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1 **Geochemical correlation in an exhumed**
2 **submarine channel complex (Tabernas**
3 **Basin, SE Spain): comparison to**
4 **sedimentological correlation at various**
5 **length-scales**
6

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18

19 **Abstract**

20

21 Whole-rock, inorganic, geochemical data have previously been used to aid characterisation
22 and stratigraphic correlation of fossil-poor clastic sedimentary deposits although this approach
23 has not yet been calibrated by testing chemostratigraphic correlations against physical
24 stratigraphic correlations from outcrop. Chemical data from a well-exposed siliciclastic
25 succession in a Tortonian (Late Miocene) submarine slope channel system in the Tabernas
26 Basin of Southern Spain were generated using X-ray fluorescence supplemented by X-ray
27 diffraction, SEM analysis and light microscopy. Amongst the >60 elements measured nearly
28 a quarter of them have proved to be useful or reliable for geochemically-based correlation at
29 the tested scales (~10m, ~50m, ~100m). These elements are SiO₂, K₂O, Al₂O₃, CaO, and
30 TiO₂, as well as Zr, Nb, Th, Rb, Cs, As, and the Rare Earth Elements; La, Nd, and Ce. High
31 resolution, bed-to-bed geochemical correlation is feasible over short distances (~10m).
32 Geochemical data from sections in beds that are traceable suggest that a given stratigraphic
33 level seems to be geochemically homogeneous with respect to some key elements.
34 Geochemical data also provide a useful aid for high resolution sedimentary correlation, at
35 distances of several tens of meters up to at least 100m. Since each individual bed seems to be
36 broadly homogenous in composition, at a larger scale it is be possible to discern a provenance
37 signal within geochemical data. Chemical stratigraphy thus seems to work even in
38 stratigraphically-complicated submarine channel complexes.

39

40 **Keywords**

41 Sandstone, correlation, geochemistry, sequence stratigraphy, submarine channel system,
42 Tabernas Basin, geochemical correlation, chemostratigraphy

43

44 **1 Introduction**

45

46 Biostratigraphy and sequence stratigraphy, two widely used subsurface correlation techniques,
47 are not always robust, especially in fossil-poor deposits, and alternative tools such as
48 petrography and heavy mineral data, palaeomagnetic data or isotope techniques are required
49 (e.g. Preston et al. 1998; Pearce 1999; Ratcliffe et al. 2004). Chemical stratigraphy provides
50 an objective, quick, and relatively low cost method of performing correlation using whole-
51 rock, inorganic, geochemical data. Variations in geochemical characteristics respond to
52 changes in mineralogy, which in turn are controlled by a number of variables, such as: grain
53 size, origin of sedimentary grains, extent of weathering in the hinterland at the time sediments
54 were being created, geochemical processes in the depositional environment, or even
55 diagenesis after deposition if there has been a net import or export of material at the sample
56 scale (e.g. Taylor & McLennan 1985; McLennan 1989; Dypvik & Harris 2001; Garcia et al.
57 2004). Thus, chemical stratigraphy reflects diagnostic sediment features such as: gross
58 lithology, provenance and sedimentary facies and potentially provides a method for the
59 subdivision and correlation of sedimentary successions.

60

61 Chemostratigraphic techniques have been successfully applied to stratigraphic subdivision
62 and inter-well correlation in a range of published cases (e.g., Ehrenberg and Siring 1992;
63 Racey et al. 1995; Preston et al. 1998; Pearce et al. 1999; Hutchison et al. 2001; Ratcliffe et
64 al. 2004, 2006; Friis et al. 2007). In some cases, the results of chemostratigraphy have proved
65 to be ambiguous due to noisy data and consequent lack of consistent patterns and thus not
66 ideal for stand-alone sedimentary correlation (e.g., Andersson et al. 2004; North et al. 2005).
67 Furthermore, published studies of chemical stratigraphy have tended to lack integration with
68 sedimentological and sequence stratigraphic correlation methods. Published test cases of
69 geochemical correlation compared to sequence stratigraphic or sedimentological

70 interpretation, based on outcrop analyses, are rare. North et al. (2005) examined the validity
71 and limitations of the geochemical approach to high-resolution correlation within fluvial-
72 deltaic successions at the parasequence scale. At the other end of scale, Hussain (2007),
73 attempted to use elemental geochemistry for stratigraphic correlation of two Lower
74 Palaeozoic formations at a distance of over 1250 km.

75
76 The [single](#) objective of the present study was to test the reliability of geochemically-derived
77 stratigraphic correlations against unequivocal physical correlations of sediments in an
78 exhumed Tortonian (Late Miocene) submarine channel system exposed in the Tabernas
79 Basin, SE Spain (Fig. 1, 2a). [Geochemically-derived correlation of wells is typically](#)
80 [performed using cuttings samples meaning that petrographic study to support the geochemical](#)
81 [correlations is typically limited or absent. In some studies detailed heavy mineral population](#)
82 [studies are used to achieve correlation \(e.g. Morton et al., 2005\); this is quite distinct from](#)
83 [geochemical correlation and was not part of this study.](#) Submarine slope channels are major
84 conduits for sediment transport from the hinterland to the deep basin, and typically preserve
85 multiple phases of erosion and filling with axial to margin facies transitions that result in a
86 complicated depositional architecture (e.g. Hodgson et al. 2011; McHargue et al. 2011). Since
87 the detailed applicability, efficiency and resolution of chemical stratigraphic correlations and
88 subdivisions are restricted by the amount of statistical noise in the geochemical signals, this
89 study has investigated bed-scale geochemical variations between physically correlated
90 sections. Geochemical correlations, therefore, have been compared to conventionally-logged
91 and correlated sections at different scales (Fig. 1) to test the application of chemical
92 stratigraphy in the correlation of individual, physically-traceable beds and so address the
93 following specific questions:

94 (1) What elements and element ratios are best for geochemical correlation?

95 (2) What controls the geochemical variations in these sediments?

- 96 (3) Does geochemical stratigraphic correlation work when compared to physical
97 stratigraphic correlations?
- 98 (4) To what degree do geochemical trends follow depositional trends (sedimentary facies
99 and grain size control) and channel axis to channel margin variation, since this
100 potentially reduces the applicability of geochemical data for regional correlation?
- 101 (5) Are there distinct geochemical fingerprints for individual beds that allow identification
102 of marker horizons and correlation of sections over distances of several tens to
103 hundreds of metres in channel downstream and channel axis to channel margin
104 direction?

105

106 **2 Material and Methods**

107

108 2.1 Geology of the investigation area

109

110 The Neogene Tabernas Basin is a small, fault-controlled, intramontane basin resting on the
111 Internal Zone of the Betic Cordillera in SE Spain (Fig. 2a) (Kleverlaan 1987; 1989a; b;
112 Haughton 2000; Pickering et al. 2001; Hodgson 2002; Hodgson and Haughton 2004). It
113 contains a succession of >1 km of predominantly marine sediments in an overall
114 transgressive-regressive succession. The base of the basin-fill comprises Tortonian (Late
115 Miocene) non-marine to shallow-marine conglomerates, which are overlain by deep marine
116 marls with intercalated submarine channel and distributive systems (Kleverlaan 1989a;
117 Pickering et al 2001). Intra-basinal tectonics led to the development of mini-basins and
118 ponded turbidites intercalated with megabeds in the early Messinian (Late Miocene)
119 (Haughton 2000; Hodgson and Haughton 2004). The overlying shallowing upward trend
120 culminates with local deposition of salt associated with the Messinian Salinity Crisis,

121 followed by formation of an unconformity and fan delta deposition during the Pliocene
122 (Kleverlaan 1989a).

