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1 **An elemental and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic restitution of contaminated**
2 **pore waters from sandy sediments of the Peciko**
3 **gas field (Mahakam Delta, Indonesia)**

4
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16 **keywords:** restored pore waters; H₂O and dilute HCl leachates; $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; major, trace
17 and rare-earth elemental contents; Peciko gas field; Mahakam Delta (Indonesia)

18
19
20 **Abstract**

21 Pore waters of hydrocarbon-bearing sand layers from gigantic Peciko gas reservoir
22 located to the South of the Mahakam Delta in Indonesia were reconstructed and studied by
23 applying the restored pore-water technique. The method is based on the Sr isotopic
24 compositions of rock chips leached with de-ionized water aided, here, by the associated
25 contents of major, metal and rare-earth elements (REEs). The soluble minerals were also
26 leached with dilute hydrochloric acid and analyzed for their Sr isotopic compositions.

27 The main founding is that many of the recovered H₂O leachates were most probably
28 contaminated during coring, which induced abnormally high metal and REE contents. The
29 leachates considered free of pollution yield $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that increase progressively with
30 depth, which suggests a recent supply of surface waters to the upper pore waters. It seems also
31 that only a few sedimentary horizons are interconnected at intermediate depths. Furthermore,
32 the minerals dissolved by dilute HCl yield quite systematically lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the

33 associated pore waters, which suggests a crystallization earlier than the recent flushing of the
34 upper sediments by surface-type waters.

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36

37 **1. Introduction**

38

39 The chemical evolution of oil-field waters and their migration paths have often been
40 reconstructed successfully on the basis of their chemical and stable isotope data (e.g., Sulin,
41 1947; De Sitter, 1947; Degens et al., 1964; White, 1965; Clayton et al., 1966; Rittenhouse,
42 1967; Hitchon et al., 1971; Kharaka et al., 1973; Kharaka and Berry, 1974; Collins, 1975;
43 Carpenter, 1978). As fluid-rock interactions play key roles in the compositional evolution of
44 these waters, a reconstruction of their interactions requires varied chemical and isotopic
45 information. For instance, such studies ignored largely the potential benefits that may come
46 from Sr isotopic investigations until Chaudhuri's (1978) publication, which was confirmed by
47 many further studies (e.g., Sunwall and Pushkar, 1979; Starinsky et al., 1983; Chaudhuri et
48 al., 1983; Stueber et al., 1984; Chaudhuri et al., 1987; Furlan et al., 1995). These studies not
49 only provided valuable clues to the understanding of the chemical evolution of oil-field
50 waters, but also improved the comprehension of the diagenetic history of their host rocks.

51 While long-distance migrations of pore waters through various rock types of any
52 sedimentary basin often obscure the reconstruction of their geochemical evolution, their study
53 may provide valid information within a finite space and during a limited time in a basin. In
54 this context, it appeared of interest to test the Sr isotope compositions of restored formation
55 waters following the "Residue Salt Analysis" concept of Stolum et al. (1993) complemented
56 by elemental analyses of the leachates, and by Sr isotopic data obtained on the soluble
57 minerals of the studied rocks by interaction with dilute hydrochloric acid. The purpose was to
58 pursue testing that isotopic technique by identifying connections between producing units of
59 larger hydrocarbon reservoirs. More precisely, the isotopic technique was applied here,
60 together with elemental analyses of the H₂O leachates on hydrocarbon-bearing sand units of
61 the gigantic Peciko reservoir to the South of the Mahakam Delta in Indonesia.

62

63 **2. Geological and hydrodynamic background**

64

65 The Mahakam delta is located on the eastern side of Borneo Island in Indonesia (Fig.
66 1). Active since the Pliocene, the river deposited more than 10,000 m of interlayered lithic

67 sandstone and shale units into the delta (Duval et al., 1992). The collecting basin corresponds
68 to the limited drainage surface of the nearby island that does not host any Sr-rich carbonate-
69 type rocks. This lack of outcropping carbonates is of some importance in the further
70 discussion, because it means that the river waters were not enriched in overwhelming Sr
71 contents that could have imprinted preferentially the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the local surface waters
72 from deposited sediments. The surface drained by the Mahakam River is only of about 75,000
73 km^2 , which means that the chemical signatures of the present-day pore waters are most likely
74 not obscured by multiple and extensive interactions with various types of rocks during a long-
75 distance migration, as is the case for pore waters from large sedimentary basins of North
76 America (e.g., Chaudhuri et al., 1987; Banner et al., 1989). The gentle Miocene deformation
77 of the Mahakam sedimentary sequence into successive anticlines was followed by some late
78 reactivations (Letouzey et al., 1990). Consequently, the oil and gas fields of the Mahakam
79 Delta basin relate to anticline traps oriented parallel to the coastline with the Peciko-Handil-
80 Tambora-Badak axis being the closest to the shore (Fig. 1).

81 Onshore exploration of hydrocarbons in the area started before the turn of the last
82 century. A system of hydrodynamic brine circulations flowing in opposite directions was
83 described (Grosjean et al., 1994) due to an onshore uplift allowing meteoric waters to invade
84 permeable intervals of the stratigraphic section, mostly at the faulted edges of the deltaic
85 offshore system. Also, a deeper and slower, but more extensive, circulation of brines was
86 driven by overpressures found in distal shales (Burrus et al., 1992). The available chemical
87 and isotopic data of formation waters from proximal (Tambora and Handil) and distal (Attaka
88 and Bekapai) oil fields provided more information about the recent to present-day mass
89 transfers (Furlan et al., 1995). For instance, the Ca and Sr contents decrease in the formation
90 waters, whereas the Sr/Ca ratio suggests a combined precipitation of albite and dissolution of
91 K-feldspar, while the associated decrease of the released K in the running waters was
92 consumed by an on-going illitization. The variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the waters were
93 related to the dissolution of these K-feldspar minerals.

94 The influence of down-dip hydrodynamic circulations on the lateral sealing of the
95 local stratigraphic traps was explained by a system consisting of meteoric waters driven by
96 gravity (e.g., Stones and Hoeger, 1973). Drilling of the Peciko-1 well in the early 1990s into
97 the northwestern area of the field was somehow determining as pressure-depth plots could be
98 documented in the upper sections that showed aligned gas-pressure curves. These curves
99 revealed that many large reservoirs were detected, each consisting of multiple-metric sand
100 bodies. Thicker shale inter-beds could also be correlated regionally on the basis of

101 intersecting sand bodies that resulted from flooding events in the deltaic environment with
102 seals as useful tools for the pressure profiles.

103 Twenty-three core samples were collected for the present study along the Peciko-3 and
104 Peciko-8 wells drilled into the northwestern Peciko gas field (Fig. 1). Nine of these samples
105 belong to the upper zone of the P3 well between the markers MF7 and MF75 from 2,730 to
106 2,780 m depth (Fig. 2). Seven more samples were collected in the upper intermediate P3-ZI
107 zone between the markers MF8 and FS85.1 from 3,110 to 3,180 m. Three more samples are
108 from lower intermediate zone P3-ZII between the markers FS85.4 and FS85.6 at about 3,380
109 m, while the four last samples belong to the deeper P3-ZP zone below the marker MF9, at
110 3,510 to 3,560 m. Nine additional samples were collected in the nearby Peciko-8 well; two of
111 them being parts of the upper zone at 2932.6 and 2959.4 m, two others belonging to the
112 intermediate zone at 3,320.4 and 3,322.4 m, while the last five range between 3,506 and 3,538
113 m.

114

115 **3. Analytical procedure**

116

117 The analytical procedure is based on the concept of Stolum et al. (1993) called
118 “Residue Salt Analysis”. Those authors demonstrated that hydrocarbon-bearing reservoirs
119 from a North Sea reservoir communicate or not on the basis of Sr isotopic data of deionized-
120 water leachates of the reservoir rocks. If two reservoirs were or still are connected, the
121 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the rock leachates should overlap as they may be considered to be
122 representative of seeping formation brines. Conversely, in the case of non-communicating
123 reservoirs, the same isotopic ratios should not overlap. The cores studied here were first hand-
124 cleaned by removing the external centimeter-thick layer potentially contaminated by drilling
125 mud. Then, they were gently reduced into centimeter-large chips by hammer crushing, and the
126 rock chips were subjected to a one-hour interaction in a satellite rotating equipment with
127 deionized water at a 2 to 1 water/rock weight ratio. Afterwards, the leachates and residues
128 were centrifuged at about 4,500 rpm during 1 hr, the leachates being collected for analysis
129 and the residues for further leaching. This further leaching was similar to the previous one,
130 except for the reagent, the de-ionized water being replaced by ultra-pure HCl diluted to 1M at
131 an acid-rock weight ratio set at a 1 to 1 for a 15-mn interaction.

132 The leachates were dried in Teflon© beakers and the residues dissolved in HNO₃ acid
133 before analysis. The contents of the major, trace and rare-earth elements (REEs) were
134 analyzed on an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) for

135 the major elements and on an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) for
136 the trace and REEs, following Samuel et al.'s (1985) procedure. Reproducibility tests were
137 made routinely by a systematic analysis of the international BE-N and GL-O standards that
138 give a reproducibility of the equipment at a 2.5% uncertainty for the major elements that
139 doubles at 5% for the trace elements, and again at 10% for the REEs.

140 The Sr isotopic data were determined on a mass spectrometer with a multi-collector.
141 Strontium of the leachates was separated and purified using a chemical procedure similar to
142 that reported by Schaltegger et al. (1994) and loaded on Ti-filaments for analysis. The
143 $^{87}\text{Sr}/^{86}\text{Sr}$ value of the NBS 987 standard was 0.710257 ± 0.000015 ($2\sigma_{\text{mean external}}$) for 4
144 independent analyses during the study. A systematic internal uncertainty of $2\sigma/\sqrt{N}$ is given
145 for each measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio on the basis of a hundred measured ratios (Table 1).

146

147 **4. Results**

148

149 4.1. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the H_2O and HCl leachates

150 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the H_2O leachates increases with depth: the upper scatter ranges
151 from 0.70852 to 0.70898 at 2,700-2,800 m depth and increases to 0.70987 at 3,500 m (Table
152 1). If combined with the Rb/Sr ratio, which might have an impact due to the production of
153 ^{87}Sr due to the decay of ^{87}Rb relative to time, it might result from mixtures with various
154 ratios. The data points fit two lines in a diagram with steep slopes that include most data
155 points with intercepts with the $^{87}\text{Sr}/^{86}\text{Sr}$ abscissa at about 0.7084. Five more dispersed data
156 points with higher Rb/Sr ratios are also scattered to the lower right side of the diagram (Fig.
157 3A). The H_2O leachates of the Peciko-8 samples display a similar pattern for the $^{87}\text{Sr}/^{86}\text{Sr}$
158 ratio relative to the Rb/Sr ratio (Fig. 3B). All their data, except one, fit again two lines with
159 steep slopes that intercept again the abscissa at about 0.7084. Interestingly, the data points
160 that plot outside the two lines in the two drillings belong to the uppermost samples.

161 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the HCl leachates display a similar spread relative to depth than
162 those of the corresponding H_2O leachates, in both drill wells (Fig. 4). The ratios increase
163 progressively with depth, being more scattered in the Peciko-8 drilling well. They are also
164 systematically lower than those of the corresponding H_2O leachates except for the sample at
165 2778.7 m depth in the Peciko-3 well (Table 1; Fig. 5A). In fact, the overall differences among
166 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the two types of leachates range from 2.9×10^{-5} to 98.1×10^{-5} (Fig. 5B).
167 The largest differences ($> 50.0 \times 10^{-5}$) were obtained mostly in the leachates of the deeper
168 samples from the two wells.

169 A comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the successive H_2O and HCl leachates of the
170 same rock samples shows that the ratios of the formers are higher than those of the latters,
171 except the already mentioned sample (Fig. 5A). This overall behavior is confirmed by the data
172 of the leachates from second drilling well (Fig. 5B). The two diagrams show also that the
173 difference among the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the two types of leachates is somewhat stratified, the
174 larger differences being for the deeper H_2O leachates relative to those with HCl . However, no
175 clearly organized stratification can be observed within each collection depth.

176

177 4.2. The major and trace elemental contents of the H_2O leachates

178 A preliminary comment about the changing contents of the major and trace elements
179 from H_2O leachates is probably appropriate to avoid any confusion. The released contents
180 were made, here, on “restored” waters and not strictly on “pore” waters. The purpose was not
181 to discuss the concentrations of formation waters taken at different depths, but to compare
182 extraction contents of “reconstructed” fluids. The goal was, therefore, not to calculate
183 concentrations that are also dependent on the relative porosity of the host rocks, but to follow
184 an analytical dispersion of the contents relative to depth. However, it can certainly be agreed
185 that the porosity of the deeper samples is lower than that of less deeply collected samples.

186 In turn, the contents in major elements of the restored formation waters obtained here
187 by leaching the rock samples from the two wells with de-ionized water show a general
188 tendency to decrease with depth (Fig. 6). The elemental contents of the same waters from the
189 second drilling well fit the range of those from first drilling, except for a very high Fe_2O_3
190 content in its deeper section. Also to be noticed are the generally low Rb and Fe contents
191 (Table 2; Fig. 7), the contents of elements such as Al , Rb and Sr that appear to be quite widely
192 dispersed at the intermediate depth range of 3,100-3,200 m.

193 To overcome the missing porosity values of the sediments, some major and trace
194 elements were also compared relative to their sampling depth in the sediments. The spread of
195 the Si/Al ratio becomes wider towards depth, which is mainly due to a downward decrease of
196 the Al contents (Table 2; Fig. 7). On the other hand, the Si/Fe ratio decreases with depth
197 increase, except for one value. Widely scattered near the surface, the Ca/Sr decreases also
198 with depth, except again, one deeper value. Chosen because of potential interactions between
199 formation waters and carbonates, this Ca/Sr ratio is the widest dispersed at the upper
200 collection depths (Table 1), while decreasing significantly at the two intermediate depths and
201 increasing again in the deepest. These changes appear to be mostly related to the changes in
202 the Sr contents. The Rb/Sr ratio that might impact the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the formation waters

203 due to the leaching of radiogenic ^{87}Sr released from alkali-rich soluble minerals, is also
204 decreasing with depth, except one intermediate sample, which can be related to a Sr increase
205 in the deeper extracts (Fig. 7). It shows a clear difference between the restored waters of the
206 two drillings. The ratios of the H_2O leachates from Peciko-3 well are quite higher than those
207 of the sister drilling, especially in the deepest collection range.

