values of a selection of Kupferschiefer samples were collected by INAA – an
86 analytical method based on powder sample and not requiring any reference materials. These
87 data were used to compare the accuracy of ICP-OES and XRF data.

88

89 **Materials and Methods**

90 *Sample Materials*

91 A set of 7 samples was selected to represent Kupferschiefer from different localities in Germany
92 and Poland (Tab. 2). Sample M-KS was collected from a low grade Kupferschiefer surface
93 stockpile (Kamradt et al., 2012) , while W-KS was collected underground at the Wettelrode
94 Fortschritt shaft for this project. Well-mineralized Kupferschiefer samples were further collected
95 at different sites from the Polish Polkowice-Sieroszowice and Rudna mines. In addition, a
96 flotation concentrate from the Lubin concentrator of KGHM (Poland) was included. Although
97 this concentrate originates from a mixture of different mineralized lithotypes (Kupferschiefer-,
98 sandstone- and carbonate-type ores) it was deemed necessary to consider this material as part
99 of this methodological study.

100 *Table 2: List of samples and their respective origin*

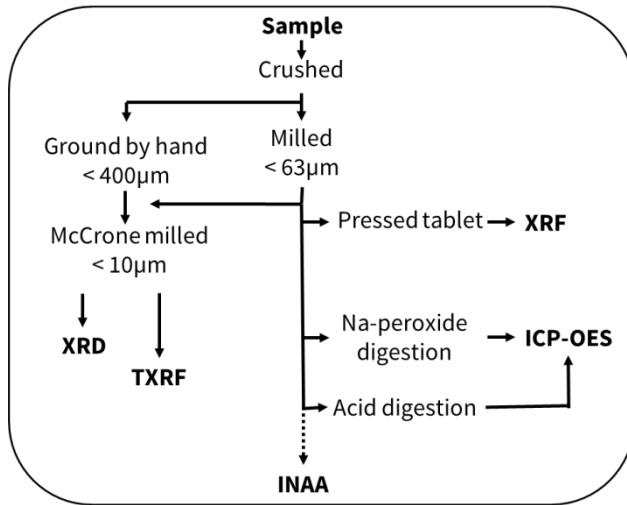
101

	Wettelrode	Mansfeld dump	Polkowice	Rudna	Lubin
Kupferschiefer	W-KS	M-KS	P-KS-2	R-KS-1	L-KS-Con*
samples			P-KS-3	R-KS-2	

* flotation concentrate

102

103 At least 3kg of each sample were collected and subsequently crushed, milled \leq to 63 μ m with a
104 planetary ball mill, dried, and then split following the procedure shown in Fig. 1.



105

106 *Figure 1: Illustration of the sample treatment and subsequent geochemical and mineralogical*
 107 *analysis*

108

109 Mineralogical data were gathered using X-ray diffraction (XRD). This mineralogical information
 110 was used to correct XRF spectra evaluation by designing a suitable component list, choice of a
 111 suitable digestion technique, and validation of the final geochemical results. An overview of the
 112 mineralogical composition of all samples is provided in table 3. Details regarding mineralogical
 113 studies on this suite of samples are presented in a companion study (Rahfeld et al., submitted
 114 2017).

115 *Table 3: Quantitative mineralogical composition of sample material without organic content by*
 116 *XRD. Values reported in weight percent with a conservatively estimated relative error of 15%.*
 117 *The organic carbon content was determined separately by CNS analysis. (Carbonates: dolomite,*
 118 *ankerite, and calcite; Clays: white mica, kaolinite, and chlorite; Cu-sulfides: chalcocite, bornite,*
 119 *chalcopyrite, covellite; Sulfides: pyrite, galena, and sphalerite)*

120

	Quartz	Carbonates	Clays	Feldspar	Cu-Sulfides	Sulfides	C _{org}
M-KS	18	36	26	9	<2	3	2.2
W-KS	22	8	38	6	5	7	14.4
R-KS-1	11	38	24	5	7	10	7.9
R-KS-2	9	21	40	8	5	7	7.4
P-KS-2	19	38	27	3	8	< 1	7.1
P-KS-3	17	5	32	1	32	< 1	9.3
L-KS-Con	8	13	17	4	25	13	9.1

121

122 *Reference Materials*

123 At present time, no geological reference material of black shale composition with base metal
124 enrichment above 100 ppm (Kane et al., 1990; Pertov et al., 2007) is available. As alternative
125 reference material IGS-24, supplied by MBH Analytical Ltd, was selected - a cobalt ore with
126 concentrations of Si, Cu, Co and Ni (Lister, 1978) that are similar to those of the Kupferschiefer.
127 However, this reference material does not have the same complex mineralogical composition.
128 To test the effectiveness of the analytical approach used in this study on at least one other black
129 shale, we used the in-house standard SH-1 supplied by the University of Quebec (Henrique-
130 Pinto et al., 2017).

131 To account for the uncertainty introduced by the lack of a suitable reference material, INAA
132 measurements were carried out. INAA has the advantage that it requires no rock standards, no
133 sample digestion, and still will yield accurate results with a calibration based on single element
134 standards. Uncertainty and bias in INAA is independent of those associated with most other
135 chemical techniques as it depends on nuclear, opposed to atomic, properties of the determined
136 elements (NIST).

