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1 Erosion of Archean continents: The Sm-Nd and Lu-Hf isotopic record
2 of Barberton sedimentary rocks

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21 **Abstract**

22 Knowing the composition, nature and amount of crust at the surface of the early Earth is
23 crucial to understanding the early geodynamics of our planet. Yet our knowledge of the
24 Hadean-Archean crust is far from complete, limited by the poor preservation of Archean
25 terranes, and the fact that less attention has been paid to the sedimentary record that tracks
26 erosion of these ancient remnants. To address this problem and get a more comprehensive
27 view of what an Archean continent may have looked like, we investigated the trace element
28 and Sm-Nd, Lu-Hf isotopic records of Archean metasedimentary rocks from South Africa.
29 We focused our study on sandstone and mudstone from drill core in the Fig Tree Group (3.23-
30 3.26 Ga) of the Barberton granite-greenstone belt, but also analyzed the 3.4 Ga Buck Reef
31 cherts and still older (3.5–3.6 Ga) meta-igneous rocks from the Ancient Gneiss Complex,
32 Swaziland.

33 Based on principal component analysis of major and trace element data, the Fig Tree
34 metasedimentary rocks can be classified into three groups: crustal detritus-rich sediments, Si-
35 rich sediments and Ca-, Fe-rich sediments. The detritus-rich sediments have preserved the
36 Sm-Nd and Lu-Hf isotopic signatures of their continental sources, and hence can be used to
37 constrain the composition of crust eroded in the Barberton area in the Paleoproterozoic period.

38 Based on Sm/Nd ratios, we estimate that this crust was more mafic than today, with an

39 average SiO₂ content of 60.5 ± 2 wt.%. This composition is further supported by isotopic
40 mixing calculations suggesting that the sedimentary source area contained equal proportions
41 of mafic-ultramafic and felsic rocks. This implies that the Archean crust exposed to
42 weathering was more mafic than today but does not exclude a more felsic composition at
43 depth. Neodymium and Hf crustal residence ages show that the eroded crust was, on average,
44 ~300-400 Ma older than the deposition age of the sediments, which highlights the importance
45 of intracrustal reworking of older crust at ~3.2 Ga in the Barberton area.

46 The Si-rich sediments have slightly positive $\epsilon_{\text{Nd}}(t=3.23\text{Ga})$ but extremely radiogenic $\epsilon_{\text{Hf}}(t=3.23\text{Ga})$,
47 up to +11. Based on analyses of 3.4 Ga Buck Reef cherts, we suggest that the radiogenic Hf
48 isotopic signature of the Si-rich sediments can be accounted for by the old chert clasts or
49 detrital silicified rock fragments present in the rocks. The latter have extremely high Lu/Hf
50 ratios such that their ϵ_{Hf} values would increase dramatically, by about +100 epsilon units
51 every 100 Ma. In the Ca-, Fe-rich sediments, one sample contains carbonate that preserves the
52 typical rare-earth element features of seawater precipitates. The initial Nd isotopic
53 composition of this sample ($\epsilon_{\text{Nd}}(t=3.23\text{Ga}) = +1.7$) is within the range of previous estimates for
54 Archean anoxic seawater.

55

56 **Keywords:** Neodymium, Hafnium, Continental crust, Chert, Fig Tree group

57

58

59 **1. Introduction**

60 Archean sedimentary rocks and their metamorphic equivalents are made up of rock fragments
61 and minerals derived from the erosion of ancient continents and/or precipitates from fluids
62 such as seawater. In contrast to igneous rocks, their composition has the potential to reflect a
63 greater spectrum of materials that were exposed at the surface of the early Earth, including
64 lithologies that are no longer present at the surface. Trace and major element contents of
65 Archean sedimentary rocks have previously provided important information on the
66 composition of the early crust and oceans as well as the oxidation state of the atmosphere-
67 ocean system (Taylor and McLennan, 1985; Condie, 1993; Kamber and Webb, 2001; Bolhar
68 et al., 2005; Hofmann, 2005; Alexander et al., 2009; Bau and Alexander, 2009; Kamber,
69 2010; Thurston et al., 2012; Kamber et al., 2014; Gaschnig et al., 2014; Liu et al., 2015; Tang
70 et al., 2016; Gaschnig et al., 2016). In general, these studies suggest that the upper Archean
71 crust was more mafic, and that the oceans were anoxic and dominated by higher hydrothermal

72 inputs than today. The Sm-Nd isotopic systematics of Archean sedimentary rocks have
73 brought complementary constraints on the nature and average crustal residence age of the
74 upper Archean crust (e.g. Jacobsen and Dymek, 1988; Frost, 1993; Jahn and Condie, 1995;
75 Yamashita and Creaser, 1999; Yamashita et al., 2000). Most of the Sm-Nd data converge
76 towards the conclusion that ancient sediments received important contributions from older
77 continental crustal material, implying that enough felsic crust had formed in the early Archean
78 to be registered in their sedimentary provenance. This interpretation receives some support
79 from *in situ* Lu-Hf isotopic analyses of detrital and magmatic Archean zircons (Belousova et
80 al., 2010; Griffin et al., 2014) even though the latter have more variable compositions and
81 may record a higher contribution of juvenile material in the early Archean.

82 In this paper, we report trace element concentrations and coupled whole-rock Lu-Hf and Sm-
83 Nd isotopic analyses of Archean metasedimentary rocks to see whether the two isotopic
84 systems when used in combination, can provide new insights on the crustal composition and
85 evolution of the Eastern Kaapvaal craton and potentially the composition of Paleoproterozoic
86 seawater. Except for the few measurements reported for example by Vervoort et al. (1999),
87 Hoffman et al. (2010) and Viehmann et al. (2014), whole-rock Lu-Hf isotopic compositions
88 of ancient metasedimentary rocks have generally not been measured. Most studies have
89 concentrated instead on *in situ* Lu-Hf isotopic analyses of detrital Archean zircons. This
90 approach, however, may capture the composition of only the most felsic portions of the
91 Archean crust, because zircons are common in felsic magmas, but very rare in mafic ones.
92 Here, we chose to investigate whole-rock Lu-Hf isotopic systematics rather than *in situ*
93 analyses of zircons to get a more comprehensive view of the composition of the eroded crust
94 and oceans in the Barberton area and to facilitate the comparison of Sm-Nd and Lu-Hf
95 isotopic data.

96 Use of sedimentary rocks as natural samples of the average composition of surrounding crust
97 requires a careful evaluation of the effect of sedimentary processes. While weathering and
98 post-depositional processes are generally well discussed in most studies dealing with Archean
99 rocks, the effects of other sedimentary processes such as different erodibility of mafic and
100 felsic rocks, or mineral sorting during sediment transport, are not systematically evaluated by
101 geochemists. Yet, these processes have been shown to bias the composition of modern
102 sediments and significantly affect interpretations of sediment provenance (e.g. Patchett et al.,
103 1984; Garzanti et al., 2010; Garzanti et al., 2011; Dhuime et al., 2011; Garçon et al., 2013;
104 Garçon et al., 2014; Sauzéat et al., 2015). Here, we evaluate and correct for sedimentary

105 effects in order to extract valuable information from the Archean sedimentary record.

106 This study focuses on Paleoproterozoic sedimentary samples – mainly sandstones and mudstones
107 – from core obtained by the International Continental Scientific Drilling Program (ICDP) in
108 the Fig Tree Group of the Barberton granite-greenstone belt, in the eastern part of the
109 Kaapvaal Craton in South Africa. The Barberton granite-greenstone belt is an emblematic
110 Paleoproterozoic terrane. Its outcrops of plutonic and volcanic rocks, in particular the komatiite
111 sequences, have been widely studied for their chemical and isotopic compositions (Condie
112 and Hunter, 1976; Clemens et al., 2006; Grosch et al., 2011; Stiegler et al., 2012; Furnes et
113 al., 2012; Robin-Popieul et al., 2012; Furnes et al., 2013; Kröner et al., 2013), including
114 whole-rock Sm-Nd and Lu-Hf isotopic analyses (Lahaye et al., 1995; Chavagnac, 2004;
115 Clemens et al., 2006; Van Kranendonk et al., 2009; Puchtel et al., 2013; Kröner et al., 2013;
116 Blichert-Toft et al., 2015). Investigations of Barberton metasedimentary rocks, however, are
117 scarcer although they are among the best-preserved Paleoproterozoic sedimentary sequences that
118 can be found on Earth. In particular, Fig Tree metasedimentary rocks have been studied for
119 trace and major element concentrations (Condie et al., 1970; Toulkeridis et al., 1999;
120 Hofmann, 2005) and *in situ* Lu-Hf isotopic analyses on zircons separated from one coarse-
121 grained greywacke (Zeh et al., 2013). Only a small number of whole-rock Rb-Sr, Sm-Nd and
122 Pb-Pb isotopic compositions have been measured (Toulkeridis et al., 1994; 1998; 1999).
123 Toulkeridis et al. concluded, however, that all three radiogenic isotopic systems were
124 disturbed by later thermal events and provided little useful information on the eroded crust in
125 the Barberton area. In this paper, we re-visit the Sm-Nd isotopic systematics of Fig Tree
126 metasedimentary rocks and additionally explore their whole-rock Lu-Hf isotopic
127 compositions using a larger dataset from core samples rather than samples from surface
128 outcrops.

129

130 **2. Geological overview of the eastern Kaapvaal craton**

131 The Barberton granite-greenstone belt and the Ancient Gneiss Complex (Figure 1a) contain a
132 rare, well-preserved 550 Ma (ca. 3.66-3.11 Ga) record of Archean crustal evolution. The
133 construction of this part of the craton is mostly thought to be through subduction-accretion
134 mechanisms with a major collision phase at ca. 3.23 Ga (de Wit et al., 1992; de Ronde and de
135 Wit, 1994; Lowe, 1994; Lowe and Byerly, 1999; Moyen et al., 2006; Schoene and Bowring,
136 2010; de Wit et al., 2011; Furnes et al., 2012) though alternative models have been suggested;
137 e.g. convective overturn of a dense upper crust and more buoyant middle crust (Van
138 Kranendonk et al., 2009) or evolution of a plume-related oceanic plateau (Chavagnac, 2004).

139 In the subduction-accretion model, the eastern portion of the Kaapvaal craton is said to result
140 from the assembly of at least two micro-continental blocks along NE-SW suture zones such
141 as the Inyoka fault system (cf. Figure 1c). The Ancient Gneiss Complex and the northern and
142 southern parts of the Barberton belt are often seen as possible building blocks sutured in the
143 ca. 3.23 Ga convergent event (e.g. de Wit et al., 1992; Lowe, 1994; Schoene and Bowring,
144 2010). The tectono- and chrono-stratigraphy of the Ancient Gneiss Complex and the
145 Barberton belt have been widely described and discussed in the literature since the 1970's
146 (e.g. M. J. Viljoen and R. P. Viljoen, 1969; Hunter, 1970; Anhaeusser, 1973; Eriksson, 1980;
147 de Wit, 1982; Kröner et al., 1989; Armstrong et al., 1990; Kröner et al., 1991; Kamo and
148 Davis, 1994; Kröner and Tegtmeier, 1994; Lowe and Byerly, 1999; Kröner, 2007; Schoene et
149 al., 2008; Schoene and Bowring, 2010; de Wit et al., 2011; Furnes et al., 2013). Here, we
150 present a brief geological overview and summarize a few observations and interpretations that
151 provide the key for understanding the following discussion.

152 The Ancient Gneiss Complex contains the oldest rocks yet discovered in the Kaapvaal craton.
153 It consists of deformed and metamorphosed tonalite-trondhjemite-granodiorites (TTGs)
154 interlayered with amphibolites known as the Ngwane gneiss (3.66-3.50 Ga; Compston and
155 Kröner, 1988; Kröner et al., 1989; Schoene et al., 2008; Zeh et al., 2011; Kröner et al., 2014)
156 and by a series of metasedimentary and metavolcanic rocks called the Dwalile metamorphic
157 suite (ca. 3.55 Ga; Kröner and Tegtmeier, 1994) (Figure 1c). The two units are intruded by
158 younger mafic-silicic banded orthogneisses and by a suite of tonalitic to granodioritic rocks
159 (Schoene and Bowring, 2010). The Ancient Gneiss Complex is now separated from the
160 Barberton greenstone belt by the 3.1 Ga-old Mpuluzi and Pigg's Peak granitic batholiths (e.g.
161 Kamo and Davis 1994; cf. Figure 1c).

162 The Barberton granite-greenstone belt is a succession of tilted, folded and variably
163 metamorphosed volcanic and sedimentary units, the Swaziland Supergroup, surrounded by
164 orthogneiss complexes (e.g. Stolzburg and Steynsdorp complexes > 3.43 Ga; Kamo and
165 Davis, 1994) and younger granitoid intrusions (e.g. Kaap Valley and Dalmien plutons at ca.
166 3.23 Ga; Armstrong et al., 1990; Kamo and Davis, 1994). The oldest unit of the Swaziland
167 Supergroup, the 3.54-3.27 Ga-old Onverwacht group, consists of mafic and ultramafic rocks –
168 komatiites and basalts mainly – with minor felsic volcanic and sedimentary rocks (see recent
169 reviews by de Wit et al., 2011 and Furnes et al., 2013). The Onverwacht Group is overlain by
170 the predominantly sedimentary Fig Tree (3.26-3.23 Ga; Kröner et al., 1991; Byerly et al.,
171 1996) and Moodies Groups (3.23-3.11(?) Ga; Heubeck and Lowe, 1994) which consist of
172 conglomerate, sandstone, shale, banded chert, banded iron formation and dacitic volcanic

173 rocks. In the subduction-accretion model, the Fig Tree and Moodies Groups could represent
174 the fill of an evolving foreland basin fed by the erosion products of an orogenic complex
175 (Lowe and Byerly, 1999).

176

177 **3. Materials and methods**

178

179 The study focuses on mudstones and sandstones recovered at different depths in two cores -
180 BARB 4 and BARB 5 - drilled in the Mapepe formation of the Fig Tree Group. Drilling
181 locations, simplified core logs and sampling depths are shown in Figure 1 and a detailed
182 description of the samples is provided in Supplementary File A. Additionally, three drill core
183 samples of chert from the Barberton area and fourteen outcrop samples of meta-igneous rocks
184 from the Ancient Gneiss Complex from the Dwalile and Ngwane units were analyzed to see
185 whether they could represent potential sources for the studied metasedimentary rocks (see
186 white stars in Figure 1c and sample description in Supplementary File A).

187 We analyzed the trace element concentrations and the Sm-Nd-Lu-Hf isotopic compositions of
188 the metasedimentary rocks from BARB 4 and BARB 5 drill cores, the three Buck Reef cherts
189 and four meta-igneous rocks from the Ancient Gneiss Complex. The remaining ten meta-
190 igneous rocks from the Ancient Gneiss Complex were analyzed for Sm-Nd isotopic
191 compositions only. The detailed analytical procedure can be found in Supplementary File B.
192 Major element concentrations of BARB 5 samples are available in Galic (2015). Samples
193 preceded by “SWZ” were previously analyzed for trace and major elements by Hunter et al.
194 (1984).

195

196 **4. Results**

197 **4.1. Trace element concentrations**

198 Measured trace element concentrations are reported in Supplementary Table A. They are
199 shown normalized to the present-day upper continental crust composition (average UCC of
200 Rudnick and Gao, 2014) and the post-Archean shale (average PAAS of Nance and Taylor,
201 1976 reported by Taylor and McLennan, 1985) in Figure 2. Metasedimentary rocks from the
202 BARB 4 and BARB 5 drill cores share similar trace element distributions that resemble, to
203 first order, the present-day upper continental crust (Figure 2a). Such concentrations are
204 consistent with previously-analyzed siliciclastic rocks from the Fig Tree group (e.g.
205 Hofmann, 2005). Trace element patterns are sub-parallel, which likely reflects a dilution
206 effect by variable amounts of silica and/or carbonate. The samples show low concentrations

207 of incompatible elements relative to present-day upper continental crust and post-Archean
208 shale, with slightly more depletion in the more highly incompatible elements. This is
209 illustrated by the average $(\text{Pr}/\text{Yb})_{\text{N, PAAS}}$ ratio of 0.50 ± 0.20 (2s) calculated for all
210 metasedimentary rocks, where N, PAAS denotes normalization to the post-Archean shale ratio.
211 With the exception of a few outliers, the patterns show depletion of Sr and Pb, and
212 enrichment of Ba, Cr, Co and Ni. When normalized to post-Archean shale (Figure 2d), most
213 samples have positive Eu anomalies, but no significant Ce anomalies. A few samples, one in
214 particular (i.e. Ca-rich BARB 5-102.68) shows strong positive La and Eu anomalies
215 $((\text{La}/\text{La}^*)_{\text{N, PAAS}} = (\text{La}/(3\text{Pr}-2\text{Nd}))_{\text{N, PAAS}} = 1.5; (\text{Eu}/\text{Eu}^*)_{\text{N, PAAS}} = (\text{Eu}/(0.5\text{Sm}+0.5\text{Gd}))_{\text{N, PAAS}} =$
216 $1.8)$ together with a superchondritic Y/Ho ratio of 51.2 (Figure 2b) that is a typical feature of
217 seawater precipitates (Bau, 1996; Bolhar et al., 2004).

218 The three chert samples are distinguished from the detrital sediments by low concentrations in
219 almost all trace elements, up to a hundred to a thousand times less abundant than the present-
220 day upper continental crust for Cs, Rb, Ba, Th, Sr, Zr, Hf and Ti (Figure 2b). The chert
221 breccia is generally more REE-rich ($\Sigma\text{REE} = 41.8$ ppm) than the black chert ($\Sigma\text{REE} = 3.5$
222 ppm), itself more enriched in REE than the translucent chert ($\Sigma\text{REE} = 0.3$ ppm). All cherts
223 show strong depletions in the more highly incompatible elements and thus low $(\text{Pr}/\text{Yb})_{\text{N, PAAS}}$
224 ratios (i.e. 0.17, 0.22 and 0.04 for the chert breccia, the black chert and the translucent chert,
225 respectively; Figure 2e). The absence of a negative Ce anomaly, the presence of a positive Eu
226 anomaly and the magnitude of depletion in the incompatible elements are typical of Archean
227 cherts and banded iron formations (e.g. Bolhar et al., 2004; Hofmann, 2005; Bau and
228 Alexander, 2009; Thurston et al., 2012; Ledevin et al., 2014).

229 As can be expected, the four samples that we analyzed from the Ancient Gneiss Complex
230 show different trace element patterns as a function of their lithology (Figure 2c-2f). The
231 Ngwane gneiss is the most enriched in Th, U, Nb, Ta, REE, Zr, Hf and Ti but also the most
232 depleted in transition metals such as V, Cr, Co, Ni, Cu, Zn (Figure 2c). It has a LREE-
233 depleted pattern and a slightly negative Ce anomaly relative to PAAS (Figure 2f). By
234 contrast, the trace element distribution of the Dwalile basalt is almost the opposite with its
235 very low concentrations in Th, U, Nb, Ta, REE, Zr, Hf and Ti and its strong enrichment in Cr,
236 Co and Ni relative to present-day upper continental crust. Finally the two amphibolites share
237 similar trace element patterns that resemble present-day upper continental crust and PAAS
238 compositions. The two samples have a positive Eu anomaly relative to PAAS.

239

240 **4.2. Sm-Nd and Lu-Hf isotopic compositions**

241 Neodymium and Hf isotopic compositions are reported in Table 1 together with $^{147}\text{Sm}/^{144}\text{Nd}$
242 and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios determined by isotope dilution. Also shown are initial isotopic
243 compositions calculated at the sediment deposition age (i.e. 3.23 Ga) relative to the chondritic
244 uniform reservoir (CHUR) using the reference values of Bouvier et al. (2008).
245 Metasedimentary rocks from BARB 4 and BARB 5 show only a small range in $^{147}\text{Sm}/^{144}\text{Nd}$
246 ratios (average $^{147}\text{Sm}/^{144}\text{Nd} = 0.133 \pm 0.020$ (2s)) but variable $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ($0.0063 <$
247 $^{176}\text{Lu}/^{177}\text{Hf} < 0.0437$). In a consistent way, their Nd isotopic compositions recalculated at 3.23
248 Ga span a small range of values ($-2.0 < \epsilon_{\text{Nd}}(t=3.23\text{Ga}) < +1.7$) while their $\epsilon_{\text{Hf}}(t=3.23\text{Ga})$ are
249 extremely variable ($-1.5 < \epsilon_{\text{Hf}}(t=3.23\text{Ga}) < +13.1$), reaching Hf isotopic compositions even more
250 radiogenic than that of the depleted mantle (calculated, as a simple approximation, at 3.23 Ga
251 following a linear evolution from a chondritic composition at 4.55 Ga to a present-day
252 extreme MORB value of $\epsilon_{\text{Hf}}(0) = +20$; i.e. $(^{176}\text{Hf}/^{177}\text{Hf})_{\text{MORB}, t=0} \sim 0.283350$).