208 The contents of metallic elements (Cr, Co, Ni, Cu, Zn, Br, Ba, Cs and Sn) from H_2O
209 leachates were also determined (Table 3). While those of Cs and Sn remain systematically
210 low, which testifies for reliable data, those of the other metals are extremely varied with very
211 high values, for instance from 2.3 to 637 ng/g for Cr or from 1.1 to 923 ng/g for Ni in
212 leachates from Peciko-3 well (Fig. 8). In fact, Co, Ni, Cu and Zn vary together within very
213 wide ranges in three leachates of this Peciko-3 drill hole. The Br contents are also very
214 variable between 13.7 and 661 ng/g in the leachates of the same well. The uppermost samples
215 are systematically widely spread with very high contents. These large scatters for the H_2O
216 leachates, and especially the high contents of similar metals for the reconstructed pore waters
217 of quite homogeneous host rocks, are somehow surprising and even suspicious.

218

219 4.3. The contents and distribution of the rare-earth elements in the H_2O leachates

220 The total REE concentrations also range widely from 0.46 to 359 ng/g for the H_2O
221 leachates when the patterns are complete that is to say without any of the REEs below
222 detection limit (Table 4). As for the metal contents, the higher contents are somewhat
223 intriguing: two total amounts are beyond 340 ng/g and two others are at 117-144 ng/g. Three
224 of those were obtained on leachates from upper section of the Peciko-3 well and one from
225 deeper part of the Peciko-8 well. In fact, such high REE contents are not expected in H_2O
226 leachates, as natural waters are known to yield low to very low REE concentrations due to the
227 low solubility of the REEs and their tendency to adsorb preferentially onto particle surfaces
228 (e.g., Taylor and McLennan, 1985).

229 The total REE contents above 100 ng/g give smooth patterns relative to the Post
230 Archean Australian Shales (PAAS) taken here as reference, with a regular increase from La
231 until Eu, an almost regular flat plateau for the successive Eu, Gd and Tb and a final, smooth
232 decrease until Lu (Fig. 9, upper row). This configuration is still obtained for leachates with
233 contents up to 27-ng/g with, however, a more irregular distribution for the heavy REEs
234 (HREEs; Fig. 9, middle row). Below total contents of 4 ng/g, the patterns become much more
235 irregular with higher Eu values relative to the PAAS that are equivalent to those of Gd (Fig. 9,
236 middle row). In the REEs patterns of H_2O leachates with total values below 1 ng/g, the Eu

237 content is systematically the lowest of the surrounding REEs, that of Tb becoming the highest
238 (Fig. 9, lower row). Of course, such low concentrations are somehow biased by high
239 uncertainties beyond the usual +/-10% uncertainty given by the repetitive analysis of the
240 international standards, which probably contributes, at least partly, to the observed irregular
241 shapes.

242 If discarding all REE contents above a total of 27.1 ng/g, the contents range from 0.34
243 to 10.3 ng/g for the patterns with no more than one element below the detection limit (Table
244 4). Based on this adjustment, the total contents decrease relative to collection depth with
245 systematic contents below 1 ng/g in the H₂O leachates of the deeper samples from both wells.
246 However, for analytical reasons and consequently because of the large uncertainties in such
247 low contents, only the REE spectra amounting between 10 and 1 ng/g were evaluated further.
248 Also of interest, the La/Yb ratio varies widely from 0.08 to 3.30, with five values that could
249 not be measured because the contents of either La and/or Yb were below the detection limit.
250 In the detail, high contents of REEs and of metals were found together in two samples of the
251 Peciko-3 well at 2,768 and 2,779 m depth, as well as in two samples of the Peciko-8 well at
252 2,932 and 3,516 m depth. These large scatters with abnormal high values, together with those
253 of the metals, suggest clearly a contamination to be identified.

254

255 **5. Discussion**

256

257 Among the preliminary observations are the ⁸⁷Sr/⁸⁶Sr ratios of the restored formation
258 waters increasing with depth, whereas their elemental contents decrease correlatively. The Sr
259 isotopic ratios of the HCl leachates from the same samples are also systematically lower than
260 those of the corresponding H₂O leachates, including an increase with depth. And, importantly,
261 the distribution patterns of the REEs relative to the PAAS reference, as well as the high metal
262 contents, seem to depend more on their amounts than on the burial depth.

263

264 5.1. The meaning of the elemental and Sr isotopic data of the H₂O leachates

265 The increasing ⁸⁷Sr/⁸⁶Sr ratios of the H₂O leachates downward the sedimentary
266 sequence, with a decrease of the elemental contents, (Fig. 4 and 6) suggests an overall
267 chemical heterogeneity of the leachates, as well as a kind of stratification from upper to
268 deeper sampling depth. This combination is confirmed by the data of the H₂O leachates of the
269 samples from the second well. The individual data of the successive collection strata also
270 show that no identical to close ⁸⁷Sr/⁸⁶Sr values are obtained on most successive restored water

271 samples. This observation is confirmed by the REE data that are highly variable in their
272 contents for each collection layer, as well as by their distribution patterns relative to the
273 PAAS reference.

274 For instance, the widely spread REE and metal contents of the restored pore waters
275 need an explanation. Spontaneously, such data may be due to a contamination, either natural
276 or anthropogenic, due to an addition of natural waters from outside the field and/or, probably,
277 resulting from a human activity. If one agrees that this contamination is highest with REE
278 contents at about 350 ng/g in the leachates and that it is vanishing at about 5 ng/g, the range
279 can be compared to the corresponding major and trace elements and to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.
280 Those leachates with such high REE contents yield also high Ca and Sr contents above 100
281 and 200 ng/g, respectively (Table 5). In turn a solid indicator of the contamination seems to
282 be the Ca/Sr ratio that is beyond about 0.5 in most samples. If the same criteria are applied to
283 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the leachates, those contaminated have a tendency to occur rather on the
284 high side of the elemental data, especially at the upper collection level (Fig. 6; the gray dots).
285 These low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to contemporaneous pore-water layers could then be due,
286 based on the REE data, to the addition of present-day water and/or drilling fluids that could
287 have been used during the exploration drillings.

288 Combined with the Rb/Sr ratio, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the H_2O leachates from very
289 upper sampling depths plot away from common evolution lines, representing in turn a further
290 argument in favor of a recent to very recent external supply (Fig. 5A). Indeed, all leachates
291 with data points outside the two lines could result, at least partly, from recent addition(s) of
292 external natural waters. About the potential origin of these waters, McArthur et al. (2001)
293 showed that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ocean water increased after the Oxfordian, albeit with
294 small reversals, to reach a today's high of 0.709175 that is far beyond the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the
295 restored waters determined here. It can then be stated that the water used during the injection
296 of any kind of product into the drill holes was not ocean water, but rather that of the
297 Mahakam River in the delta.

298 In summary and beyond the analytical heterogeneity due to a probable pollution by the
299 drilling of the wells, the elemental and Sr isotopic data show that there is no straight
300 continuity in most successive collected samples of the two wells studied here. There are
301 almost never elemental and Sr isotopic continuities in successively analyzed H_2O leachates,
302 whatever the burial depth of the host samples. About the drilling pollutant, it obviously
303 increases the REE, Ca, Sr and metal contents and decreases the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the leachates.

304

305 5.2. The meaning of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the H_2O and the HCl leachates

306 The differences among the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the H_2O and the HCl leachates are widely
307 scattered from 2.9×10^{-5} to 98.1×10^{-5} in favor of the H_2O leachates, the larger differences
308 occurring at depth. Before discussing a possible geochemical continuity among the upper and
309 deeper restored waters, two preliminary hypotheses can be launched beyond the already
310 evidenced contamination: (1) either the overall increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio relative to depth
311 is due to a variable incorporation of ^{87}Sr into the pore fluids resulting from interactions with
312 host minerals fueled by an increasing diagenetic action monitored by a general increase of the
313 burial temperature, or (2) the deeper fluids are significantly “older” than the upper ones with
314 probable impermeable units in between, an argument that is supported by the elemental and
315 Sr isotopic differences even in the same sequences of both wells.

316 The trend of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio relative to depth is in favor of a communicating pool.
317 Not only the ratio is increasing with depth, but it is also accompanied by a continuous
318 decrease of its spread. Another argument in favor of a unique pool is the continuous decrease
319 of the elemental contents of the H_2O leachates relative to depth, as well as the reduction of
320 their spread. Both can be considered to be beyond the impact of the porosity at depth: the
321 contents have a tendency to decrease, which suggests the highest contamination in the upper
322 levels, with a quite significant spread reduction. Given as examples, the spreads of Si, Ca and
323 Sr provide similar decreasing trends relative to depth, considering that they do not represent
324 concentrations *stricto sensu*, as already stated (Fig. 6). In any case, the observed changes
325 suggest that the restored fluids were progressively less loaded with depth increase, while the
326 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio increases correlatively, which favors the hypothesis of the unique pool.
327 However, this sketch does not really apply to the Sr contents that remain quite constant
328 relative to depth, except one single sample of the upper level at 2764.5 m and two samples at
329 the intermediate depths at 3116.9 and 3140.9 m of the Peciko-3 well. Also to be considered is
330 the fact that the spread of the leachates suspected to be contaminated (gray dots in Fig. 6) is
331 quite decreasing with depth.

332 Conversely, if the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would be age dependent, that is to say higher ratios
333 for older formation waters, the deepest leachates should also yield, correlatively, the higher
334 Rb contents. Indeed, higher Rb contents are expected to give the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
335 relative to time and consequently older “age data” for the mobile Sr in the deeper formation
336 waters, which is not the case here. The correlation among the $^{87}\text{Sr}/^{86}\text{Sr}$ and the Rb/Sr ratios
337 provides three groups of data (Fig. 10): the two upper yield the higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with the
338 largest Rb/Sr spread for the uppermost data of the two drilling wells. Older formation waters

339 in the deepest grouping would also need the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios to support a
340 relationship induced by an age impact and this again is not the case. In summary, an older
341 “age” for the deeper water samples seems not to be the case either.

342 As already stated, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the H₂O leachates are almost systematically
343 higher than those of the HCl leachates, except at 2,768.1 m depth. Also, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of
344 both types of leachates plot farther from line of equivalent values when depth increases. The
345 hypothesis explaining this almost systematic difference seems to combine the facts that: (1)
346 the minerals dissolved by the dilute HCl, probably of carbonate, chloride and/or sulfate types,
347 yield lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the non-contaminated pore waters of the same samples, and
348 (2) the difference among the Sr isotopic ratios of the two leachates increases with depth.
349 These two observations apply, in turn, to all samples of the two studied wells (Fig. 5). The
350 differences in the Sr isotopic ratios of the successive H₂O and HCl leachates are also
351 supportive for a crystallization of the HCl-soluble minerals before a recent flushing of pore
352 waters, and for a progressive increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio relative to depth. In two cases,
353 those of the samples at 2766.1 and 2778.7 m depth of the Peciko-3 well, the analytical
354 uncertainties of the H₂O and HCl leachates overlap, with a large analytical uncertainty in the
355 second case. It is, therefore, plausible that the soluble minerals and the pore waters were
356 isotopically homogeneous once, at least for these two samples. In turn, this homogeneity
357 being not the usual issue here, confirms that a supplementary water supply seems to have
358 invaded the sediments after the soluble mineral crystallized and therefore very recently with a
359 different $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than that of the occurring soluble minerals. However, some
360 interconnection between the connected samples should be visible in this case, which is not as
361 obvious for the data of the H₂O leachates from two wells.

362

363 5.3. The meaning of the REE contents and patterns in the H₂O leachates

364 It is probably appropriate to recall here that REEs are lithophyte, electropositive,
365 mostly trivalent and refractory. Their use in geochemistry is based on systematic variations of
366 their ionic radius, as well as on the complexation capacities of two of them to change their
367 redox state: cerium as Ce^{3+} and Ce^{4+} , and europium as Eu^{2+} and Eu^{3+} . Also to be remembered
368 is the fact that REE patterns characterizing sedimentary materials are often very uniform as
369 they are representative of the upper continental crust (Taylor and McLennan, 1985), which is
370 easily tested by comparing any REE spectrum to the pattern of the PAAS reference. These
371 patterns are usually identified by a negative Eu anomaly due to varied oxidation-reduction
372 conditions and a more or less positive Eu anomaly that focuses specifically on some

373 partitioning of detrital plagioclases that were progressively altered. In this context, seawater is
374 generally characterized by marked Ce depletions due to an oxidation into Ce^{IV} and its
375 separation from other REE by preferential uptake onto Mn^{IV} oxide.

376 The REE patterns characterized by low to very low contents display scattered
377 distributions relative to the PAAS, which is partly due to analytical aspects inherent for
378 extremely low contents (Fig. 9, lower row). The patterns also yield a systematic irregular
379 increase from Eu to Gd and Tb, as well as a systematic low La/Yb ratio. The low to very low
380 total REE contents relative to depth include almost automatically REEs with contents below
381 the detection limit. The fact that fluids contain usually very low contents of REEs makes that
382 the primary role of these REEs is here in the detection of a contamination of the pore waters
383 by their abnormally high contents in the H₂O leachates. Together with high metal contents,
384 they allow identifying and discarding the contaminated waters. It might be added that
385 increased contents of heavy REEs could also be theoretically due to the use of surface water
386 during drilling that diffused into the sandy matrix with the drilling pollutants. On the basis of
387 these constraints, twelve H₂O leachates of the Peciko-3 well remain eligible for representing
388 the restored pore waters, as well as four leachates of the Peciko-8 well. In the former drilling,
389 they were collected close to 2,737 and 2,747 m in the upper part, between 3,118 and 3,183 m
390 in the intermediate level, and the five deepest samples. Four leachates from second drilling
391 well are also in these values: that close to 3,506 m and the three deepest samples between
392 3,534 and 3,538 m depth.

393 If now one considers the ⁸⁷Sr/⁸⁶Sr ratio of the non-contaminated H₂O leachates, it is
394 clear that the two uppermost clean water samples are not in continuous connection and that
395 they seem, with lower Sr isotopic values, to have been mixed with present-day surface waters.
396 In the intermediate sequence, the four samples located between about 3,118 and 3,177 m
397 depth could be part of a communicating pool, while the deepest leachates of the Peciko-3 well
398 seem to be presently isolated with the highest ⁸⁷Sr/⁸⁶Sr ratios of the whole water sequence.
399 Also none of the highest Sr isotopic data from deepest leachates of the second drilling well
400 overlap and, therefore, are probably not connected directly.

401

402 5.4. The meaning of the combined elemental contents and Sr isotopic signatures

403 The HCl leaching dissolved carbonates and sulfates that crystallized either during the
404 recent invasion of the pore waters or previously to it. This second hypothesis is the most
405 appropriate as the two types of leachates yield almost never the same ⁸⁷Sr/⁸⁶Sr ratio. Not
406 contemporaneous with the current pore waters, the HCl soluble minerals precipitated then

407 probably before the present-day fluids diffused into the sediments. In fact, identical $^{87}\text{Sr}/^{86}\text{Sr}$
408 ratios for the two types of leachates was only obtained at 2,766 and 2,779 m depth, where the
409 soluble minerals could be somehow contemporaneous with the pore waters, both with
410 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within analytical uncertainty.