137

138 *Sample digestion for ICP-OES*

139 Two digestion techniques were utilized in the preparation of solutions for ICP-OES analyses.
140 Peroxide digestion (PD), a type of caustic fusion, was carried out in zirconium crucibles using a
141 mixture of 0.5000 g sample material, 6g Na₂O₂, and 1g Na₂CO₃, based on the FluXana operating
142 instruction (FXSOP-0083-01). The digestion was completed with a Vulcan 2-station gas fusion

143 machine. An adapted fusion program composed of 240 s pre-fusion (150 m³/h gas – 20 m³/h
144 oxygen – 800 m³/h air) followed by 180 sec fusion (150-20-500) and 180sec cooling was
145 implemented to minimize the explosiveness of the reaction. The pre-fusion settings produced
146 the smallest possible flame and kept the initially violent reaction of the peroxide with the
147 organic matter well contained. Afterwards, the cooled zirconium crucible was dropped into a
148 beaker with 70 ml deionized water (DI-H₂O) and covered by a watch glass. 70 ml 16% HCl was
149 added as soon as the reaction had come to an end, causing a change in the solution color and
150 transparency from turbid to clear. The crucible was removed and cleaned with 16% HCl and
151 deionized H₂O. The remaining solution was boiled for 3 minutes to achieve full dissolution and
152 conversion. Under the addition of DI-H₂O, 200 ml of solution were transferred into a PET bottle
153 using a measuring cylinder.

154 A second set of solutions was prepared by acid digestion (AD) in glassy carbon vessels. In this
155 approach, 0.1000 g of each sample was dissolved in 50 ml DI-H₂O with an addition of 2.5 ml
156 HNO₃. Samples P-KS-2, P-KS-3, R-KS-2, and W-KS with high TOC contents were treated with 5ml
157 HNO₃ and 3 ml HF overnight and at a temperature of 100°C. Afterwards, the solutions were
158 heated to 50 °C (60 min) and 100°C (30 min) before vaporization. In all four samples a dark
159 residue remained in the solution that was subsequently filtered. Samples M-KS, and R-KS-2 were
160 dissolved in 3ml HNO₃ and 5ml HF. A dark residue remained and required a filtration step.

161

162 *Inductively coupled plasma optical emission spectroscopy*

163 The ICP-OES measurements were conducted at the Department of Mineralogy at the Technical
164 University Bergakademie Freiberg. Two standard solutions were prepared for calibration. One of

165 these was composed of Merck multi-element solution number four (ME-IV) containing Ag, Al,
166 As, Ba, Ca, Cu, Co, Fe, K, Mg, Pb, Zn and the other a solution of Mo, V, Sb, Se, Si, Ti . The working
167 solutions were prepared with a dilution factor of 1:100 and 1:10. All ICP-OES measurements
168 were carried out using a Perkin Elmer Optima 3300DV spectrometer and autosampler AS 90.
169 The spectrometer was operated at 1.3 kW, with 0.8 L min⁻¹ Ar nebuliser gas, 15.0 L min⁻¹
170 plasma gas and 0.5 L min⁻¹ auxiliary gas in cross flow dispersion. As part of ongoing quality
171 control, a blank and a reference material were analyzed with each batch of samples. Every third
172 sample was run in duplicate. The results of the duplicates are reported as averages.

173

174 *Wavelength-dispersive-X-ray fluorescence spectrometry*

175 For XRF, pressed powder pellets with a diameter of 40 mm were prepared using 10g milled
176 sample material and 2g pure wax (C-wax, C₁₈H₃₆O₂N₂). This mixture was homogenized in a
177 mixing mill. The tablets were pressed at 18kN for 30 seconds. The sample material could not be
178 calcined, because temperatures above 780°C led to sintering and prohibited removal of the
179 material from the crucible. Therefore, primary, untreated material was used. Total carbon (TC)
180 data supplied by CNS analyses was used for a correct calculation of element concentrations.

181 All WD-XRF analyses were executed using a PANalytical AxiosMAX spectrometer with 60 kV and
182 a current of 66 mA at lower, 25 kV with 160 mA at higher wavelengths. The spectrometer is
183 equipped with a Rh-anode X-ray tube. The wavelength dispersive system uses five crystals (LiF
184 (2 0 0), Ge (1 1 1), PE (0 0 2), PX1 and LiF (2 2 0)). The K α lines of Ag, Al, As, Ba, Ca, Cl, Cr, Co, Cu,
185 F, Fe K, Mg, Mn, Na, Ni, P, Rb, Si, Sr, Ti, V, Y, Zn and L β line of Pb were selected for the
186 quantification. Quantitative analysis was performed by the PANalytical 'standardless' analytical
187 program *Omnian* (Axios, 2005).

188

189 *Total reflection X-ray fluorescence spectrometry*

190 A homogenous suspension was prepared by mixing 100 mg of fine powdered sample material
191 with 5 ml of an aqueous 1 vol % Triton X-100 solution (Klockenkämper and Von Bohlen, 2015).
192 For convenience, McCrone milled material with a particle size below 10 μm – identical to that
193 commonly used for quantitative X-ray powder diffraction analysis – was used. 40 μg Bi and 40
194 μg Y solution were added as internal standards to the suspension. Aliquots of 10 μl were
195 pipetted onto 30 mm quartz-glass carriers and dried. The measurement was completed with a
196 S2 Picofox instrument from Bruker. The air-cooled spectrometer is equipped with a metal
197 ceramic X-ray tube, a Mo-target and a Ni/C-multilayer monochromator. The tube was operated
198 at 50 kV and 600 μA . The measurement itself was completed with a silicon drift detector (SDD)
199 with a resolution of less than 160 eV and the Spectra processing software. Measurements were
200 repeated twice. Reported values are averages.