123

124 This study focussed on the ‘Solitary Channel’, one of five slope channel complexes of late
125 Tortonian age (Late Miocene) in the Sartenella Formation that are encased in hemipelagic and
126 pelagic bioturbated marlstones with bundles of turbidite beds (Haughton 2000; Pickering et al.
127 2001; Hodgson and Haughton 2004). The trend of the channel complex has been mapped for
128 at least 7 km along the palaeoflow direction, which is, in part, coincident with the course of a
129 post-depositional fault complex (Pickering et al. 2001; Figure 2b). The westerly, more
130 confined, part of the slope channel complex is composed of at least five different stacked
131 channel units (Fig. 3). The channel-fills preserve a typical fill pattern from basal debrites,
132 through inclined turbidites, to intrachannel, bioturbated, fine-grained deposits, which display
133 evidence of channel back-filling (Pickering et al. 2001) and channel sinuosity (Abreu et al.
134 2003). Downslope, to the east, the channel becomes less confined (Pickering et al. 2001).

135

136 The primary sediment of the channel-fill was derived from the metamorphic ridges of the
137 Sierra de los Filabres (higher metamorphic grade Nevádo-Filabride complex) in the north and
138 the Sierra Gador (lower grade Alpujarride complex) in the west (Fig. 2a), which were exposed
139 in the hinterland at that time (Kleverlaan 1989a). The Nevado-Filabride complex consist of:
140 (1) >5 km of monotonous graphitic mica-schists and quartzite of pre-Permian age, locally
141 intruded by Permian granite (Priem et al. 1966); (2) a Permo-Triassic sequence of
142 metamorphosed feldspathic sandstones and carbonates, and (3) an association of metabasic
143 rocks (of late Jurassic age) and serpentinite slivers, marble and calcareous mica schist (of
144 Cretaceous age) (García-Dueñas et al. 1988). The overlying Alpujarride Complex is separated
145 from the Nevaso-Fliabride complex by the Betic Movement Zone (Platt and Vissers 1980),

146 and is composed of Permo-Triassic aluminous phyllite and quartzite, and a thick sequence of
147 middle to late Triassic dolomitised platform carbonates.

148

149 2.2 Sampling strategies

150

151 To study small scale correlations in the submarine slope channel complex using geochemical
152 methods, the erosionally-confined up-stream (westerly) part of the system was chosen (west
153 of the A-92 motorway; Fig. 2b). Here, the channel complex extends for approximately 2 km
154 to the SW from exit 376 of the A-92 motorway, where it passes into the subcrop. In detail, the
155 study area covers outcrops both perpendicular (Rambla Lanujar) and parallel (Campsa) to the
156 palaeoflow direction (Fig. 3).

157

158 [Sampling was systematically undertaken to test the various hypotheses outlined in the](#)
159 [introduction](#). Samples were collected from vertical sections ([pseudo-wells](#)) in order to
160 produce geochemical correlations at a variety of scales for which the conventional
161 stratigraphy was already documented, and traceable in the outcrops. [At some locations, access](#)
162 [and safety limited sample collection but](#) on average the vertical (stratigraphic) sampling
163 density was three samples per metre. [There was no sampling bias by grain size](#). More than
164 300 samples were collected from a total of 20 logged sections. In order to avoid alteration
165 effects due to recent weathering at outcrop, concerted effort was made to collect fresh
166 material.

167

168 Small-scale geochemical correlations have been tested at Campsa (Fig 3a) and in Rambla
169 Lanujar (Fig. 3b-d) on sections 10 to 15 m apart, by the sampling of individual beds that are
170 physically traceable from one section to the next. Sampling happened, as far as practically
171 possible, at the same vertical position in the same bed. Larger scale correlations within

172 individual sedimentary units have been tested in Rambla Lanujar (Fig. 3b, d) by sampling of
173 sections within lithostratigraphically-correlateble packages at distances over several tens to
174 hundred metres.

175 Samples were between 100 g and 250 g in order to adequately sample different lithoclasts. In
176 conglomerates with lithoclast sizes exceeding granule to small pebble grain sizes, only the
177 sand to granule sized matrix was sampled in order to avoid significant dilution effects by
178 individual large lithoclasts.

179

180 2.3 Analytical techniques

181

182 Elemental analysis for chemical stratigraphy was carried out using energy dispersive X-ray
183 fluorescence analysis (ED-XRF). This methodology was favoured due to its high precision
184 and accuracy and its simultaneous analysis of a wide range of elements. The samples were
185 crushed to a fine powder in a tungsten carbide ball mill. Approximately 12g was sub-sampled
186 from each sample. This was then mixed with a wax binding agent that is inert to X-rays and
187 pressed in an aluminium holder, forming a pellet. The analyses were performed using a batch
188 process on a Panalytical Epsilon-5 ED-XRF modified to perform a multi-element scan using a
189 22 minute analytical program per sample. Sixty one elements were analysed, including ten
190 major oxides (SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅ and MnO), all
191 expressed as a weight percent (wt%). In addition, 33 trace elements (Ag, As, Ba, Bi, Cd, Co,
192 Cr, Cs, Cu, Ge, Hf, Hg, In, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Tl, U, V, W,
193 Y, Zn and Zr), 14 Rare Earth Elements (REEs; La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,
194 Tm, Yb and Lu), and the halogens, Cl, Br and I, plus sulphur (S), have been determined with
195 results reported in mg/kg (~ppm). The elements S, Cl, Br, Sr, B, Ag and Bi have been
196 excluded from interpretation due to being [at or below](#) detection levels in most samples.

197

198 All elements analysed by XRF have been calibrated to 25 international standards. As part of
199 the instrument calibration, X-ray intensity was plotted against concentration for each element
200 in each standard, and a relationship determined (generally this is a straight line with an R^2
201 >0.9). The precision of a given reading varies according to the specific element and
202 concentration. As a general rule, precision is estimated to be better than within 10% for all
203 elements.

204

205 Various correlations were attempted starting with simple element and mineral concentration
206 diagrams, and then moving on to a variety of element ratios and indices. Given the vast
207 number of elements analysed there are a very wide number of element ratio options to plot as
208 a function of depth. In this paper we have chosen the concentration and ratio data that best
209 highlight the correlations. To that end, we have here plotted the major minerals and oxide
210 concentrations and the following ratios and indices as a function of depth and compared these
211 to the physically-correlated stratigraphy: TiO_2/Zr , $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$, $\text{Al}_2\text{O}_3/\text{TiO}_2$,
212 $(\text{CaO}+\text{Na}_2\text{O})/\text{K}_2\text{O}$.

213

214 In order to integrate geochemical data with mineral concentration data, X-ray diffraction
215 analysis (XRD) was performed using a Panalytical X pert Pro XRD instrument. A copper X-
216 ray tube operated at 40kV and 40mA was used. Powder samples were loaded into cavity
217 holders and rotated continuously during the scan, completing one rotation every 2 seconds.
218 Programmable anti-scatter slits and a fixed mask maintained an irradiated sample area of
219 10x15mm, with an additional 2° incident beam antiscatter slit producing a flat background in
220 raw data from 3.60° . Scans covered the 2θ range of $3.66-70.00^\circ$ over a scan time of 44
221 minutes and 26 seconds, with 0.02 Rad Soller slits in both the incident and diffracted beam
222 paths. The X'Celerator detector was set to scan in continuous mode with full length (2.122°)
223 active and pulse-height discrimination levels set to 45-80% with a nickel filter employed.

224 "HighScore Plus®" analysis software and automated Rietveld refinement methods were used
225 with reference patterns from the International Centre for Diffraction Data, Powder Diffraction
226 File-2, Release 2008. [XRD mineral quantity data were quantified using the reference](#)
227 [intensity ratio technique \(Hillier 2003\).](#)

228

229 For petrographic purposes, a subset of 18 samples was studied by thin section analyses using
230 transmitted, polarised light optical microscopy, backscattered electron microscopy (BSEM)
231 and secondary X-ray analysis (EDAX) using a Philips XL30 scanning electron microscope.