411 Restoring pore waters of sediments is analytically quite easy. However, the restored
412 fluids appear more sensitive to contamination than the associated soluble minerals, at least
413 here. To test such anthropogenic pollution, the REE contents of the restored waters seem to be
414 an appropriate basis to discard those fluids containing large amounts of REEs, together with
415 high metal contents. Beyond these analytical aspects that are useful in the selection of
416 samples representative of “natural” environments, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of restored waters also
417 represent an efficient tool to trace the connectivity of superposed pore-water systems. Here in
418 the case of the Peciko gas field, the superposed channelizing horizons seem not to be often
419 interconnected, at least nearby the drilling wells, unless drilling cemented somehow the sands
420 around. Such characteristics are also of interest if a reservoir field is studied for potential CO_2
421 storage for instance.

422

423 **6. Conclusions**

424

425 In an attempt to restore the pore waters of the hydrocarbon-bearing sand units from
426 Peciko gas reservoir in the southern Mahakam Delta (Indonesia), the host rocks were leached
427 with de-ionized water to analyze the major, trace and rare earth elemental contents of the
428 separates with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. After water leaching, the rocks were also treated with dilute
429 hydrochloric acid to analyze the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the associated soluble minerals.

430 Abnormally high REE and metal contents suggest that most of the recovered H_2O
431 leachates were contaminated, most probably during drilling. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the non-
432 polluted leachates increase progressively with depth, suggesting in turn that the pore waters
433 from upper sandy layers were mixed, probably recently, with local waters of riverine origin.
434 Also, only a few water levels at intermediate depths yield analytically similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
435 suggesting interconnections. On the other hand, the minerals that were dissolved by dilute
436 hydrochloric acid yield quite systematically lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the associated pore
437 waters. These minerals most probably crystallized before the invasion of the sedimentary
438 sequence by recent to present-day pore waters. Also, the superposed pore-water horizons
439 seem not to have been interconnected in the gas field, at least near the drilling wells.

440

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451 their contribution to the analytical procedure.

452

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534

535 **Table and figure captions**

536

537 **Figure 1:** Location of the Peciko gas field in the Mahakam delta (modified from Furlan et al.,
538 1995).

539 **Figure 2:** North-to-South cross section of the northern Peciko gas field. The cross section
540 illustrates the reservoir units (in black) between the Peciko-3 and Peciko-8 drillings. In
541 the upper zone they are sub-horizontal towards the North and sub-vertical to the South.

542 In the lower zone, they are tilted in both flanks and steeper to the South (modified from
543 Grosjean et al., 1994).

544 **Figure 3:** The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to the corresponding Rb/Sr ratios of the H₂O leachates
545 from Peciko-3 well in the diagram (A) and from Peciko-8 well in the diagram (B). The
546 depths of the samples with data points away from the lines are given next to the dots.

547 **Figure 4:** The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the H₂O and HCl leachates relative to depth in the two
548 Peciko drillings. The data of the Peciko-3 well are to the left and those of the Peciko-8
549 well are to the right. The two upper diagrams display the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the H₂O
550 leachates and the two lower those of the HCl leachates.

551 **Figure 5:** The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the H₂O vs. HCl leachates relative to depth in the Peciko-3
552 (A) and in the Peciko-8 (B) drill wells.

553 **Figure 6:** The contents of four major elements of the H₂O leachates relative to depth in the
554 Peciko-3 well (in the four upper diagrams) and of Rb and Sr (in the two lower
555 diagrams). The arrows (full and dashed) underline the spread of the data relative to
556 collection depth. The leachates susceptible to have been contaminated are shown by the
557 gray dots.

558 **Figure 7:** Elemental ratios of six major and two trace elements of the H₂O leachates relative
559 to depth in the Peciko-3 well.

560 **Figure 8:** The contents of three metal-trace elements of the H₂O leachates relative to depth in
561 the Peciko-3 well. The arrows (full and dashed) underline the spread of the data relative
562 to collection depth.

563 **Figure 9:** The REE patterns of the H₂O leachates relative to the PAAS reference. The
564 numbers below each diagram stand for the REEs from La to Lu and the dashed lines are
565 drafted to show the graphic relation between the two REE end members.

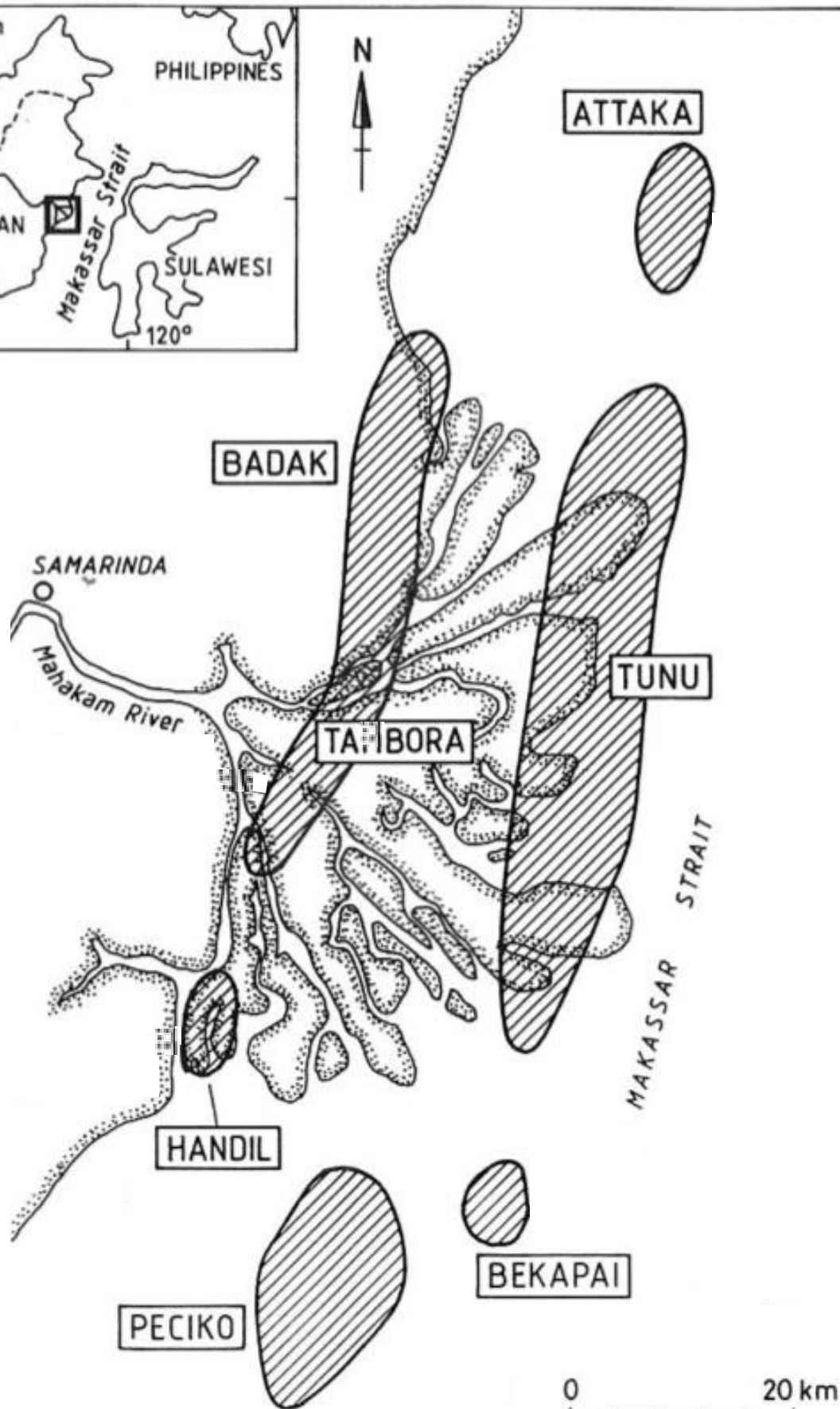
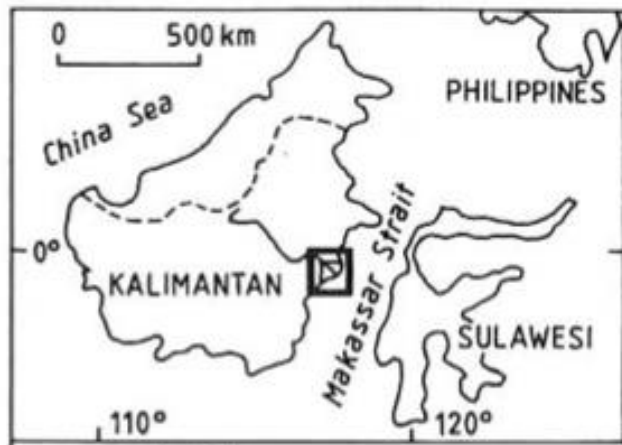
566 **Figure 10:** The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to the corresponding Rb/Sr ratios of the H₂O leachates
567 from Peciko-3 well in the diagram (A) and from Peciko-3 well in the diagram (B). The
568 depths of the samples with data points away from the lines are given next to the dots.

569
570 **Table 1:** The contents in major elements of the H₂O leachates.

571 **Table 2:** The contents in trace elements of the H₂O leachates.

572 **Table 3:** The contents in rare-earth elements of the H₂O leachates.

573 **Table 4:** The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the H₂O and HCl leachates and the difference in the $^{87}\text{Sr}/^{86}\text{Sr}$
574 ratios of both in the same leachates at the same depths.



North

South

drill holes

NWP8

NWP3

2000
(m)