253 Chert samples have generally higher $^{147}\text{Sm}/^{144}\text{Nd}$ ratios than the metasedimentary rocks from
254 BARB 4 and BARB 5 ($^{147}\text{Sm}/^{144}\text{Nd} = 0.1437, 0.2893, 0.1796$ for the black chert, translucent
255 chert and chert breccia, respectively). More importantly, they are characterized by extremely
256 high $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, up to a 100 times higher than common rocks ($^{176}\text{Lu}/^{177}\text{Hf} = 0.1843,$
257 $0.1253, 1.3324$ for the black chert, translucent chert and chert breccia, respectively). The high
258 Lu/Hf ratios are consistent with their trace element patterns that show strong depletion in
259 LREE and Hf relative to HREE (Figure 2b and 2e). Cherts share similar $\epsilon_{\text{Nd}}(t=3.23\text{Ga})$ with
260 BARB 4 and BARB 5 metasedimentary rocks ($\epsilon_{\text{Nd}}(t=3.23\text{Ga}) = -1.0, -0.1, -0.4$ for the black
261 chert, translucent chert and chert breccia, respectively). Hf isotopic compositions recalculated
262 at 3.23 Ga for the cherts are extremely radiogenic ($\epsilon_{\text{Hf}}(t=3.23\text{Ga})$ from +23 to +72) even though
263 these values are associated with large uncertainties of up to $15\epsilon_{\text{Hf}}$ units as explained at the end
264 of Supplementary File B.

265 Rocks from the Ancient Gneiss Complex have variable $^{147}\text{Sm}/^{144}\text{Nd}$ (0.0898 to 0.2068; n=14)
266 and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios (0.0075 to 0.0270; n=4). Since the meta-igneous rocks were analyzed to
267 see whether they could be the parent sources of the Fig Tree sediments, we report their initial
268 Nd and Hf isotopic compositions recalculated at the sediment deposition age (i.e. 3.23 Ga) in
269 Table 1. Initial Nd isotopic compositions recalculated at sediment deposition age span a

270 relatively large range ($\epsilon_{\text{Nd}} (t=3.23\text{Ga}) = -3.4$ to $+2.0$, $n=14$), just like their initial Hf isotopic
271 compositions $\epsilon_{\text{Hf}} (t=3.23\text{Ga})$ values ($\epsilon_{\text{Hf}} (t=3.23\text{Ga}) = -2.5$ to $+2.5$, $n=4$). The Dwalile and Ngwane
272 units share similar $\epsilon_{\text{Nd}} (t=3.23\text{Ga})$ averaging -1.0 ± 1.4 (1s, $n=14$) and -1.0 ± 1.6 (1s, $n=4$),
273 respectively.

274

275 **5. Discussion**

276 ***5.1. Classification of metasedimentary rocks from BARB 4 and BARB 5 drill cores***

277 The major and trace element composition of mature detrital sediments is mainly controlled by
278 sedimentary processes, in particular mineral sorting (or hydrodynamic sorting) that occurs
279 during sediment transport. Sorting during long transportation favors the formation of coarse-
280 grained sediments enriched in quartz and heavy minerals while fine-grained sediments tend to
281 be enriched in phyllosilicates such as clays (see for example Garzanti et al., 2011; Lupker et
282 al., 2011). BARB 4 and BARB 5 sandstones contain limited amounts of detrital quartz
283 (usually $<10\%$) and instead consist mainly of angular and unsorted lithic clasts ($>90\%$) (cf.
284 Supplementary File A for the petrographic description of the samples). This composition
285 reflects both incomplete weathering and short sediment transport distances, indicating that the
286 geochemistry of the studied Archean sediments is not controlled by simple mineral sorting
287 effects and cannot be understood using the reasoning applied to mature sediments. To
288 understand which processes controlled the chemical composition of the samples, we
289 performed a principal component analysis (PCA) using both major and trace element
290 concentrations normalized to their standard deviations. The PCA results show that the first
291 two principal components (PC1 and PC2) explain $\sim 70\%$ of the total variance in chemical
292 composition. Loading factors for PC1 and PC2 are shown in Figure 3 (purple arrows) together
293 with scores obtained for each sample in the new coordinate system (i.e. circles and squares in
294 Figure 3). In detail, 56% of the total variance is explained by PC1, which is defined by
295 positive correlations with Al_2O_3 , TiO_2 , K_2O , Na_2O , P_2O_5 and all trace elements but Cu.
296 Principal component 2 (PC2) explains $\sim 13\%$ of the total variance and is defined by relatively
297 high weights from CaO, MnO, MgO, FeO_T , Sr, Y and a few MREE, but negative correlation
298 with SiO_2 . Given the loading factors, we suggest that variations along PC1 reflect variable
299 proportions of chemical sedimentary components (negative scores) and crustal detritus
300 (positive scores). Variations along PC2 differentiate two different types of chemical
301 sedimentary components and reflect variable proportions of Ca-, Fe-rich phases (positive

302 scores) and Si-rich phases (negative scores). Petrographic observations of the samples
303 indicate that the Ca-, Fe-rich phases could be secondary or primary carbonate, iron oxide
304 and/or pyrite while Si-rich phases correspond to secondary silica, detrital quartz, chert clasts
305 and/or clasts of silicified rocks. Based on their scores, we differentiate three groups of
306 samples in Figure 3:

307 (1) Samples that positively contribute to PC1 (gray points in Figure 3) can be classified as
308 “crustal detritus-rich sediments”.

309 (2) Samples that negatively contribute to PC1 but positively contribute to PC2 (dark pink
310 points in Figure 3) can be classified as “Ca-, Fe-rich samples”.

311 (3) Samples that negatively contribute to PC1 and negatively contribute to PC2 can be
312 classified as “Si-rich samples” (pale pink points in Figure 3).

313 Our classification of metasedimentary rocks from PCA results is based on chemical
314 compositions that can be used to explain the samples’ Nd-Hf isotopic systematics. In the
315 following discussion, the isotopic compositions of each group are considered separately to
316 investigate different aspects of the Archean such as the formation and evolution of the crust or
317 the prevailing environmental conditions. Note that the PCA method can be more generally
318 applied to classify any type of sediment and/or screen for outliers prior to the interpretation of
319 isotopic data.

320

321 ***5.2. The Archean crust of Barberton from detrital sedimentary rocks***

322 *5.2.1. Robustness of Lu-Hf and Sm-Nd isotopic compositions*

323 The studied metasedimentary rocks from the BARB 4 and BARB 5 drill cores are largely
324 detrital (i.e. sandstone and mudstone), but their petrography and chemical composition
325 indicate that they contain a significant amount of chemical precipitates, such as the Ca-, Fe-,
326 Si-rich phases identified in thin sections and by the PCA (cf. Figure 3). While some of the
327 chemical sedimentary components are likely primary, some of these phases are clearly
328 secondary, meaning that they formed after the deposition of the sediments, so that they may
329 have overprinted the “truly-detrital” signature of the sediments. Toulkeridis et al. (1994;
330 1998; 1999) reached this conclusion following their study of the metasedimentary rocks from
331 the Fig Tree group. They highlighted the resetting of Rb-Sr, Sm-Nd and Pb-Pb isotopic
332 compositions by post-depositional events at ~2.6 and ~3.1 Ga, particularly in Fig Tree
333 carbonates and greywackes. To minimize this issue, we chose to focus on metasedimentary
334 rocks classified as “crustal detritus-rich sediments” only and evaluate whether their isotopic

335 compositions can be used to study the nature and age of the eroded crust in the Barberton area
 336 during the Paleoproterozoic period.

337 In igneous rocks, one can easily assess whether the Sm-Nd and Lu-Hf isotopic systematics of
 338 cogenetic samples or minerals have been perturbed after their crystallization by plotting the
 339 data on isochron diagrams (cf. Supplementary File C for an example with the meta-igneous
 340 rocks from the Ancient Gneiss Complex). This approach is not as simple for sedimentary
 341 rocks. Sedimentary rocks are mixtures of erosion products derived from different sources that
 342 are often not cogenetic, and hence do not share the same initial isotopic compositions. For
 343 example, a shale and a sandstone formed at the same time may contain variable proportions of
 344 juvenile mafic rock and recycled felsic crust (cf. Garçon and Chauvel, 2014). If the isotopic
 345 compositions of the shale and the sandstone are significantly different at the sediment
 346 deposition time, and the range of parent-daughter ratios is relatively small, then the slope
 347 defined by the data on an isochron diagram has no age significance because it is dominated by
 348 isotopic differences inherited from different, unrelated source rocks. By contrast, if all
 349 components of the sediment have similar isotopic compositions at the time of deposition, but
 350 different parent-daughter ratios - either due to their initial nature or because the ratios were
 351 changed by processes involved in sediment transportation/deposition - then the situation
 352 resembles the isochron case and the slope in the isochron diagram corresponds to an age that
 353 is close to the sediment deposition age. The extent to which the sediment isotopic
 354 heterogeneity at deposition age propagates into isochron age inaccuracy can be quantitatively
 355 evaluated. In brief, the variation of slope ($d\alpha$), or the variation of age (dt) produced by
 356 sediment heterogeneity on the isochron age can be defined, for the Lu-Hf isotopic system, as:

$$dt = \frac{1}{\lambda} * \frac{d\alpha}{e^{\lambda t}} \quad \text{with} \quad d\alpha = \frac{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_{max,t} - \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_{min,t}}{\left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_{max,0} - \left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_{min,0}}$$

357 where λ is the radioactive decay constant, $\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_{max,t} - \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_{min,t}$ the variability of
 358 isotopic compositions at sediment deposition age (t) and $\left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_{max,0} - \left(\frac{^{176}\text{Lu}}{^{177}\text{Hf}}\right)_{min,0}$ is the
 359 range of variability of parent-daughter ratios measured at present-day.

360 This calculation shows that a range of $\sim 2\varepsilon$ units in the isotopic composition of sediments
 361 deposited at 3.23 Ga coupled to parent-daughter ratios varying between 0.11 and 0.14 for
 362 $^{147}\text{Sm}/^{144}\text{Nd}$ and 0.006 and 0.020 for $^{176}\text{Lu}/^{177}\text{Hf}$, as for the crustal detritus-rich sediments
 363 (Figure 4) will significantly perturb the slope of the array in an isochron diagram, and hence

364 the age defined by this trend. Even such minor sediment heterogeneity will generate an age
365 variation (dt) of ± 0.5 Ga and ± 0.2 Ga for the Sm-Nd and Lu-Hf isotopic systems,
366 respectively. This effect must be taken into account when evaluating sediment isotopic data.
367 In Figure 4, crustal detritus-rich sediments define linear trends whose slopes correspond to
368 Sm-Nd and Lu-Hf ages of 3.13 ± 0.48 Ga and 3.37 ± 0.38 Ga, respectively. The large age
369 uncertainties and the high MSWD of the correlations reflect the scatter of the data around the
370 best-fit lines, which can be generated by sediment isotopic heterogeneity at deposition age as
371 discussed above and/or an open system behavior after sediment deposition. Here, both the
372 Sm-Nd and Lu-Hf ages are consistent, within error, with the sediment deposition age of the
373 Fig Tree group (i.e. 3.23-3.26 Ga). This means that (1) the two isotopic systems have not been
374 significantly perturbed in the crustal detritus-rich sediments since their deposition age, and (2)
375 their isotopic composition was relatively homogenous when they formed at 3.23-3.26 Ga.
376 Assuming that the two isotopic systems were not disturbed after 3.23 Ga thus implies that the
377 isotopic composition of the crustal detritus-rich sediments at deposition age ranged between -
378 1.6 and +0.1 for ϵ_{Nd} , with an average at -0.9 ± 1.0 (2s) and between -0.8 and +4.0 for ϵ_{Hf} , with
379 an average at $+0.6 \pm 3.2$ (2s).

380

381 *5.2.2. Sediment provenance and composition of the eroded crust*

382 *5.2.2.a. What are the sources of the sediments?*

383 The Nd-Hf isotopic compositions of crustal-detritus rich sediments are shown in Figure 5a
384 together with the composition of their potential sources in the Barberton area and the Ancient
385 Gneiss Complex. Both Nd and Hf isotopic compositions of the sediments are consistent with
386 a mixture of mafic and felsic sources, as suggested by previous studies (Condie et al., 1970;
387 Toulkeridis et al., 1999; Hofmann, 2005; Drabon et al., 2014). However, the large scatter in
388 compositions of the potential source rocks, and the lack of Hf isotopic data, in particular for
389 young felsic units, precludes further inferences about the nature of the eroded terranes from
390 Figure 5a. Furthermore, sedimentary processes fractionate the Lu-Hf more easily than the Sm-
391 Nd isotopic system mainly because Lu is not hosted in the same minerals as Hf whereas Sm
392 and Nd are usually carried by the same phases (Patchett et al., 1984; McLennan, 1989;
393 Garçon et al., 2013; Garçon et al., 2014; Bayon et al., 2015). The focus is thus on the Sm-Nd
394 isotopic system (Figure 5b and 5c) to constrain both the sources of the sediments and the
395 composition of the eroded crust.

396 The first important conclusion that can be drawn from Figure 5b and 5c is that very few
397 igneous rocks from the Barberton area or the Ancient Gneiss Complex share the Nd isotopic

398 compositions of the Fig Tree metasedimentary rocks. This could mean that the source of the
399 sediments has not been sampled, or more likely that the sediments do not derive from the
400 erosion of a unique lithological source. The Nd isotopic compositions of the sediments are
401 indeed well explained as mixtures of mafic-ultramafic and felsic sources derived solely from
402 the Barberton area (Figure 5b). Contributions from both young and old felsic rocks are needed
403 to account for the most unradiogenic Nd isotopic compositions. This requires that the
404 sediments were sourced from at least three distinct units from the Barberton area. Rocks from
405 the Ancient Gneiss Complex alone are not radiogenic enough to account for the entire range
406 of Nd isotopic compositions measured in Fig Tree metasedimentary rocks (cf. Figure 5c). We
407 do not exclude a contribution from rocks from the Ancient Gneiss Complex, but suggest that
408 the more likely sources of the Fig Tree sediments are mafic-ultramafic and felsic rocks from
409 the Onverwacht group and maybe the surrounding intrusions of the Barberton area (Figure
410 5b). This interpretation is in agreement with previous petrographic studies describing Mapepe
411 detrital sediments as mixtures of terrigenous debris derived from the uplift and erosion of the
412 Onverwacht Group, felsic volcanic rocks and the previously formed units of the lower Fig
413 Tree Group (e.g. Nocita, 1989; Lowe and Nocita, 1999; Drabon et al., 2014).

414

415 *5.2.2.b. Proportion of mafic vs. felsic material in the sediments and the eroded crust*

416 Figure 5b also provides important information regarding the relative proportions of mafic vs.
417 felsic material in the sediments and in the eroded crust. The Sm-Nd isotopic systematics
418 indicate that Fig Tree sediments are made up of 30 to 65% mafic erosion products. Most
419 samples, and all the mudstones, contain ~50-65% mafic material, while two sandstones (the
420 outliers identified in Figure 5b) contain only ~30% mafic material and ~70% felsic erosion
421 products. The contrasting provenance of fine and coarse-grained sediments is not surprising
422 and has been previously observed in modern sedimentary systems. Garçon and Chauvel
423 (2014) showed that mafic volcanic rocks tend to be over-represented in fine-grained
424 sediments and under-represented in coarse-grained ones because mafic-ultramafic volcanic
425 rocks yield more clays and dissolved species than their felsic equivalents. Since the
426 proportions of mafic materials are not quantitatively transferred from sources to sediments,
427 those deduced from mudstone isotopic compositions overestimate the abundance of mafic
428 contributions compared to what was exposed at the surface. Conversely, proportions of felsic
429 material in the two outlier sandstones are overestimated compared to their likely relative
430 abundances in the terrane eroding to provide the material deposited in the sediments. Hence,
431 we suggest that the composition of the eroded crust was between the endmember proportions

432 indicated by the mud- and sandstones, and was likely made up of near-equal proportions of
433 mafic and felsic rocks (i.e. 50:50).

434 Another way to constrain the proportion of mafic vs. felsic rocks exposed in the Barberton
435 area at ~ 3.2 Ga is to focus on the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the sediments. Due to their different
436 degrees of incompatibility, Sm and Nd are partitioned differently by differentiation processes
437 within the crust. This generates a range of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios in crustal rocks that is, in part,
438 related to the rock's SiO_2 content, except for Si-undersaturated rocks, but these are essentially
439 absent from the Paleoproterozoic record. Inspired by the recent studies of Tang et al. (2016) and
440 Dhuime et al. (2015), we compiled about 3400 analyses from the GEOROC database to
441 explore the precise inverse correlation between the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of crustal rocks and
442 their SiO_2 content (Figure 6, see caption for more details). This correlation has been known
443 since the early days of the application of the Sm-Nd system to crustal rocks but has not been
444 exploited quantitatively. The compilation excluded settings like ocean islands and continental
445 rifts because their $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are dominated by mantle source enrichment which
446 overwhelms the effect on Sm/Nd of crustal differentiation, the process we want to explore in
447 this study. Figure 6 shows that the relationship between $^{147}\text{Sm}/^{144}\text{Nd}$ ratio and SiO_2 content of
448 crustal rocks is well defined and, more importantly, very consistent with the values reported
449 for the present-day average upper continental crust (see red box in Figure 6). Assuming that
450 alteration and hydrodynamic sorting do not significantly fractionate Sm from Nd in sediments
451 (McLennan, 1989; Garçon et al., 2013; Bayon et al., 2015), the average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of
452 crustal detritus-rich mud- and sandstones can be interpolated on the fitted curve of Figure 6 to
453 estimate the average SiO_2 content in the eroded Archean crust. This gives an average SiO_2
454 concentration of 60.5 ± 2 wt.% (blue box in Figure 6), showing that the portion of Archean
455 upper crust that eroded to provide the sedimentary material in the Barberton area was
456 significantly more mafic than the present-day upper continental crust (Rudnick and Gao,
457 2014). Note that the interpolated SiO_2 content is entirely consistent with previous
458 interpretations from Figure 5b since a mixture of 50% of mafic rocks ($\text{SiO}_2 = \sim 50$ wt.%) and
459 50% of felsic rocks ($\text{SiO}_2 = \sim 70$ wt.%) results in an average SiO_2 content of 60 wt.%.

460 The high proportion of mafic component in the sedimentary source area is also well reflected
461 by the trace element signature of the crustal-detritus-rich sediments, in particular the strong
462 enrichments in Cr, Co and Ni (see Figure 2a). These elements are typical of mafic-ultramafic
463 rocks (cf. trace element pattern of the Dwalile basalt in Figure 2c) and are present in far lower
464 concentrations in modern sediments that are derived from the erosion of a more felsic upper
465 crust (Taylor and McLennan, 1985; Garçon and Chauvel, 2014; Gaschnig et al., 2014;

466 Gaschnig et al., 2016). Ratios of immobile trace elements such as Th/Sc and La/Yb, shown in
467 Figure 7 and often used as provenance tracers in sediments, further support the above
468 interpretations. Due to their high proportion of mafic components, the crustal detritus-rich
469 sediments from Barberton have significantly lower La/Yb and Th/Sc ratios than the post-
470 Archean shale (PAAS) and modern upper crust (Figure 7). Their trace element composition is
471 compatible with a mixture of detritus derived from local mafic-ultramafic and felsic rocks; the
472 two sandstones being the more enriched in felsic erosion products. Note that the relative
473 proportions deduced from trace element ratios (Figure 7) do not agree with those obtained
474 from their $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (Figure 6). This is because mixing proportions calculated using
475 trace element ratios are largely under-constrained due to the paucity and scattering of the data
476 available in the literature for felsic rocks from the Barberton area (cf. Figure 7). Further
477 analyses of felsic volcanic, volcanoclastic and plutonic rocks from the Barberton area are
478 required to resolve this inconsistency.

479

480 *5.2.2.c. Was the Archean crust really more mafic than today?*

481 The mafic composition inferred above for the crust eroded in the Barberton area implies that a
482 smaller proportion of differentiated, sialic crustal components was present in the sedimentary
483 source area at ~3.2 Ga. Perhaps differentiated silicic crustal rocks were not proximal to the
484 sedimentary basin. More likely, a larger portion of the surface was covered by subaerial mafic
485 volcanic rocks because the studied sediments sampled the crust before the big wave of
486 plutonism that produced the 3.1 Ga granitoids that dominate the present-day exposure of the
487 eastern Kaapvaal region (cf. Figure 1). A growing number of studies now converge to the idea
488 that Archean upper crust had a more mafic composition than modern upper continental crust.
489 This was first suggested by the pioneering studies of Taylor and McLennan (1985) and
490 Condie (1993) showing that both Archean cratonic shales and sediments from greenstone
491 belts derived from more mafic sources than post-Archean sediments. In particular, Condie's
492 results on cratonic shales imply that the mafic composition of the upper Archean crust was
493 not restricted to greenstone belt-tectonic setting only. Our results and the more recent studies
494 of Gaschnig et al. (2016) and Tang et al. (2016) using larger datasets in time and space,
495 clearly strengthen this view at a global scale.