201

202 *Instrumental neutron activation analysis (INAA)*

203 A suite of 25 elements was measured by INAA in five of the seven samples considered in this
204 study (Tab. 2). Two hundred milligram of powdered sample material were filled into
205 polyethylene capsules and then irradiated at the University of Mainz TRIGA research reactor
206 with thermal neutrons at 100 kW_{th} . The samples were first irradiated in the pneumatic system
207 of the TRIGA Mainz research reactor in a neutron flux of $1.7\text{e}12 \text{ n/cm}^2 \text{ s}$ for 1 min to detect the
208 isotopes with relatively short half-lives (electronic supplement). Three measurements were
209 taken: one immediately after irradiation, a second after about 5 min decay and a third one after

210 ~20 min decay. For isotopes with longer half-lives a second irradiation was performed in the
211 carousel facility for 6h at 0.7×10^{12} n/cm²s. The samples were measured after a week and a month
212 of cooling time. A Ti and Fe standard was measured together with the samples as flux monitor
213 for the pneumatic and carousel measurements.

214 Samples from the carousel were measured with a high purity germanium detector in 7 cm
215 distance to the detector with less than 3 % dead time. The short-lived isotopes were measured
216 with a high purity germanium detector (HP-Ge) equipped with a loss-free-counting system (LFC,
217 Westphal, 2008) at a distance of 9 and 19 cm to the detector. The measurements were
218 performed and analyzed using the Genie 2000 software, version 3.2 (Copyright Canberra
219 Industries Inc., 2009). Elemental contents were determined relative to single element standards
220 which were irradiated and counted under the same conditions. The measurement uncertainty
221 of the element concentrations were determined based on the relative peak area uncertainty.

222 The Mo concentration was measured by INAA using the 739 keV line of the isotope ⁹⁹Mo after a
223 week of cooling time. Mo has an increased uncertainty of up to 12 % due to increased peak area
224 uncertainty. The aluminum concentration was calculated from the ²⁸Al activation product.

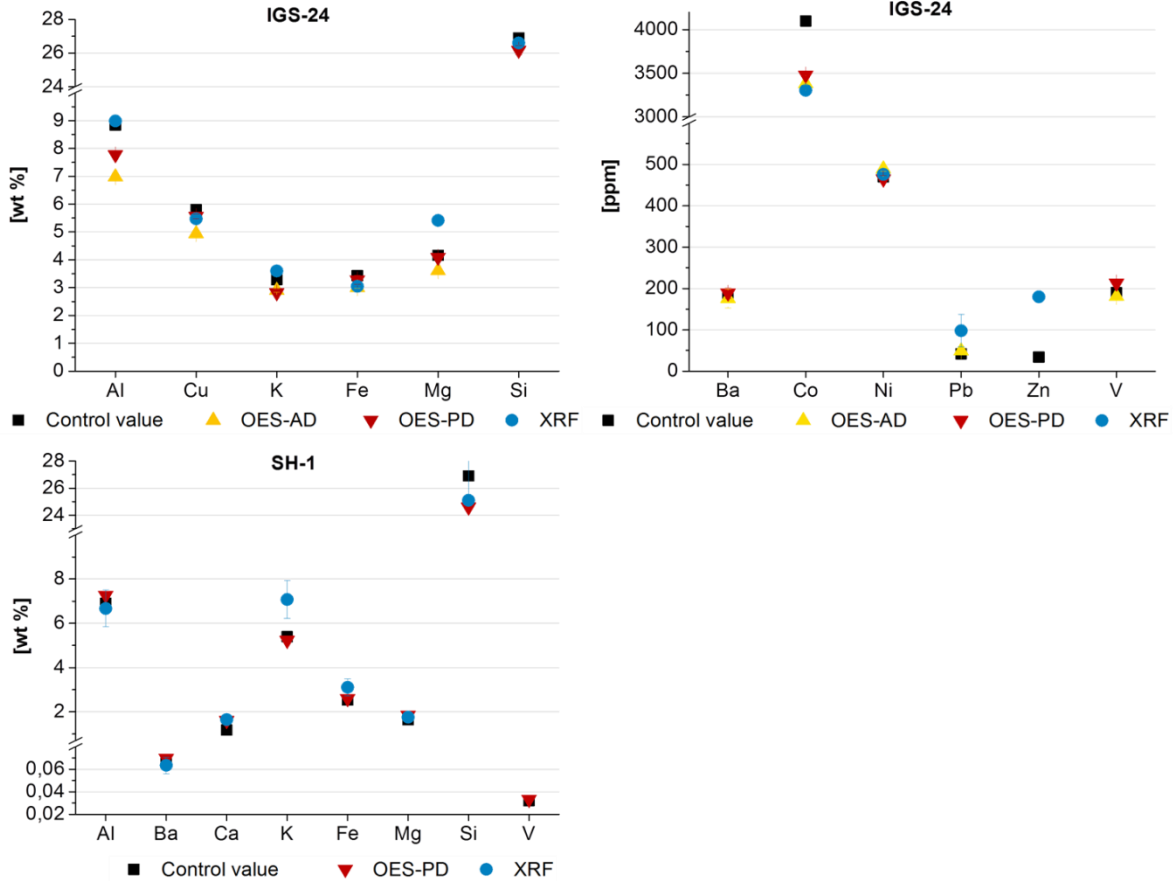
225 Measurement of a Si standard determined that 1.2 % ²⁸Al is formed in the activation of 100% Si.
226 The average Si content of about 13 wt% in the samples corresponds to an error of 0.1 wt% that
227 was deduced from the calculated Al concentration. Only low or no activity of isotope ³¹Si could
228 be found to determine the Si concentration in the samples by INAA, due to low gamma-ray
229 intensities and the low neutron capture cross section ($\approx 0.07\%$) of ³¹Si. Calculation of Si
230 concentrations based on ²⁹Al did not yield realistic results that could be related to the observed
231 mineralogical composition. To have an alternative estimate of the realistic Si content, Si within

232 the samples was calculated based on quantitative XRD measurements of quartz, clay minerals
233 and feldspar (Tab. 3, Fig. 4).