2500

3000

3500

4000

FS 59

MF 7

UPPER
ZONE

MF 75

FM 8

FS 85.1

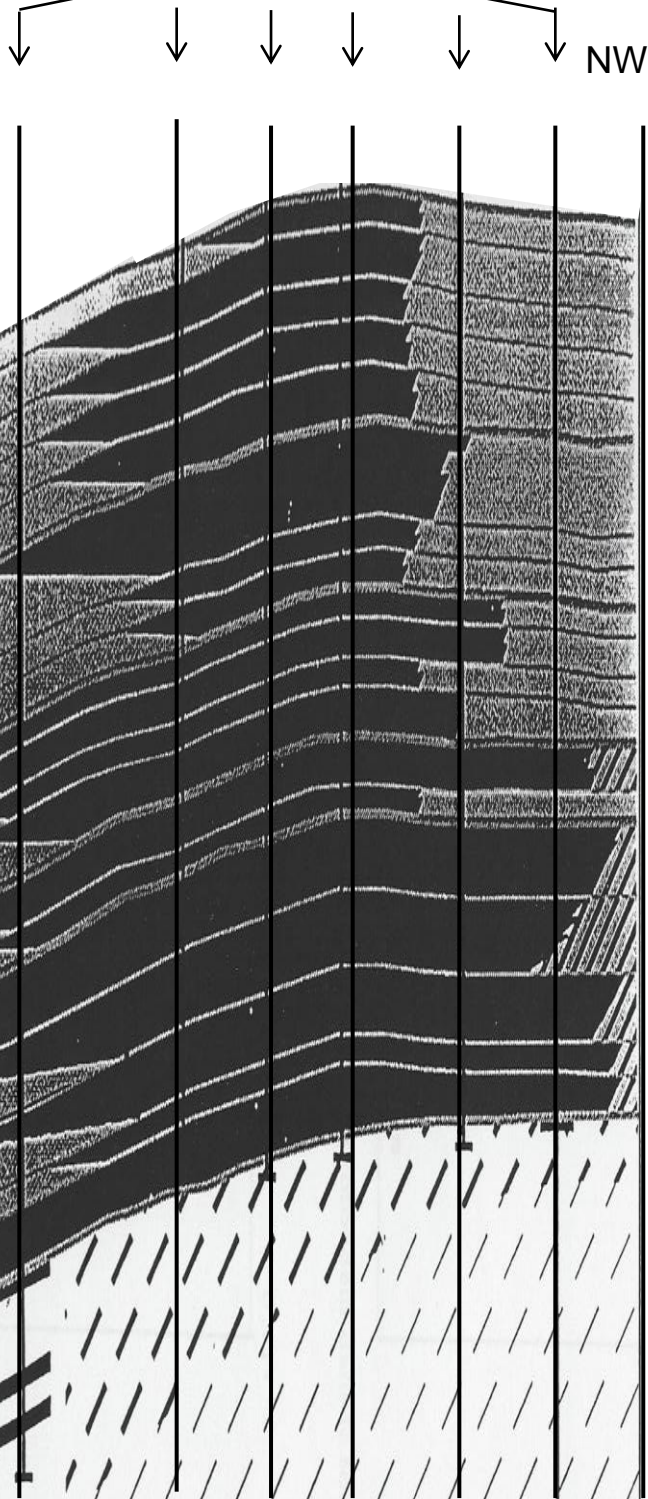
FS 85.4

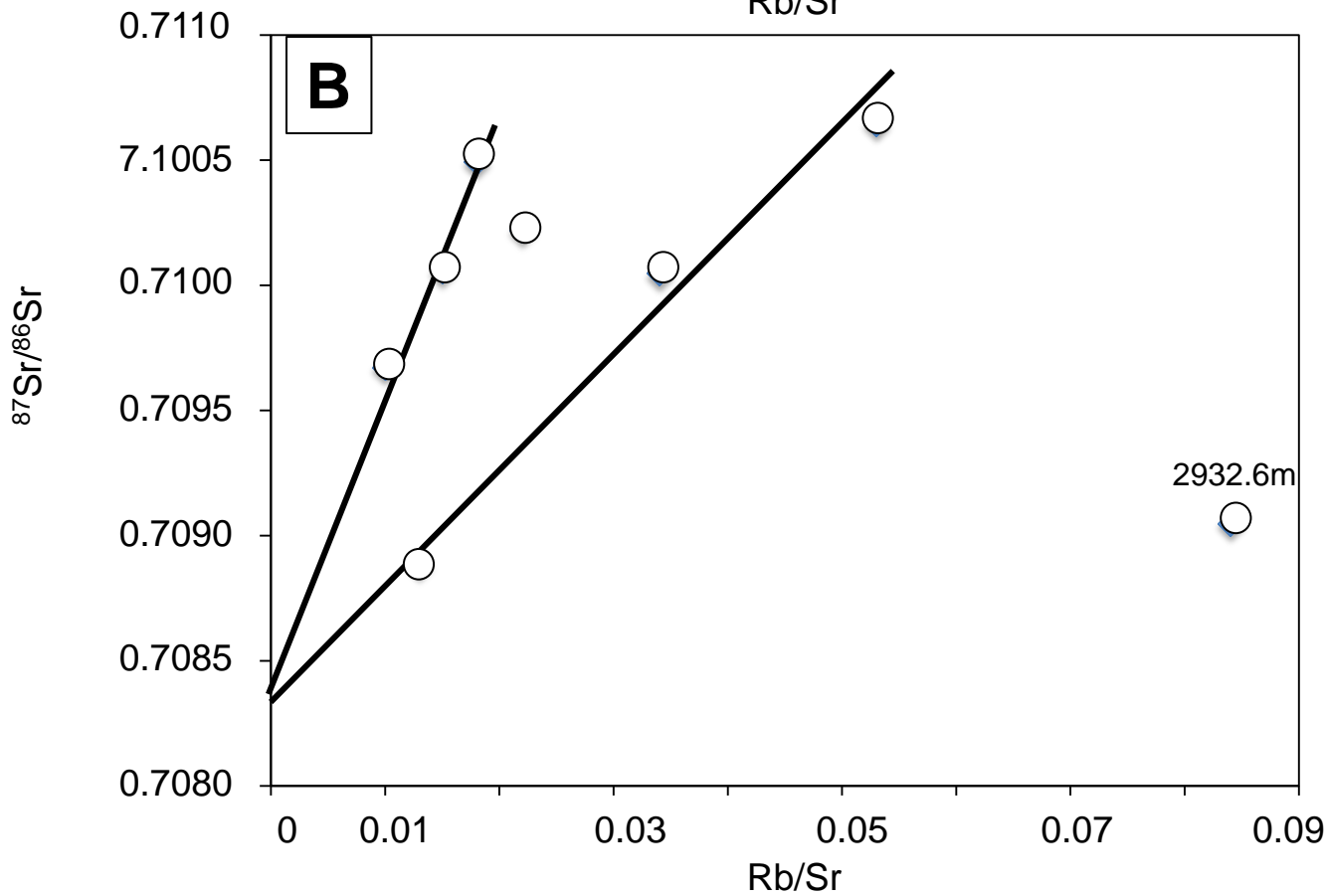
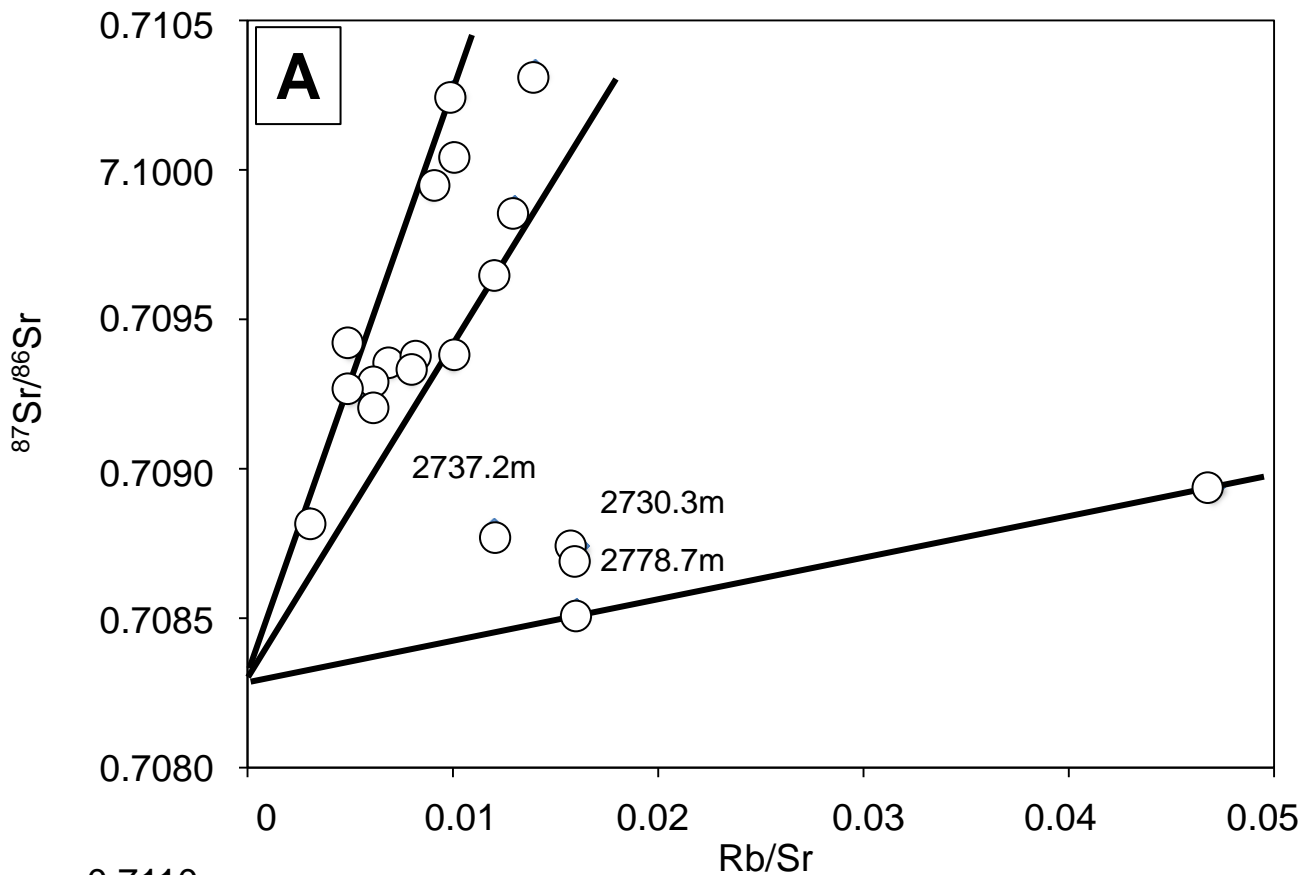
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LOWER
ZONE

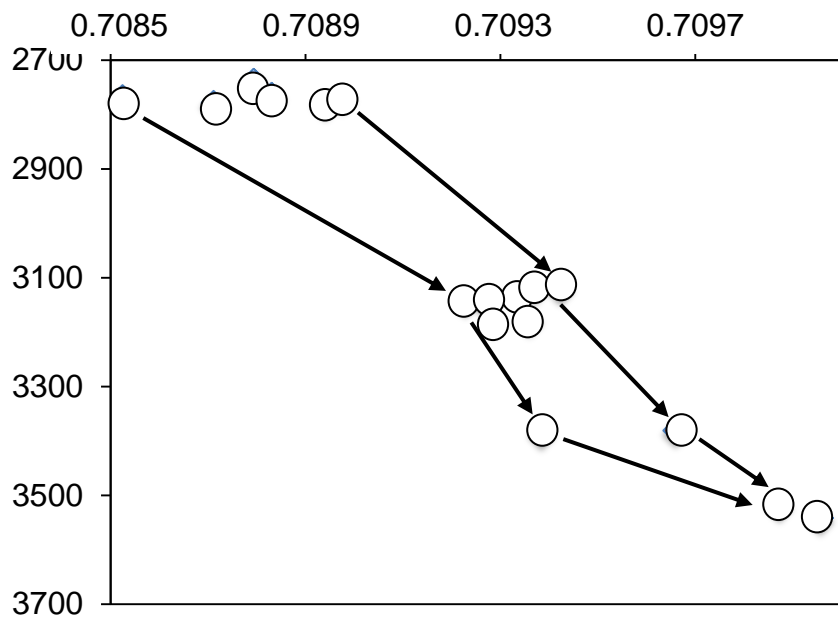
FM 9

2 km

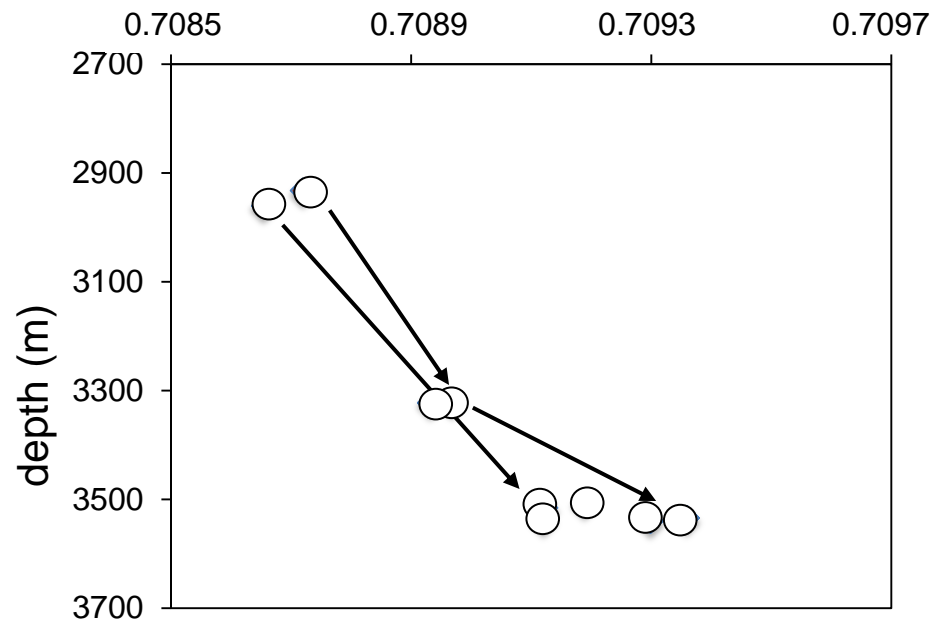
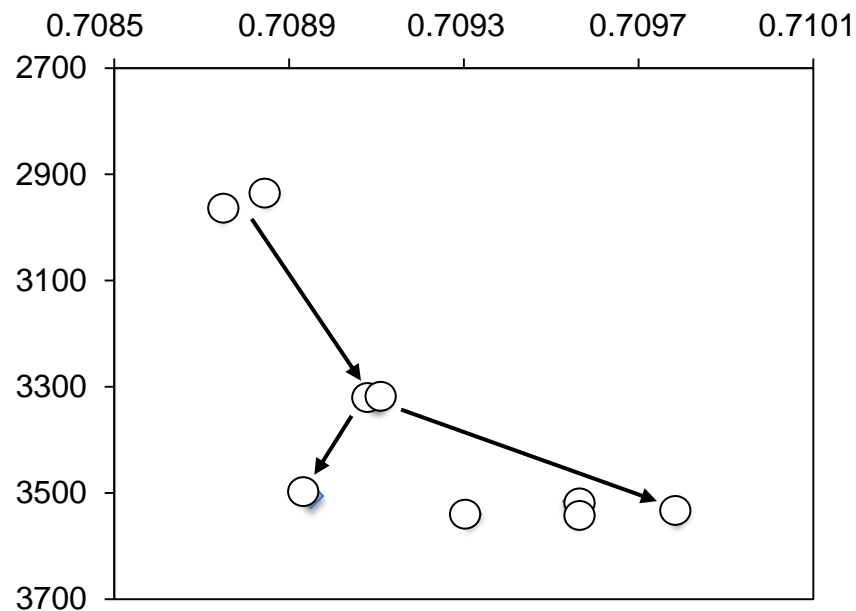
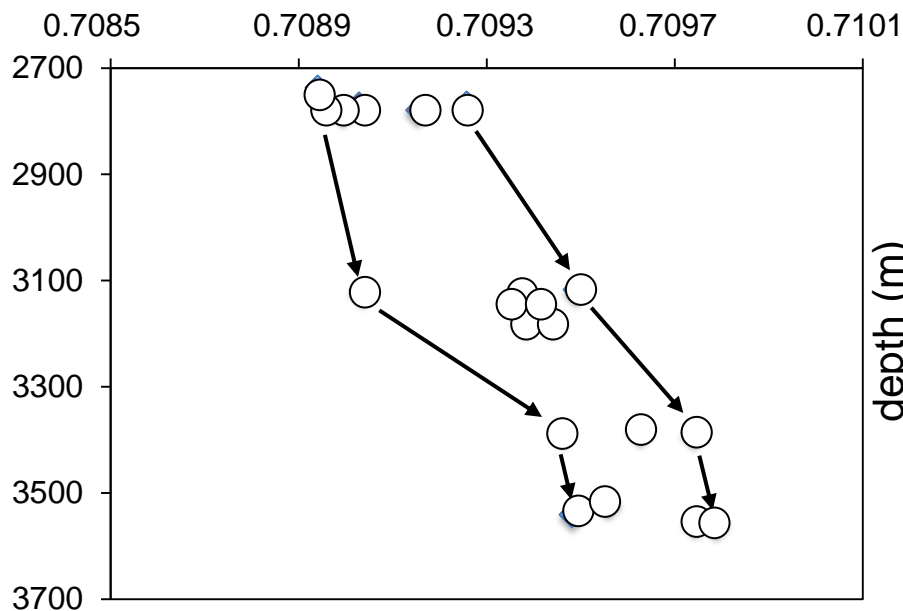