496 The depth in the crust to which the high proportion of mafic rocks extends however is
497 difficult to estimate. Most of the above studies, including ours, rely on sediment that samples
498 the surface crust exposed to weathering, which may not be representative of bulk upper
499 Archean crust composition. In South Africa, geoelectric and gravity data (De Beer et al.,

500 1988) suggest that the Barberton belt, in particular the mafic-ultramafic Onverwacht group,
501 extends to a minimum depth of 4 km and a maximum of 8 km. Assuming that the Archean
502 upper crust was 10 to 15 km-thick (Rudnick and Fountain, 1995), the mafic composition may
503 be representative of nearly half of the upper Archean crust. Deeper in the Kaapvaal crust,
504 seismic studies indicate that the middle and lower portions of the crust are felsic to
505 intermediate in composition, excluding the Bushveld area (James et al., 2003; Nair et al.,
506 2006; Youssof et al., 2013). Felsic to intermediate deep crust is also inferred from seismic
507 data beneath the Paleo- to Neoproterozoic terranes of the Northern Canadian Shield (Thompson
508 et al., 2010) and the Zimbabwe craton (Nair et al., 2006). By contrast, geophysical data
509 suggest the presence of a thick mafic crust beneath Indian terranes that formed prior to 2.6 Ga
510 (Das et al., 2015). A more mafic mid- to lower crust is more in line with the conclusions of
511 Rudnick and Fountain (1995), Keller and Schoene (2012) and Dhuime et al. (2015). To
512 summarize, studies based on sediments show clearly that Archean continents had more mafic
513 rock exposure than post-Archean continental crust. To which depth in the crust this higher
514 proportion of mafic rocks extended is still unclear and needs to be further investigated to
515 affirm that the bulk Archean crust was more mafic than today.

516

517 *5.2.3. Crustal growth history and building of the Eastern Kaapvaal craton*

518 Nd and Hf model ages, also called crustal residence ages, are useful to estimate the average
519 extraction age of rocks from their mantle sources, often assumed to be the depleted mantle.
520 Here we calculate the model ages for the crustal detritus-rich sediments in order to evaluate
521 the average age of the Archean crust that was eroded in the Barberton area (details about the
522 calculations are provided in the caption of Figure 8). Figure 8 shows that most crustal
523 detritus-rich sediments converge towards roughly one Nd and Hf model age of ~3.5-3.6 Ga.
524 Hf model ages are slightly younger than Nd ages for a given sediment because they were
525 calculated in one stage, using the Hf isotopic compositions and the $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of
526 sediments as if they were representative of those of the eroded crust. However, sedimentary
527 processes, in particular mineral sorting, can modify Lu-Hf isotopic systematics, which may
528 bias the calculated Hf model ages towards slightly younger values. By subtracting the
529 deposition age of the sediments from the model ages, we calculate that the eroded Archean
530 terrane was on average ~300-400 Ma older than the deposition age of the sediments at ~3.2
531 Ga. This interval is much shorter than the average crustal residence age of the present-day
532 upper crust (i.e. 1.8 ± 0.4 Ga; Jacobsen, 1988) but corresponds, as today, to ~1/3 of the age of
533 the Earth at sediment deposition time. The 1/3 ratio suggests that a relatively large proportion

534 of older crust was exposed at the surface and likely remelted during the major collision event
535 that contributed to building the eastern Kaapvaal craton at ca. 3.23 Ga.

536 The importance of intracrustal reworking in the making of the eastern Kaapvaal craton has
537 been highlighted by several studies, in particular Schoene et al. (2009) based on Sm-Nd
538 isotopic compositions of 3.66 to 2.70 Ga-old granitoids and Zeh et al. (2009; 2011; 2013)
539 based on Hf isotopic compositions of zircons. To see whether the Barberton sediment data are
540 consistent with the crustal growth history depicted by previous studies, we report the initial
541 epsilon Nd-Hf of crustal detritus-rich sediments as a function of time in Figure 9, together
542 with published Nd-Hf isotopic compositions of whole-rocks from the Barberton and Ancient
543 Gneiss complex areas and Hf isotope data of detrital zircons from the Fig Tree and Moodies
544 units. The general decreasing trend towards more negative epsilon values in younger magmas
545 that is particularly well-defined by the zircon data in Figure 9b confirms that most felsic
546 magmas formed after 3.3 Ga inherited a component from an older felsic crust. Except for the
547 two 3.23 Ga samples with radiogenic Hf isotopic compositions, the crustal detritus-rich
548 sediments consistently plot within the general decreasing trend, indicating that intracrustal
549 remelting of older crust was not restricted to just a few igneous bodies but was sufficiently
550 widespread and important to be recorded by sediments draining large continental areas at 3.23
551 Ga. Nd-Hf data (Figure 9) indicate that the old remelted felsic crust could have been extracted
552 from the depleted mantle at 3.5-3.6 Ga, which is consistent with the formation ages and the
553 Nd-Hf isotopic compositions of some of the oldest rocks from the Barberton area and the
554 Ancient Gneiss Complex (Figure 9).

555

556 ***5.3. The Archean environment as seen by chemical sedimentary components***

557 *5.3.1. Cherts and silicification: effect on Lu-Hf isotopic systematics of sedimentary rocks*

558 Nd and Hf isotopic compositions of Si- and Ca-, Fe-rich sediments can provide insights on
559 the Archean environment because they are rocks formed under Archean surface condition.

560 Figure 10 shows ϵ_{Nd} and ϵ_{Hf} of Si and Ca-, Fe-rich sediments recalculated at 3.23 Ga, the

561 deposition age of the sediments. The most striking feature is the extremely radiogenic ϵ_{Hf}

562 values of the Si-rich sediments, up to +11, which is much higher than the predicted

563 composition of the depleted mantle at 3.23 Ga as shown in Figure 10. These unusually high ϵ

564 ϵ_{Hf} values could be theoretically explained by a post-depositional disturbance of sufficient

565 intensity to decrease the Lu/Hf ratio or affect the Hf isotopic composition of the sediments

566 after their deposition. However, the studied samples have been subjected to only low-grade
567 metamorphic conditions (up to greenschist facies) and silicification is such a low-temperature
568 process (<200°C) that it seems unlikely that it would have affected Hf isotopic compositions.
569 More importantly, the Si-rich sediments have a small range of $\epsilon_{\text{Nd}}(t=3.23 \text{ Ga})$ values that strongly
570 resembles those of the crustal detritus-rich sediments (Figure 10). In the Sm-Nd isochron
571 diagram (Figure 11), the Si-rich sediments define a trend whose slope corresponds to an age
572 of ~3.8 Ga, which is not well constrained due to limited range in Sm/Nd but clearly not reset
573 by a later event. The last two observations suggest that the Sm-Nd isotopic system has not
574 been significantly disturbed in Si-rich sediments after their deposition. Therefore, if the high ϵ
575 $\text{Hf}(t=3.23 \text{ Ga})$ values result from a post-depositional disturbance, one needs to find a process able
576 to significantly perturb Lu-Hf isotopic systematics but not Sm-Nd. This is, in our opinion,
577 very unlikely.

578 The sediments classified as “Si-rich” are all sandstones, mostly coarse-grained and from the
579 BARB 4 drill core (Table 1). Petrographic studies show that BARB 4 coarse-grained
580 sandstones represent composites of common silicified rocks from the Barberton area and
581 additionally contain a high amount of chert clasts (Drabon et al., 2014). The overabundance
582 of chert clasts explains why these sediments have been classified as “Si-rich” by the PCA. We
583 suggest that the presence of the chert clasts can also account for their extremely radiogenic
584 initial Hf isotopic compositions. To test this hypothesis, we analyzed three chert samples
585 (translucent chert, black chert and chert breccia) from the Buck Reef formation (3.42 Ga,
586 Kröner et al., 1991) lying at the base of the Kromberg formation in the Onverwacht group.
587 These cherts are older than the Fig Tree metasedimentary rocks and are thus good candidates
588 for sources of the chert clasts in the studied sediments. Analyses of these cherts show that
589 they have extremely low concentrations of most trace elements and higher Lu, Sm and Nd
590 concentrations compared to Hf (see Figure 2b-2e) that translate into unusually high Lu/Hf
591 ratios. The three cherts define linear trends in both the Sm-Nd and Lu-Hf isochron diagrams
592 (Figure 12). The slopes of these trends yield ages of ~3.3 Ga, which are consistent within
593 error with the estimated age of formation of the Buck Reef cherts at ~3.42 Ga (Lowe and
594 Byerly, 1999).

595 The present-day Hf isotopic compositions of the cherts are among the most radiogenic
596 compositions ever measured for terrestrial rocks, reaching $^{176}\text{Hf}/^{177}\text{Hf}(t=0)$ ratios of ~0.37, that
597 is, a remarkable $\epsilon_{\text{Hf}}(t=0)$ of +2931, and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios up to ~1.33 (Figure 12). The Lu/Hf

598 ratios of the three cherts are so elevated that, at 3.23 Ga, only a few hundred million years
599 after their formation, they would have developed extremely radiogenic Hf isotopic
600 compositions ($\epsilon_{\text{Hf}}(t=3.23\text{Ga}) = +23$ to $+72$; Table 1 and Figure 10). Their Nd isotopic
601 compositions at 3.23 Ga are nonetheless close to chondritic values and very similar to all
602 other metasedimentary rocks from the BARB 4 and BARB 5 drill cores (Table 1; Figure 10).
603 Given the highly unusual Nd-Hf isotopic compositions of cherts, we suggest that the presence
604 of old chert clasts and silicified lithic grains in the Si-rich sediments explain their unusually
605 high $\epsilon_{\text{Hf}}(t=3.23\text{Ga})$ but normal $\epsilon_{\text{Nd}}(t=3.23\text{Ga})$. Binary isotopic mixing between cherts and crustal
606 detritus-rich sediments is consistent with this interpretation. Figure 10 shows that the
607 proportion of silicified clasts must be as high as 90% to account for the radiogenic Hf isotopic
608 compositions of Si-rich sediments, proportions that are in agreement with measured SiO_2
609 contents and petrographic observations showing that the Mapepe sandstones are commonly
610 made up of ~90% of lithic silicified/chert clasts.

611 This result potentially has more global implications as it could help explain the decoupling of
612 Nd and Hf isotopic compositions seen in other sedimentary rocks. Fig Tree sedimentary rocks
613 are highly silicified and represent an extreme case where cherts and silicified clasts constitute
614 up to 90% of the rock. The amount of chert clasts needed to significantly shift the bulk
615 sediment Hf isotopic composition however depends on the lapse of time between the
616 formation of the cherts and their erosion to form the sediments. The older the chert clasts, the
617 more radiogenic their Hf isotopic compositions are, the less chert clasts are needed to
618 significantly affect the bulk Hf isotopic composition of the sediment. The presence of 20% of
619 Archean cherts, such as sample B3-227-Ch3, in a modern sediment having the same
620 composition as the modern upper crust (i.e. $\epsilon_{\text{Hf}}(t=0) = -13$ and $C_{\text{Hf}} = 5.3$ ppm; Chauvel et al.,
621 2014) would for example shift the bulk Hf isotopic composition of the modern sediment by
622 about $+6\epsilon$ units.

623

624 *5.3.2. Chemical sediments: proxies for Archean seawater compositions?*

625 The origin of cherts and other chemical sediments as primary or secondary precipitates is still
626 debated in the literature (e.g. Paris et al., 1985; Weis and Wasserburg, 1987; Lowe and
627 Byerly, 1999; Hofmann, 2005; Tice and Lowe, 2006; Rouchon and Orberger, 2008; Ledevin
628 et al., 2014). Discussing the formation of these chemical sediments in detail is beyond the
629 scope of this manuscript but we can evaluate whether the chemical precipitates have

630 preserved a seawater signal and can be used to provide insights on the Nd-Hf isotopic
631 systematics of Archean seawater. Seawater and its chemical precipitates have typical trace
632 element signatures that develop mainly in aqueous systems. This is because the behavior of
633 trace elements in aqueous media is controlled not only by ion charge and radius as in most
634 igneous rocks (charge and radius controlled i.e. CHARAC behavior) but additionally depends
635 on chemical complexation, in particular the type of ligands and the electron configuration of
636 the aqueous complexes (Bau, 1996). Typical features of seawater-like trace element
637 signatures, as summarized by Bolhar et al. (2004) and Bau (1996), include superchondritic
638 Y/Ho and Zr/Hf ratios (i.e. non-CHARAC ratios), positive La and Gd anomalies in post-
639 Archean shale-normalized REE-Y diagrams, depletion in LREE and MREE relative to HREE,
640 and low REE and HFSE concentrations. The Buck Reef cherts and most of the Ca-, Fe- rich
641 sediments however have typical CHARAC-like Y/Ho and Zr/Hf ratios (Figure 13) and do not
642 exhibit any particularly strong La or Gd anomalies (Figure 2d and 2e). This indicates that
643 these chemical sediments likely did not precipitate from seawater and/or that the primary
644 seawater-like signature is blurred by the presence of detrital particles (Bolhar et al., 2004);
645 hence they cannot be used to study the Nd-Hf isotopic systematics of Archean seawater, at
646 least not in a simple, straightforward way.

647 One sample from the BARB 5 drill core (sample BARB5-102.68) however has a very
648 peculiar petrographic and chemical composition compared to other Ca-, Fe-rich
649 metasedimentary rocks. This sample is mainly composed of carbonate grains and iron oxides
650 at grain boundaries and has one of the strongest enrichments in Ca, Fe and Mg ($\text{CaO} = 37.8$
651 $\text{wt.}\%$; $\text{FeO}_T = 17.3 \text{ wt.}\%$; $\text{MgO} = 14.8 \text{ wt.}\%$; Galic, 2015), but also a superchondritic Y/Ho
652 ratio of ~ 51.2 (Figure 13), a positive La anomaly when normalized to post-Archean shale, and
653 a depletion in LREE relative to HREE (Figure 2d). Sample BARB5-102.68 thus has the main
654 features of a marine precipitate, suggesting that its REE-Y distribution, hence its Nd isotopic
655 composition, has preserved a seawater-like signature. Note that the Zr/Hf ratio of this sample
656 is chondritic (i.e. CHARAC behavior, see Figure 13), which may suggest that its Hf and/or Zr
657 are not sourced from seawater or, alternatively, that seawater had a chondritic Zr/Hf ratio as
658 suggested by Bau and Alexander (2009). The lack of Ce anomaly and the positive Eu
659 anomaly (Figure 2d) are common features in Archean sediments (e.g. Bolhar et al., 2004;
660 Hofmann, 2005; Bau and Alexander, 2009; Thurston et al., 2012) and can be taken as
661 evidence for anoxic conditions and higher hydrothermal inputs to the ancient oceans (e.g.
662 Fryer, 1977; Appel, 1983; Derry and Jacobsen, 1990). Interestingly, carbonate BARB5-

663 102.68 has the most radiogenic Nd isotopic composition of our dataset ($\epsilon_{\text{Nd}}(t=3.23\text{Ga}) = \sim +1.7$;
664 Table 1; Figure 10). We acknowledge that the composition of the Archean oceans cannot be
665 estimated from one sample, but we note that this ϵ_{Nd} value is compatible with Alexander et
666 al.'s (2009) suggestion that bulk anoxic seawater had a relatively constant $\epsilon_{\text{Nd}}(t)$ of
667 approximately +1 to +2 during the Archean period. The radiogenic Nd isotopic composition
668 of the Archean oceans may be accounted for by a combination of higher hydrothermal input
669 and higher contribution of dissolved material derived from the weathering of juvenile mafic-
670 ultramafic rocks (Kamber, 2010). The ϵ_{Nd} of the carbonate is indeed very similar to the
671 average Nd isotopic composition of mafic-ultramafic rocks from the Barberton area (cf.
672 Figure 5b), which could reflect their over-representation in seawater (cf. Dessert et al., 2003),
673 just as they are over-represented in shale compared to sandstone (cf. section 5.2.2.b).

674

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686

687 **Table Caption**

688 **Table 1:** Sm-Nd and Lu-Hf isotopic compositions of metasedimentary rocks from the
689 Barberton area and meta-igneous rocks from the Ancient Gneiss Complex.

690 *Duplicate* stands for complete dissolution duplicate. s_N are in-run standard errors. Epsilon
691 values are calculated relative to the present-day CHUR composition of Bouvier et al. (2008).

692

693 **Figure Caption**

694 **Figure 1:** The Barberton area and the Ancient Gneiss Complex.

695 (a) Location of the Kaapvaal craton in South Africa and Swaziland. (b) Legend of the
696 geological map. (c) Geological map of the eastern Kaapvaal craton modified after Schoene et
697 al. (2009) and Ledevin et al. (2014). Sampling locations of cherts from the Barberton area and
698 meta-igneous rocks from the Ancient Gneiss Complex are indicated by white stars. (d)
699 Simplified core logs of BARB 4 and BARB 5 drilled in the Mapepe formation of the Fig Tree
700 group in the Barberton area. Sampling depths are indicated by white stars.

701

702 **Figure 2:** Trace element patterns

703 *Left panels:* trace element concentrations of (a) BARB 4 and BARB 5 metasedimentary
704 rocks, (b) cherts and (c) meta-igneous rocks from the Ancient Gneiss Complex normalized to
705 the present-day upper continental crust composition of Rudnick and Gao (2014). *Right*
706 *panels:* REE + Y concentrations of (d) BARB 4 and BARB 5 metasedimentary rocks, (e)
707 cherts and (f) meta-igneous rocks from the Ancient Gneiss Complex normalized to post-
708 archean shale composition (PAAS; Nance and Taylor, 1976; Taylor and McLennan, 1985).

709 In panels (d), (e) and (f), Pm and Tm are shown to respect the slope of the REE pattern. The
710 Rb concentration of the Dwalile basalt shown in (c) was below detection limits, hence we
711 interpolated the pattern between Ba and Cs. Detection limit is defined as 3 times the number
712 of counts/sec measured on blanks for one analytical sequence.

713

714 **Figure 3:** Results of the principal component analysis (PCA) of major and trace elements

715 The PCA allows the classification of metasedimentary rocks from BARB 4 and BARB 5 drill
716 cores into three groups of samples: the crustal detritus-rich sediments (dark grey), the Ca-, Fe-
717 rich sediments (dark pink) and the Si-rich sediments (light pink). Purple arrows are graphic
718 representations of loading factors (i.e. weight of each variable on PC1 and PC2). The
719 coordinates of each sample in the new PC1 vs. PC2 space (i.e. sample scores) are shown by
720 squares (BARB 4) and circles (BARB 5).

721

722 **Figure 4:** Sm-Nd and Lu-Hf isochron diagrams for crustal-detritus rich sediments.

723 (a) Present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratios as a function of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. (b) Present-day
724 $^{176}\text{Hf}/^{177}\text{Hf}$ ratios as a function of $^{176}\text{Lu}/^{177}\text{Hf}$ ratios. Shaded areas indicate 95% confidence
725 level. Measurement errors are smaller than the symbol sizes.

726

727 **Figure 5:** Nd and Hf isotopic compositions of crustal detritus-rich sediments compared to
728 their potential rock sources from the Barberton area and the Ancient Gneiss Complex.

729 (a) $\epsilon_{\text{Hf}}(t=3.23 \text{ Ga})$ as a function $\epsilon_{\text{Nd}}(t=3.23 \text{ Ga})$; (b) and (c) $\epsilon_{\text{Nd}}(t=3.23 \text{ Ga})$ as a function of $^{147}\text{Sm}/^{144}\text{Nd}$
730 ratios. Literature data are from Carlson et al. (1983), Kröner and Tegtmeier (1994), Lahaye et
731 al. (1995), Kröner et al. (1996), Chavagnac (2004), Clemens et al. (2006), Schoene et al.
732 (2009), van Kranendonk et al. (2009), Furnes et al. (2012), Kröner et al. (2013), Puchtel et al.
733 (2013), Kröner et al. (2014), Blichert-Toft et al. (2015) and Hoffmann et al. (2016). For the
734 Barberton area, young felsic rocks include gneisses, tonalites and granodiorites from
735 Nelspruit and Stentor basements, Kaap Valley and Nelshoogte plutons, and Vlakplaats area;
736 old felsic rocks include a tonalitic dike (Komati formation) and felsic volcanics (Theespruit
737 and Hooggenoeg formations) from the Onverwacht group together with gneisses and tonalite-
738 granodiorites from Stolzburg and Steynsdorp terranes; mafic and ultramafic rocks are all from
739 the Onverwacht group and include basalts, komatitic basalts, komatiites and a few gabbros
740 from the Theespruit, Komati, Hooggenoeg, Kromberg, Mendon and Weltevreden formations.
741 For the Ancient Gneiss Complex, young felsic rocks include gneisses, tonalites and
742 granodiorites from the Usutu and Nhlngano suites; old felsic rocks include mostly tonalitic
743 and grey gneisses from the Ngwane and Twasela units; mafic and ultramafic rocks include
744 komatiites to basalts from the Dwalile suite. To our knowledge, no Hf isotopic data are
745 available in the literature for young felsic rocks from the Barberton area and the Ancient
746 Gneiss Complex as well as for mafic and ultramafic rocks from the Ancient Gneiss Complex.
747 Colored stars show averages for each group of sources, averages that were used as
748 endmembers in the isotopic mixtures. Ticks and numbers next to the mixing lines indicate the
749 proportion of mafic-ultramafic materials in the mixtures (one tick every 10%). Error bars are
750 fixed at $\pm 0.3 \epsilon$ unit for Nd and $\pm 0.8 \epsilon$ unit for Hf (see Supplementary File B). They are
751 smaller than the symbol size for $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. All epsilon values were recalculated
752 relative to the CHUR composition of Bouvier et al. (2008).