234

235 **Results obtained for reference materials**

236 IGS-24 was used primarily to compare the performance of the acid (AD) and peroxide digestion
237 (PD) process as applied to a Cu- and Si-rich sample material. Si and Cu were determined with a
238 high accuracy by both OES-PD and XRF. OES-AD underestimated the Cu content by about 14 %.
239 Peroxide digestion had an overall higher accuracy with an average deviation of only 6.5 and 7.7
240 % in major and trace elements compared to 14.7 and 11.9% in acid digested samples measured
241 by ICP-OES (Fig. 2). In particular, Al, Co, and Ni could be detected with a lower deviation to the
242 standard. Co was underestimated with all three techniques, whereby OES-PD showed the best
243 performance. SH-1 (Fig. 2) was digested with peroxide to test specifically the suitability of this
244 procedure for black shales. No results regarding the base metals are available, since their
245 concentration in this reference sample is below the detection limit of the analytical methods
246 used. OES-PD has an average deviation from the in-house standard by 5.9 %, while XRF has an
247 increased deviation from the standard of 13 %. Both OES-PD and XRF underestimated the Si
248 content by about 8%. Results with high accuracy (< 5 % deviation) were obtained for Al, Ba, Fe,
249 Mg, and V using OES-PD.



250
 251 *Figure 2: Illustration of element concentrations determined by OES-AD, OES-PD, and XRF in IGS-*
 252 *24 and SH-1*

253
 254
 255 **Assessment of analytical data**

256 The number of elements contained in significant concentrations the Kupferschiefer and the
 257 number of methods used in this study does not allow a full presentation of the collected data.
 258 The complete data set can, however, be found in the electronic supplement. Data gathered by
 259 INAA serves as reference to judge the accuracy of the tested analytical techniques in the
 260 absence of a suitable reference material. The relative deviation of the analytical results to the
 261 ones determined by INAA is expressed in %. In most diagrams, the error bars of the INAA
 262 measurements are not visible since they usually range within 5 %.

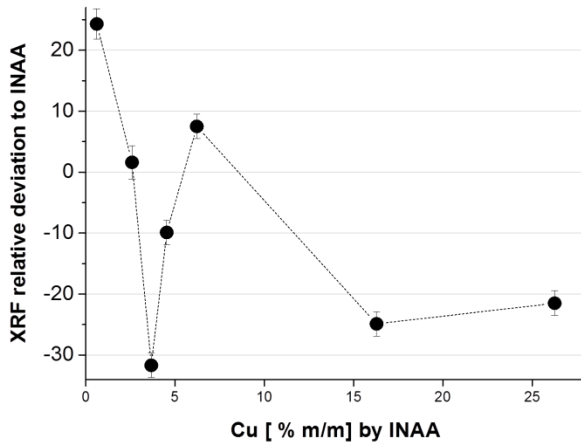
263 This study illustrates the difficulties and pitfalls of various analytic methods suffering from the
 264 Kupferschiefer black shale's complexity. An overview of technique-specific sources of error,
 265 their occurrence and influence on the applied technique is given in table 4 and addressed
 266 individually in the following section.

267
 268 *Table 4: Overview of major sources of error in the measurements of different analytical*
 269 *techniques*
 270

Error source	OES-AD	OES-PD	XRF	TXRF
Pre-treatment	Low recuperation of Al, Cu, Co, Ni, Si, As, C _{org}	Incomplete digestion (Si, Al, Co, Ni) Loss of Ag	-	Digestion (see AD and PD)
Measurement	-	Matrix effects (Na) High detection limits	Matrix effects (sulfides)	Low energy resolution (full peak overlaps)
Processing	-	-	Correction with secondary data from CNS and XRD	Strong peak overlap (including internal standard)

271
 272 *Base metal concentrations*
 273 The Cu content was successfully measured in all samples using INAA. The copper concentration
 274 was extrapolated from the ⁶⁶Cu isotope activity in samples taken from the pneumatic tube after
 275 1-minute irradiation and generally about 6 to 15 minutes decay. ⁶⁶Cu was chosen for the
 276 calculation of the Cu concentration based on the large peak to background ratio and high
 277 neutron cross section. The samples carry diverse but overall high Cu concentrations ranging
 278 from 0.6 to 26 wt% (Fig. 4). Measurements of Cu by ICP-OES, XRF, and TXRF show a large spread
 279 of results (Fig. 4). The largest mismatch was found in TXRF data that underestimated the Cu
 280 concentration in the Kupferschiefer samples vastly (ca. 37 % relative) compared to INAA data.

281 The XRF results deviate in individual measurements by a range of 2 to 25 % from INAA. While
282 the results indicate clearly that high Cu concentrations are underestimated, low concentrations
283 can also be overestimated (Fig. 3).



284

285 *Figure 3: Relationship between Cu concentration determined by INAA and relative deviation of*
286 *WD-XRF results*
287

288 Best and most consistent results were delivered by ICP-OES analyses of AD and PD samples with
289 a relative deviation from INAA results of only 5 %. About 5 % higher Cu concentrations were
290 measured in PD samples compared to AD. Lower concentrations of Cu in AD samples are
291 attributed to incomplete digestion of organic matter compared to PD. Systematic
292 overestimation of Cu content due to the Na-rich PD solution by ICP-OES, could be disproven by
293 the measurements of IGS-24 where instead only a minor underestimation by 4.1% was
294 detected.