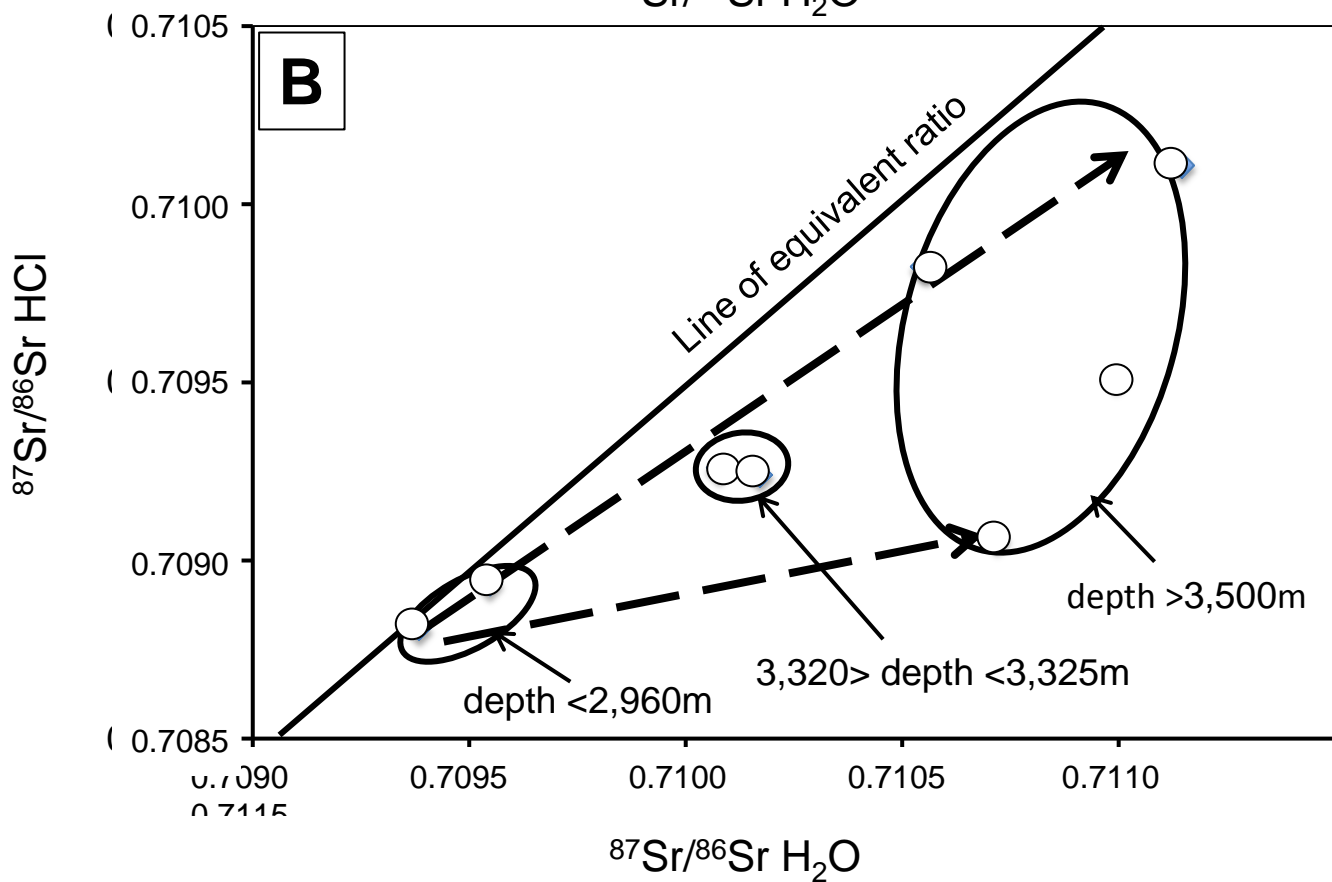
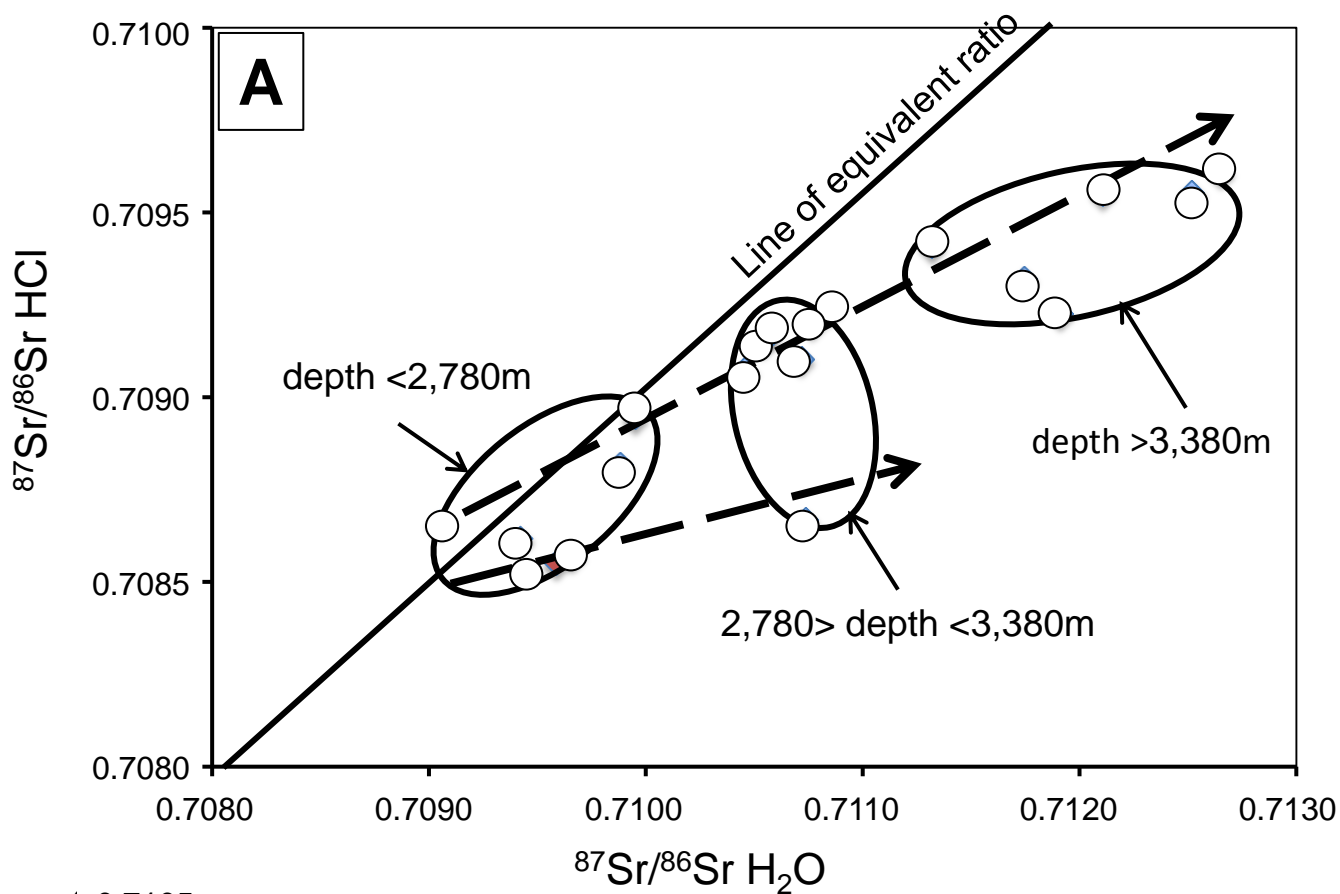


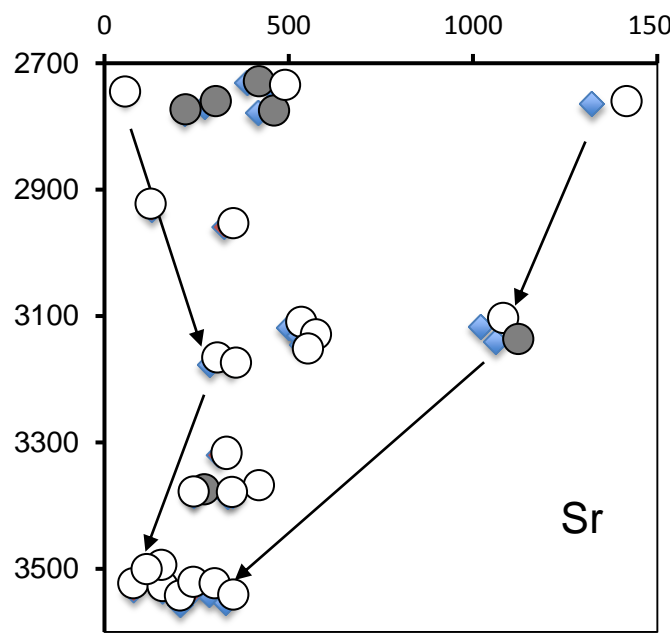
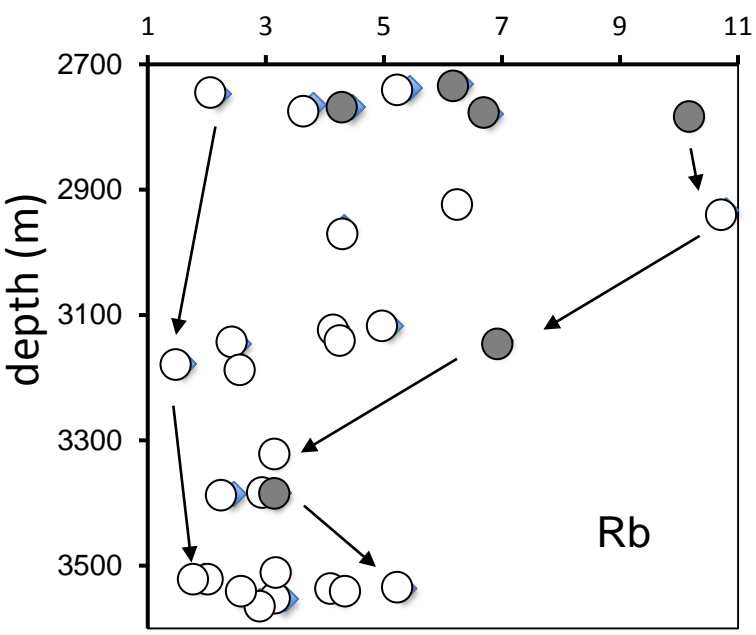
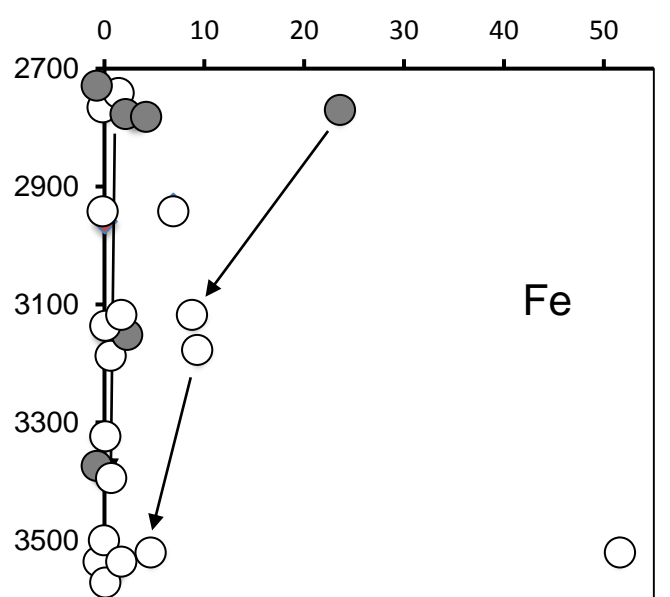
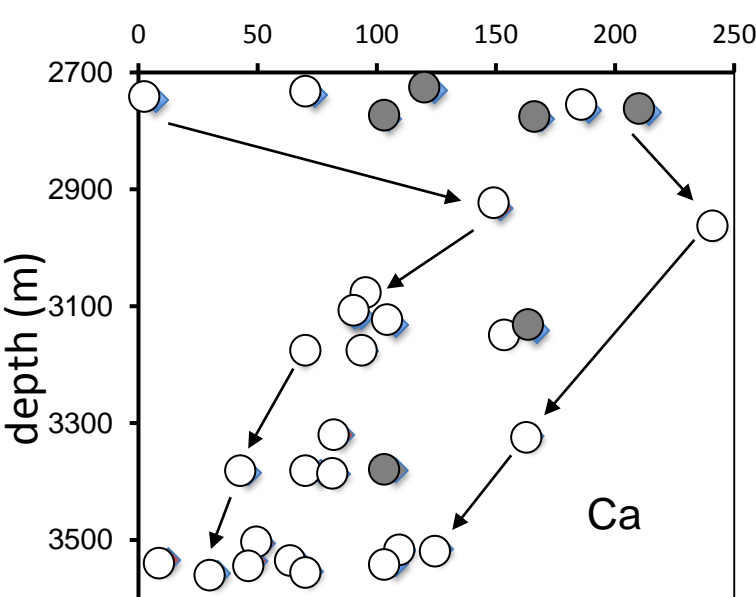
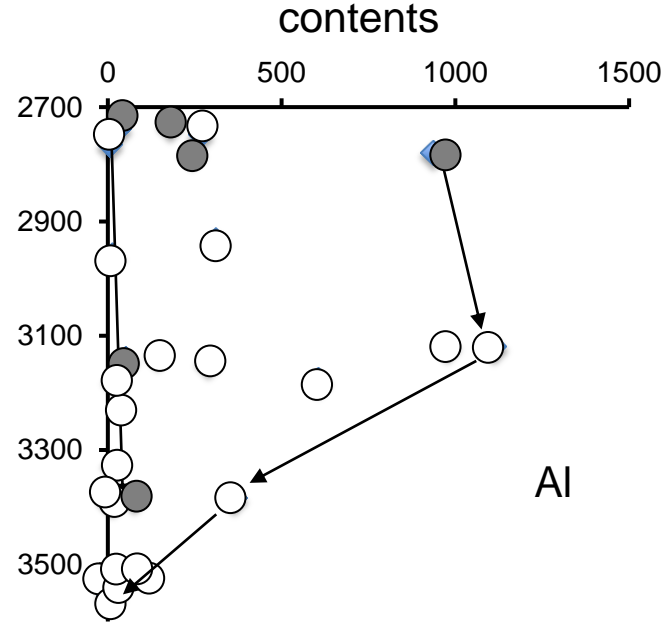
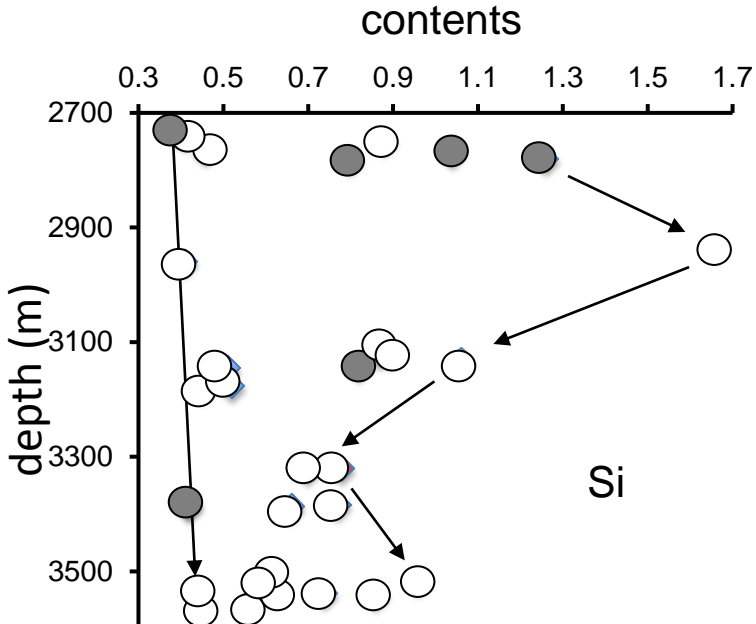
Peciko-3