753

754 **Figure 6:** Relationship between $^{147}\text{Sm}/^{144}\text{Nd}$ ratio and SiO_2 content of crustal rocks based on
755 a compilation of 3397 volcanic and plutonic rocks from convergent margins, oceanic plateaus
756 and Archean cratons.

757 Data are from the GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc>). We used
758 samples for which $^{147}\text{Sm}/^{144}\text{Nd}$ ratios were precisely determined by isotopic dilution only.
759 Like Dhuime et al. (2015), black dots correspond to median $^{147}\text{Sm}/^{144}\text{Nd}$ ratios calculated for
760 each 1 wt.% SiO_2 interval (error bars indicate 2 s.e.). The best fit to the data is shown by the
761 black line. The gray shaded area indicates the 95% confidence interval. The range of

762 $^{147}\text{Sm}/^{144}\text{Nd}$ ratios and SiO_2 contents known for the present-day upper continental crust are
763 shown by the red box ($^{147}\text{Sm}/^{144}\text{Nd} = 0.1012\text{-}0.1193$ after Chauvel et al. (2014) and references
764 therein; $\text{SiO}_2 = 66.6 \pm 2.4$ (2s) wt.% after Rudnick and Gao (2014)). The blue box
765 corresponds to the average composition of the eroded Barberton crust that we estimated using
766 the average $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the crustal detritus-rich sediments from BARB 4 and BARB
767 5 drill cores. UCC stands for upper continental crust.

768

769 **Figure 7:** La/Yb and Th/Sc ratios of the crustal detritus-rich sediments compared to their
770 potential rock sources from the Barberton area (log-log scale).

771 Symbols and colors as in Figure 5. Data for mafic-ultramafic rocks (basalts and komatiites
772 from the Onverwacht group mainly) are from Furnes et al. (2012), Robin-Popieul et al.
773 (2012), and Puchtel et al. (2013). Data for felsic rocks include silicic metavolcaniclastic rocks
774 from the Theespruit Formation of the Onverwacht Group and plutonic rocks from the
775 Nelshoogte, Steynsdorp, Stolzburg, Theespruit, Kaap Valley and Dalmien plutons (Glikson,
776 1976; Kohler and Anhaeusser, 2002; Kleinhanns et al., 2003; Kröner et al., 2013). UCC
777 stands for upper continental crust (data from Rudnick and Gao, 2014) and PAAS for post-
778 Archean shale (data from Taylor and McLennan, 1985). Ticks and numbers next to the
779 mixing line indicate the proportion of mafic-ultramafic material in the mixtures (one tick
780 every 10%). Note the sinusoidal form of the mixing line due to the use of a log-log scale.
781 Measurement errors are smaller than the symbol sizes.

782

783 **Figure 8:** Nd and Hf model ages (or crustal residence ages) of crustal detritus-rich sediments.
784 Model ages were calculated in one stage assuming that the depleted mantle has linearly
785 evolved from a CHUR composition (Bouvier et al., 2008) at 4.55 Ga to a present-day
786 composition of $\epsilon_{\text{Nd}(t=0)} = +8.2$ and $\epsilon_{\text{Hf}(t=0)} = +13.0$ corresponding to the average composition
787 of MORB compiled from the petDB database (<http://www.earthchem.org/petdb>) and
788 additional data from C. Chauvel. Error bars are at ± 0.1 Ga to account for variations in the
789 depleted mantle compositions and uncertainties on measured ϵ_{Nd} , ϵ_{Hf} , $^{147}\text{Sm}/^{144}\text{Nd}$ and
790 $^{176}\text{Lu}/^{177}\text{Hf}$ ratios.

791

792 **Figure 9:** Temporal evolution of initial Nd and Hf isotopic compositions of whole-rocks and
793 detrital zircons from the Barberton area and the Ancient Gneiss Complex.

794 Whole-rock data are from the literature (see caption of Figure 5 for references). Hf data for
795 detrital zircons are from Zeh et al. (2013). As in Figure 8, the depleted mantle composition is
796 assumed to have linearly evolved from a chondritic composition at 4.55 Ga to the present-day
797 average composition of MORB ($\epsilon_{\text{Nd}(t=0)} = +8.2$; $\epsilon_{\text{Hf}(t=0)} = +13.0$). The evolution of the 3.5 Ga
798 and 3.6 Ga felsic crusts is calculated using a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.11 and a $^{176}\text{Lu}/^{177}\text{Hf}$ ratio
799 of 0.009, which correspond to the medians of the parent-daughter ratios of old felsic rocks
800 from the Barberton area and the Ancient Gneiss Complex. All epsilon values are calculated
801 relative to the CHUR composition of Bouvier et al. (2008).

802

803 **Figure 10:** Nd and Hf isotopic compositions of Fig Tree metasedimentary rocks and Buck
804 Reef cherts at 3.23 Ga.

805 The field of composition for depleted mantle (DM; purple box) was calculated back at 3.23
806 Ga following a linear evolution from a chondritic composition at 4.55 Ga to present-day
807 average and extreme MORB compositions. The black line represents the mixing curve
808 between the chert breccia and the average composition of the crustal detritus-rich sediments.

809 Ticks represent increments of 10% of chert in the mixture. Error bars are fixed at $\pm 0.3 \epsilon$ unit
810 for Nd and $\pm 0.8 \epsilon$ unit for Hf, except for cherts for which the measurement errors on ϵ_{Hf}
811 ($t=3.23\text{Ga}$) are much higher (see Supplementary File B). All epsilon values are calculated using
812 the CHUR composition of Bouvier et al. (2008).

813

814 **Figure 11:** Sm-Nd isochron diagram for Si-rich sediments.

815 Shaded areas indicate 95% confidence level. Measurement errors are smaller than the symbol
816 sizes.

817

818 **Figure 12:** Sm-Nd and Lu-Hf isochron diagrams for Buck Reef cherts.

819 (a) Present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratios as a function of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. (b) Present-day
820 $^{176}\text{Hf}/^{177}\text{Hf}$ ratios as a function of $^{176}\text{Lu}/^{177}\text{Hf}$ ratios. Measurement errors are smaller than the
821 symbol sizes.

822

823 **Figure 13:** Plot of Y/Ho ratios vs. Zr/Hf ratios showing Barberton metasedimentary rocks
824 and cherts as well as fields for seawater, hydrothermal vein, Fe-Mn crusts, and CHARAC

825 samples (i.e. samples for which the behavior of trace elements is controlled by their charge
826 and radius; CHarge And RADIUS Controlled).

827 Figure modified from Bau (1996). Metasedimentary rocks and cherts from Barberton are
828 color-coded as in Figure 10.

829

830 **References**

831 Alexander B. W., Bau M. and Andersson P. (2009) Neodymium isotopes in Archean seawater
832 and implications for the marine Nd cycle in Earth's early oceans. *Earth and Planetary
833 Science Letters* **283**, 144–155.

834 Anhaeusser C. R. (1973) The Evolution of the Early Precambrian Crust of Southern Africa.
835 *Philosophical Transactions of the Royal Society* **273**, 359–388.

836 Appel P. (1983) Rare earth elements in the early Archean Isua iron-formation, West
837 Greenland. *Precambrian Research* **20**, 243–258.

838 Armstrong R. A., Compston W., de Wit M. and Williams I. S. (1990) The stratigraphy of the
839 3.5–3.2 Ga Barberton Greenstone Belt revisited: a single zircon ion microprobe study.
840 *Earth and Planetary Science Letters* **101**, 90–106.

841 Bau M. (1996) Controls on the fractionation of isoivalent trace elements in magmatic and
842 aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contrib
843 Mineral Petrol* **123**, 323–333.

844 Bau M. and Alexander B. W. (2009) Distribution of high field strength elements (Y, Zr, REE,
845 Hf, Ta, Th, U) in adjacent magnetite and chert bands and in reference standards FeR-3
846 and FeR-4 from the Temagami iron-formation, Canada, and the redox level of the
847 Neoproterozoic ocean. *Precambrian Research* **174**, 337–346.

848 Bayon G., Toucanne S., Skonieczny C., André L., Bermell S., Cheron S., Dennielou B.,
849 Etoubleau J., Freslon N., Gauchery T., Germain Y., Jorry S. J., Ménot G., Monin L.,
850 Ponzevera E., Rouget M. L., Tachikawa K. and Barrat J. A. (2015) Rare earth elements
851 and neodymium isotopes in world river sediments revisited. *Geochimica et
852 Cosmochimica Acta* **170**, 17–38.

853 Belousova E. A., Kostitsyn Y. A., Griffin W. L., Begg G. C., O'Reilly S. Y. and Pearson N. J.
854 (2010) The growth of the continental crust: Constraints from zircon Hf-isotope data.
855 *Lithos* **119**, 457–466.

856 Blichert-Toft J., Arndt N. T., Wilson A. and Coetzee G. (2015) Hf and Nd isotope systematics
857 of early Archean komatiites from surface sampling and ICDP drilling in the Barberton
858 Greenstone Belt, South Africa. *American Mineralogist* **100**, 2396–2411.

859 Bolhar R., Kamber B. S., Moorbath S., Fedo C. M. and Whitehouse M. J. (2004)
860 Characterisation of early Archean chemical sediments by trace element signatures. *Earth
861 and Planetary Science Letters* **222**, 43–60.

862 Bolhar R., Kamber B. S., Moorbath S., Whitehouse M. J. and Collerson K. D. (2005)
863 Chemical characterization of earth's most ancient clastic metasediments from the Isua

- 864 Greenstone Belt, southern West Greenland. *Geochimica et Cosmochimica Acta* **69**, 1555–
865 1573.
- 866 Bouvier A., Vervoort J. D. and Patchett P. J. (2008) The Lu–Hf and Sm–Nd isotopic
867 composition of CHUR: Constraints from unequilibrated chondrites and implications for
868 the bulk composition of terrestrial planets. *Earth and Planetary Science Letters* **273**, 48–
869 57.
- 870 Byerly G. R., Kröner A., Lowe D. R. and Todt W. (1996) Prolonged magmatism and time
871 constraints for sediment deposition in the early Archean Barberton greenstone belt:
872 evidence from the Upper Onverwacht and Fig Tree groups. *Precambrian Research* **78**,
873 125–138.
- 874 Carlson R. W., Hunter D. R. and Barker F. (1983) Sm–Nd age and isotopic systematics of the
875 bimodal suite, ancient gneiss complex, Swaziland. *Nature* **305**, 701–704.
- 876 Chauvel C., Garçon M., Bureau S., Besnault A., Jahn B.-M. and Ding Z. (2014) Constraints
877 from loess on the Hf–Nd isotopic composition of the upper continental crust. *Earth and*
878 *Planetary Science Letters* **388**, 48–58.
- 879 Chavagnac V. (2004) A geochemical and Nd isotopic study of Barberton komatiites (South
880 Africa): implication for the Archean mantle. *Lithos* **75**, 253–281.
- 881 Clemens J. D., Yerron L. M. and Stevens G. (2006) Barberton (South Africa) TTG magmas:
882 Geochemical and experimental constraints on source-rock petrology, pressure of
883 formation and tectonic setting. *Precambrian Research* **151**, 53–78.
- 884 Compston W. and Kröner A. (1988) Multiple zircon growth within early Archaean tonalitic
885 gneiss from the Ancient Gneiss Complex, Swaziland. *Earth and Planetary Science*
886 *Letters* **87**, 13–28.
- 887 Condie K. C. (1993) Chemical composition and evolution of the upper continental crust:
888 contrasting results from surface samples and shales. *Chemical Geology* **104**, 1–37.
- 889 Condie K. C. and Hunter D. R. (1976) Trace element geochemistry of Archean granitic rocks
890 from the Barberton region, South Africa. *Earth and Planetary Science Letters* **29**, 389–
891 400.
- 892 Condie K. C., Macke J. E. and Reimer T. O. (1970) Petrology and geochemistry of early
893 Precambrian graywackes from the Fig Tree Group, South Africa. *Geological Society of*
894 *America Bulletin* **81**, 2759–2776.
- 895 Das R., Saikia U. and Rai S. S. (2015) The deep geology of South India inferred from Moho
896 depth and Vp/ Vs ratio. *Geophys. J. Int.* **203**, 910–926.
- 897 De Beer J. H., Stettler E. H., Plessis Du J. G. and Blume J. (1988) The deep structure of the
898 Barberton greenstone belt: a geophysical study. *South African Journal of Geology* **91**,
899 184–197. Available at: b.
- 900 de Ronde C. and de Wit M. (1994) Tectonic history of the Barberton greenstone belt, South
901 Africa: 490 million years of Archean crustal evolution. *Tectonics* **13**, 983–1005.

- 902 de Wit M. (1982) Gliding and overthrust nappe tectonics in the Barberton greenstone belt.
903 *Journal of Structural Geology* **4**, 117–136.
- 904 de Wit M. J., Furnes H. and Robins B. (2011) Geology and tectonostratigraphy of the
905 Onverwacht Suite, Barberton Greenstone Belt, South Africa. *Precambrian Research* **186**,
906 1–27.
- 907 de Wit M. J., Roering C., Hart R. J., Armstrong R. A., de Ronde C., Green R. W. E., Tredoux
908 M., Ellie P. and Hart R. A. (1992) Formation of an Archaean continent. *Nature* **357**, 553–
909 562.
- 910 Derry L. A. and Jacobsen S. B. (1990) The chemical evolution of Precambrian seawater:
911 evidence from REEs in banded iron formations. *Geochimica et Cosmochimica Acta* **54**,
912 2965–2977.
- 913 Dessert C., Dupré B., Gaillardet J., François L. M. and Allègre C. J. (2003) Basalt weathering
914 laws and the impact of basalt weathering on the global carbon cycle. *Chemical Geology*
915 **202**, 257–273.
- 916 Dhuime B., Hawkesworth C. J., Storey C. D. and Cawood P. A. (2011) From sediments to
917 their source rocks: Hf and Nd isotopes in recent river sediments. *Geology* **39**, 407–410.
- 918 Dhuime B., Wuestefeld A. and Hawkesworth C. J. (2015) Emergence of modern continental
919 crust about 3 billion years ago. *Nature Geoscience* **8**, 552–555.
- 920 Drabon N., Lowe D. R. and Heubeck C. E. (2014) Petrography of sandstones from drill cores
921 BARB4 and BARB5, Paleoproterozoic Mapepe Formation, Barberton greenstone belt, South
922 Africa: Implications for provenance and tectonic reconstructions. In Abstract AGU fall
923 meeting. San Francisco.
- 924 Eriksson K. A. (1980) Transitional sedimentation styles in the Moodies and Fig Tree Groups,
925 Barberton mountain land, South Africa: evidence favouring an Archean continental
926 margin. *Precambrian Research* **12**, 141–160.
- 927 Frost C. D. (1993) Nd isotopic evidence for the antiquity of the Wyoming province. *Geology*
928 **21**, 351–354.
- 929 Fryer B. J. (1977) Rare earth evidence in iron-formations for changing Precambrian oxidation
930 states. *Geochimica et Cosmochimica Acta* **41**, 361–367.
- 931 Furnes H., de Wit M. and Robins B. (2013) A review of new interpretations of the
932 tectonostratigraphy, geochemistry and evolution of the Onverwacht Suite, Barberton
933 Greenstone Belt, South Africa. *Gondwana Research* **23**, 403–428.
- 934 Furnes H., Robins B. and de Wit M. J. (2012) Geochemistry and petrology of lavas in the
935 upper onverwacht suite, Barberton Mountain Land, South Africa. *South African Journal*
936 *of Geology* **115**, 171–210.
- 937 Galic A. (2015) Unravelling atmospheric photolysis and ocean redox chemistry from
938 Paleoproterozoic pyrite. A multiple sulfur and iron stable isotope study.
- 939 Garçon M. and Chauvel C. (2014) Where is basalt in river sediments, and why does it matter?

- 940 *Earth and Planetary Science Letters* **407**, 61–69.
- 941 Garçon M., Chauvel C., France-Lanord C., Huyghe P. and Lavé J. (2013) Continental
942 sedimentary processes decouple Nd and Hf isotopes. *Geochimica et Cosmochimica Acta*
943 **121**, 177–195.
- 944 Garçon M., Chauvel C., France-Lanord C., Limonta M. and Garzanti E. (2014) Which
945 minerals control the Nd–Hf–Sr–Pb isotopic compositions of river sediments? *Chemical*
946 *Geology* **364**, 42–55.
- 947 Garzanti E., Andò S., France-Lanord C., Censi P., Pietro Vignola, Galy V. and Lupker M.
948 (2011) Mineralogical and chemical variability of fluvial sediments 2. Suspended-load silt
949 (Ganga–Brahmaputra, Bangladesh). *Earth and Planetary Science Letters* **302**, 107–120.
- 950 Garzanti E., Andò S., France-Lanord C., Vezzoli G., Censi P., Galy V. and Najman Y. (2010)
951 Mineralogical and chemical variability of fluvial sediments 1. Bedload sand (Ganga–
952 Brahmaputra, Bangladesh). *Earth and Planetary Science Letters* **299**, 368–381.
- 953 Gaschnig R. M., Rudnick R. L., McDonough W. F., Kaufman A. J., Hu Z. and Gao S. (2014)
954 Onset of oxidative weathering of continents recorded in the geochemistry of ancient
955 glacial diamictites. *Earth and Planetary Science Letters* **408**, 87–99.
- 956 Gaschnig R. M., Rudnick R. L., McDonough W. F., Kaufman A. J., Valley J. W., Hu Z., Gao
957 S. and Beck M. L. (2016) Compositional evolution of the upper continental crust through
958 time, as constrained by ancient glacial diamictites. *Geochimica et Cosmochimica Acta*
959 **186**, 316–343.
- 960 Glikson A. Y. (1976) Trace element geochemistry and origin of early Precambrian acid
961 igneous series, Barberton Mountain Land, Transvaal. *Geochimica et Cosmochimica Acta*
962 **40**, 1261–1280.
- 963 Griffin W. L., Belousova E. A., O'Neill C., O'Reilly S. Y., Malkovets V., Pearson N. J.,
964 Spetsius S. and Wilde S. A. (2014) The world turns over: Hadean–Archean crust–mantle
965 evolution. *Lithos* **189**, 2–15.
- 966 Grosch E. G., Kosler J., McLoughlin N., Drost K., Slama J. and Pedersen R. B. (2011)
967 Paleoproterozoic detrital zircon ages from the earliest tectonic basin in the Barberton
968 Greenstone Belt, Kaapvaal craton, South Africa. *Precambrian Research* **191**, 85–99.
- 969 Heubeck C. and Lowe D. R. (1994) Depositional and tectonic setting of the Archean Moodies
970 Group, Barberton Greenstone Belt, South Africa. *Precambrian Research* **68**, 257–290.
- 971 Hoffmann J. E., Kröner A., Hegner E., Viehmann S., Xie H., Iaccheri L. M., Schneider K. P.,
972 Hofmann A., Wong J., Geng H. and Yang J. (2016) Source composition, fractional
973 crystallization and magma mixing processes in the 3.48–3.43 Ga Tsawela tonalite suite
974 (Ancient Gneiss Complex, Swaziland) – Implications for Palaeoproterozoic geodynamics.
975 *Precambrian Research* **276**, 43–66.
- 976 Hoffmann J. E., Münker C., Polat A., König S., Mezger K. and Rosing M. T. (2010) Highly
977 depleted Hadean mantle reservoirs in the sources of early Archean arc-like rocks, Isua
978 supracrustal belt, southern West Greenland. *Geochimica et Cosmochimica Acta* **74**, 7236–
979 7260.