295 Zn concentrations range from tens of ppm to weight percent in the studied sample suite. The
296 available Zn-INAA data supports the accuracy of OES results with an average deviation of only 7
297 % (Fig. 4). The average deviation of OES-AD from INAA is slightly increased relative to OES-PD
298 due to the larger error associated with the measurement of smaller Zn concentrations. The Zn

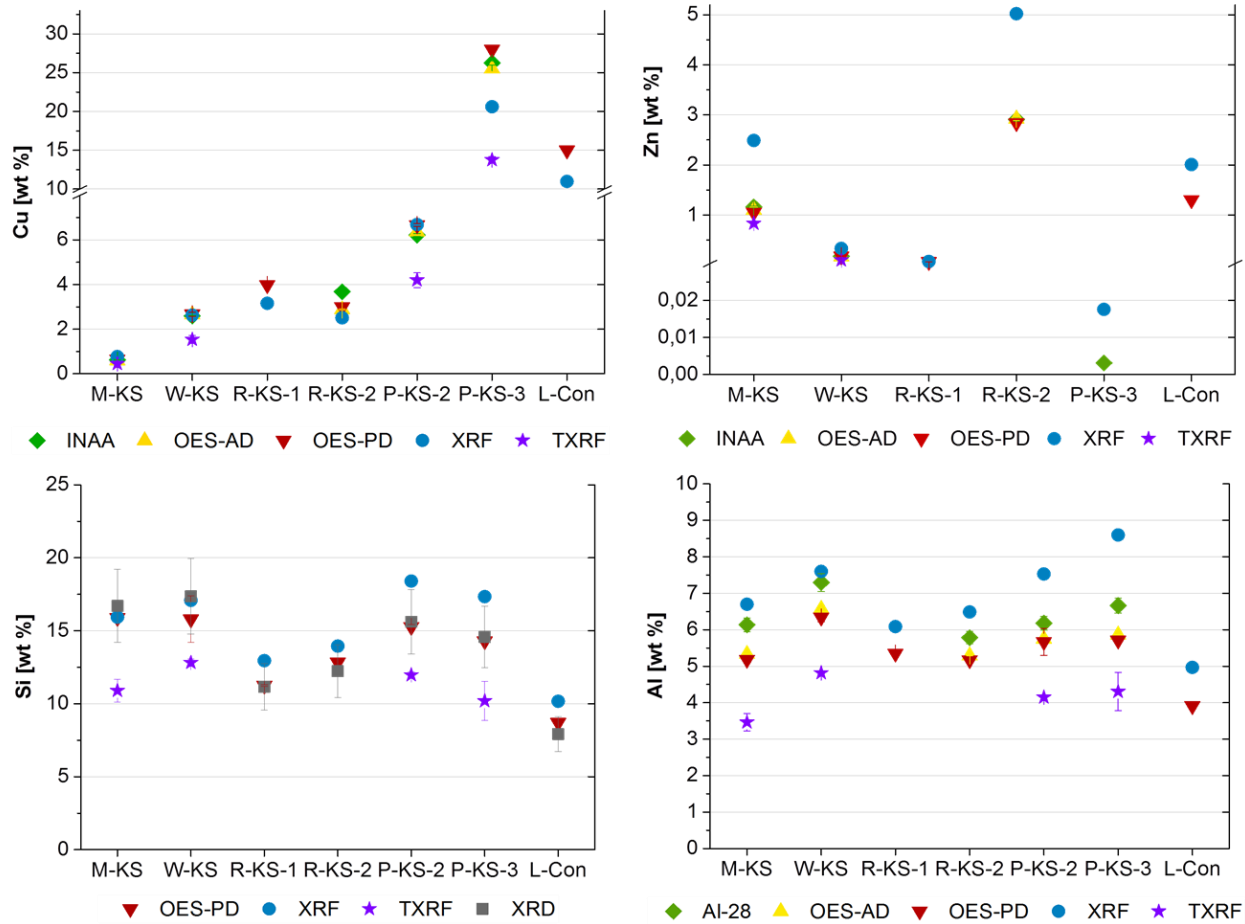
299 detection limit of OES-AD and PD is below 30 ppm and 100 ppm, respectively. The primary
300 cause for high detection limits associated with OES-PD appears to be the plasma condition that
301 is directly influenced by the matrix components (Kragten and Parczewski, 1981; Olesik, 1991).
302 Especially the addition of large quantities of Na to the flame increases the background in the
303 ICP-OES continuum by recombination of ionized Na^+ and electrons (Olesik, 1991; Taylor, 2001;
304 Hug, 2011; Harris, 2014, 2014). To circumvent this issue, a higher degree of dilution is required,
305 lowering the detection limit (Hill, 2007), but also with the advantage of lowering the slightly
306 increased viscosity in PD solutions caused by the high salt content. No clogging issues were
307 observed in this study, but they can occur and should be considered (Boulyga et al., 2004).

308

309 *Silicate-bound major element concentrations*

310 Si cannot be measured in AD solutions, since it was expelled as $\text{H}_2\text{SiF}_6/\text{SiF}_4$ in the digestion
311 process (Hill, 2007; Harris, 2014). ICP-OES results of peroxide digested samples appear to
312 underestimate the Si content by an average of 5 % in relation to the values obtained from XRD,
313 whereas a relative overestimation by 9 % is obtained by XRF (Fig. 4). These values are, however,
314 well within the relative estimated error of 15 % of the XRD analysis. The same effect of Si
315 underestimation by OES-PD was observed in the reference measurements SH-1 (-8.6 %) and to a
316 minor degree in IGS-24 (-2.7 % deviation). This is most likely the result of incomplete dissolution
317 of silicates during digestion (Heinrich and Hermann, 1990), despite a visually complete digestion
318 with no noticeable residues or lack of clarity. The same effect is observed for Al with both OES-
319 AD (relative deviation of 10 %) and PD (12 %), as well as in the reference sample IGS-24.