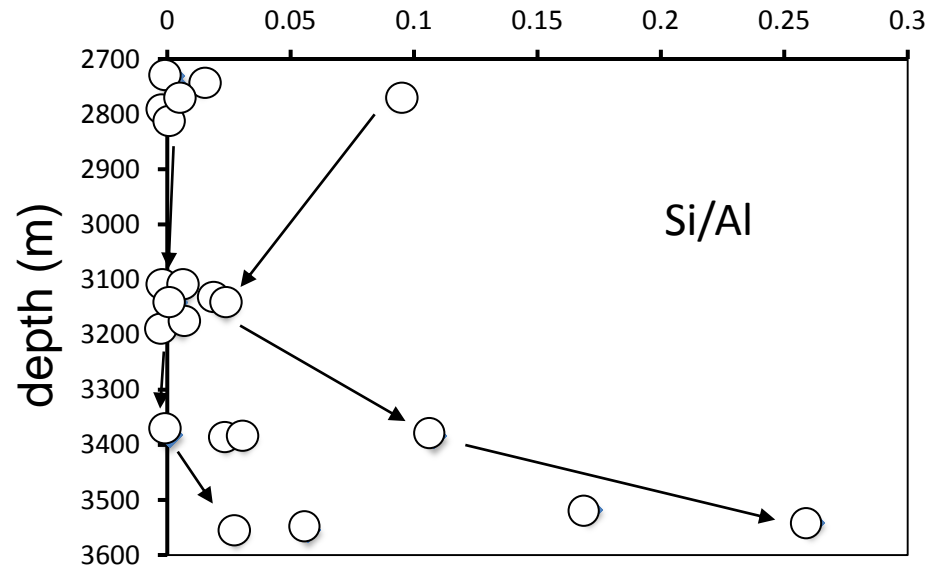
Peciko-8

 $^{87}\text{Sr}/^{86}\text{Sr}$ of H_2O leachates $^{87}\text{Sr}/^{86}\text{Sr}$ of HCl leachates