- 980 Hofmann A. (2005) The geochemistry of sedimentary rocks from the Fig Tree Group,
981 Barberton greenstone belt: Implications for tectonic, hydrothermal and surface processes
982 during mid-Archaean times. *Precambrian Research* **143**, 23–49.
- 983 Hunter D. R. (1970) The ancient gneiss complex in Swaziland. *Transactions of the*
984 *Geological Society of South Africa* **73**, 107–150.
- 985 Hunter D. R., Barker F. and Millard H. T. (1984) Geochemical investigation of Archaean
986 bimodal and Dwalile metamorphic suites, ancient gneiss complex, Swaziland.
987 *Precambrian Research* **24**, 131–155.
- 988 Jacobsen S. B. (1988) Isotopic constraints on crustal growth and recycling. *Earth and*
989 *Planetary Science Letters* **90**, 315–329.
- 990 Jacobsen S. B. and Dymek R. F. (1988) Nd and Sr isotope systematics of clastic
991 metasediments from Isua, West Greenland: Identification of pre-3.8 Ga Differentiated
992 Crustal Components. *Journal of Geophysical Research* **93**, 338–354.
- 993 Jahn B. M. and Condie K. C. (1995) Evolution of the Kaapvaal Craton as viewed from
994 geochemical and Sm-Nd isotopic analyses of intracratonic pelites. *Geochimica et*
995 *Cosmochimica Acta* **59**, 2239–2258.
- 996 James D. E., Niu F. and Rokosky J. (2003) Crustal structure of the Kaapvaal craton and its
997 significance for early crustal evolution. *Lithos* **71**, 413–429.
- 998 Kamber B. S. (2010) Archean mafic–ultramafic volcanic landmasses and their effect on
999 ocean–atmosphere chemistry. *Chemical Geology* **274**, 19–28.
- 1000 Kamber B. S. and Webb G. E. (2001) The geochemistry of late Archaean microbial
1001 carbonate: implications for ocean chemistry and continental erosion history. *Geochimica*
1002 *et Cosmochimica Acta* **65**, 2509–2525.
- 1003 Kamber B. S., Webb G. E. and Gallagher M. (2014) The rare earth element signal in
1004 Archaean microbial carbonate: information on ocean redox and biogenicity. *Journal of*
1005 *the Geological Society* **171**, 745–763.
- 1006 Kamo S. L. and Davis D. W. (1994) Reassessment of Archean crustal development in the
1007 Barberton Mountain Land, South Africa, based on U-Pb dating. *Tectonics* **13**, 167–192.
- 1008 Keller C. B. and Schoene B. (2012) Statistical geochemistry reveals disruption in secular
1009 lithospheric evolution about 2.5 Gyr ago. *Nature* **485**, 490–493.
- 1010 Kleinhanns I. C., Kramers J. D. and Kamber B. S. (2003) Importance of water for Archaean
1011 granitoid petrology: a comparative study of TTG and potassic granitoids from Barberton
1012 Mountain Land, South Africa. *Contrib Mineral Petrol* **145**, 377–389.
- 1013 Kohler E. A. and Anhaeusser C. R. (2002) Geology and geodynamic setting of Archaean
1014 silicic metavolcaniclastic rocks of the Bien Venue Formation, Fig Tree Group, northeast
1015 Barberton greenstone belt, South Africa. *Precambrian Research* **116**, 199–235.
- 1016 Kröner A. (2007) Chapter 5.2 The Ancient Gneiss Complex of Swaziland and Environs:

- 1017 Record of Early Archean Crustal Evolution in Southern Africa. In *Earth's oldest rocks*
1018 Developments in Precambrian Geology. Elsevier. pp. 465–480.
- 1019 Kröner A. and Tegtmeier A. (1994) Gneiss-greenstone relationships in the Ancient Gneiss
1020 Complex of southwestern Swaziland, southern Africa, and implications for early crustal
1021 evolution. *Precambrian Research* **67**, 109–139.
- 1022 Kröner A., Byerly G. R. and Lowe D. R. (1991) Chronology of early Archean granite-
1023 greenstone evolution in the Barberton Mountain Land, South Africa, based on precise
1024 dating by single zircon evaporation. *Earth and Planetary Science Letters* **103**, 41–54.
- 1025 Kröner A., Compston W. and Williams I. S. (1989) Growth of early Archean crust in the
1026 Ancient Gneiss Complex of Swaziland as revealed by single zircon dating.
1027 *Tectonophysics* **161**, 271–298.
- 1028 Kröner A., Hegner E., Wendt J. I. and Byerly G. R. (1996) The oldest part of the Barberton
1029 granitoid-greenstone terrain, South Africa: evidence for crust formation between 3.5 and
1030 3.7 Ga. *Precambrian Research* **78**, 105–124.
- 1031 Kröner A., Hoffmann J. E., Xie H., Munker C. and Hegner E. (2014) Generation of early
1032 Archean grey gneisses through melting of older crust in the eastern Kaapvaal craton,
1033 southern Africa. *Precambrian Research* **255**, 823–843.
- 1034 Kröner A., Hoffmann J. E., Xie H., Wu F., Munker C., Hegner E., Wong J., Wan Y. and Liu
1035 D. (2013) Generation of early Archean felsic greenstone volcanic rocks through crustal
1036 melting in the Kaapvaal, craton, southern Africa. *Earth and Planetary Science Letters*
1037 **381**, 188–197.
- 1038 Lahaye Y., Arndt N., Byerly G., Chauvel C., Fourcade S. and Gruau G. (1995) The influence
1039 of alteration on the trace-element and Nd isotopic compositions of komatiites. *Chemical*
1040 *Geology* **126**, 43–64.
- 1041 Ledevin M., Arndt N., Simionovici A., Jaillard E. and Ulrich M. (2014) Silica precipitation
1042 triggered by clastic sedimentation in the Archean: New petrographic evidence from cherts
1043 of the Kromberg type section, South Africa. *Precambrian Research* **255**, 316–334.
- 1044 Liu X. M., Kah L. C., Knoll A. H., Cui H., Kaufman A. J., Shahar A. and Hazen R. M. (2015)
1045 Tracing Earth's O₂ evolution using Zn/Fe ratios in marine carbonates. *Geochem. Persp.*
1046 *Let.* **2**, 24–34.
- 1047 Lowe D. R. (1994) Accretionary history of the Archean Barberton greenstone belt (3.55-3.22
1048 Ga), southern Africa. *Geology* **22**, 1099–1102.
- 1049 Lowe D. R. and Byerly G. R. (1999) *Geologic Evolution of the Barberton Greenstone Belt,*
1050 *South Africa*, Geological Society of America - Special Paper 329.
- 1051 Lowe D. R. and Nocita B. W. (1999) Foreland basin sedimentation in the Mapepe Formation,
1052 southern-facies Fig Tree Group. In *Geologic Evolution of the Barberton Greenstone Belt,*
1053 *South Africa* (eds. D. R. Lowe and G. R. Byerly). Geological Society of America Special
1054 Papers. pp. 233–258.
- 1055 Lupker M., France-Lanord C., Lavé J., Bouchez J., Galy V., Métivier F., Gaillardet J.,

- 1056 Lartiges B. and Mugnier J.-L. (2011) A Rouse-based method to integrate the chemical
1057 composition of river sediments: Application to the Ganga basin. *Journal of Geophysical*
1058 *Research* **116**, F04012.
- 1059 McLennan S. M. (1989) Rare earth elements in sedimentary rocks: influence of provenance
1060 and sedimentary processes. In *Geochemistry and mineralogy of rare earth elements* (eds.
1061 B. R. Lipin and G. A. McKay). Reviews in Mineralogy and Geochemistry. pp. 169–200.
- 1062 Moyen J.-F., Stevens G. and Kisters A. (2006) Record of mid-Archean subduction from
1063 metamorphism in the Barberton terrain, South Africa. *Nature* **442**, 559–562.
- 1064 Nair S. K., Gao S. S., Liu K. H. and Silver P. G. (2006) Southern African crustal evolution
1065 and composition: Constraints from receiver function studies. *Journal of Geophysical*
1066 *Research* **111**, 1–17.
- 1067 Nance W. B. and Taylor S. R. (1976) Rare earth element patterns and crustal evolution-1.
1068 Australian post-Archean sedimentary rocks. *Geochimica et Cosmochimica Acta* **40**,
1069 1539–1551.
- 1070 Nocita B. W. (1989) Sandstone petrology of the Archean Fig Tree Group, Barberton
1071 greenstone belt, South Africa: Tectonic implications. *Geology* **17**, 953–956.
- 1072 Paris I., Stanistreet I. G. and Hughes M. J. (1985) Cherts of the Barberton greenstone belt
1073 interpreted as products of submarine exhalative activity. *The Journal of Geology* **93**, 111–
1074 129.
- 1075 Patchett P. J., White W. M., Feldmann H., Kielinczuk S. and Hofmann A. W. (1984)
1076 Hafnium/rare earth element fractionation in the sedimentary system and crustal recycling
1077 into the Earth's mantle. *Earth and Planetary Science Letters* **69**, 365–378.
- 1078 Puchtel I. S., Blichert-Toft J., Touboul M., Walker R. J., Byerly G. R., Nisbet E. G. and
1079 Anhaeusser C. R. (2013) Insights into early Earth from Barberton komatiites: Evidence
1080 from lithophile isotope and trace element systematics. *Geochimica et Cosmochimica Acta*
1081 **108**, 63–90.
- 1082 Robin-Popieul C. C. M., Arndt N. T., Chauvel C., Byerly G. R., Sobolev A. V. and Wilson A.
1083 (2012) A New Model for Barberton Komatiites: Deep Critical Melting with High Melt
1084 Retention. *Journal of Petrology* **53**, 2191–2229.
- 1085 Rouchon V. and Orberger B. (2008) Origin and mechanisms of K–Si-metasomatism of ca.
1086 3.4–3.3Ga volcanoclastic deposits and implications for Archean seawater evolution:
1087 Examples from cherts of Kittys Gap (Pilbara craton, Australia) and Msauli (Barberton
1088 Greenstone Belt, South Africa). *Precambrian Research* **165**, 169–189.
- 1089 Rudnick R. L. and Fountain D. M. (1995) Nature and composition of the continental crust: A
1090 lower crustal perspective. *Reviews of Geophysics* **33**, 267–309.
- 1091 Rudnick R. L. and Gao S. (2014) 4.1 - Composition of the Continental Crust. In *Treatise on*
1092 *Geochemistry (Second Edition)* (ed. H. D. H. K. Turekian). Treatise on Geochemistry
1093 (Second Edition). Elsevier, Oxford. pp. 1–51.
- 1094 Sauzéat L., Rudnick R. L., Chauvel C., Garçon M. and Tang M. (2015) New perspectives on

- 1095 the Li isotopic composition of the upper continental crust and its weathering signature.
1096 *Earth and Planetary Science Letters* **428**, 181–192.
- 1097 Schoene B. and Bowring S. A. (2010) Rates and mechanisms of Mesoarchean magmatic arc
1098 construction, eastern Kaapvaal craton, Swaziland. *Geological Society of America Bulletin*
1099 **122**, 408–429.
- 1100 Schoene B., de Wit M. J. and Bowring S. A. (2008) Mesoarchean assembly and stabilization
1101 of the eastern Kaapvaal craton: A structural-thermochronological perspective. *Tectonics*
1102 **27**, 1–27.
- 1103 Schoene B., Dudas F. O. L., Bowring S. A. and de Wit M. (2009) Sm-Nd isotopic mapping of
1104 lithospheric growth and stabilization in the eastern Kaapvaal craton. *Terra Nova* **21**, 219–
1105 228.
- 1106 Stiegler M. T., Cooper M., Byerly G. R. and Lowe D. R. (2012) Geochemistry and petrology
1107 of komatiites of the Pioneer Ultramafic Complex of the 3.3 Ga Weltevreden Formation,
1108 Barberton greenstone belt, South Africa. *Precambrian Research* **212-213**, 1–12.
- 1109 Tang M., Chen K. and Rudnick R. L. (2016) Archean upper crust transition from mafic to
1110 felsic marks the onset of plate tectonics. *Science* **351**, 372–375.
- 1111 Taylor S. R. and McLennan S. M. (1985) *The continental crust: Its composition and*
1112 *evolution*, Blackwell Scientific Pub., Palo Alto, CA.
- 1113 Thompson D. A., Bastow I. D., Helfrich G., Kendall J.-M., Wookey J., Snyder D. B. and
1114 Eaton D. W. (2010) Precambrian crustal evolution: Seismic constraints from the
1115 Canadian Shield. *Earth and Planetary Science Letters* **297**, 655–666.
- 1116 Thurston P. C., Kamber B. S. and Whitehouse M. (2012) Archean cherts in banded iron
1117 formation: Insight into Neoproterozoic ocean chemistry and depositional processes.
1118 *Precambrian Research* **214-215**, 227–257.
- 1119 Tice M. M. and Lowe D. R. (2006) The origin of carbonaceous matter in pre-3.0 Ga
1120 greenstone terrains: A review and new evidence from the 3.42 Ga Buck Reef Chert. *Earth*
1121 *Science Reviews* **76**, 259–300.
- 1122 Toulkeridis T., Clauer N., Kröner A., Reimer T. and Todt W. (1999) Characterization,
1123 provenance, and tectonic setting of Fig Tree greywackes from the Archaean Barberton
1124 greenstone belt, South Africa. *Sedimentary Geology* **124**, 113–129.
- 1125 Toulkeridis T., Goldstein S. L., Clauer N. and Kröner A. (1994) Sm-Nd dating of Fig Tree
1126 clay minerals of the Barberton greenstone belt, South Africa. *Geology* **22**, 199–202.
- 1127 Toulkeridis T., Goldstein S. L., Clauer N. and Kröner A. (1998) Sm–Nd, Rb–Sr and Pb–Pb
1128 dating of silicic carbonates from the early Archaean Barberton Greenstone Belt, South
1129 Africa: evidence for post-depositional isotopic resetting at low temperature. *Precambrian*
1130 *Research* **92**, 129–144.
- 1131 Van Kranendonk M. J., Kröner A., Hegner E. and Connelly J. (2009) Age, lithology and
1132 structural evolution of the c. 3.53 Ga Theespruit Formation in the Tjakastad area,
1133 southwestern Barberton Greenstone Belt, South Africa, with implications for Archaean

- 1134 tectonics. *Chemical Geology* **261**, 115–139.
- 1135 Vervoort J. D., Patchett P. J. and Blichert-Toft J. (1999) Relationships between Lu–Hf and
1136 Sm–Nd isotopic systems in the global sedimentary system. *Earth and Planetary Science*
1137 *Letters* **168**, 79–99.
- 1138 Viehmann S., Hoffmann J. E., Munker C. and Bau M. (2014) Decoupled Hf–Nd isotopes in
1139 Neoproterozoic seawater reveal weathering of emerged continents. *Geology* **42**, 115–118.
- 1140 Viljoen M. J. and Viljoen R. P. (1969) An introduction to the geology of the Barberton,
1141 granite-greenstone terrain. *Geological Society of South Africa, Special Publication* **2**, 9–
1142 28.
- 1143 Weis D. and Wasserburg G. J. (1987) Rb–Sr and Sm–Nd Systematics of Cherts and Other
1144 Siliceous Deposits. *Geochimica et Cosmochimica Acta* **51**, 959–972.
- 1145 Yamashita K. and Creaser R. A. (1999) Geochemical and Nd isotopic constraints for the
1146 origin of Late Archean turbidites from the Yellowknife area, Northwest Territories,
1147 Canada. *Geochimica et Cosmochimica Acta* **63**, 2579–2598.
- 1148 Yamashita K., Creaser R. A. and Villeneuve M. E. (2000) Integrated Nd isotopic and U–Pb
1149 detrital zircon systematics of clastic sedimentary rocks from the Slave Province, Canada:
1150 evidence for extensive crustal reworking in the early- to mid-Archean. *Earth and*
1151 *Planetary Science Letters* **174**, 283–299.
- 1152 Youssof M., Thybo H., Artemieva I. M. and Levander A. (2013) Moho depth and crustal
1153 composition in Southern Africa. *Tectonophysics* **609**, 267–287.
- 1154 Zeh A., Gerdes A. and Barton J. M. (2009) Archean Accretion and Crustal Evolution of the
1155 Kalahari Craton--the Zircon Age and Hf Isotope Record of Granitic Rocks from
1156 Barberton/Swaziland to the Francistown Arc. *Journal of Petrology* **50**, 933–966.
- 1157 Zeh A., Gerdes A. and Heubeck C. (2013) U–Pb and Hf isotope data of detrital zircons from
1158 the Barberton Greenstone Belt: constraints on provenance and Archean crustal
1159 evolution. *Journal of the Geological Society* **170**, 215–223.
- 1160 Zeh A., Gerdes A. and Millonig L. (2011) Hafnium isotope record of the Ancient Gneiss
1161 Complex, Swaziland, southern Africa: evidence for Archean crust-mantle formation and
1162 crust reworking between 3.66 and 2.73 Ga. *Journal of the Geological Society* **168**, 953–
1163 964.

Table 1

Table 1: Sm-Nd and Lu-Hf isotopic compositions of metasedimentary rocks from the Barberton area and meta-igneous rocks from the Ancient Gneiss Complex.

Sample name	Depth (m)	Unit/Formation	Type of sample	PCA result	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd ₀	²⁵ N	¹⁴³ Nd/ ¹⁴⁴ Nd at 3.23Ga	ϵ_{Nd} at 3.23Ga	Lu (ppm)	Hf (ppm)
Metasedimentary rocks from BARB 4 drill core													
BARB4-119.17	119.17	Fig Tree/Mapepe Fm	Very coarse- grained sandstone	Si-rich	0.62	2.80	0.1338	0.511202	0.000006	0.508345	-2.0	0.076	1.038
BARB4-122.31	122.31	Fig Tree/Mapepe Fm	Fine-grained sandstone	Ca-, Fe- rich	1.39	5.38	0.1565	0.511728	0.000005	0.508386	-1.2	0.133	0.798
BARB4-123.50	123.5	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.87	12.68	0.1368	0.511311	0.000005	0.508390	-1.1	0.299	2.408
BARB4-129.19	129.19	Fig Tree/Mapepe Fm	Fine-grained sandstone	Si-rich	1.03	4.37	0.1425	0.511453	0.000008	0.508411	-0.7	0.143	1.654
BARB4-133.61	133.61	Fig Tree/Mapepe Fm	Coarse-grained sandstone	Si-rich	1.11	4.46	0.1507	0.511659	0.000011	0.508442	-0.1	0.131	1.362
BARB4-134.67	134.67	Fig Tree/Mapepe Fm	Mudstone	Ca-, Fe- rich	1.61	7.04	0.1380	0.511435	0.000003	0.508489	0.8	0.163	0.902
BARB4-141.64	141.64	Fig Tree/Mapepe Fm	Fine-grained sandstone	Ca-, Fe- rich	1.40	5.72	0.1474	0.511571	0.000004	0.508424	-0.4	0.131	0.995
BARB4-145.67	145.67	Fig Tree/Mapepe Fm	Very coarse- grained sandstone	Si-rich	0.74	3.31	0.1343	0.511232	0.000005	0.508364	-1.6	0.080	1.380
<i>Duplicate</i>					0.72	3.23	0.1348	0.511228	0.000004	0.508351	-1.9	0.079	1.339
BARB4-155.69	155.69	Fig Tree/Mapepe Fm	Coarse-grained sandstone	Si-rich	0.99	4.20	0.1423	0.511427	0.000007	0.508388	-1.1	0.110	1.218
<i>Duplicate</i>					1.03	4.35	0.1428	0.511444	0.000004	0.508395	-1.0	0.112	1.327
BARB4-197.64	197.64	Fig Tree/Mapepe Fm	Coarse-grained sandstone	Si-rich	0.82	3.58	0.1382	0.511373	0.000010	0.508423	-0.5	0.080	1.387
BARB4-208.90	208.9	Fig Tree/Mapepe Fm	Coarse-grained sandstone	Si-rich	1.14	5.04	0.1363	0.511329	0.000006	0.508419	-0.5	0.144	1.547
BARB4-314.33	314.33	Fig Tree/Mapepe Fm	Very coarse-grained sandstone	Si-rich	1.02	4.71	0.1311	0.511155	0.000007	0.508355	-1.8	0.133	1.246
BARB4-338.47	338.47	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	3.35	15.39	0.1316	0.511196	0.000005	0.508387	-1.2	0.300	2.905
BARB4-346.46	346.46	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	3.90	18.78	0.1255	0.511116	0.000006	0.508437	-0.2	0.409	3.131
<i>Duplicate</i>					3.89	18.95	0.1241	0.511117	0.000004	0.508468	0.4	0.411	3.147
Metasedimentary rocks from BARB 5 drill core													
BARB5-102.68	102.68	Fig Tree/Mapepe Fm	Mudstone	Ca-, Fe- rich	1.49	7.39	0.1217	0.511132	0.000004	0.508534	1.7	0.204	0.662
BARB5-108.46	108.46	Fig Tree/Mapepe Fm	Fine-grained sandstone	Crustal detritus- rich	6.18	31.87	0.1173	0.510917	0.000011	0.508412	-0.7	0.385	8.694
BARB5-315.46	315.46	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.04	9.63	0.1278	0.511143	0.000004	0.508414	-0.6	0.206	2.102
BARB5-319.79	319.79	Fig Tree/Mapepe Fm	Fine-grained sandstone	Crustal detritus- rich	3.05	15.24	0.1208	0.510946	0.000004	0.508367	-1.6	0.265	3.383
<i>Duplicate</i>						13.69		0.510961	0.000006			0.246	3.280
BARB5-349.44	349.44	Fig Tree/Mapepe Fm	Coarse-grained sandstone	Si-rich	1.18	5.45	0.1311	0.511169	0.000004	0.508371	-1.5	0.127	1.442
BARB5-355.54	355.54	Fig Tree/Mapepe Fm	Coarse-grained sandstone	Ca-, Fe- rich	0.55	2.37	0.1392	0.511384	0.000004	0.508412	-0.7	0.060	0.329
<i>Duplicate</i>					0.55	2.39	0.1391	0.511356	0.000003	0.508387	-1.2	0.056	0.313
BARB5-425.78	425.78	Fig Tree/Mapepe Fm	Mudstone	Ca-, Fe- rich	1.80	9.72	0.1117	0.510909	0.000004	0.508524	1.5	0.172	1.891
BARB5-429.38	429.38	Fig Tree/Mapepe Fm	Mudstone	Ca-, Fe- rich	1.41	6.49	0.1313	0.511157	0.000004	0.508354	-1.8	0.151	1.732
BARB5-520.31	520.31	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.62	12.34	0.1282	0.511125	0.000004	0.508388	-1.1	0.213	2.552
BARB5-615.03	615.03	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.52	11.52	0.1325	0.511226	0.000005	0.508397	-1.0	0.220	2.205
BARB5-620.45	620.45	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.53	11.51	0.1330	0.511215	0.000004	0.508375	-1.4	0.252	2.524
BARB5-724.69	724.69	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.07	9.62	0.1303	0.511155	0.000002	0.508373	-1.4	0.212	1.865
BARB5-730.51	730.51	Fig Tree/Mapepe Fm	Mudstone	Crustal detritus- rich	2.78	12.92	0.1300	0.511226	0.000005	0.508451	0.1	0.298	2.317
Chert samples from BARB 3 drilled in Buck Reef													
B3-227-Ch1	227.34	Buck Reef	Black chert		0.12	0.50	0.1437	0.511465	0.000003	0.508397	-1.0	0.030	0.023
B3-227-Ch2	227.34	Buck Reef	Translucent chert		0.01	0.03	0.2893	0.514615	0.000006	0.508440	-0.1	0.006	0.007
B3-402-Ch3	402.9	Buck Reef	Chert breccia		2.16	7.25	0.1796	0.512258	0.000003	0.508423	-0.4	0.406	0.042
Meta-igneous rocks from the Ancient Gneiss Complex													
KV84-2A		Dwalile suite	Amphibolite		0.29	1.19	0.1464	0.511466	0.000005	0.508340	-2.1	0.025	0.475
<i>Duplicate</i>					0.29	1.26	0.1405	0.511351	0.000015	0.508351	-1.7		
KV84-2B		Dwalile suite	Amphibolite		2.59	9.55	0.1639	0.511890	0.000006	0.508391	-1.1		
KV84-2C		Dwalile suite	Amphibolite		3.60	13.77	0.1582	0.511708	0.000014	0.508330	-2.3		
KV84-5B		Dwalile suite	Amphibolite		1.00	3.23	0.1873	0.512410	0.000017	0.508411	-0.7		
SWZ-12		Dwalile suite	Metabasalt		0.77	2.25	0.2078	0.512946	0.000029	0.508509	1.2		
KV84-5C		Ngwane	Garnet amphibolite		8.69	37.33	0.1407	0.511386	0.000034	0.508381	-1.3		
KV84-5D		Ngwane	Garnet amphibolite		4.63	25.29	0.1107	0.510713	0.000004	0.508349	-1.9	0.311	3.036
<i>Duplicate</i>					4.49	24.58	0.1105	0.510668	0.000018	0.508309	-2.5		
KV84-1A		Ngwane	Grey gneiss		5.10	27.63	0.1115	0.510703	0.000028	0.508323	-2.4		
SWZ-4		Ngwane	Quartz monzonite gneiss		2.39	16.09	0.0898	0.510293	0.000018	0.508376	-1.4		
SWZ-5		Ngwane	Siliceous gneiss		9.66	45.53	0.1282	0.511086	0.000020	0.508350	-1.9		
SWZ-10		Ngwane	Metabasalt		1.68	5.21	0.1953	0.512668	0.000029	0.508498	1.0		
SWZ-19		Ngwane	Amphibolite		3.69	18.42	0.1210	0.510882	0.000004	0.508299	-2.9	0.271	2.133
<i>Duplicate</i>					3.68	18.59	0.1197	0.510913	0.000025	0.508358	-1.7		
SWZ 29		Ngwane	Amphibolite		3.08	10.41	0.1789	0.512308	0.000038	0.508488	0.8		
SW-31		Ngwane	Siliceous gneiss		18.18	71.07	0.1547	0.511721	0.000003	0.508419	-0.5	2.692	14.142
<i>Duplicate</i>					18.06	71.12	0.1536	0.511687	0.000003	0.508408	-0.7	2.625	14.490