232

233 **3 Results**

234

235 3.1 Sedimentary facies

236

237 The sedimentary facies of channel axes are dominated by matrix-supported sandy
238 conglomerates and medium- to very coarse-grained sandstone beds, generally <1-m-thick
239 (locally bioclastic). The sediments were deposited by debris flows and high concentration
240 turbidity currents (Haughton 2000; Pickering et al. 2001). Also, clast-supported cobble-grade
241 conglomerates are present, interpreted to represent channel lag deposits from high-
242 concentration sediment gravity flows. The sandstones and conglomerates are predominantly
243 texturally immature, sharp-based, weakly normally graded, and locally bioturbated.

244 Amalgamation surfaces, indicated by muddy and sandy rip-up clast horizons, are common.

245 Intra-channel thin-bedded marly siltstones and mudstones are preserved towards channel
246 margins (Haughton 2000; Pickering et al. 2001; Abreu et al. 2003), although locally marly
247 silt-prone beds are also interbedded with sandstones and conglomerates in off-axis settings.

248 The siltstones, together with thin-bedded (cm-scale), finer-grained sandstones, were deposited
249 as low density turbidity currents.

250

251 3.2 Sedimentary petrography

252

253 The sandstone samples are poorly- to moderately-sorted litharenites (Fig. 4a, b). The main
254 detrital components are quartz, fossil fragments (mainly foraminifers, shell fragments),
255 metamorphic lithoclasts (mica schists, quartzites, quartz chlorite schists, and quartzite
256 schists), micas (muscovite together with some paragonite and extensively chloritised biotite),
257 chlorite (greenish chlorite flakes, plus chlorite that has replaced biotite with anomalous blue
258 interference colour of chlorite suggesting a Fe-rich specimen). Transparent accessory minerals
259 (mainly heavy minerals) generally make up less than 1 % of the petrographic composition.
260 They are composed of brownish and euhedral tourmaline, colourless and subrounded zircon,
261 colourless monazite, colourless Ca-Fe-rich garnet, brownish and subrounded rutile, and
262 apatite (with garnet and tourmaline dominating). Broadly, the accessory minerals are
263 uniformly distributed throughout the sandstones either as detrital framework grains or, in the
264 case of zircon and tourmaline, additionally in lithic clasts. The opaque mineral assemblage
265 (≤ 3 %) consists of Ti-oxides, some with traces of Fe. The opaque Ti-(Fe)oxide grains show
266 subhedral shapes and patchy Ti and Fe distribution (most likely former ilmenite altered to
267 TiO₂ minerals, Pe-Piper et al. 2011). Also, skeletal shapes and trellis-like structures occur,
268 which suggest secondary, authigenic TiO₂ formation (Pe-Piper et al. 2011). The sandstones
269 contain a negligible quantity of detrital matrix. Locally, intensely deformed, weak lithoclasts
270 have created pseudomatrix especially in the coarser grained sandstones (e.g. Worden et al.
271 2000). Diagenetic features also include trace quartz cement overgrowths and the ubiquitous
272 occurrence of calcite cement (5 to >20%).

273

274 The fine-grained samples (siltstones and mudstones) are poorly-sorted and contain mica
275 (predominantly muscovite) and chlorite dominating over quartz and fossil fragments (mainly

276 pelagic foraminifers, shell fragments). Accessory phases are zircon, garnet, apatite, Fe oxides
277 (in part these are haematite pseudomorphs that have replaced framboidal pyrite), and [trace](#)
278 [quantities of pyrite only found in the finest-grained samples](#) (Fig. 4c).

279

280 A few samples are calcarenitic turbidites composed of well-sorted, sand-sized, siliciclastic
281 (quartz, sparse lithoclasts, glauconite) and calcareous detritus (pellet-like micrite fragments,
282 other carbonate intraclasts, bioclasts (pelagic and benthic foraminifers, shell fragments),
283 sparitic recrystallised detritus), some mixed siliciclastic-micritic matrix and sparitic carbonate
284 cement.

285

286 3.3 Bulk geochemical and mineralogy data

287

288 The geochemical data from XRF analysis are presented as Table 1. XRD bulk mineralogy
289 data are listed in Table 2. The main minerals present include quartz, muscovite, minor
290 paragonite, chlorite, traces of biotite, calcite and minor dolomite, and locally a small quantity
291 of kaolinite. These geochemical and mineralogical data will now be presented in terms of the
292 stratigraphic context.

293

294 3.4 Small-scale (10m correlation) application: individual beds

295

296 Small-scale correlations have been tested in three different outcrops by sampling vertical
297 sections within laterally-traceable turbidite beds in down-dip directions, and from channel-
298 axis to channel-margin settings (see Figs. 3, 5). Of the >60 elements measured by ED-XRF, a
299 relatively limited number proved to be useful in stratigraphic correlation, showing identical
300 trends and similar concentrations in traceable beds.

301

302 3.4.1 Major element data

303

304 Amongst the major elements, silicon and potassium, and to a lesser extent aluminium and
305 calcium, proved useful for correlation purposes. The element concentration data of nearly 140
306 from 158 samples of the sections in Figure 5, together with XRD mineral data, are plotted
307 against bed number in Figure 6. The good bed-to-bed correlations of SiO_2 and K_2O are
308 apparently related to the concentration of quartz and muscovite respectively (Fig. 6). Al_2O_3
309 roughly follows the K_2O trend. CaO shows good correlation with calcite.

310

311 Bivariate plots illustrate the linkage between major element data and major host mineral
312 concentrations including all samples considered in this study (>300 samples) (Fig. 7). Scatter
313 indicates that individual elements are not exclusively hosted within one mineral. The good
314 correlation of silica and quartz (Fig. 7a) confirms that the majority of silica is provided by
315 quartz. Alumina concentrations are generally linked to the phyllosilicate fraction although
316 they show some variation with individual phyllosilicate minerals (Fig. 7b). Within the
317 analysed samples major alumina sources are mica (muscovite, paragonite, biotite), and
318 chlorite. The good potassium-muscovite correlation (Fig. 7c) confirms that the main
319 potassium-supplying mineral is muscovite. Calcium concentrations show a distinct
320 relationship to calcite abundance (Fig. 7d), although minor dolomite is also present.

321

322 Within the bed-to-bed plots of XRF-defined element concentrations and XRD-defined
323 mineral quantities, there are stratigraphic trend-breaks that can be linked to major changes in
324 lithology (Fig. 6). K_2O , muscovite and Al_2O_3 have their highest concentrations in the finest
325 grained beds. Conversely, SiO_2 and quartz are enriched in the sandy lithologies. However,
326 pebbly sandstones show intermediate concentrations for K_2O , muscovite and Al_2O_3 and SiO_2
327 and quartz, reflecting the more lithic content of these sediments (Fig. 8). CaO and calcite

328 reveal a more complicated pattern, having the lowest concentrations in the very coarse-
329 grained sandstone beds and in the interbedded mudstone horizons, but having higher
330 concentrations in medium-grained packages and their associated mudstones.

331

332 SiO_2 and Al_2O_3 concentrations largely reflect grain-size. Al_2O_3 -rich units are phyllosilicate-
333 rich fine-grained lithologies and SiO_2 -rich units are sand-rich. There is a negative correlation
334 between Al_2O_3 and SiO_2 ($R = -0.46$) which suggests a sandstone-mudstone mixing trend.