320 TXRF grossly underestimates the Si (28 %) and Al (36 %) concentration. The very variable
321 element composition of Kupferschiefer samples is considered the most likely source for this
322 systematic error. (Klockenkämper and Von Bohlen, 2015) describe in detail the capabilities of
323 TXRF and discuss the limits of energy-dispersive spectroscopy by TXRF. Especially elements in
324 the low energy region (< 10 keV) of EDS spectra (e.g. Al, Si, Fe, Co, Cu, among others) suffer
325 from interferences. The probability of energy line interferences strongly increases in multi-
326 element samples (Klockenkämper und Von Bohlen 2015). The error caused by overlapping peaks
327 is often elevated in energy-dispersive systems in comparison to wavelength dispersive ones,
328 despite the availability of correction programs (Jenkins, 1999). Furthermore, quantification of
329 TXRF results depends strongly on the reliability of the internal standard and is based on a
330 determination of net intensities in each spectrum. Bi and Y were the best possible internal
331 standards, not contained in significant concentrations in the samples themselves. However,
332 both still suffer from peak overlaps especially by Pb, which is contained in significant
333 concentrations (up to 4.5 wt% measured by OES-AD) in the Kupferschiefer samples studied.



334

335 *Figure 4: Illustration of Cu, Zn, Si and Al concentrations determined by INAA (Al from Al28), OES-*
 336 *PD/AD, XRF, TXRF, and XRD (based on calculation of Si content in quartz, sheet silicates and*
 337 *feldspars)*

338

339 *Trace element concentrations*

340 While ICP-OES is commonly used to determine trace element concentrations, it is well known

341 that one has to be cautious with XRF trace element results (Jenkins et al., 1995). The latter is

342 supported by the rather erratic results received from the studied samples (Fig. 5). Generally,

343 XRF overestimates Ag, As, Co, Ni, Mo and V by about 57 %, compared to INAA.

344 The best results for Ag were achieved with ICP-OES of AD samples. OES-AD Ag results deviate by

345 ~15 % from the concentration determined by INAA and generally appear to underestimate the

346 Ag content. The measurement of silver in solution is known to be challenging due to the number
347 of insoluble salts that can be formed (Joerger et al., 2000; Averill and Elderedge, 2006). Ag was
348 expected to precipitate as chloride in the solution created by peroxide digestion because of the
349 addition of hydrochloric acid. This assumption is supported by consistently lower Ag
350 concentrations (about 12%) reported for PD samples analyzed by ICP-OES comparatively to AD
351 measurement solutions. XRF overestimates the Ag content in all but those samples that are
352 most enriched in Cu- and Ag (P-KS-03 and L-KS-Con), by an average of 22 % compared to INAA
353 data. Ag was not determined by TXRF due to interferences caused by Ar within the ambient
354 atmosphere (Klockenkämper and Von Bohlen, 2015).

355 OES-PD and INAA data on As are in good agreement. Deviation is greatest for OES-AD samples,
356 where As is underestimated (W-KS). It is safe to assume that a major fraction of As is lost as
357 volatile oxide during the AD digestion process – whereas it is evidently retained to a greater part
358 during the PD process (Yu et al., 2001; Hill, 2007; Harris, 2014). The results may be further
359 improved by the use of a lid during the caustic fusion. Low As concentrations could not be
360 detected in PD samples due to a detection limit of 140 ppm.