Figure 1

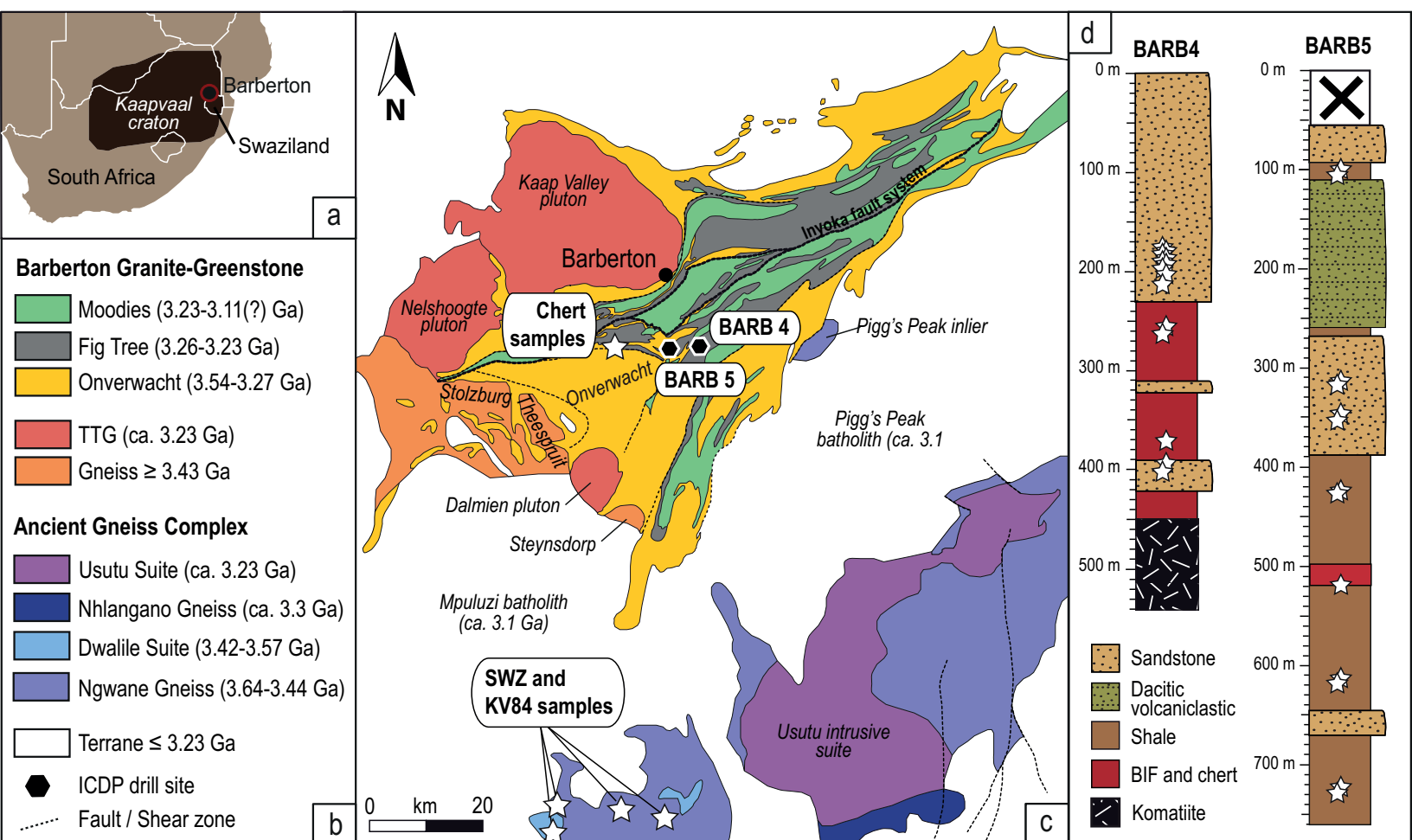


Figure 1

Figure 2

Figure 2

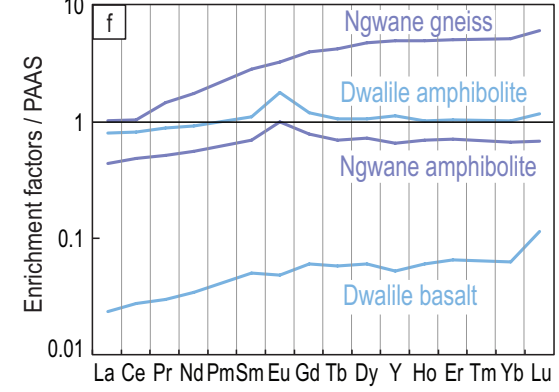
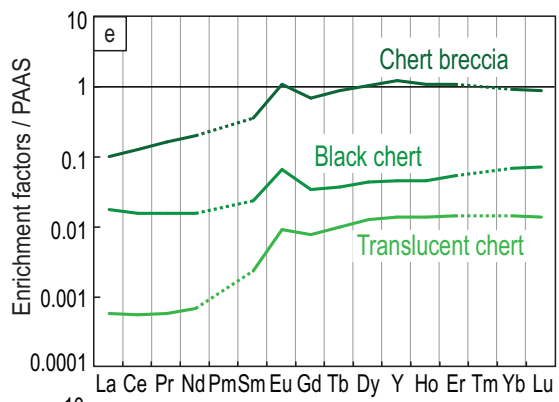
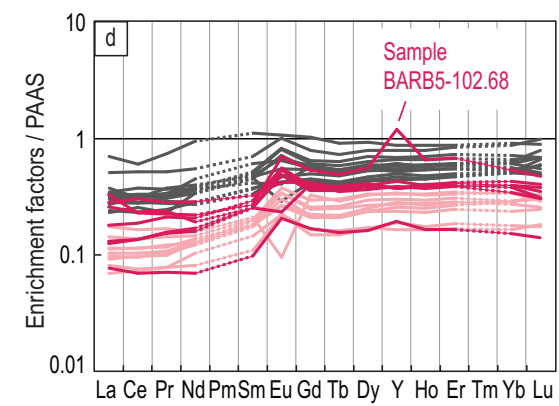
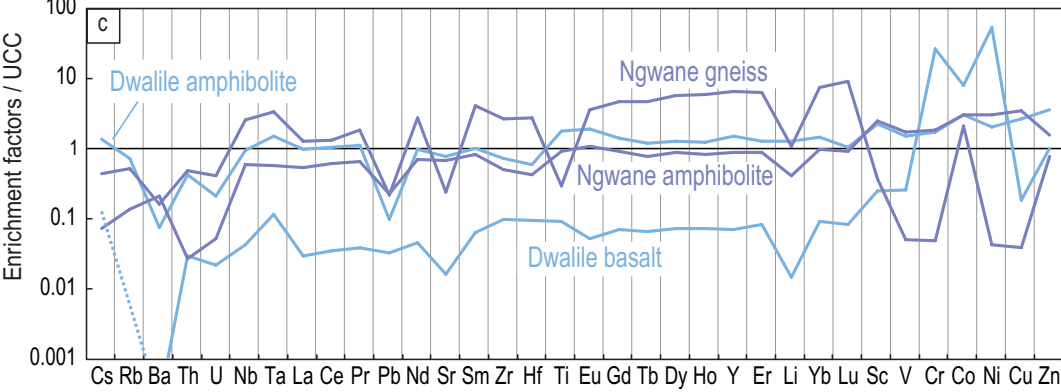
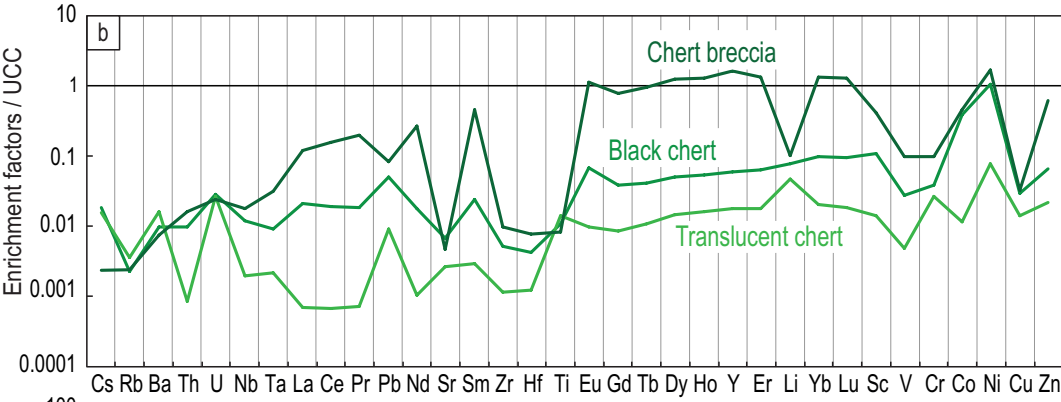
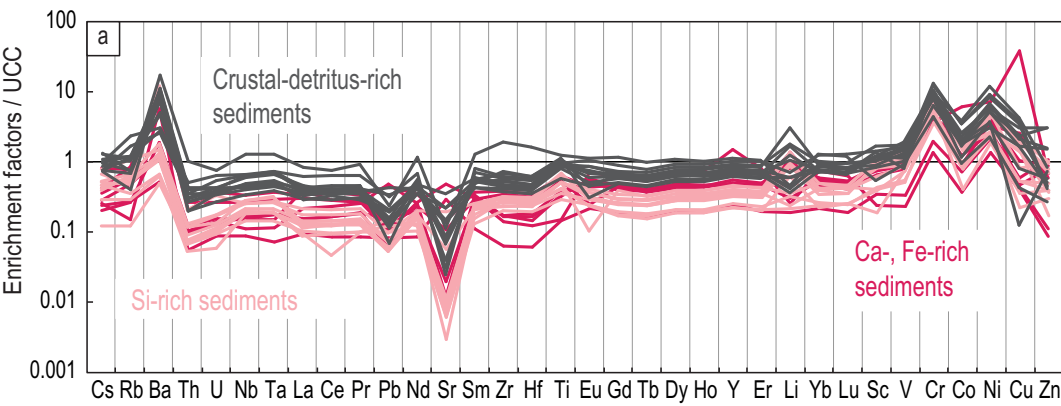