335 However, dilution by carbonate may blur this trend. Reappraisal of the data set renormalised
336 to 0% CaO thus leads to a much stronger correlation ($R = -0.92$) (Fig. 9). However, the very
337 coarse-grained sandstones and sandy conglomerates exhibit intermediate concentrations in
338 this mixing trend (Fig. 9), again reflecting the more lithic content of these sediments

339

340 3.4.2 Trace element data

341

342 The trace element bed-to-bed correlations are best for are TiO_2 , Nb, Zr and Th (and Hf to
343 lesser extent) (Fig. 10). In a bivariate plot, Nb exhibits a strong positive correlation with TiO_2
344 ($R = 0.93$, Fig. 11a), both being more abundant in sand- than silt-size fractions. Although Th
345 follows the Zr-stratigraphic variation (Fig. 10), these two elements display a rather poor
346 mutual correlation (Fig. 11b), although both tend to be more abundant in siltstones than
347 sandstones. TiO_2 and Zr do not exhibit a simple relationship suggesting that abundances of
348 titaniferous minerals and zirconium bearing minerals do not co-vary, and that they are
349 concentrated in different grain size fractions (Fig. 11c). TiO_2 uniformly has the lowest
350 concentrations in the finest grained beds (sandy siltstones) and highest abundances in sandy
351 horizons, with preferential enrichment in medium to coarse sand size fractions (Fig. 8). The
352 highest Zr abundances seem to be preferentially associated with sandy siltstones and fine-
353 grained sandstones, but they also occur in medium- and coarse-grained beds (Fig. 8).

354 Normalisation of both TiO_2 and Zr to Al_2O_3 excludes the influence of CaO dilution (Fig. 11d).
355 The resulting triangular distribution is typically observed for elements whose abundances are
356 not exclusively explained by sand-silt mixing trends (Garcia et al. 2004). The trends can be
357 explained as mixing lines between different compositional end members: (1) Al-rich siltstones
358 and sandstones with low normalised Zr- and TiO_2 -concentrations, (2) Al-poor sandstones with
359 a relative TiO_2 -enrichment compared to Zr, and (3) Al-poor sandstones with a relative Zr-
360 enrichment compared to TiO_2 .

361

362 TiO_2 is characteristically found in heavy minerals such as rutile, anatase, brookite, ilmenite,
363 titanomagnetite, titanite. [Diagenetic alteration of Ti-minerals is possible \(Pe-Piper et al. 2011\)](#)
364 [but the solubility of Ti is so low that it is unlikely to have undergone any degree of](#)
365 [metasomatism. Bulk Ti concentrations thus likely reflect the initial sediment's Ti](#)
366 [concentration and can safely be used for correlation purposes despite Ti-mineral diagenetic](#)
367 [reactions.](#) Zr is typically associated with zircon. Whole-rock Zr concentrations are considered
368 to provide a good measure of the zircon abundance in sediments (Preston et al. 1998). From
369 thin section analysis (light microscopy, BSEM and EDAX) TiO_2 occurrence in the sandstones
370 can be assigned to detrital rutile grains (negligible to trace amounts) as well as to the opaque
371 fraction (<3 %), which is entirely composed of detrital and authigenic Ti-oxides (most likely
372 former ilmenite altered to TiO_2 minerals). EDAX analyses of the mica have confirmed the
373 occurrence of some TiO_2 in the mica. The strong positive correlation between Nb and TiO_2
374 (Fig. 11a) suggests that Nb is present as a trace element in detrital Ti-rich minerals. Thorium
375 shows some covariation with Zr (Fig. 10) implying that it must occur either within zircon or is
376 within minerals co-deposited with zircon (Fig. 11b).

377

378 A few further elements also provided good bed-to-bed correlation (Fig. 12), including Rb, Cs,
379 and arsenic and the Rare Earth Elements; La, Ce, and Nd.

380

381 It is likely that zircon is the dominant host mineral for the REEs in the samples since they
382 correlate with Zr (Figs. 12 1). Furthermore, the REEs could be linked with heavy minerals in
383 the same grain size range as zircon and, for example monazite. The low abundances of REEs
384 in sand fractions can be generally attributed to dilution by quartz. Clay minerals can also have
385 relatively high REE concentrations (Taylor and McLennan 1985; McLennan 1989), so REE
386 enrichment in the mudstones (Fig. 12) may indicate that they sit directly in phyllosilicates.

387

388 In the vertical sections (Fig. 12) increasing arsenic abundances are linked to siltstone and
389 mudstone beds, where [trace quantities of altered pyrite](#) and Fe oxides have been detected
390 during SEM examination, and which contain abundant mica minerals (Fig. 6). There is
391 negligible correlation of arsenic with bulk iron concentrations ($R = 0.23$) despite the reported
392 association of As with diagenetically-reduced Fe-compounds and sulphides, such as pyrite
393 (Belzile and Lebel 1986; Moore et al. 1988; Thomson et al. 1998; Bodin et al. 2007).

394 However, pyrite is only a [trace mineral \(predominantly below detection in most samples\)](#) and
395 Fe is also present in many other minerals (e.g. chlorite, biotite, garnet, Ti-Fe-oxides). The
396 weak positive correlation with both Al_2O_3 ($R = 0.53$) and K_2O ($R = 0.50$) thus only implies a
397 linkage of arsenic to silty and muddy sediments (perhaps adsorbed on phyllosilicates;
398 Seddique et al. 2008).

399

400 Rubidium seems to be closely associated with K_2O , since it can substitute for potassium in
401 minerals such as alkali feldspars and micas. The good linear correlation of Rb with K_2O (Fig.
402 13a) suggests it is primarily linked to micas, Cs also follows the rubidium trend implying it is
403 also present in micaceous minerals (Fig. 13b). However, in cross plots K_2O , Rb, and Cs data
404 are distributed in triangles implying addition of two distinct alkaline element-bearing
405 minerals. A possible explanation is the confirmed presence of more than one K-bearing mica

406 beside muscovites (paragonite) that has a different K/Rb and Cs/Rb ratios to muscovite. The
407 siltstone samples have the highest K₂O, Rb and Cs concentrations. The positive correlation of
408 Cs with K₂O (and Rb) in sandstone samples probably reflects the mica content in lithoclasts
409 and discrete mica flakes.

410

411 3.5 Meso-scale application (50-100m correlation): sedimentological units

412

413 Meso-scale correlations have been tested by comparing sections of different outcrops, which
414 represent the same stratigraphic level. At these scales it is not feasible to directly trace
415 individual beds due to outcrop discontinuity. Lithostratigraphic correlation has been used for
416 comparison with chemostratigraphic variations.

417

418 In the first meso-scale case study (Rambla Lanujar; Figs. 3, 14), two sections (LNI, LN-G)
419 with similar sedimentary successions and at a distance of about 50 m in the channel down-dip
420 direction have been compared, based on the recognition of stratigraphically-traceable
421 sedimentological trends in the outcrop (Fig. 14a, units 1-5) with unit 5 at the base and unit 1
422 at the top of the succession. In stratigraphic order (unit 5) sandy pebbly conglomerates (unit
423 4) laminated medium-grained sandstones interbedded with siltstones (unit 3) dominantly thin-
424 bedded siltstones, (unit 2) laminated medium-grained sandstones interbedded with siltstones
425 and (unit 1) massive coarse to very coarse sandstone beds with interbedded siltstones. The
426 dominant mineralogy and corresponding major elements follow these lithological trends, with
427 elevated quartz and SiO₂ concentrations generally occurring in sand-prone units, elevated
428 mica and K₂O concentrations in the silt-prone packages. In very coarse-grained sandstones
429 and sandy conglomerates, quartz, SiO₂, mica and K₂O show intermediate abundances. These
430 trends allow the geochemical identification, characterisation and tracing of the major
431 lithological units (Fig. 14a, units 1-5).