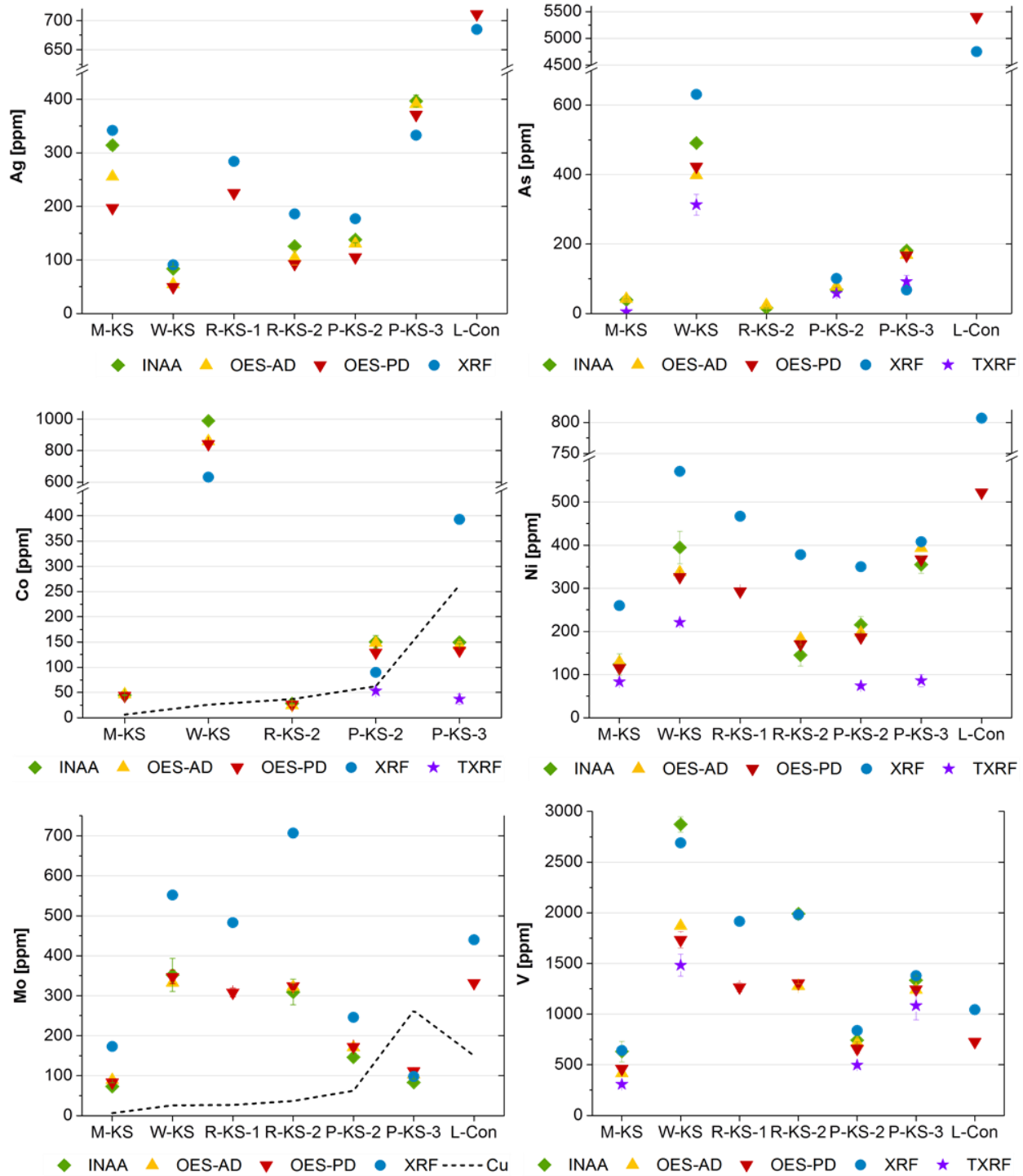
361 Co is underestimated by XRF in contrast to other trace elements with the exception of the Cu-
362 rich sample P-KS-3 where the Co concentration is grossly overestimated compared to INAA data.
363 Co concentrations detected in PD and AD samples measured by OES are very similar to those
364 determined by INAA with an average deviation of -8.5 %. Underestimation of Co was also found
365 in IGS-24 and implies a higher resistance of Co to digestion.

366 OES-AD and PD results for Mo match closely (~3 % deviation). They deviate by about ~11 % from
367 the values determined by INAA, but remain in most cases within the high uncertainty of INAA

368 for Mo. The concentrations measured by XRF are much higher, except in sample P-KS-3 (Fig. 5).
369 The XRF analysis of Mo, Co, and Ni, but also Al, and Si appears to be influenced by the
370 abundance of Cu (eg. P-KS-3, Fig. 4, 5), resulting in over- or underestimation of the respective
371 trace element concentrations. These observations are most likely influenced by matrix effects in
372 the pressed pellets. Such effects have been observed by a number of authors (Spangenberg et
373 al., 1994; Sieber, 2002). While the absorption contrast between the lighter (Si, Al) and heavier
374 elements (Cu, Pb, Zn) is a source of concern, more so are element interactions causing
375 secondary absorption and enhancement reactions (Mainardi et al., 1982; Jenkins et al., 1995;
376 Jenkins, 1999). In extreme cases, secondary fluorescence causing enhancement can account for
377 50% observed emissions (Tertian, 1982).

378 V concentrations measured by XRF closely match the ones determined by INAA, with only a
379 slight average deviation of about 4.9%. ICP-OES detected in all samples considerably lower V
380 concentrations with average deviation of 23 % from the concentrations determined with INAA.

381



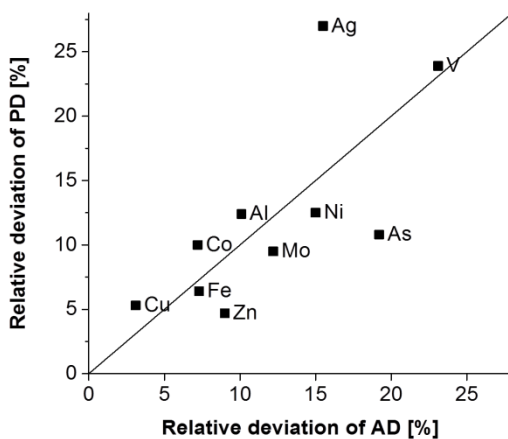
382
 383 *Figure 5: Illustration of trace element (Ag, As, Co, Mo, Ni, V) concentrations determined by INAA,*
 384 *OES-PD, XRF, and TXRF. The dotted line marks the relative copper concentration within the*
 385 *samples based on INAA*
 386

387

388 **Assessment of analytical techniques**

389 *ICP-OES*

390 A comparison of the results collected with ICP-OES and INAA show a high accuracy for the base
391 metals Co, Cu, Ni, Mo, Zn (Fig. 6) as well as for Si and Al. Variations are larger and less
392 consistent for other elements. The volatile As was determined with a relatively high accuracy by
393 OES-PD but deviated stronger in OES-AD measurements. The opposite was observed for Ag. The
394 measurements itself possess a low relative standard deviation (RSD) of less than 0.5 and 5 % at
395 concentrations above and below 1000 ppm respectably.