Figure 3

Figure 3

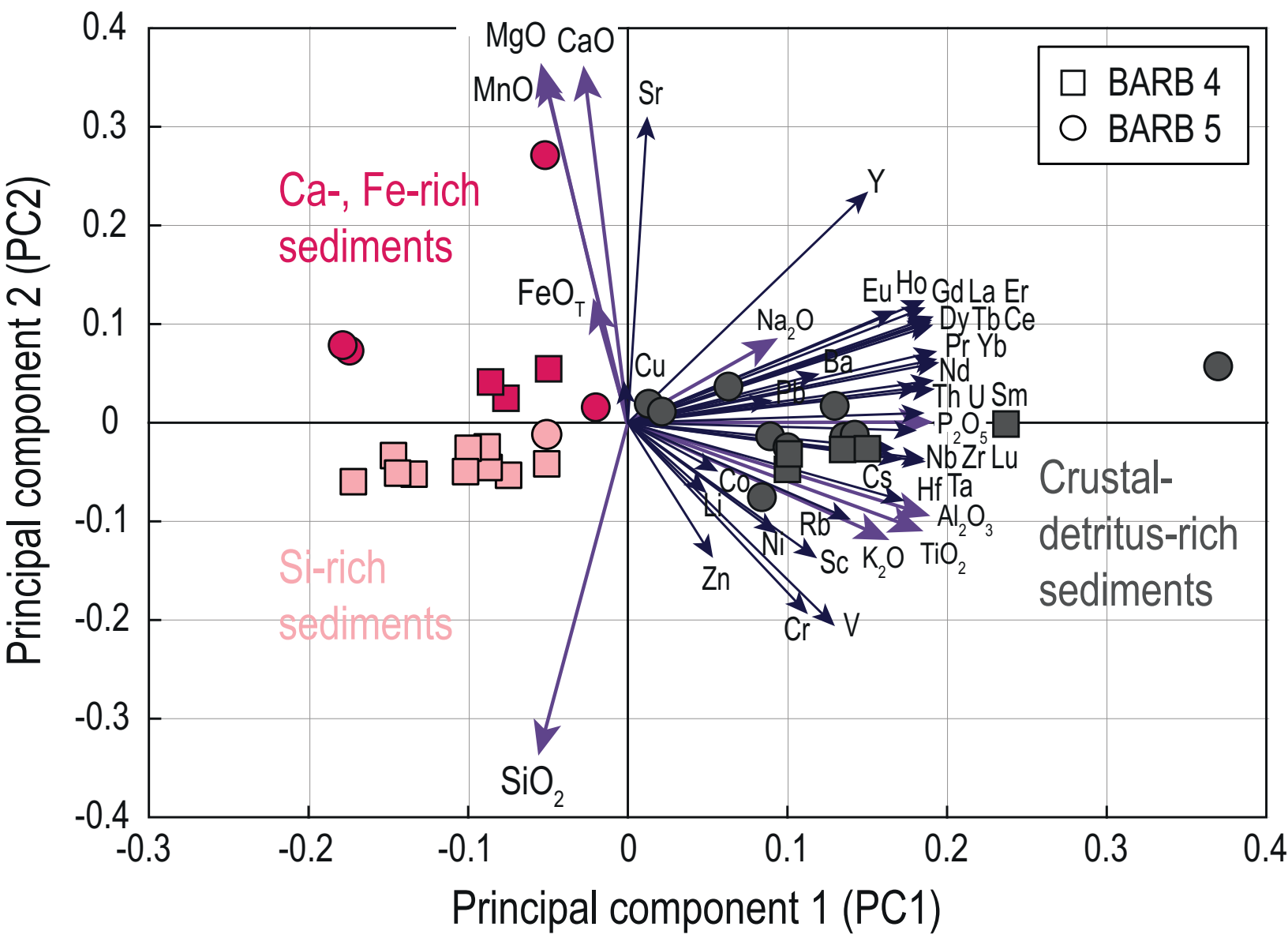


Figure 4

Figure 4

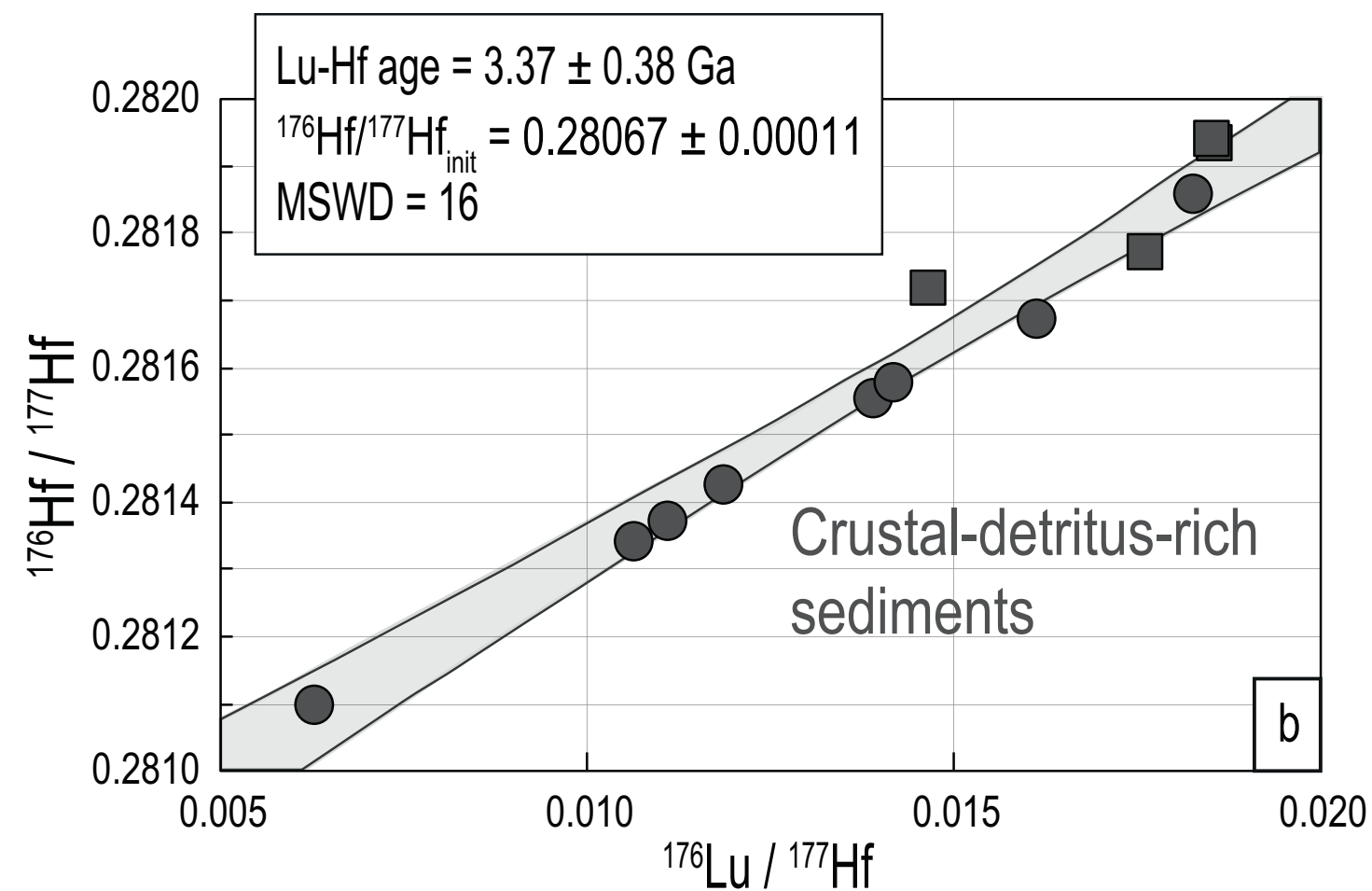
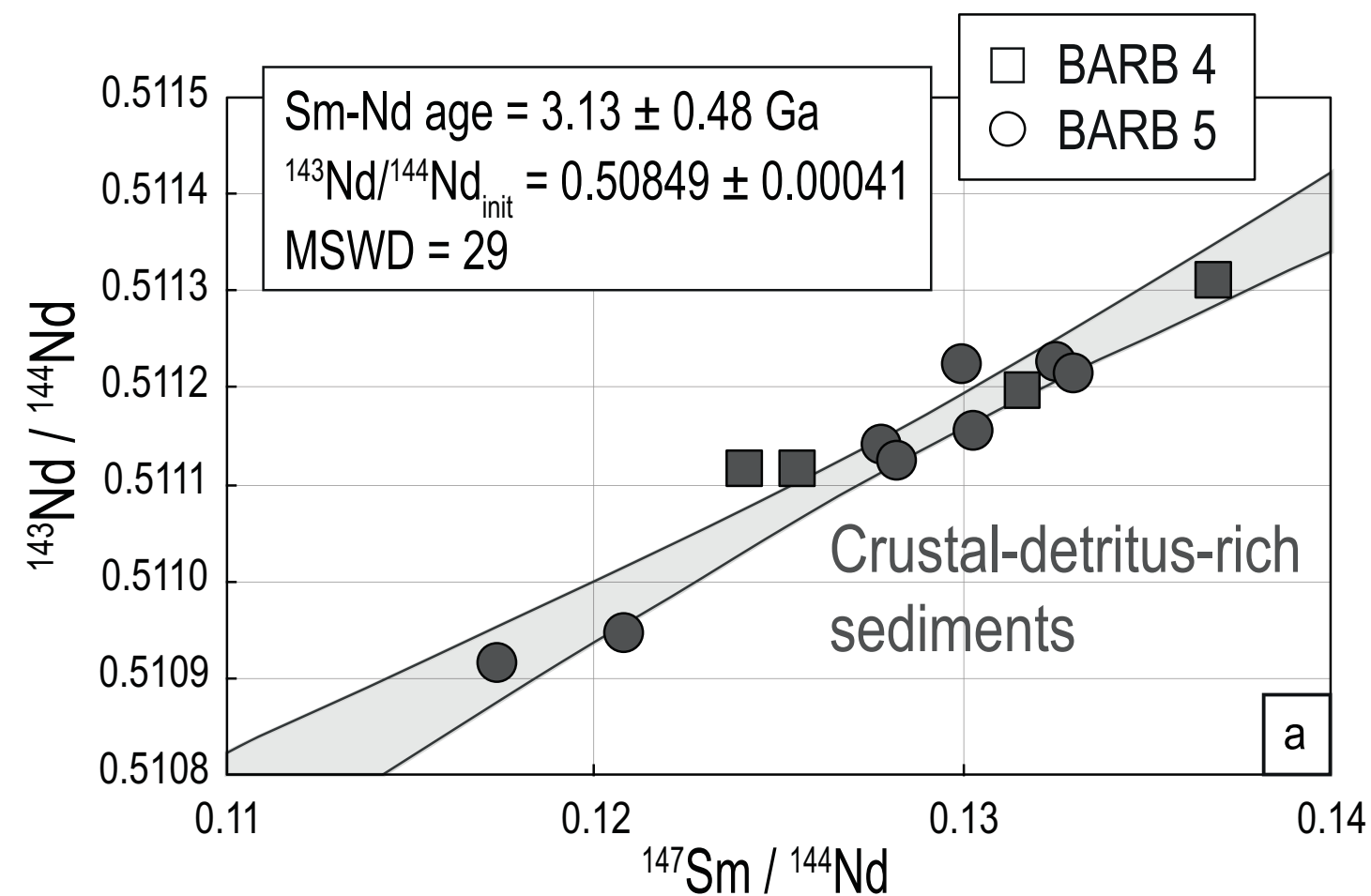
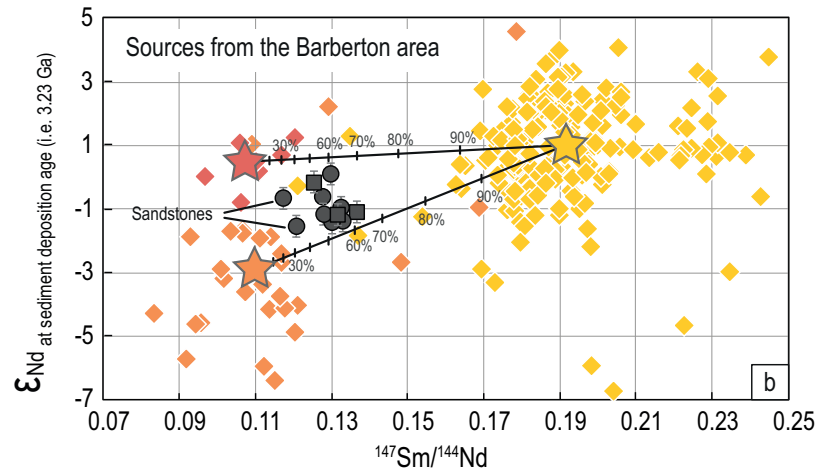
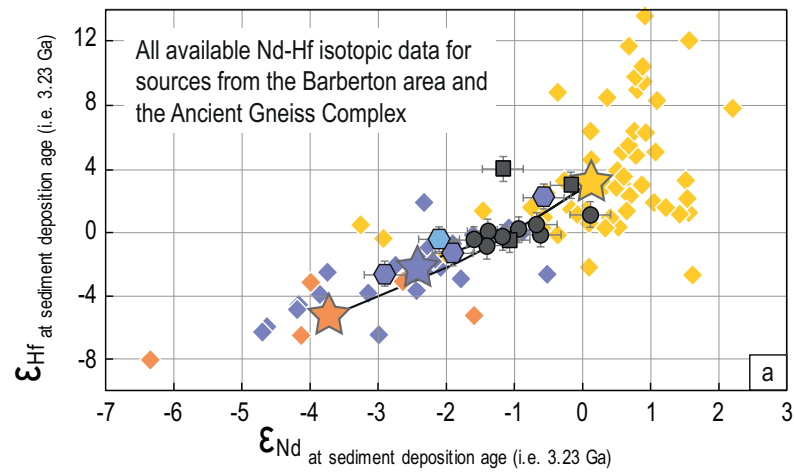


Figure 5

Figure 5



<i>This study</i>	<i>Literature data</i>
Barberton Greenstone Belt	Barberton Greenstone Belt
Crustal detritus-rich sediments	Young felsic rocks (3.23-3.26 Ga)
■ BARB 4 - Fig Tree group	Old felsic rocks (3.45-3.53 Ga)
● BARB 5 - Fig Tree group	Mafic and ultra-mafic rocks (3.27-3.53 Ga)
Ancient Gneiss Complex	Ancient Gneiss Complex
⬡ Ngwane unit	Young felsic rocks (3.23-3.33 Ga)
⬢ Dwalile suite	Old felsic rocks (>3.45 Ga)
	Mafic and ultra-mafic rocks (>3.45 Ga)