432

433 Secondary trends of both individual major and trace elements and element ratios additionally
434 allow subdivision of the major lithological units into geochemically-defined, traceable sub-
435 units (Fig. 14a, subunits a-e). These sub-units are based on vertical trends (upward increasing
436 or decreasing element abundances and ratios), and marker horizons indicated by significant
437 depletions or enrichments of individual elements compared to the same lithologies, e.g.:

- 438 - Compositionally very mature sandstone beds with distinct K_2O , Al_2O_3 , muscovite and
439 Rb depletion, SiO_2 , quartz and TiO_2 enrichment, very high SiO_2/Al_2O_3 and low
440 Al_2O_3/TiO_2 ratios (e.g. base of 2a, subunit 4c, base of 4e),
- 441 - Siltstones with distinct K_2O , Al_2O_3 , muscovite, Rb and some Zr enrichment (e.g., top
442 of 2a, in 4b, 4d),
- 443 - Siltstones with distinct CaO and carbonate enrichment (e.g., upper part of 3).

444 In order to mimic drill cuttings in the way they are produced and collected during oil
445 exploration and field appraisal, and to reduce grain-size related noise the dataset was
446 recalculated using a moving average of three samples (Fig. 14b, c). The correlatable patterns
447 identified in Figure 14a are more obvious with the moving average approach and the
448 geochemically based subdivisions are more pronounced. The lithostratigraphic unit 4
449 represents a very good example. Individual, chemically-defined sub-packages (4a-e) can be
450 traced between both sections by distinct enrichments or depletions of individual elements or
451 minerals, or increasing and decreasing element ratios, respectively.

452

453 A second meso-scale case study, also at Rambla Lanujar (Figs. 3, 15), was undertaken using
454 two sections (LN-G-IV, LSIV) also at a distance of about 50 m. As in the previous case
455 (Figs. 14a-c), both sections have a similar depositional trend, but show some variability in
456 lithological composition (Fig. 15). Furthermore, section LN-G-IV lacks vertical continuity
457 related to the outcrop situation. Using a recalculated dataset based on a moving average of

458 three samples, nevertheless a reasonable geochemical correlation is possible, based on the
459 recognition of traceable major lithologies and geochemical trends :

- 460 - the basal coarse clastics (lithostratigraphic unit 4) display high SiO₂, K₂O, and TiO₂
461 contents, and Zr enrichments at the top,
- 462 - lithostratigraphic unit 3 is characterised by decreasing SiO₂, K₂O, and Zr contents,
463 increasing CaO content, chemical maturity ($\log_{10}[\text{SiO}_2/\text{Al}_2\text{O}_3]$), $\log_{10}(\text{Fe}_2\text{O}_3/\text{K}_2\text{O})$ and
464 TiO₂/Zr ratios as well as decreasing Al₂O₃/TiO₂ ratios in the lower part (chemical
465 subunit b) and reverse trends in the upper part (subunit a),
- 466 - lithostratigraphic unit 2 comprises a mud-dominated part of the section LSIV that is
467 not accessible in section LN-G-IV, but displays low SiO₂, K₂O and TiO₂ contents, low
468 TiO₂/Zr ratios and chemical maturity, high CaO contents and high Al₂O₃/TiO₂ ratios,
- 469 - lithostratigraphic unit 1 reflects channel reactivation represented by sand-dominated
470 deposits, which show increasing SiO₂, TiO₂ and Zr contents and TiO₂/Zr ratios;
471 however other elements and ratios display large variability, although the K₂O and
472 reverse CaO trend could warrant further chemical based subdivision.

473

474 Two additional case studies at Rambla Lanujar considered sections at distances of up to 100
475 m perpendicular to the palaeoflow direction (Fig. 3, 16). As for Figures 14b-c and 15 the
476 geochemical dataset was recalculated based on an moving average of three samples. The first
477 example (sections LSV, LSVb Fig. 3, 16a) displays two sections in channel unit V (Fig. 3).
478 Section LSV represents a setting closer to the channel axis consisting of very coarse, pebbly
479 sandstone beds at the base passing into sand-silt-interbeddings and mud-prone beds towards
480 the top. Section LSVb is situated at the northern margin of the channel unit. Here the
481 intrachannel sandstone beds pinch out abruptly forming intercalations in intrachannel
482 mudstone successions. It is possible to trace back an individual, very coarse, thin sandstone
483 bed in section LSVb to the basal coarse clastics of section LSV providing a lithostratigraphic

484 marker horizon for correlation purposes (lithostratigraphic unit 2 in Fig. 16a, see base of unit
485 V in Fig. 3b). Geochemical data (moving average) display additional trends that allow
486 subdivision and correlation of the overlying sandstone-mudstone interbeddings (subunits a–c
487 of lithostratigraphic unit 1 in Fig. 16a). From base to top these subunits are characterised:

- 488 - in subunit c; by lower SiO₂ values, increasing CaO contents, decreasing TiO₂ and Zr
489 contents, and a higher log₁₀(Fe₂O₃/K₂O) ratio (compared to lithostratigraphic unit 2)
- 490 - in subunit b; by higher contents of SiO₂, basal TiO₂ enrichment, increasing
491 Al₂O₃/TiO₂ ratio, decreasing chemical maturity and lower log₁₀(Fe₂O₃/K₂O) ratio,
- 492 - in subunit a; in section LSV by additional trends being not represented in section
493 LSVb

494

495 The second example of correlation at distances of ~100m (Fig. 16b) displays two sections in
496 channel unit II with section LSIII situated closer to the channel margin and section LNII
497 representing the channel axis (Fig. 3). The sections are located on the eastern (LNII) and
498 western (LSII) Rambla Lanujar river valley with no potential for a physical tracing of
499 lithostratigraphic units. Nevertheless, in both sections overall fining upward is recognisable,
500 which represents decreasing energies during channel fill. Consequently, the axial section LNII
501 is characterised by basal clast-supported conglomerates representing the channel thalway
502 deposits, followed by very coarse sandstone beds and sandstone-mudstone interbeddings. In
503 section LSIII succession starts with thick basal sandstone beds passing into interbedded sand-
504 mud towards the top. Based on chemostratigraphy and element data (moving average of three
505 samples) subdivision and correlation is possible (subunits a–c in Fig. 16b). From base to top
506 the subunits are characterised:

- 507 - in subunit c; by lower SiO₂, higher CaO, lower TiO₂, low an decreasing TiO₂/Zr ratios,
- 508 - in subunit b; by higher SiO₂ contents, decreasing CaO content, higher TiO₂ content as
509 well as TiO₂/Zr ratios, and higher chemical maturity,

510 - in subunit a; by lower SiO₂ content, increasing CaO content, low TiO₂ content,
511 increasing Zr content, low TiO₂/Zr ratios, high Al₂O₃/TiO₂ ratios, and low chemical
512 maturity,
513 - from subunit c to subunit a an increase in Zr content and Th content.
514 -
515 The 100m distance between the lithologically correlated sections results in a stronger
516 variability in the lithological composition than for the closer-spaced sections, and a
517 lithostratigraphic correlation between axial and marginal sections is less straightforward.
518 However, element concentration data reflect the overall fining upward trends in individual
519 channel fills (SiO₂, CaO, chemical maturity) and the geochemical data provide correlatable
520 patterns (SiO₂, TiO₂, Zr, TiO₂/Zr, Al₂O₃/TiO₂, local chemical maturity and log₁₀(Fe₂O₃/K₂O)
521 ratios).
522
523

524

525 **4 Discussion**

526

527 Amongst the >60 elements measured by ED-XRF nearly a quarter of them have proved to be
528 useful or reliable for geochemically-based correlation at the tested scales (~10m, ~50m,
529 ~100m) for this succession. These elements are SiO₂, K₂O, Al₂O₃, CaO, and TiO₂, as well as
530 Zr, Nb, Th, Rb, Cs, As, and the Rare Earth Elements; La, Nd, and Ce. The following
531 discussion therefore focuses on these elements.