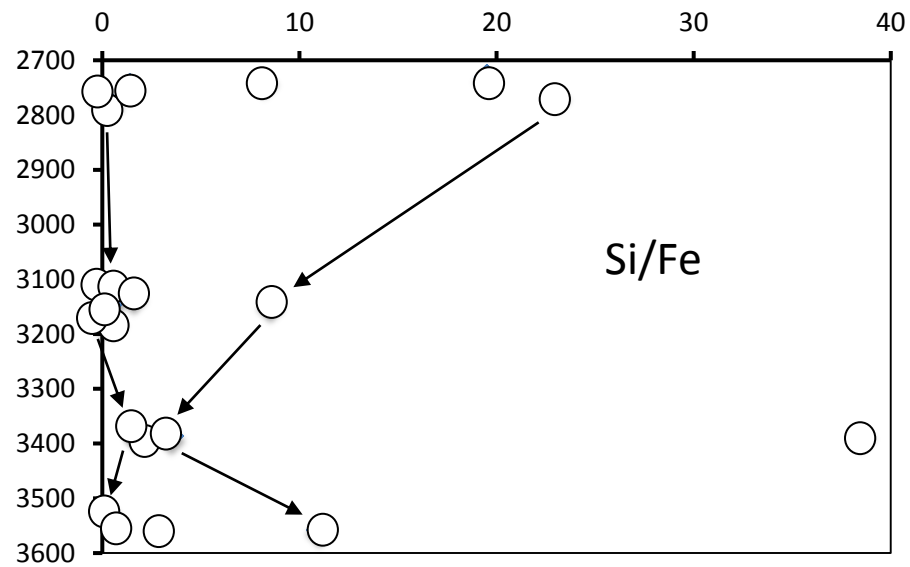




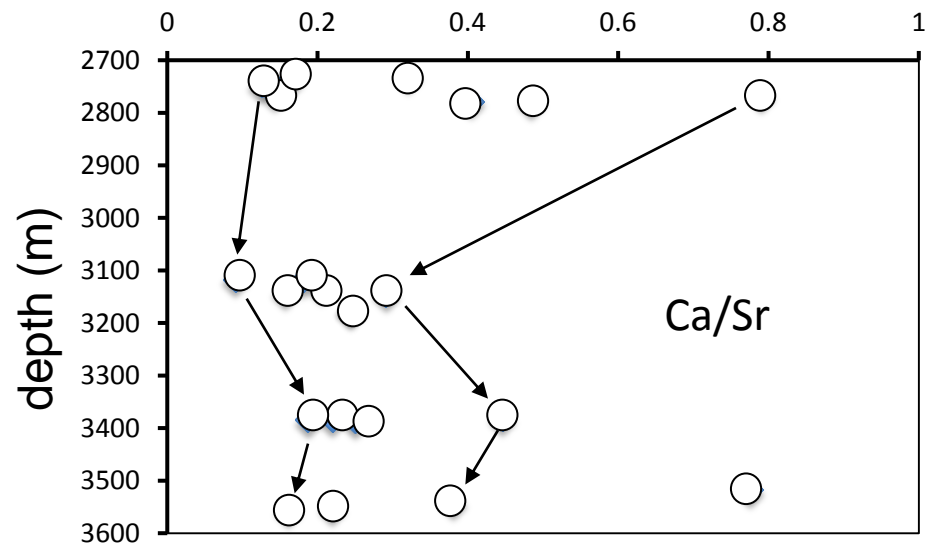
ratios



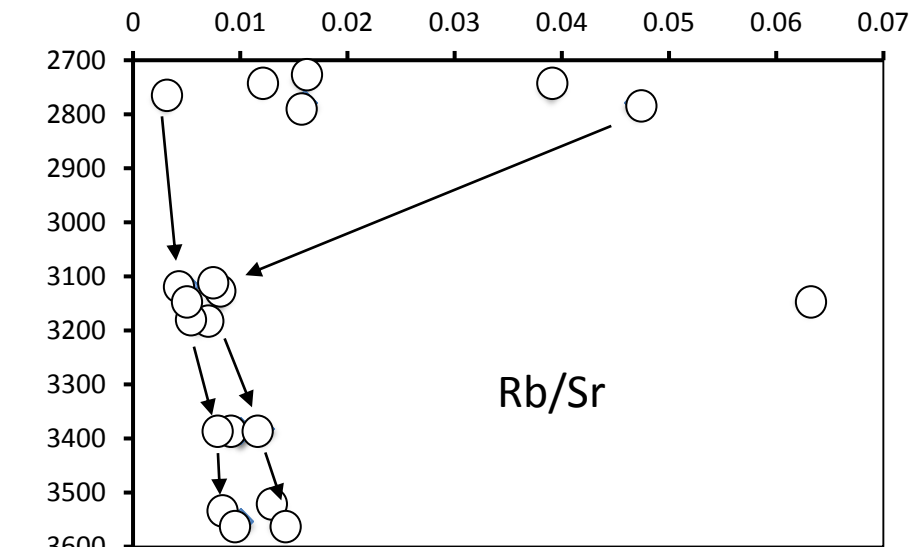
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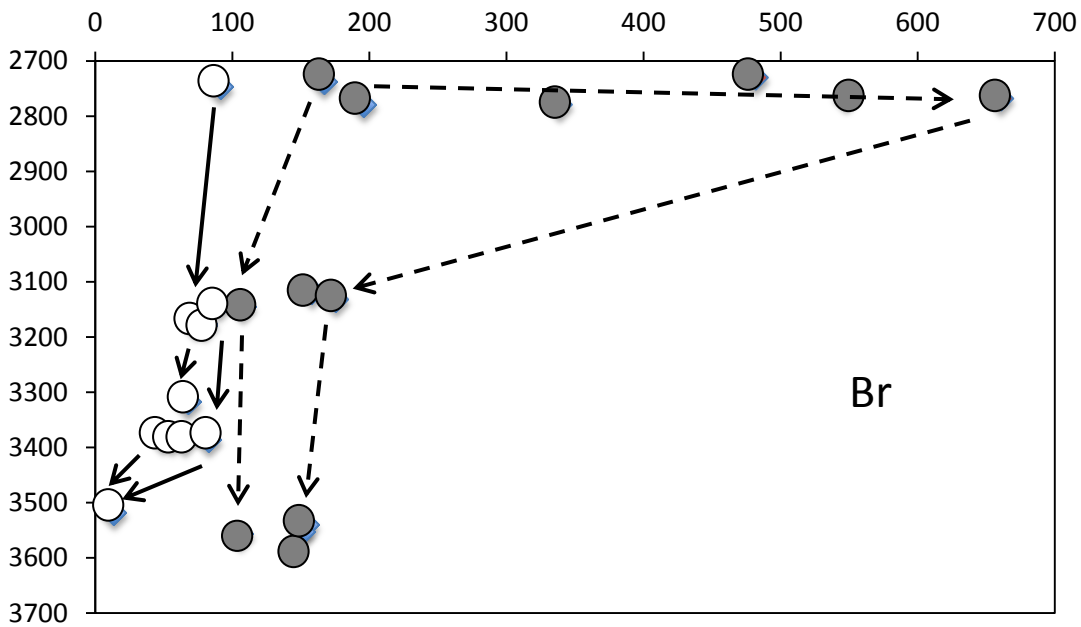
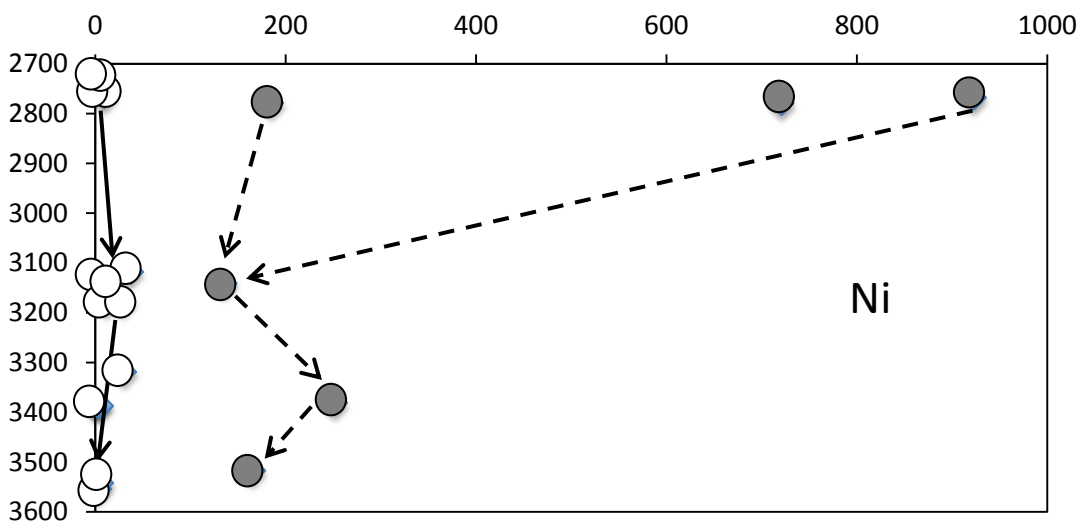
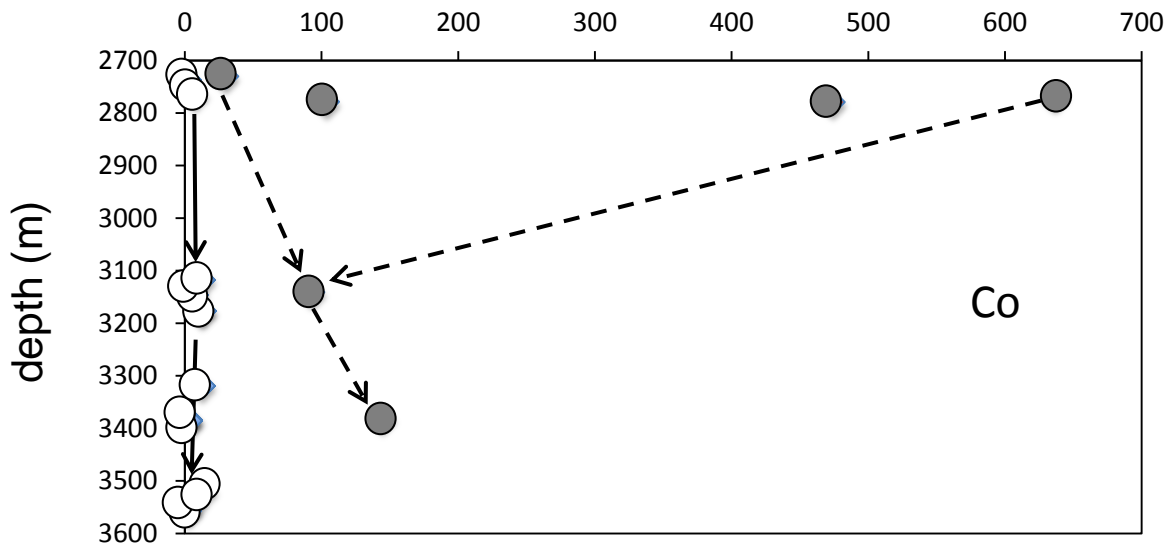
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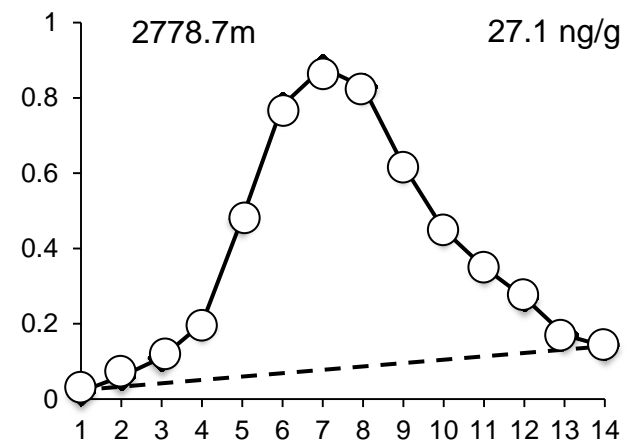
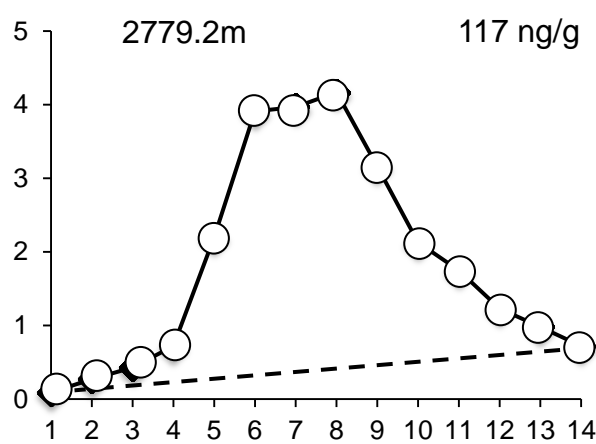
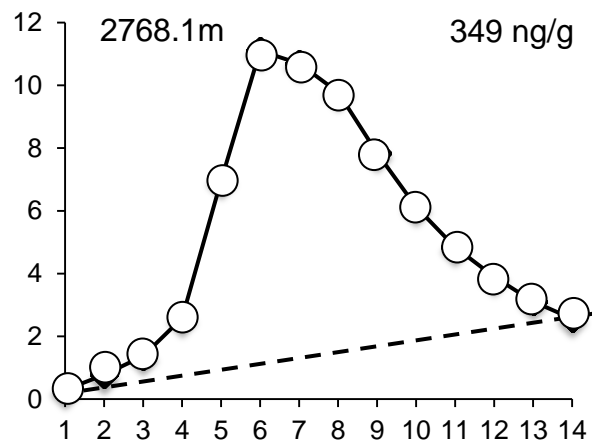
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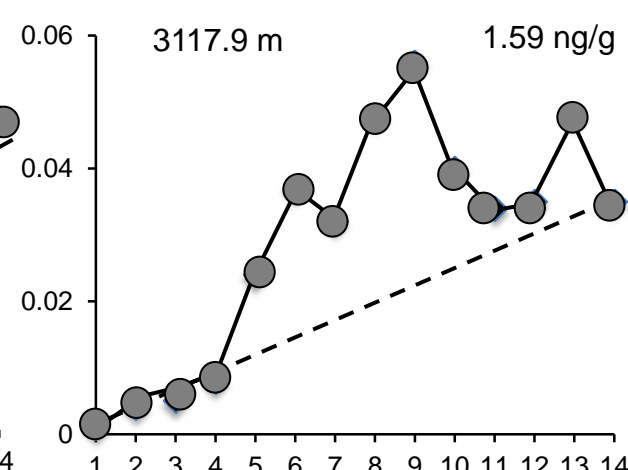
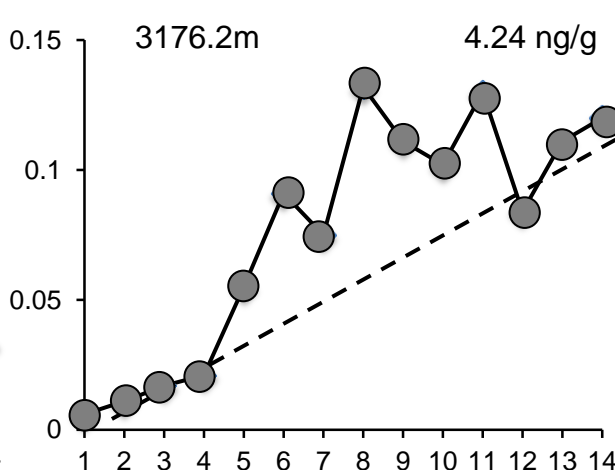
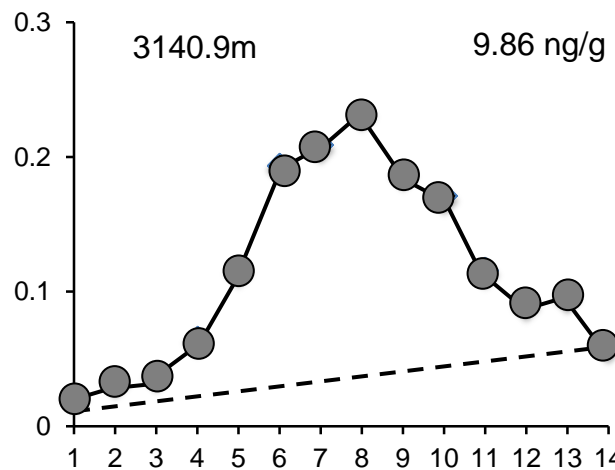
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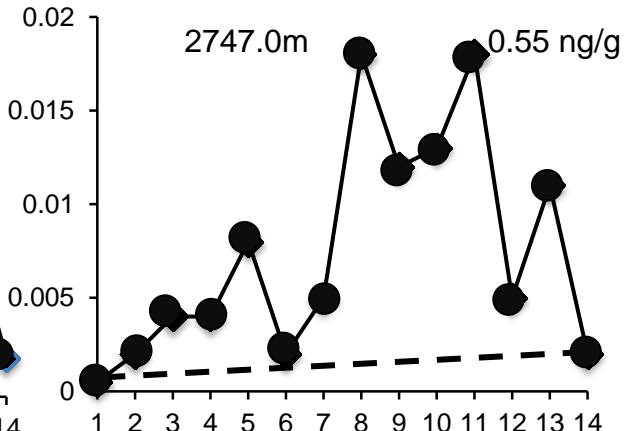
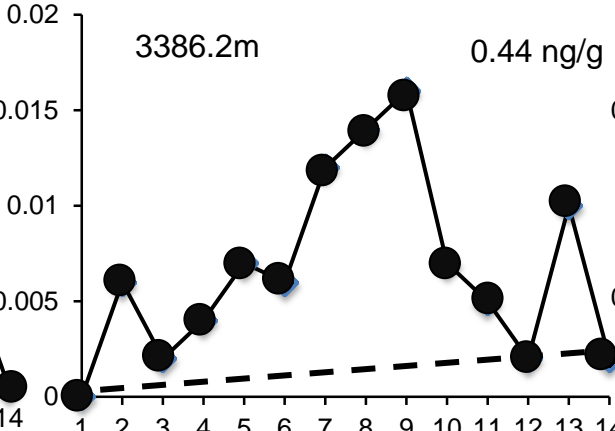
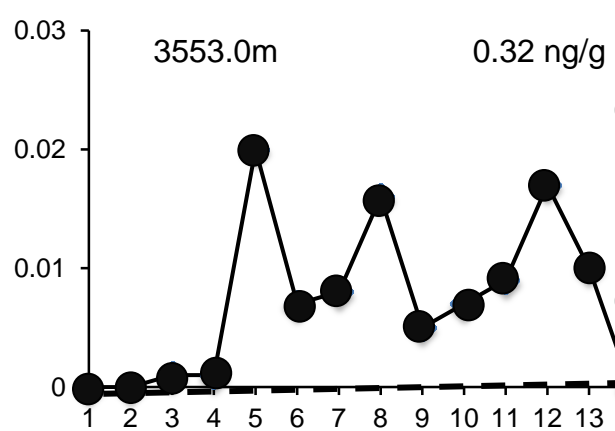
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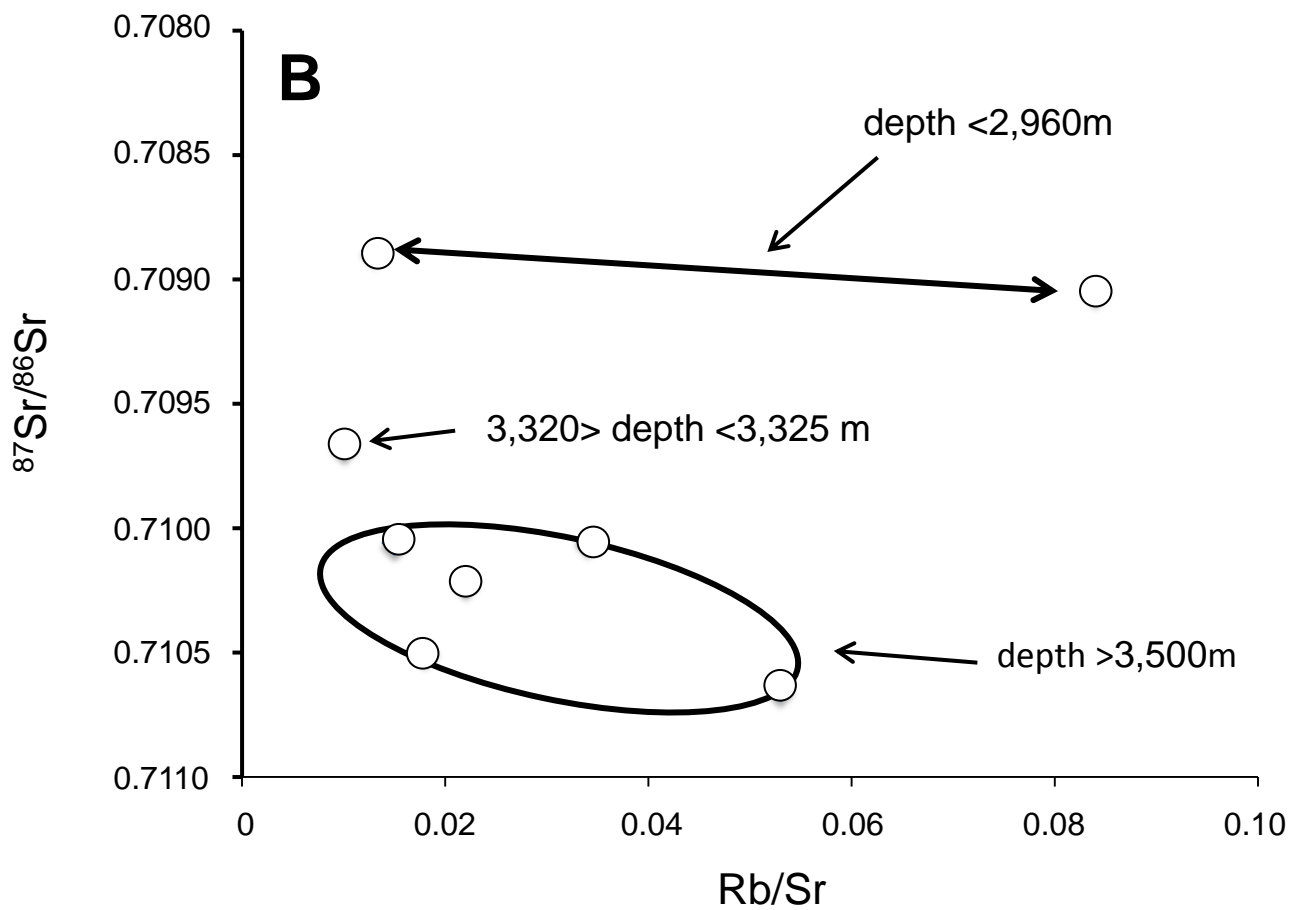
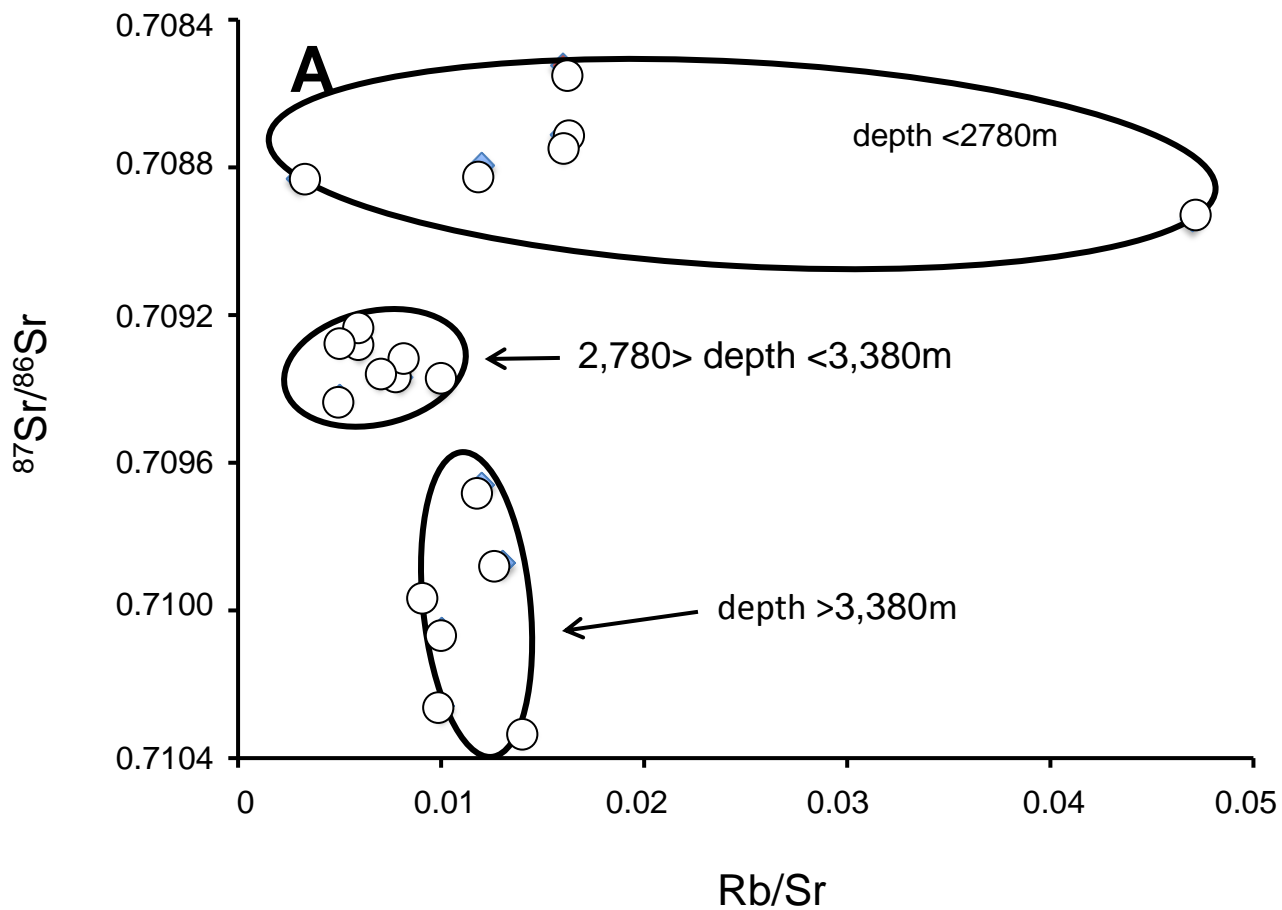