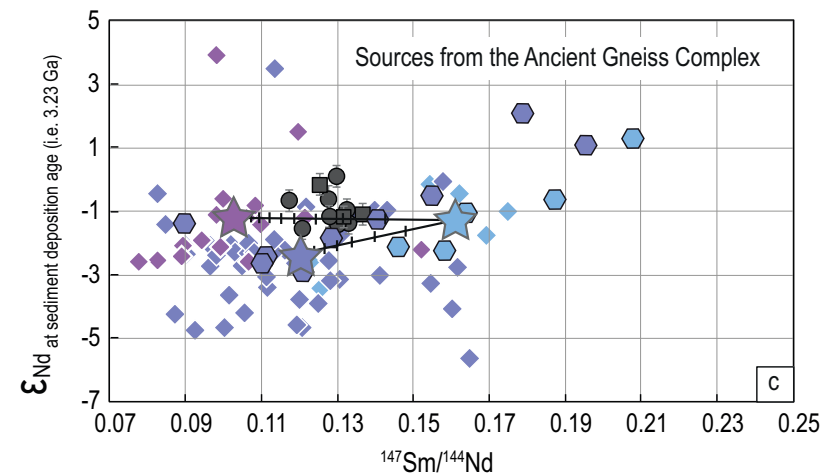


Figure 6

Figure 6

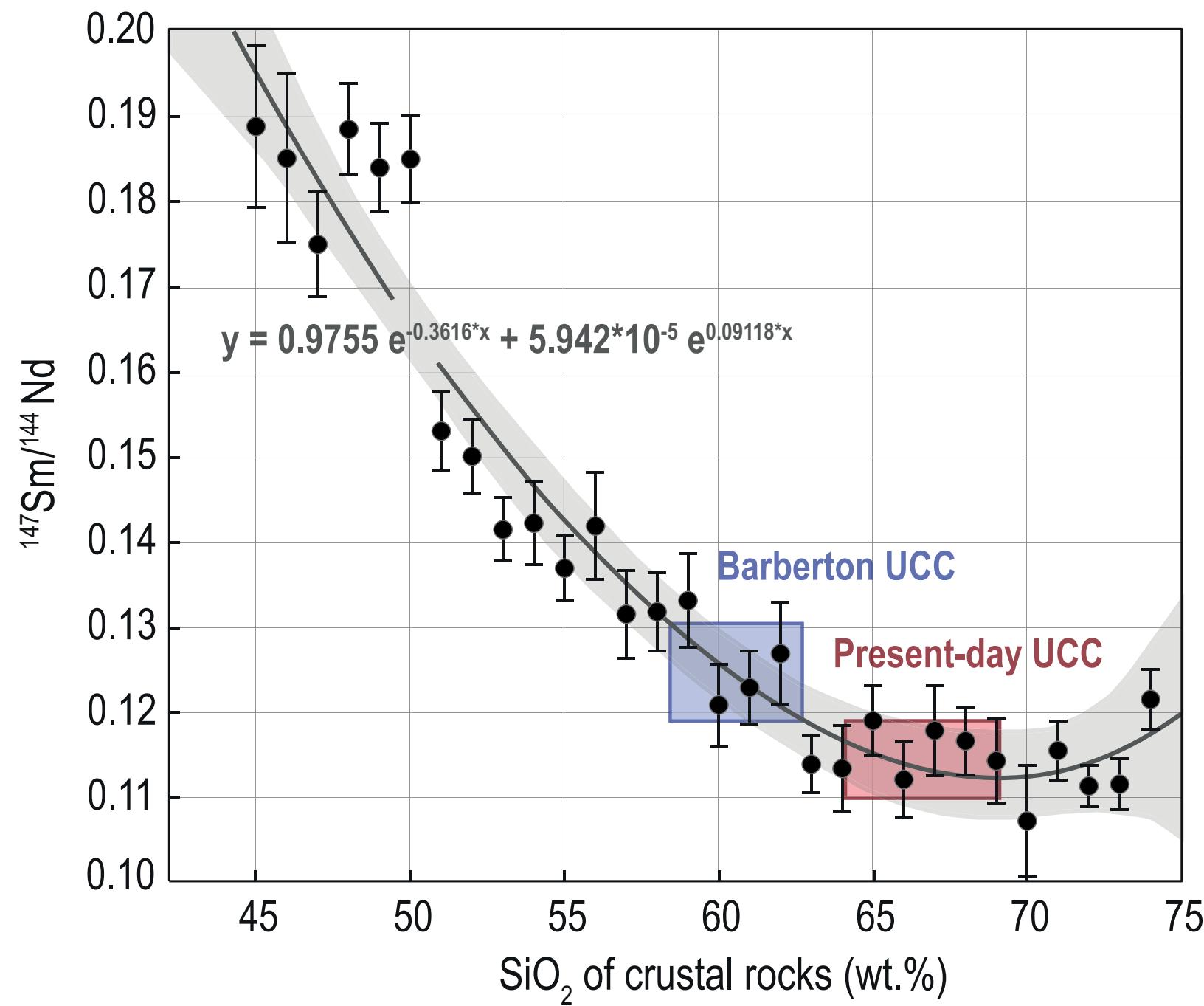


Figure 7

Figure 7

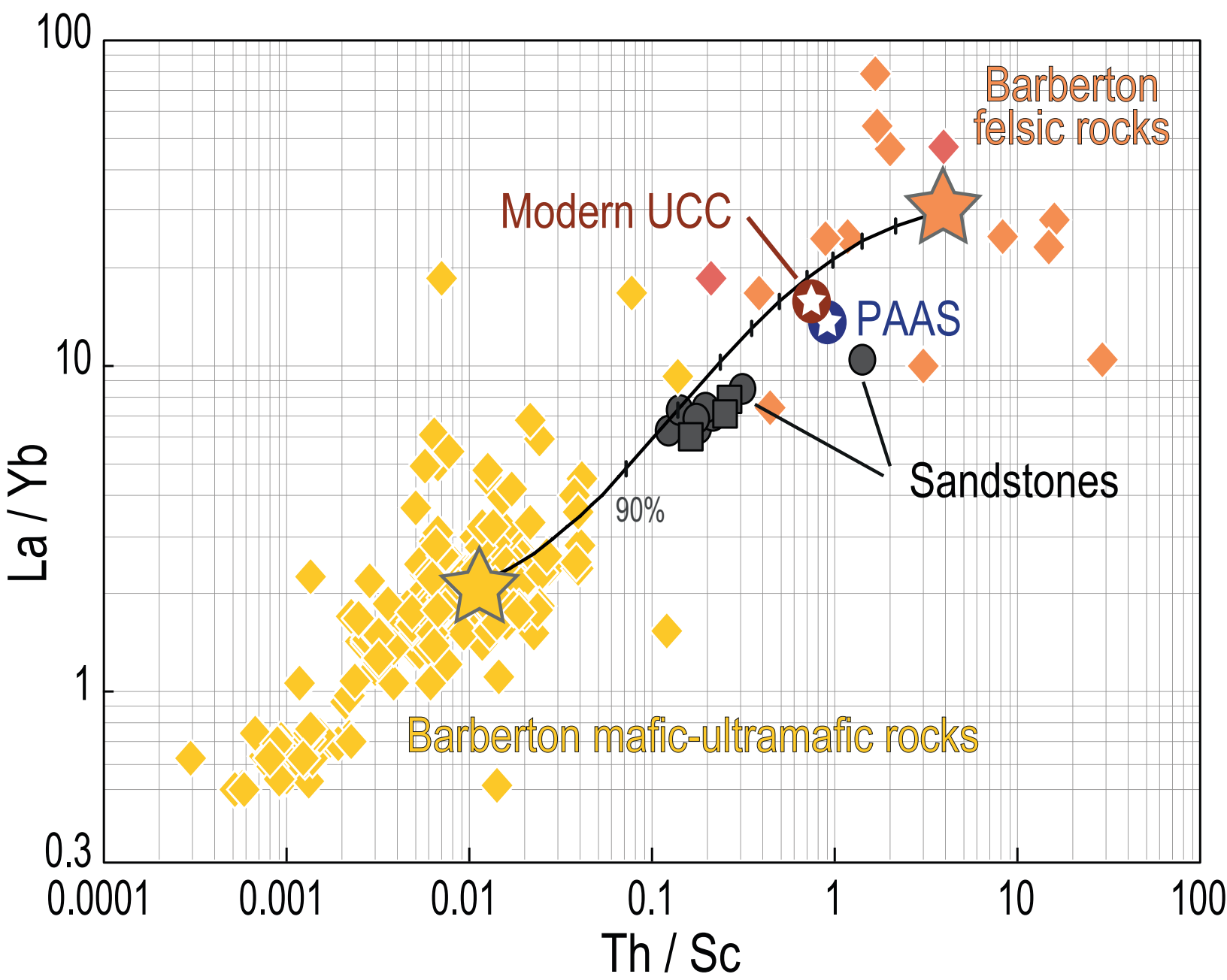


Figure 8

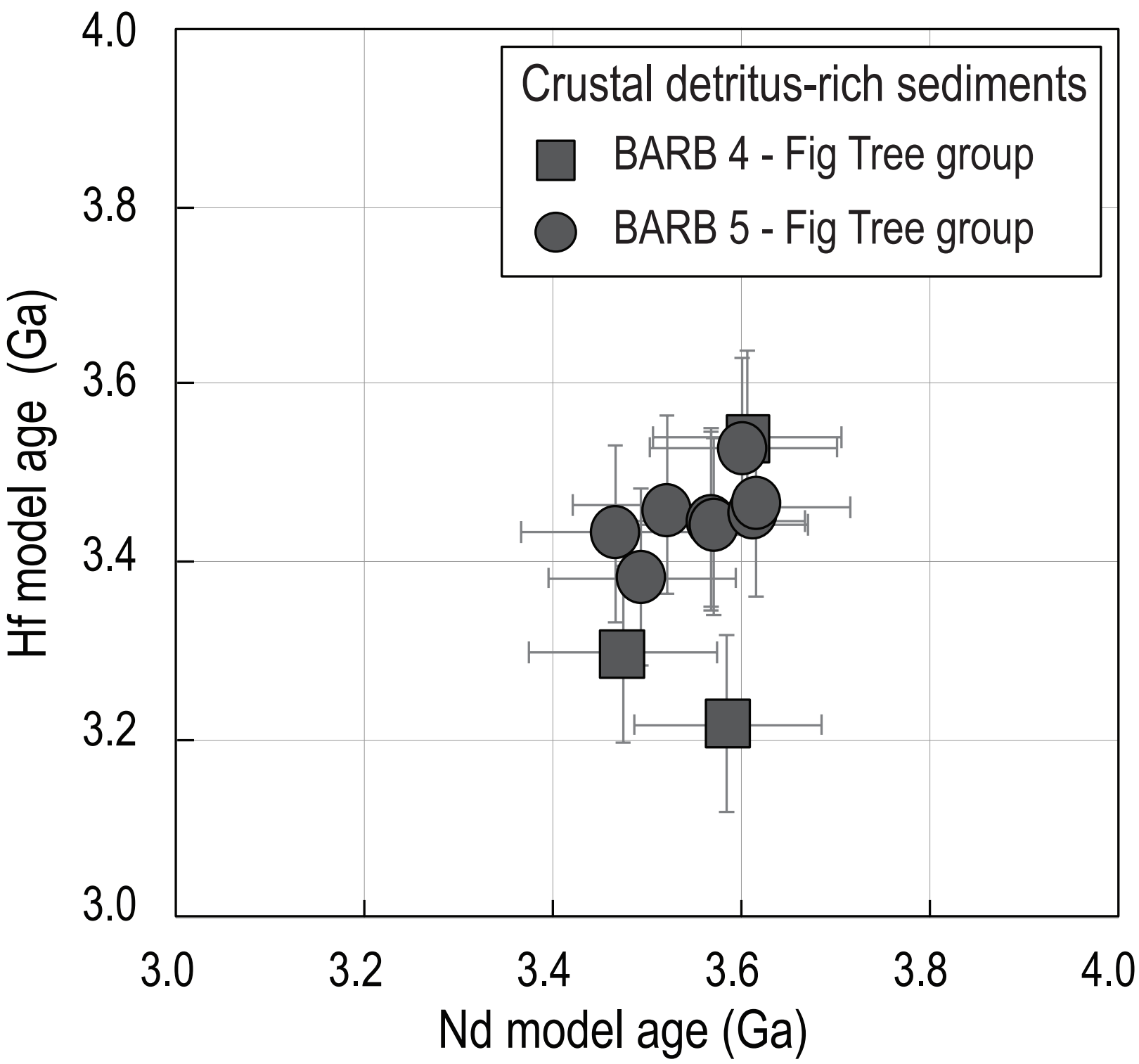


Figure 9

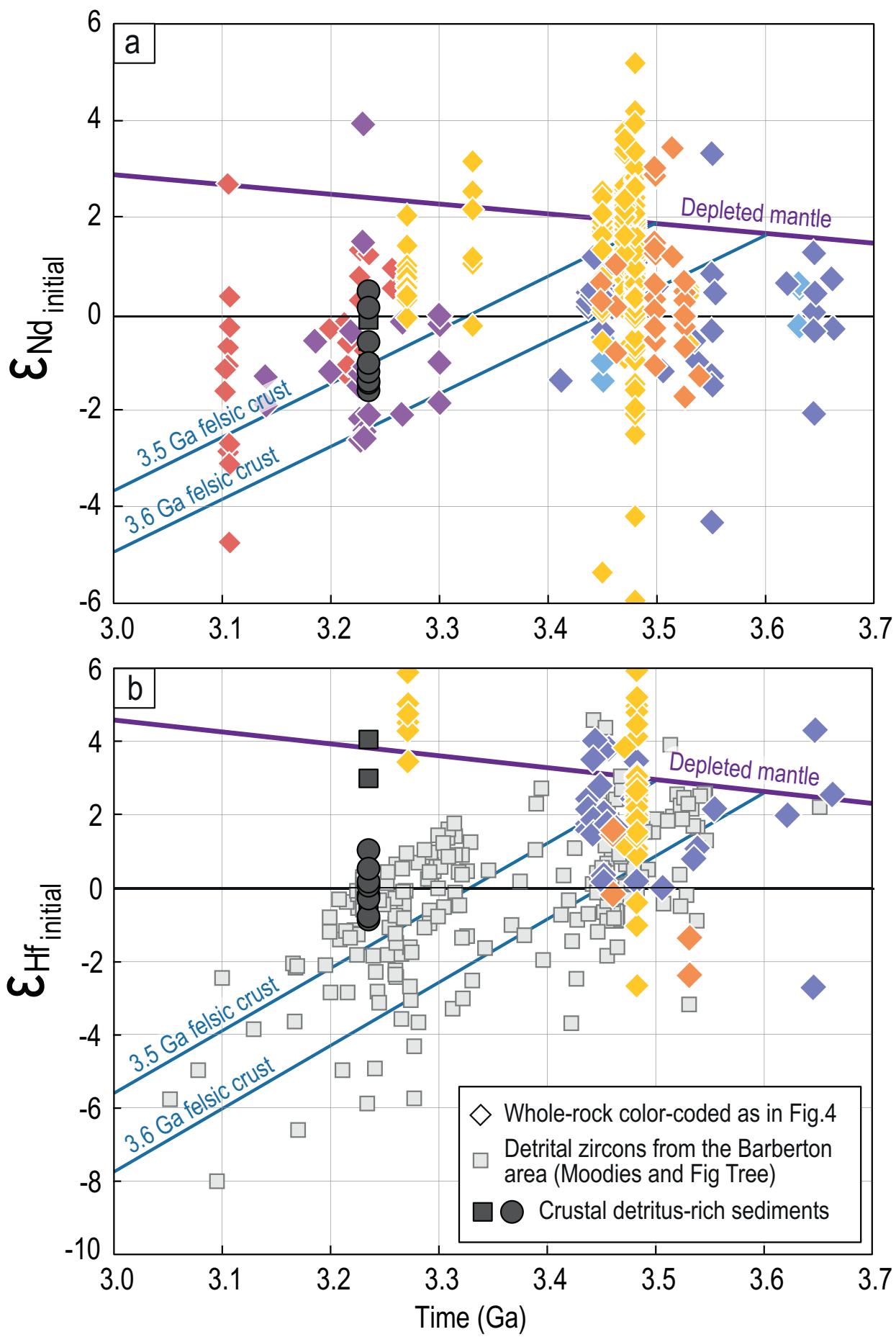


Figure 10

Figure 10

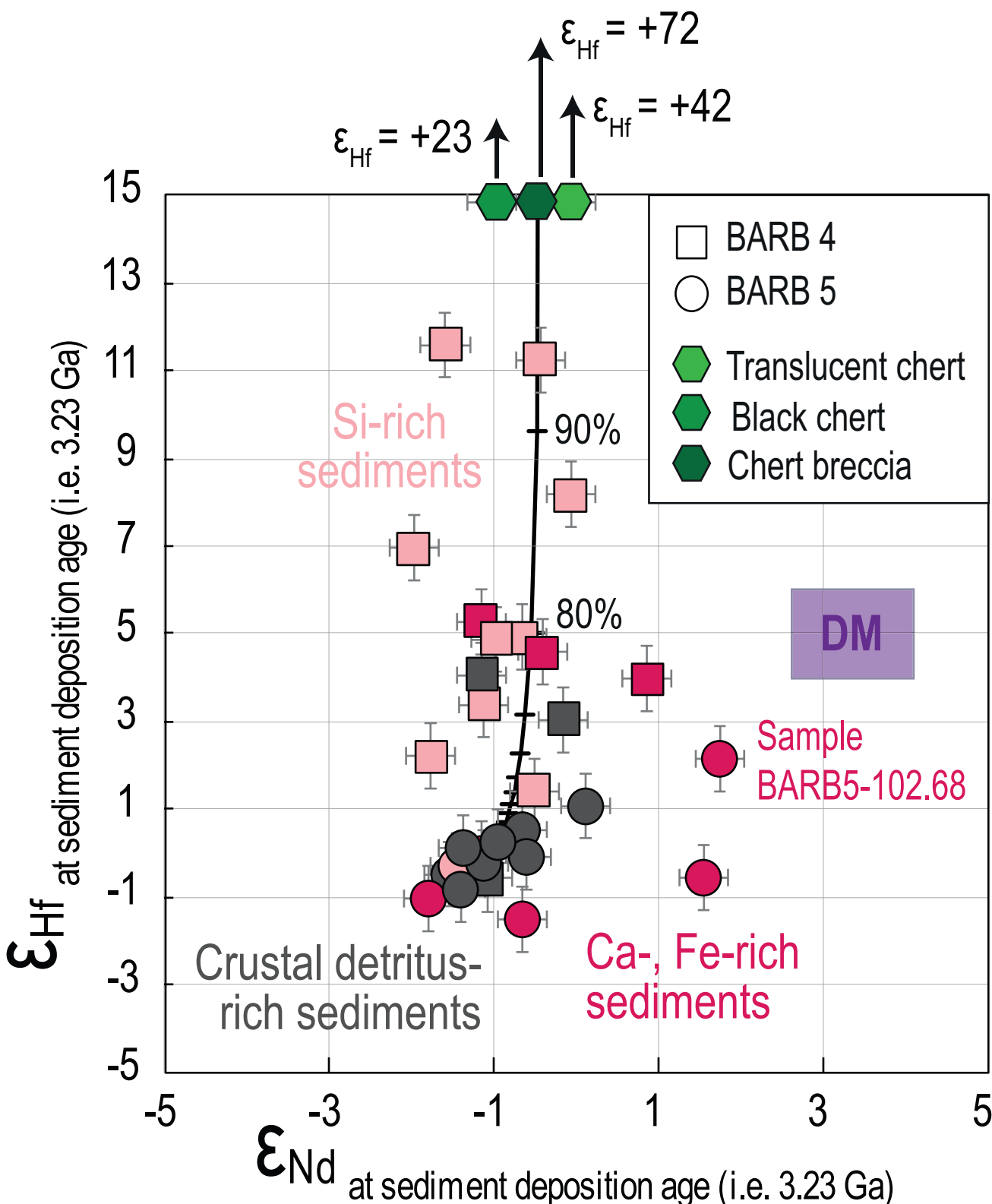
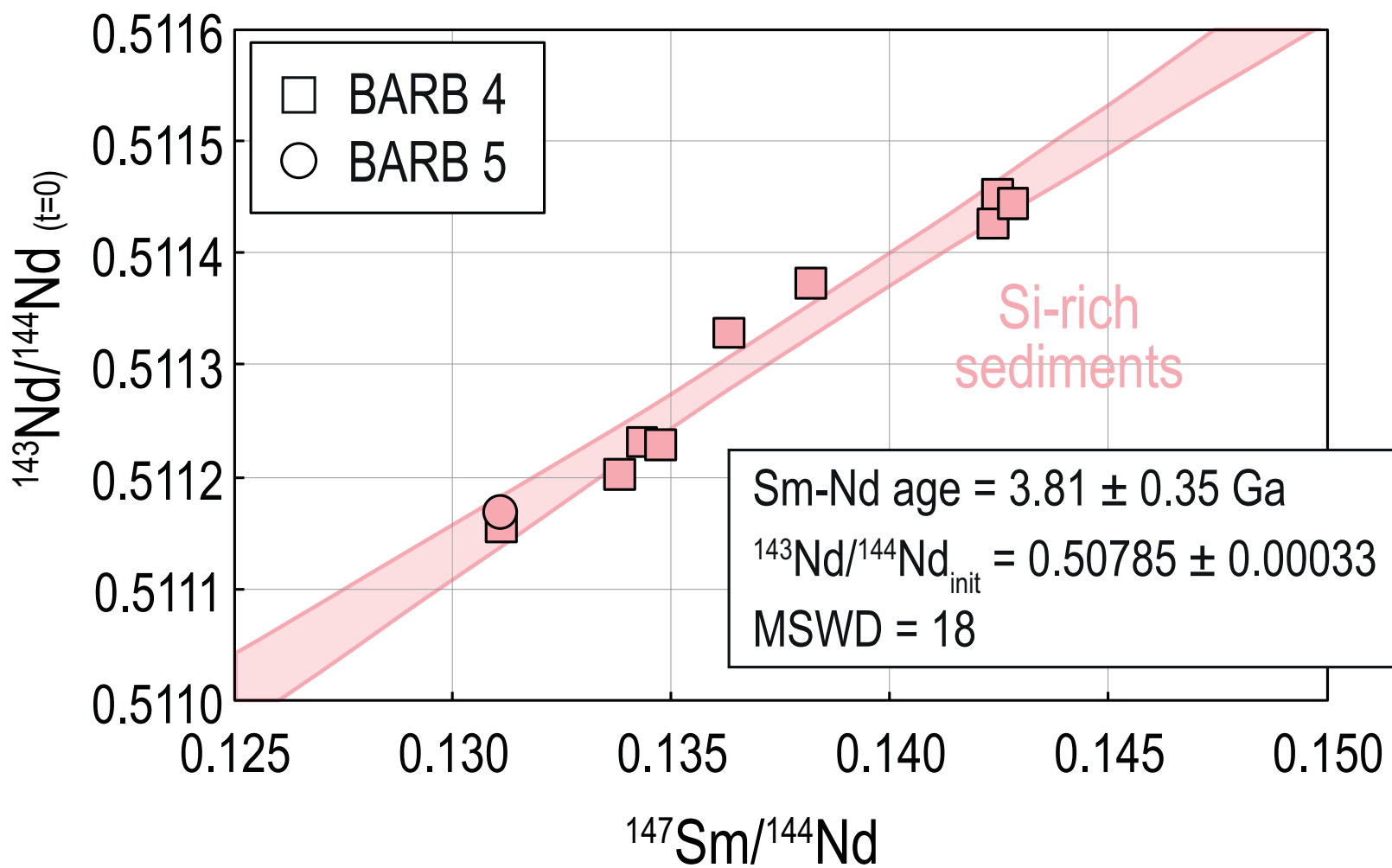


Figure 11



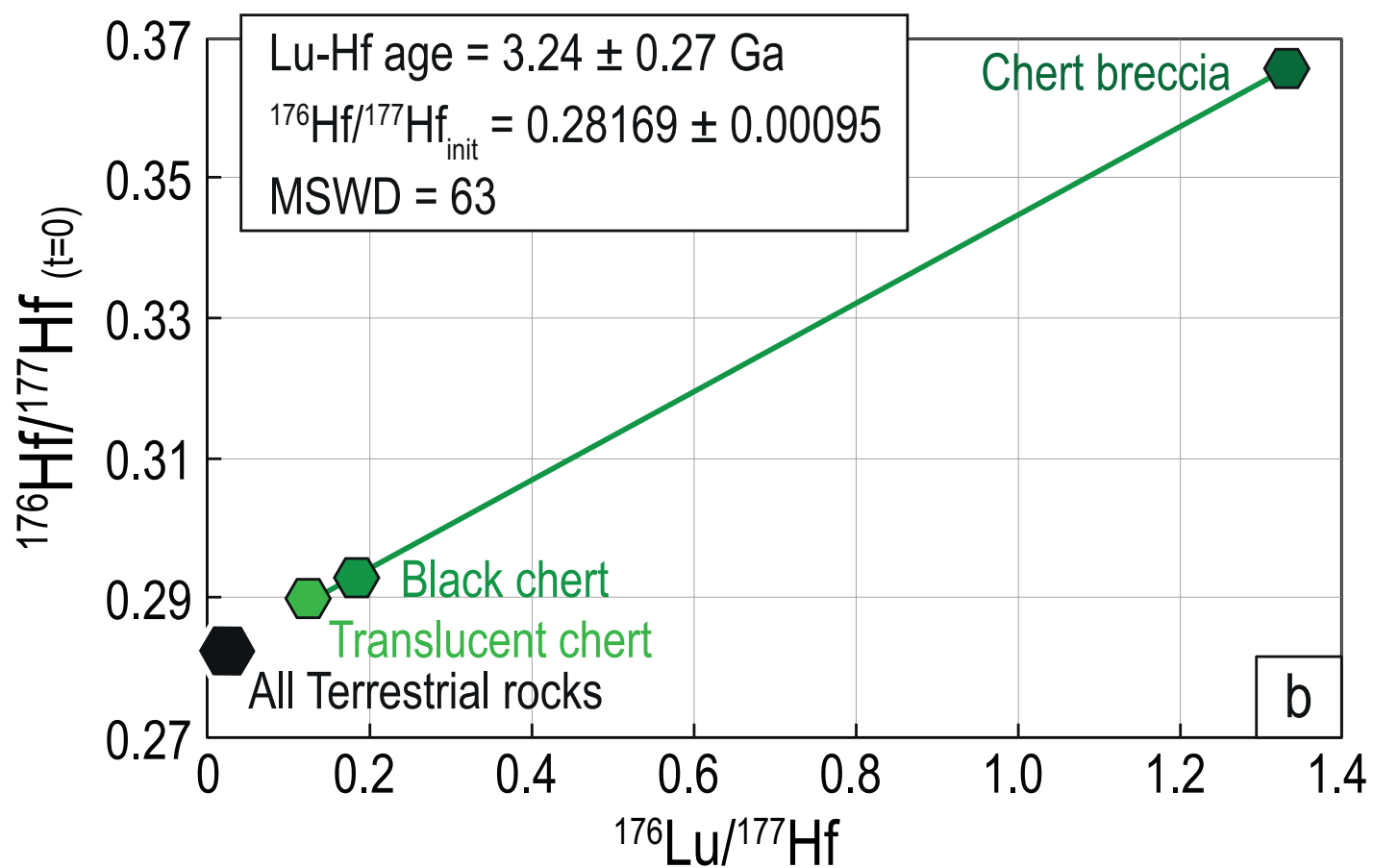
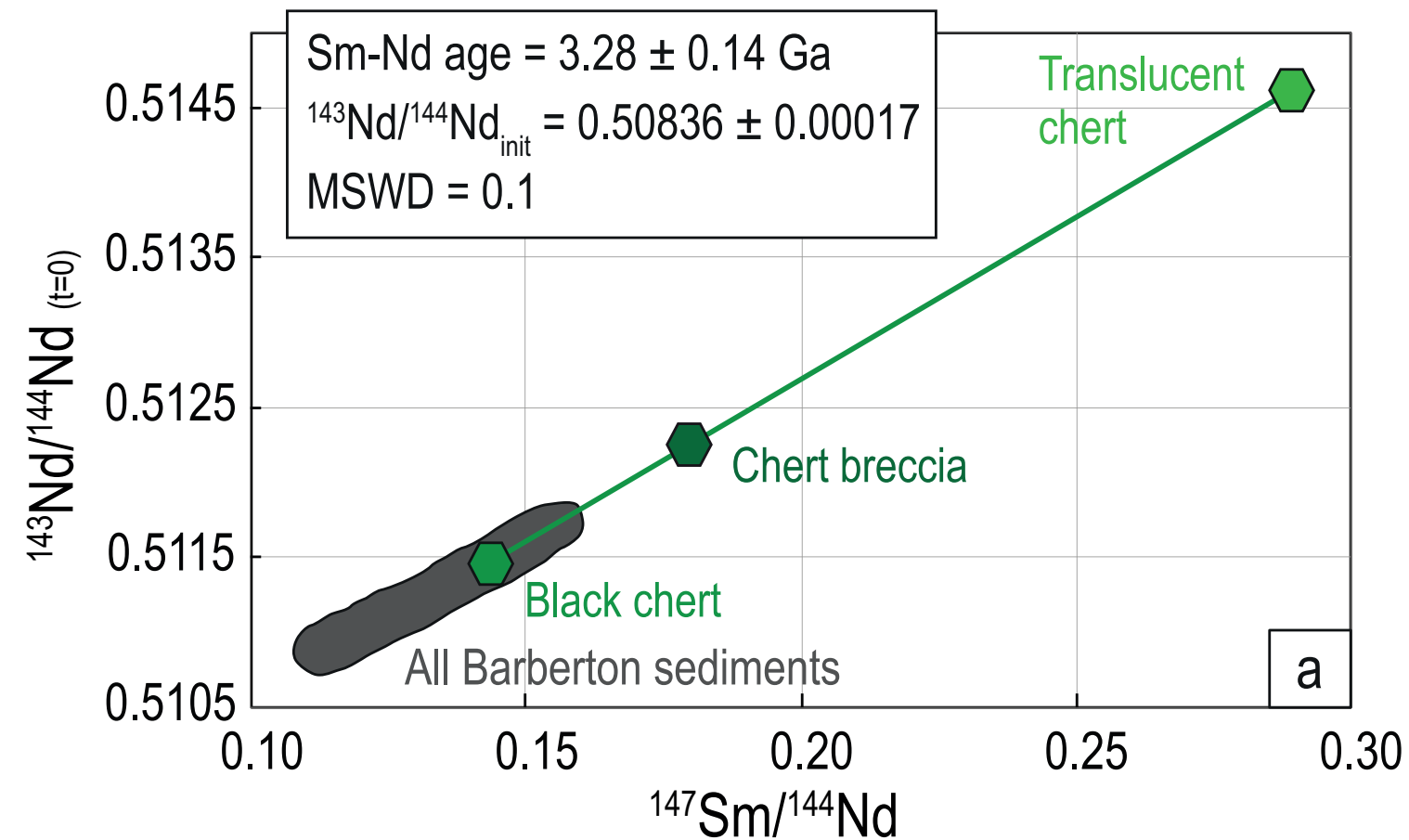
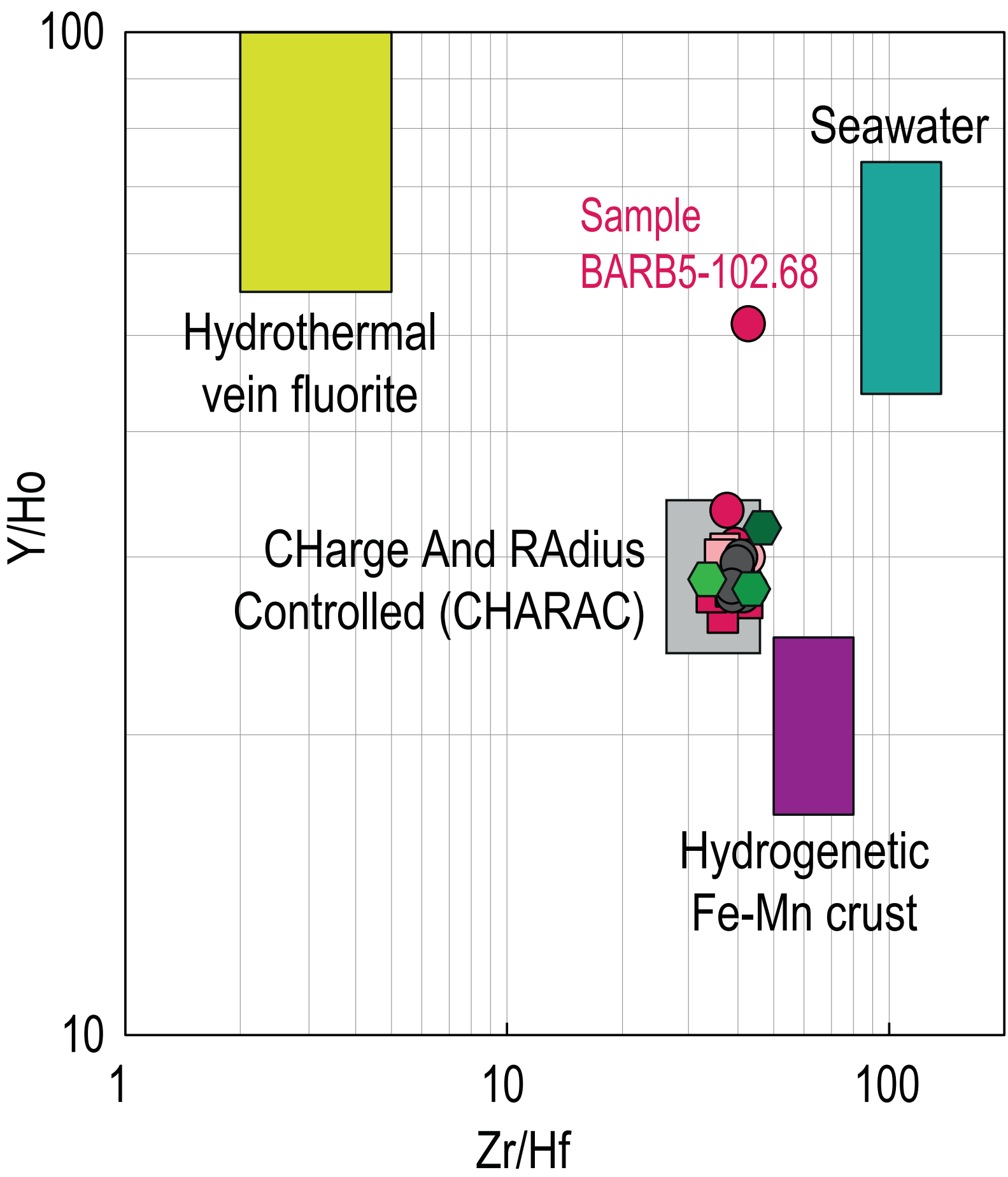


Figure 13



Supplementary Table A

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Supplementary Table B

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Supplementary File A

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Supplementary File B

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Supplementary File C

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