532

533 4.1 Grain size and lithological controls on element abundances

534

535 The grain-size dependent relationship with geochemistry is depicted in Figure 9 with low
536 Si/Al ratios in the silt-prone samples and with increased Si/Al concentrations in the
537 sandstones. However, increasing Si/Al ratios do not uniformly reflect increasing grain size,
538 since the coarse and very coarse-grained samples fall between the Al-rich end member and
539 the Si-rich end member. The same holds true for the potassium concentrations. This
540 variability is consistent with the general tendency of coarse-grained fractions concentrating
541 the lithic fragments. This is apparent in thin section (Fig. 4), which reveal coarse schist
542 lithoclast fragments (mica, chlorite), which contribute much Al₂O₃ and K₂O to the most
543 coarse sedimentary rocks (Fig. 8).

544

545 In general, argillaceous lithologies contain significantly more abundant and more varied trace
546 element and REE concentrations than interbedded sandstones. Rubidium and Cs are typically
547 enriched in mudstones and siltstones (Taylor 1965; Fralick and Kronberg 1997) and their
548 linear correlations with Al₂O₃ and K₂O reflect the enrichment of mica in the siltstone fraction
549 (Fig. 13).

550

551 From the vertical distribution of the Zr concentrations in this study (Fig. 10) it seems that Zr
552 is preferentially associated with the finer horizons. The results suggest the presence of fine-
553 grained Zr bearing phases (enrichment in sandy siltstones and very fine-grained sandstones)
554 and coarser-grained Zr bearing phases (some enrichments in medium- to coarse-grained
555 sandstone beds; Fig. 8). In medium- to coarse-grained sandstone samples, zirconium was
556 found in thin section as small grains (up to 100 μm), but also as silt-sized detrital grains
557 within metasedimentary lithic fragments. This observation supports the conclusion that, with
558 zircon grains rarely exceeding 250 μm (Poldervaart 1955), fine-grained and silty sand
559 represents the most favourable size range for zirconium (Garcia et al. 2004).

560

561 The low TiO_2 concentrations in the finest beds, and variable concentrations in the sandy
562 lithologies imply that TiO_2 is dominated by Ti-heavy minerals rather than occurring as a
563 species sorbed onto clay minerals (Fig. 8). In thin section, TiO_2 is linked to the presence of
564 rutile and opaque accessory minerals. Thin section analysis shows that detrital rutile exhibits
565 similar grain sizes to zircon (up to 70 μm). However, TiO_2 has a poor correlation with zircon
566 suggesting that they were not co-deposited (see Figure 11). BSEM and EDAX analyses
567 confirmed the occurrence of coarse-grained Ti-bearing opaque grains (up to $>500 \mu\text{m}$).
568 Euhedral grains with traces of Fe suggest altered Fe-Ti-oxides (e.g. ilmenite), trellis-like
569 textures and aggregation of several rutile crystals also imply secondary (diagenetic) TiO_2 -
570 mineral growth (Pe-Piper et al. 2011).

571

572 Overall the observed abundances of SiO_2 , TiO_2 and Nb seem to correlate positively with the
573 grain size. In contrast the abundances of Al_2O_3 , K_2O , Rb, As, Cs (and to some extent REE)
574 inversely correlate with grain size. Zr and Ca appear to be effectively uncorrelated with grain
575 size.

576

577 4.2 Bed-scale geochemical heterogeneities

578

579 A distinct difference was found in the element abundances of the sandstones compared to
580 siltstone, mudstones and conglomerates. However, along individual beds a number of
581 elements exhibit negligible or minor variability (see Figs. 6, 10, 12). Thus, the magnitude of
582 intra-bed variation is considerably smaller than the vertical (inter-bed) variation of these
583 elements in a section making them highly favourable for correlation purposes.

584

585 The best correlations are exhibited by SiO_2 , K_2O , TiO_2 , Nb, Th, As, and Rb. Beds are broadly
586 homogeneous for these elements over distances of up to ~20 m (Figs. 6, 10, 12) in both down-
587 flow and axis to margin directions. However even the abundances of Zr (together with REEs)
588 and Cs, and to some degree Al_2O_3 and CaO, are fairly uniform within individual beds (Fig.
589 10).

590

591 Some of these elements are a good indicator of the dominant detrital mineralogy, such as
592 quartz or mica (SiO_2 , Rb, Cs, and K_2O). Their distribution is controlled by grain size and
593 lithology (i.e., quartz-rich sandstones, phyllosilicate-rich mudstones, lithoclasts-rich
594 conglomerates). Furthermore, compositionally very mature horizons also seem to provide
595 good marker horizons for correlation over distances of up to 50 m and more (Fig. 14). The
596 high maturity relates to sorting processes favouring quartz grains over lithoclasts and micas.
597 Since lithology, grain size and sorting are a function of the energy of the transport medium, so
598 related elements represent the hydrodynamic conditions under which the individual beds have
599 been laid down.

600

601 4.3 Depositional trends and geochemical variations

602

603 These results have shown that the elements useful for geochemically-based correlations are
604 those whose abundance is controlled primarily by (1) grain size-dependent mineralogy and (2)
605 the heavy mineral content.

606

607 TiO_2 , Zr, Nb, Th, La, Ce and Nd are probably diagnostic of the lithology of the primary
608 source area due to their relative insolubility and immobility during diagenesis and weathering
609 (Taylor and McLennan 1985; Hill et al. 2000), even though e.g. Ti mobility under certain
610 conditions is reported (Pe-Piper et al. 2011) However, at the tested scales their abundance is
611 an expression of varying sedimentary facies and grain size, which cause differences in
612 mineral composition and enrichment of heavy minerals, respectively (Fig. 8).

613

614 Coarse metasedimentary lithoclasts, deposited rapidly from high density turbidity currents,
615 contribute notable amounts of SiO_2 (from quartzose clasts), TiO_2 (altered ilmenite), as well as
616 K_2O and Al_2O_3 (mica schists) and in part CaO (linked either to bioclasts or metacarbonate
617 fragments). The coarsest sediments are most enriched in SiO_2 (linked to quartz) or most
618 depleted in phyllosilicate-related elements.

619

620 Poorly- to moderately-sorted, normally-graded coarse to medium-grained, massive and planar
621 laminated sandstones (upper flow regime conditions) are characterised by decreasing amounts
622 of SiO_2 , K_2O and Al_2O_3 in finer sandstones (Fig. 8) resulting from decreasing quantities of
623 large lithoclast fragments. They are also characterised by slightly elevated average TiO_2 and
624 Zr concentrations and increasing maximum concentrations in the individual quantities of K_2O ,
625 Al_2O_3 , and TiO_2 (and Nb), Zr and SiO_2 with the largest minimum-maximum range in
626 medium-grained sandstones. This is probably caused by differences in individual sorting and

627 compositional maturity of individual beds. For example, significant SiO_2 and TiO_2 enrichment
628 (together with higher Zr concentrations), at the expense of K_2O and Al_2O_3 , seem to point to
629 increased compositional maturity. This may be due to (i) alteration and sorting processes
630 during transport, (ii) sorting effects during deposition or (iii) a provenance-related initial
631 supply of more mineralogically-mature sediment. In the last case, a possible shift of sediment
632 source from a lithoclastic source (hinterland) to sediment sourced from a siliciclastic shelf
633 material could account for those changes. In correlations of sections up to several tens of
634 metres in distance (e.g., Fig. 14) these very mature horizons seem to represent reliable marker
635 horizons. The medium to coarse and very coarse-grained sandstones seem to be the
636 favourable grain size fraction for TiO_2 enrichment, resulting from the high density of the host
637 mineral as well as a larger initial grain size of the related heavy minerals (opaque Ti oxides,
638 Ti-Fe-oxides). Besides, significant TiO_2 enrichments with no direct link to a distinct grain size
639 fraction (e.g. Fig. 16) could indicate provenance-related signals, i.e. the dominant supply of
640 certain clasts (e.g. altered ilmenite) and support the use of geochemical correlation methods.
641
642 Siltstones and very fine-grained sandstones (lower flow regime conditions) can easily be
643 distinguished from coarse (upper flow regime) sandstones by their elevated K_2O , Al_2O_3 , Rb,
644 Cs and As concentrations, and lower SiO_2 concentrations (Fig. 8), which are due to mica
645 enrichment at the expense of quartz. The amount of Rb seems to be a good indicator of the
646 proportion of fine-grained, siliciclastic material present, since elevated Rb concentrations co-
647 vary with the siltstone horizons (e.g. Fig. 12). The fine clastic horizons, furthermore, show
648 higher average and maximum Zr concentrations and a significant decrease in TiO_2
649 concentrations due to grain size differences of the related heavy minerals. The fine-grained
650 clastic horizons also exhibit higher REE and Th concentrations.