396

397 *Figure 6: Relative average deviation of OES-AD and PD measurements from INAA*

398

399 In summary it can be said, that both digestion procedures are associated with a lower accuracy
400 than is normally acceptable for ICP-OES, but deliver sufficiently accurate data (if one assumes
401 that an error of below ~15 % relative to INAA is acceptable). Acid digestion allows for a more
402 accurate determination of the silver content but requires the use of hazardous chemicals like HF,
403 especially trained personal, and more time. Sample preparation by PD is much more rapid (10-
404 20 minutes/sample), facilitating a higher sample throughput. This technique can additionally

405 retain higher concentration of volatiles and offers a complete digestion associated with a
406 slightly increased copper concentration. A serious disadvantage is the composition of the
407 matrix, which leads to high detection limits.

408

409 *WD-XRF*

410 WD-XRF measurements of pressed pellets had to be preceded by XRD and TC measurements to
411 determine the type of oxide and sulfide compounds contained in the sample in addition to the
412 total carbon content, increasing the necessary time required for analysis compared to ICP-OES.
413 The results obtained for the light elements (Si and Al) have a high but acceptable deviation of
414 about 15 % for Si and Al compared to the XRD and INAA data. The erratic, often overestimated
415 As, Co, Ni, Mo, Zn and underestimated Cu, Co concentrations, in comparison to results collected
416 by INAA and ICP-OES, are unsatisfactory. Therefore it appears to be advisable to avoid any base
417 metal and trace element measurements in Kupferschiefer by XRF.

418 The results gained with XRF on pressed pellets are not unexpected. They have clear
419 repercussions on the established operative mode to quantify base metal concentrations in
420 Kupferschiefer with XRF-based techniques. Fused glass beads are an alternative option to avoid
421 negative effects associated with pressed pellets. However, established sample preparation
422 procedures cannot be used and a suitable calibration program must be developed to recalculate
423 the original composition of the oxidized sample. A complete oxidation of the sample cannot be
424 achieved by calcination since the sintered material is impossible to remove from any crucible.
425 The subsequent fusion-step within a Pt-crucible using lithium-tetraborate flux should not be
426 attempted due to the composition of the sample material and possible destruction of the Pt-

427 crucible (Bennett and Oliver, 1992; Jenkins et al., 1995; Lupton et al., 1997; Harris, 2014).
428 Kupferschiefer is very reducing and rich in copper, arsenic, silicon and organic carbon. All of
429 these substances are known as platinum poisons that will cause structural disintegration of the
430 platinum crucible (Lupton et al., 1997). Zirconium crucibles were tested as a possible alternative
431 to platinum. They are not affected by the platinum toxins; however, tests showed that their
432 heat conductivity is insufficient to achieve complete fusion. Studies focusing on the analysis of
433 sulfide ores suggest two alternative approaches to fusion (Petin et al., 1985; Loubser and
434 Verryyn, 2008), but have not yet been verified by other authors.

435

436 *TXRF*

437 Analysis of Kupferschiefer suspensions by TXRF did not yield any useful results. All detected
438 elements were vastly underestimated by -20 to -50 % relative to INAA data. This effect could
439 also be observed in trial analysis of AD and PD solutions by TXRF, which resulted in similar
440 underestimation of element concentrations. Sample preparation itself appears therefore to only
441 affect the detection limits but not influence on the accuracy of the data (Klockenkämper and
442 Von Bohlen, 2015). The usefulness of TXRF in bulk geochemical analysis of Kupferschiefer is
443 further limited by the lack of Mo and Ag data and can therefore not be recommended. The
444 same is to be considered for other energy-dispersive XRF measurement systems.

445

446 **Conclusions**

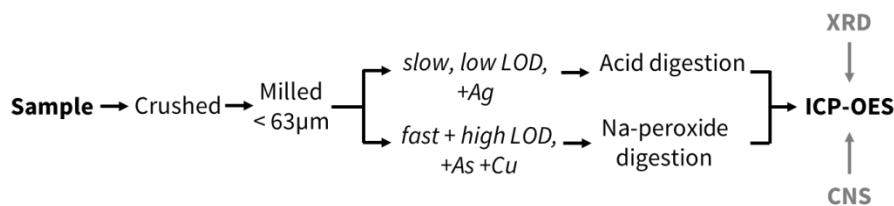
447 A critical assessment of several analytical methods for the bulk analysis of the geochemical
448 composition of mineralized Kupferschiefer illustrates that ICP-OES yields robust data whilst at

449 the same time requiring for a simple and efficient sample preparation process. Nevertheless,
 450 relative deviations relative to INAA reference data were still in the range of 5 to 20 %.

451 Measurements of acid digested (AD) solutions showed overall results with a higher accuracy but
 452 slightly lower Cu concentrations as compared to Na-peroxide digested (PD) solutions. Na-
 453 peroxide digested solutions carry the advantages of a much faster sample preparation and
 454 complete digestion. However, these advantages are offset by losses in Ag and higher detection
 455 limits.

456 In accordance with the results, both acid and peroxide digestion with subsequent ICP-OES
 457 analysis can be recommended for the analysis of Kupferschiefer (Fig. 7). Whilst ICP-OES
 458 measurements and the sample preparation through digestion are more time consuming
 459 compared to the ones used for XRF, the data quality is better and there is no explicit
 460 requirement for additional TC data, mineralogical measurements or data correction.

461 Nonetheless, additional mineralogical data (XRD) or knowledge about the TOC content (CNS) are
 462 recommended to be collected to fully understand the material and identify potential errors.



463

464 *Figure 7: Recommended flow chart for the multi-element analysis of Kupferschiefer (LOD: limit of*
 465 *detection)*
 466

467 For future work there is a vital need for a Kupferschiefer reference material that represents the
 468 complexities of base metal sulfides closely associated with abundant organic matter, with
 469 silicate and carbonate minerals. Availability of such a standard would allow a direct and precise

470 comparison of results generated in different laboratories and to estimate and trace potential
471 discrepancies.

472

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