10 > x > 1 ppb



<1 ppb





Sample ID	Si (ng/g)	Al (ng/g)	Mg (ng/g)	Ca (ng/g)	Fe (ng/g)	Mn (ng/g)	Rb (ng/g)	Sr (ng/g)	Rb/Sr	Ca/Sr	⁸⁷ Sr/ ⁸⁶ Sr (+/- 2σ)
NW Peciko-3											
C1-2730.3	0.39	179	22.3	124	0.02	2.39	6.29	387	0.016	0.320	0.708743 (16)
C1-2737.2	0.41	29.3	40.1	74.0	0.05	4.11	5.43	454	0.012	0.163	0.708794 (16)
C1-2747.0	0.88	266	2.64	7.03	0.63	bdl	2.19	56.2	0.039	0.125	-
C2-2764.5	0.46	4.9	109	189	0.02	0.47	3.80	1322	0.003	0.143	0.708830 (22)
C2-2766.1	-	-	-	-	-	-	-	-	-	-	0.708975 (16)
C2-2768.1	1.04	243	59.5	214	23.6	9.61	4.46	271	0.016	0.790	0.708524 (18)
C2-2778.7	0.80	936	75.4	169	2.83	4.89	6.80	417	0.016	0.405	0.708711 (46)
C2-2779.2	1.26	977	38.8	105	3.61	3.32	10.2	217	0.047	0.484	0.708941 (18)
C3-3116.9	0.89	1111	59.1	93.4	8.85	bdl	5.11	1021	0.005	0.091	0.709422 (18)
C3-3117.9	0.87	143	32.2	90.7	1.46	0.56	4.20	500	0.008	0.181	0.709369 (20)
C4-3131.4	1.06	51.0	47.1	108	0.67	0.36	4.26	528	0.008	0.205	0.709338 (16)
C4-3140.9	0.82	287	73.9	167	1.76	12.2	6.98	1061	0.006	0.157	0.709228 (16)
C4-3145.0	0.51	21.4	64.7	156	0.06	0.99	2.53	536	0.005	0.291	0.709271 (16)
C5-3176.2	0.52	605	32.6	95.3	9.35	1.64	2.56	344	0.007	0.244	0.709359 (16)
C5-3177.3	0.45	74.8	25.5	69.9	0.79	1.19	1.60	286	0.006	0.244	0.709285 (14)
C7-3381.0	0.42	363	71.7	108	0.07	8.51	3.01	242	0.012	0.446	0.709659 (14)
C7-3383.5	0.77	7.1	41.1	76.5	0.02	0.21	3.22	348	0.009	0.220	-
C7-3384.5	0.42	13.5	26.9	46.0	0.23	0.07	2.45	242	0.010	0.187	0.709384 (14)
C7-3386.2	0.66	27.3	29.8	83.5	0.19	0.30	3.18	334	0.010	0.250	0.710053 (18)
C8-3517.4	0.58	3.40	45.2	111	4.74	1.43	1.87	143	0.013	0.776	0.709872 (18)
C9-3540.5	0.86	3.30	26.4	108	1.34	0.44	2.61	284	0.009	0.380	0.709956 (16)
C9-3553.0	0.56	9.79	25.6	72.0	0.20	0.14	3.33	329	0.010	0.219	0.710259 (20)
C9-3556.6	0.44	15.6	14.6	33.1	0.04	0.04	2.89	205	0.014	0.161	0.710327 (16)
NW Peciko-8											
C1-2932.6	1.66	311	43.6	152	6.90	3.61	10.8	129	0.084	1.178	0.709048 (22)
C2-2959.4	0.41	13.0	208	242	0.04	18.0	4.33	325	0.013	0.745	0.708884 (18)
C3-3320.4	0.78	27.0	35.9	85.5	0.01	0.24	3.19	310	0.010	0.276	0.709671 (16)
C3-3322.4	0.70	19.1	86.8	165	0.02	6.64	-	-	-	-	0.709577 (16)
C5-3505.8	0.61	74.6	16.4	52.3	0.17	0.41	3.22	149	0.022	0.351	0.710219 (18)
C5-3515.7	0.96	107	75.1	127	51.5	9.00	1.95	128	0.015	0.992	0.710059 (20)
C6-3534.4	0.62	21.2	7.51	12.5	0.08	0.07	4.19	79.3	0.053	0.158	0.710646 (16)
C6-3536.4	0.44	24.0	27.6	49.1	0.12	0.71	5.35	158	0.034	0.311	0.710048 (16)
C6-3538.3	0.74	20.0	32.8	68.0	0.08	0.29	4.36	238	0.018	0.286	0.710495 (18)

contents are in ppb

Sample ID	Cr (ng/g)	Co (ng/g)	Ni (ng/g)	Cu (ng/g)	Zn (ng/g)	Br (ng/g)	Ba (ng/g)	Cs (ng/g)	Sn (ng/g)
NW Peciko 3									
C1-2730.3	8.82	30.3	2.50	11.6	79.9	482	87.6	0.11	bdl
C1-2737.2	3.78	2.62	2.50	5.20	0.38	167	37.6	0.06	0.003
C1-2747.0	12.9	3.10	8.89	9.63	2.02	91.2	47.8	0.06	0.022
C2-2764.5	9.25	7.31	9.17	7.42	1.85	548	26.3	0.08	0.006
C2-2768.1	38.6	637	923	442	2099	661	29.6	0.12	0.025
C2-2778.7	12.0	104	185	24.7	201	196	15.2	0.07	bdl
C2-2779.2	11.7	474	721	155	1627	339	18.3	0.12	bdl
C3-3116.9	18.3	12.7	37.1	32.6	8.26	158	28.2	0.09	0.04
C3-3117.9	13.3	12.8	30.2	30.0	5.35	67.8	29.9	0.06	bdl
C4-3131.4	28.5	5.99	7.25	7.24	6.67	175.4	25.8	0.08	bdl
C4-3140.9	32.9	93.3	136	12.2	83.0	90.5	13.6	0.14	0.017
C4-3145.0	12.1	7.42	15.5	4.89	9.32	108	16.2	0.05	0.023
C5-3176.2	15.3	13.3	28.8	9.76	12.0	73.5	25.4	0.03	bdl
C5-3177.3	13.8	12.6	11.9	5.86	13.2	80.1	22.2	0.03	bdl
C7-3381.0	13.2	145	252	3.24	169	49.2	10.2	0.06	bdl
C7-3383.5	13.1	3.20	2.27	5.15	2.85	56.0	21.0	0.04	bdl
C7-3384.5	17.6	2.34	1.11	4.14	1.89	65.9	30.2	0.04	bdl
C7-3386.2	16.9	3.14	5.40	5.56	5.08	82.8	21.7	0.05	bdl
C8-3517.4	14.4	14.2	166	2.63	44.6	13.7	14.8	0.06	bdl
C9-3540.5	12.3	6.19	5.83	3.74	16.4	154	35.0	0.06	bdl
C9-3553.0	13.7	3.00	3.15	6.09	2.24	151	18.3	0.07	bdl
C9-3556.6	13.6	2.68	bdl	6.97	1.10	106	20.8	0.04	bdl
NW Peciko 8									
C1-2932.6	22.8	764	1356	398	1529	87.9	15.5	0.30	0.007
C2-2959.4	13.0	58.0	143	7.55	13.5	67.6	9.35	0.08	bdl
C3-3320.4	13.8	1.71	0.09	5.83	5.74	29.1	18.7	0.05	bdl
C3-3322.4	27.8	32.2	46.2	4.68	85.6	44.3	14.5	0.09	0.07
C5-3505.8	10.6	8.18	13.2	25.2	12.3	13.3	29.3	0.07	bdl
C5-3515.7	6.95	492	767	112	504	17.5	11.7	0.06	bdl
C6-3534.4	16.8	4.78	9.48	29.8	4.42	35.1	32.0	0.06	bdl
C6-3536.4	12.9	25.6	38.9	16.5	43.3	21.2	25.6	0.10	bdl
C6-3538.3	14.8	2.08	bdl	2.48	4.53	33.2	19.1	0.08	bdl

bdl stands for below detection limit

Sample #	La (ng/g)	Ce (ng/g)	Pr (ng/g)	Nd (ng/g)	Sm (ng/g)	Eu (ng/g)	Gd (ng/g)	Tb (ng/g)	Dy (ng/g)	Ho (ng/g)	Er (ng/g)	Tm (ng/g)	Yb (ng/g)	Lu (ng/g)	Σ REEs (ng/g)	La/Yb
NW Peciko-3																
C1-2730.3	0.02	0.11	0.02	0.25	0.17	0.02	0.12	0.02	0.11	0.01	0.03	bdl	0.05	bdl	0.93	0.40
C1-2737.2	0.01	bdl	bdl	0.006	0.05	0.01	0.01	0.006	0.01	0.004	0.007	bdl	0.02	bdl	0.13	0.50
C1-2747.0	0.02	0.13	0.03	0.13	0.04	0.002	0.03	0.01	0.06	0.01	0.05	0.002	0.03	bdl	0.54	0.67
C2-2764.5	bdl	0.003	0.002	0.07	0.03	bdl	0.03	0.005	0.009	0.005	0.02	bdl	0.04	0.003	0.20	-
C2-2768.1	11.2	61.5	12.1	87.6	38.7	12.0	49.9	7.57	36.7	6.06	13.8	1.58	8.78	1.11	349	1.28
C2-2778.7	0.91	5.10	0.99	6.85	2.64	0.84	4.12	0.64	2.91	0.45	1.00	0.11	0.47	0.06	27.1	1.94
C2-2779.2	3.49	21.3	3.76	24.4	12.2	4.22	18.5	3.23	14.8	2.11	5.00	0.50	2.75	0.31	117	1.27
C3-3116.9	0.24	1.12	0.17	1.01	0.58	0.18	0.75	0.14	0.91	0.18	0.50	0.09	0.29	0.06	6.16	0.83
C3-3117.9	0.05	0.31	0.04	0.26	0.13	0.04	0.15	0.04	0.26	0.04	0.10	0.01	0.13	0.01	1.57	0.38
C4-3131.4	0.04	0.14	0.02	0.15	0.07	0.01	0.08	0.02	0.09	0.02	0.01	0.02	0.04	0.01	0.72	1.00
C4-3140.9	0.86	2.72	0.35	2.20	0.65	0.21	0.97	0.18	0.88	0.17	0.33	0.04	0.27	0.03	9.86	2.17
C4-3145.0	0.07	0.31	0.03	0.28	0.10	0.01	0.10	0.03	0.07	0.02	0.03	0.004	0.08	0.007	1.41	0.88
C5-3176.2	0.24	0.89	0.15	0.70	0.31	0.10	0.35	0.10	0.52	0.10	0.37	0.03	0.31	0.05	4.22	0.77
C5-3177.3	0.04	0.17	0.03	0.25	0.08	0.03	0.18	0.03	0.21	0.04	0.16	0.02	0.14	0.01	1.37	0.29
C7-3381.0	0.66	2.36	0.42	2.39	0.80	0.25	1.48	0.18	0.93	0.22	0.39	0.03	0.20	0.03	10.3	3.30
C7-3383.5	0.01	0.03	0.01	0.03	0.03	bdl	0.01	0.02	0.04	0.01	0.03	0.004	0.03	bdl	0.25	0.33
C7-3384.5	0.01	0.04	bdl	0.05	0.02	bdl	0.06	0.004	0.05	0.005	0.03	0.004	0.05	bdl	0.32	0.20
C7-3386.2	bdl	0.05	0.02	0.13	0.04	0.07	0.05	0.01	0.08	0.01	0.01	0.001	0.03	0.001	0.50	-
C8-3517.4	0.02	0.04	0.01	0.06	0.04	bdl	0.07	0.02	0.06	0.02	0.03	0.01	0.04	bdl	0.42	0.50
C9-3540.5	0.03	0.07	0.01	0.09	0.05	0.03	0.06	0.02	0.03	0.02	0.02	0.01	0.04	0.001	0.46	0.75
C9-3553.0	0.005	0.02	0.009	0.05	0.10	0.008	0.04	0.01	0.02	0.007	0.03	0.007	0.03	bdl	0.34	0.17
C9-3556.6	0.005	0.02	0.001	0.08	0.04	bdl	0.06	0.01	0.02	0.01	0.01	bdl	0.06	0.001	0.31	0.08
NW Peciko-8																
C1-2932.6	3.92	32.7	9.26	87.8	46.6	16.1	65.9	10.7	49.8	7.98	17.0	1.73	8.50	1.07	359	0.46
C2-2959.4	0.006	0.004	0.016	0.04	0.07	bdl	0.04	0.004	0.05	0.02	0.02	0.006	bdl	bdl	0.28	-
C3-3320.4	bdl	bdl	0.005	0.03	0.07	bdl	0.03	0.008	0.02	0.01	0.01	bdl	0.02	bdl	0.20	-
C3-3322.4	bdl	0.03	bdl	0.05	bdl	0.002	0.02	bdl	0.02	0.006	0.003	bdl	bdl	0.007	0.14	-
C5-3505.8	0.08	0.06	0.004	0.10	0.06	0.04	0.10	0.02	0.07	0.02	0.05	0.008	0.06	0.004	0.68	1.33
C5-3515.7	2.64	21.7	5.08	39.0	17.2	6.03	23.2	3.38	15.5	2.34	4.88	0.49	2.39	0.30	144	1.10
C6-3534.4	bdl	0.03	0.08	0.06	0.10	0.008	0.06	0.01	0.04	0.01	0.02	0.001	0.02	0.003	0.44	-
C6-3536.4	0.02	0.10	0.03	0.18	0.07	0.02	0.17	0.02	0.17	0.03	0.02	0.01	0.05	0.001	0.89	0.40
C6-3538.3	bdl	bdl	0.008	0.02	0.06	0.005	0.05	0.008	0.07	0.007	0.03	0.001	0.03	0.001	0.29	-

bdl stands for below detection limit

Sample IDs	$^{87}\text{Sr}/^{86}\text{Sr} (\pm 2\sigma)$ H ₂ O leachates	$^{87}\text{Sr}/^{86}\text{Sr} (\pm 2\sigma)$ HCl leachates	$^{87}\text{Sr}/^{86}\text{Sr}$ H ₂ O/HCl
NW Peciko-3			
C1-2737.2	0.708794 (16)	0.708551 (18)	>0.000243
C1-2747.0	-	0.708606 (18)	-
C2-2764.5	0.708830 (22)	0.708573 (16)	>0.000257
C2-2766.1	0.708975 (16)	0.708946 (16)	>0.000029
C2-2768.1	0.708524 (18)	0.708660 (18)	<0.000136
C2-2778.7	0.708711 (46)	0.708617 (50)	>0.000094
C2-2779.2	0.708941 (18)	0.708817 (20)	>0.000124
C3-3116.9	0.709422 (18)	0.709237 (18)	>0.000185
C3-3117.9	0.709369 (20)	0.708668 (14)	>0.000132
C4-3131.4	0.709338 (16)	0.709112 (18)	>0.000226
C4-3140.9	0.709228 (16)	0.709074 (18)	>0.000154
C4-3145.0	0.709271 (16)	0.709150 (18)	>0.000121
C5-3176.2	0.709359 (16)	0.709103 (18)	>0.000256
C5-3177.3	0.709285 (14)	0.709173 (18)	>0.000112
C7-3381.0	0.709659 (14)	0.709409 (18)	>0.000255
C7-3383.5	-	0.708808 (16)	-
C7-3384.5	0.709384 (14)	0.709200 (14)	>0.000184
C7-3386.2	0.710053 (18)	0.709551 (16)	>0.000502
C8-3517.4	0.709872 (18)	0.709321 (16)	>0.000551
C9-3540.5	0.709956 (16)	0.709226 (14)	>0.000730
C9-3553.0	0.710259 (20)	0.709554 (18)	>0.000705
C9-3556.6	0.710327 (16)	0.709610 (16)	>0.000717
NW Peciko-8			
C1-2932.6	0.709048 (22)	0.708935 (14)	>0.000113
C2-2959.4	0.708884 (18)	0.708811 (16)	>0.000073
C3-3320.4	0.709671 (16)	0.709242 (16)	>0.000229
C3-3322.4	0.709577 (16)	0.709260 (52)	>0.000317
C5-3505.8	0.710219 (18)	0.709062 (16)	>0.000657
C5-3515.7	0.710059 (20)	0.709818 (22)	>0.000241
C6-3534.4	0.710646 (16)	0.710110 (18)	>0.000536
C6-3536.4	0.710048 (16)	0.709824 (16)	>0.000224
C6-3538.3	0.710495 (18)	0.709514 (16)	>0.000981