651

652 Significant enrichments of CaO (30 % up to 60 %) can be attributed to accumulation of
653 predominantly calcareous beds (sandy limestone), composed of siliciclastic and carbonate
654 detritus (quartz grains, peloid micrite fragments, bioclasts) and carbonate cement. Distinct
655 CaO enrichment leads to decreasing amounts of all the other elements under consideration,
656 caused by significant dilution effects and the minor content in siliciclastic detritus. During
657 geochemical correlation of sections ≥ 100 m apart, and at axis to margin settings, these
658 limestone beds are easily recognisable and traceable. Their occurrence must be linked with
659 provenance signals, i.e., a subtle shift from sourcing sediment from an exclusively siliciclastic
660 source (hinterland as well as shelf) to sourcing sediment from carbonate shelf material.

661

662 4.4 Validity of geochemically-based correlations in this study

663

664 High resolution geochemical correlation matches lithostratigraphic correlation for closely
665 spaced (~10m) section (Figs. 6, 10, 12). The results presented here show that individual beds
666 seem to be broadly homogeneous for a range of elements, both in down-flow and axis to
667 margin directions over distances of up to ~20 m (Figs. 6, 10, 12). The elements on these
668 figures exhibit negligible or minor variability along single correlated beds. The magnitude of
669 intra-bed variation is considerably smaller than the vertical element (inter-bed) variation in a
670 section. The best correlations are exhibited by SiO₂, TiO₂, Nb, Th, As, K₂O and Rb. However
671 even the abundances of Zr (together with REEs), Cs and Al₂O₃ and CaO, are fairly uniform
672 within individual beds. North et al. (2005) obtained similar results for Nb, TiO₂, and Rb in a
673 deltaic succession. However, in contrast to our study, they reported that Zr has as much
674 variability along a lateral traverse within a single bed as they do vertically through a
675 parasequence.

676

677 The elements that permit good bed-scale geochemical based correlations are indicative of (1)
678 heavy minerals (TiO₂, Nb, Th, Zr, REEs), or (2) the dominant detrital mineralogy, such as
679 quartz or mica (SiO₂, Rb, Cs, K₂O). The abundance of these elements is controlled by the
680 hydrodynamic conditions under which the individual beds have been laid down controlling
681 grain size and sorting differences.

682

683 At the scale of several tens of metres, geochemical comparison of correlatable packages in
684 lithologically-similar sections (Figs. 14, 15) revealed that major geochemical trend-breaks
685 (here defined as sudden changes in geochemical character of the sediments) can be
686 consistently related to major changes in sedimentary facies (mudstones, sandstones,
687 conglomerates) and are traceable over distances of several tens of metres. This is notable
688 because in these sections the physical tracing of individual beds was not possible due to
689 outcrop discontinuity. Correlation in the field was based on major lithostratigraphic trends and
690 key surfaces (see lithostratigraphic correlation in Figure 14). Furthermore, it seems to be
691 possible to identify grain-size independent, correlatable sub-trends (see chemical correlation
692 in Figure 14), based on the recognition of identical geochemical patterns, minor pattern-
693 breaks or marker horizons with significant enrichments or depletions of certain elements.
694 Despite the occurrence of substantial “noise” related to minor grain size variations,
695 lithostratigraphic correlation was thus *improved* by using a high-resolution geochemical
696 subdivision of these major lithostratigraphic packages (Fig. 14). Additionally, a recalculation
697 of the dataset using a moving average of three samples (in order to more closely mimic the
698 way drill cuttings are collected and analysed during petroleum exploration and appraisal)
699 more strongly pronounced correlatable elemental patterns between sections. This implies that
700 individual lithological units, at a given stratigraphic level, and locally even individual
701 horizons, are geochemically-correlatable over several tens of metres, even in stratigraphically-
702 complicated systems such as submarine channel complexes.

703

704 Since individual beds seem to be broadly geochemically homogenous for the main elements
705 discussed previously, and individual lithological units exhibit a consistent geochemical
706 fingerprint over distances of several tens of metres, it should be possible at larger distances of
707 ~100 m, to separate a geochemical signal (e.g. major changes in composition, provenance)
708 from noise (variability related to grain size differences) using the three-point moving average.
709 With the increased distance between compared sections (up to hundreds of metres) the
710 lithological compositions and sedimentary facies are likely to change significantly (axial to
711 marginal settings) (Fig. 16). However, based on a moving average of element data, signatures
712 such as Ca-enrichment of sandy limestones (carbonate detritus, e.g. Fig. 15, 16a), high
713 compositional maturity (e.g. Fig. 16b), SiO₂ contents (e.g. Fig. 16), or significant Ti-
714 concentrations related to the quantity of opaque Ti-(Fe-) bearing detritus (e.g. Fig. 16b), are
715 generally traceable over distances of up to a hundred metres or more suggest a probable
716 provenance-related signal. The same holds true for element ratios such as TiO₂/Zr,
717 Al₂O₃/TiO₂ and log₁₀(Fe₂O₃/K₂O). Furthermore, depositional trends are reflected in
718 geochemical data trends, such as fining upward tendencies of individual channel fills (SiO₂,
719 CaO, chemical maturity). Geochemical correlation therefore is effective for sedimentary
720 sections ~100 m apart.

721

722 **8 Conclusion**

723 This study has used an integrated approach involving sedimentology, geochemistry,
724 mineralogy and petrography to test the validity of geochemical correlation with the aid of an
725 outcrop analogue study. Geochemical data have been compared to physical stratigraphic
726 correlations at a variety of scales to determine if geochemical correlations are conformable
727 with the sedimentologically-defined stratigraphic framework.

728

729 (1) Amongst the >60 elements measured by ED-XRF nearly a quarter of them have proved to
730 be useful or reliable for geochemically-based correlation at the tested scales (~10m, ~50m,
731 ~100m). These elements are SiO₂, K₂O, Al₂O₃, CaO, and TiO₂, as well as Zr, Nb, Th, Rb, Cs,
732 As, and the Rare Earth Elements; La, Nd, and Ce.

733

734 (2) The geochemical variations in these sediments are controlled by a combination of grain
735 size (for most of the major elements: SiO₂, K₂O, CaO, Al₂O₃, Fe₂O₃, TiO₂, but also for the
736 trace elements Zr, Rb, Cs, As) and subtle changes in provenance (for the elements: TiO₂, Zr,
737 Th, Rb, Nb, Cs, As, and the REEs La, Nd, and Ce).

738

739 (3) High resolution, bed-to-bed geochemical correlation is feasible over short distances
740 (~10m). Geochemical data from sections in beds traceable from outcrop suggest that a given
741 stratigraphic level seems to be geochemically homogeneous with respect to a number of
742 elements: SiO₂, K₂O, CaO, TiO₂, Al₂O₃, as well as Zr, Nb, Th, Cs, As, and the REEs La, Nd,
743 and Ce. The magnitude of the geochemical variation of these elements within a single bed is
744 negligible, or smaller than the variation vertically through the sections, making them
745 favourable for geochemical correlations. The occurrence and abundance of these correlatable
746 elements are controlled by the dominant mineralogy (quartz, mica, and carbonate) and the
747 heavy mineral content (rutile and other Ti oxides, zircon and related heavy minerals).
748 Comparisons of the element and mineral data with the lithological data suggest that
749 geochemistry, as well as mineralogy, vary systematically within the sedimentological
750 framework, and that variations are a response to changes in the hydraulic conditions under
751 which individual beds have been formed, causing differences in sedimentary facies (i.e. grain
752 size and sorting). Lateral homogeneity at bed scale implies that the hydraulic conditions must
753 have been fairly consistent over several metres in an individual bed.

754

755 (4) Geochemical data provide a useful aid for high resolution sedimentary correlation, at
756 distances of several tens of metre. Since each individual bed seems to be broadly homogenous
757 in composition, at a larger scale it is possible to separate a provenance signal from noise
758 (variability related primarily to grain size differences) within geochemical data. Distinct
759 element trend-breaks occur at the same positions as major depositional changes.

760

761 (5) There is potential to achieve high-resolution correlation based on geochemical data. The
762 occurrence of systematic stratigraphic variations in geochemistry (particular enrichments,
763 depletions or major trends) related to depositional trends allows the recognition of
764 geochemically-distinct subunits in the sections, which can be correlated to
765 lithostratigraphically-comparable and sedimentologically-similar sections.

766

767 (6) In stratigraphically-correlatable sections that span distances of hundreds of metres and that
768 exhibit significant changes in the sedimentary depositional pattern, geochemical signals
769 (including SiO₂, K₂O, CaO, TiO₂, Al₂O₃, Fe₂O₃, Zr, Th, Rb) can be traced over these longer
770 distances, permitting correlation at the channel unit scale. Chemical stratigraphy thus seems to
771 work even in stratigraphically-complicated submarine channel complexes.

772

773

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898

899 **Figure captions**

900

901 Fig. 1: Schematic sketch of a submarine channel system picturing the different scales and
902 directions of correlation attempts tested in this study.

903

904 Fig. 2. Location maps of the study area: (a) simplified geology of the Tabernas area in south-
905 eastern Spain and (b) course of the studied channel complex and location of analysed outcrops
906 (after: Hodgson 2002, Pickering et al. 2001).

907

908 Fig. 3. Studied exposures of the confined slope channel complex with location of analysed
909 sections: (a) in down-dip direction of the channel (Campsa), (b + c) in axis to margin
910 direction of the channel and in different channel units (unit I-V, Rambla Lanujar, height of
911 exposure in b approximately 40 m, see circled group of people for scale) and d) on map of
912 area of Rambla Lanujar.

913

914 Fig. 4. Petrography of the major sedimentary facies: (a) Coarse-grained pebbly sandstone,
915 poorly-sorted, with major components being quartz and schist clasts (transmitted light image,
916 XL). (b) Medium-grained sandstones, moderately-sorted, composed of quartz, mica, and
917 opaque as well as transparent accessory phases, calcite cemented (b1: transmitted light image,
918 PPL; b2: BSE image). (c) Sandy mudstone, poorly-sorted, mainly composed of quartz grains
919 and mica flakes in a dense matrix (BSE image).

920 Key: qz – quartz, m – muscovite, cl – chlorite, bi – biotite, cc – calcite cement, ti – rutile and
921 other Ti-oxides, fe – Fe-oxides, py – pyrite, gt – garnet, zr – zircon, ap – apatite.

922

923 Fig. 5. Small-scale, single bed correlations in down-flow direction (a) and axis to margin
924 directions (b, c). Sedimentary logs and correlation of the sections (Spacing between sections:
925 ca. 10 m).

926

927 Fig. 6. Major element data (XRF) that have proved useful for bed-scale correlation together
928 with their likely host minerals (XRD data). Data were plotted against bed number in the
929 section and compared to the average lithology of each bed (left). The different plots are for
930 different sections (see Fig. 4 for correlation of the sections).

931

932 Fig. 7. Cross-plots of major elements (XRF data) and their likely major host minerals (XRD
933 data), with correlation coefficients: a) SiO_2 – quartz, b) Al_2O_3 – muscovite, c) K_2O –
934 muscovite, and d) CaO – calcite.

935

936 Fig. 8. Box-Whisker plots of the grain size-dependent occurrence of some major and heavy
937 mineral-bound elements.

938 Key: M – siltstones and mudstones, Sf – fine and very fine sandstones, Sm – medium-grained
939 sandstones, Sc – coarse sandstone, Svc – very coarse to granular sandstones, Gm – matrix-
940 supported sandy conglomerates.

941

942 Fig. 9. Cross-plots of the SiO_2 and Al_2O_3 values of the samples from a CaO-free recalculation.

943

944 Fig. 10. Bed-wise correlation of primarily heavy mineral bound major and trace elements of
945 the sections in Fig. 4, plotted against bed number in section and compared to the average
946 lithology of each bed (left). Division of Zr and Nb values by ten for plotting data on the same
947 axis as for TiO_2 and Th.

948

949 Fig. 11. Element relationships of the major heavy mineral bound elements.

950

951 Fig. 12. Major, trace and rare earth element data of the sections in Fig. 4, plotted against bed
952 number in section and compared to the average lithology of each bed (left). The different
953 plots are for different sections.

954

955 Fig. 13. Element-cross plots of: a) of K_2O and Rb and b) Cs and Rb.

956

957 Fig. 14a. Geochemistry (XRF data) and mineralogy (XRD data) of channel unit I at Rambla
958 Lanujar: lithostratigraphic correlation and geochemical subdivision of sections at the eastern
959 (LNI) and western (LN-G) side of the canyon (spacing between the sections ca 50 m).

960 Correlation is based on major lithological units (units 1, 2, 3...) and chemical defined
961 subtrends (subunits a, b, c...).

962

963 Fig. 14b. Moving average of major element data (XRF) and related mineralogy (XRD data) of
964 channel unit I at Rambla Lanujar. Correlation is based on major lithological units (units 1, 2,
965 3) and chemical defined subtrends (subunits a, b, c). See legend in Fig. 13a for fills of the
966 lithological columns.

967

968 Fig. 14c. Moving average of element data and element ratios of channel unit I at Rambla
969 Lanujar. Correlation is based on major lithological units (units 1, 2, 3) and chemical defined
970 subtrends (subunits a, b, c). See legend in Fig. 13a for fills of the lithological columns.

971

972 Fig. 15. Moving average of element data and element ratios of channel unit IV at Rambla
973 Lanujar: geochemical based correlative relationship of sections towards the northern (LN-G-
974 IV) and southern (LSIV) margin of channel complex (spacing between the sections ca 50 m).

975 Correlation is based on major lithological units (basal conglomerates, sandstone-silt-
976 /mudstone interbedding) and chemically-defined subtrends (based on element and mineral
977 trends and abundancies, e.g. CaO, TiO₂, Zr, element ratios). See legend in Fig. 13a for fills of
978 the lithological columns.

979

980 Fig. 16. Moving average of element data and element ratios with assumed correlation of
981 channel axis to channel margin sections of a) channel unit V (e.g. trends of SiO₂, CaO, or
982 element ratios) and b) channel unit II (e.g. SiO₂, TiO₂ content, element ratios) at Rambla
983 Lanujar (spacing between the sections ca 80 - 100 m). See legend in Fig. 13a for fills of the
984 lithological columns.

985