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1 **Clay Mineralogy, Organic Carbon Burial, and Redox Evolution in**
2 **Proterozoic Oceans**

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14 **Clay minerals formed through chemical weathering have long been implicated in**
15 **the burial of organic matter (OM), but because diagenesis and metamorphism commonly**
16 **obscure the signature of weathering-derived clays in Precambrian rocks, clay mineralogy**
17 **and its role in OM burial through much of geologic time remains incompletely understood.**
18 **Here we have analyzed the mineralogy, geochemistry and total organic carbon (TOC) of**
19 **organic rich shales deposited in late Archean to early Cambrian sedimentary basins.**
20 **Across all samples, the predominance of $1M$ and $1M_d$ illite polytypes indicates the**
21 **diagenetic transformation of smectitic clay and/or Al-rich weathering products. In late**
22 **Neoproterozoic basins, however, igneous/detrital $2M_1$ illite (including muscovite) dominates**
23 **clay mineralogy. Correcting for K-metasomatism, paleo-weathering indices indicate that**
24 **late Archean and Mesoproterozoic samples were moderately to intensely weathered. By**
25 **contrast, paleo-weathering indices sharply decrease in late Neoproterozoic samples,**
26 **consistent with an influx of chemically immature sediments that resulted in a**
27 **predominance of micaceous clays in sampled basins. For all samples, plots of TOC vs.**
28 **paleo-weathering index suggest that weathered sediments with abundant smectitic clays**
29 **were the most effective in OM sequestration. Additionally, our samples show a positive**

30 correlation between TOC and illite crystallinity (independent of post-depositional thermal
31 effects). A late Neoproterozoic switch to detrital/igneous clays is inconsistent with
32 hypotheses for oxygen history that require an increased flux of weathering-derived clays
33 across the Precambrian-Cambrian boundary. It is, however, consistent with the empirical
34 measurements on which such hypotheses are based. Although late Neoproterozoic increases
35 in micaceous clay and chemically immature sediment could physically shield buried OM
36 from enzymatic breakdown, modal clay mineralogy cannot by itself explain an Ediacaran
37 increase in atmospheric oxygen driven by enhanced OM burial.

38

39 **Keywords:** organic carbon, Proterozoic, oxygen, clay, mineralogy, sedimentary geochemistry

40

41 1. Introduction

42 The rise of atmospheric oxygen during the last ~2400 Ma (Ma: million years) of Earth
43 history has driven profound and irreversible changes, including the oxidation of the world's
44 oceans, eukaryotic diversification, and the emergence of animal life (Cloud, 1976; Holland, 1984;
45 Canfield, 2005; Gaidos et al., 2007). Atmospheric O₂ accumulation can be driven by the burial
46 of OM (Des Marais et al., 1992; Catling and Claire, 2005), and because of their unique physico-
47 chemical properties, clay minerals -- in particular, smectites derived from chemical weathering --
48 have been implicated in OM sequestration. For this reason, clay mineral studies are central to
49 understanding OM burial and O₂ accumulation through time (e.g., Kennedy et al., 2002).
50 Surprisingly, however, relatively little is known on the nature of clay mineralogy and the
51 mechanisms behind clay-TOC interactions through much of the Precambrian, when the most
52 crucial steps in Earth's oxygenation took place (Weaver, 1989; Kennedy et al., 2006).

53 Mineralogical analyses of a large number of shales by Weaver (1967; 1989) indicated
54 that smectite minerals are absent from Precambrian clay assemblages, but abundant in late
55 Paleozoic samples. Weaver (1967; 1989) suggested that either smectitic weathering products
56 were converted to more stable illite during burial diagenesis, or much of the illite is, itself, a
57 primary precipitate formed under distinctly Proterozoic environmental conditions. Based on
58 analyses of Neoproterozoic and Cambrian shales, Kennedy et al. (2006) proposed an alternative
59 hypothesis: the absence of smectite in Proterozoic shales and its appearance near the Proterozoic-
60 Cambrian boundary reflects fundamental changes in continental weathering associated with the
61 early evolution of land plants. In this view, plant-driven increases in chemical weathering and
62 clay formation led to increases in OM burial, driving late Neoproterozoic O₂ increase.

63 To test this model and, more generally, to constrain better the evolution of clay
64 mineralogy through time, we examine the quantitative relationship between clays and OM from
65 the late Archean Eon to the early Cambrian Period. By sampling a range of high TOC
66 Proterozoic shales, we ask whether weathering style and magnitude of clay generation changed
67 fundamentally through the Proterozoic and how these results relate, if at all, to changes in the
68 carbon cycle and Neoproterozoic rise of atmospheric O₂.

69

70 **2. Sample set and methods**

71 The sample set discussed here includes late Archean (2600-2500 Ma) samples from the
72 Transvaal Supergroup, South Africa, and the Mt. McRae Shale, Australia. Paleo- and
73 Mesoproterozoic shales were sampled from the McArthur Group; the Nathan Group, and the
74 Roper Group, all in northern Australia. Neoproterozoic samples come from the Chuar Group
75 (Arizona, USA; ca. 750 Ma) and the Ediacaran Vychegda Formation (Russia), Huqf Supergroup

76 (Oman), Nama Group (Namibia), Polarisbreen Group (Svalbard), and the Redkino and Kotlin
77 horizons (northern Russia). Lower Cambrian samples come from the Tokammane Formation,
78 Svalbard. Details of age and location for each sample are listed in Table 1. All samples represent
79 siliciclastic shales, siltstones and mudrocks deposited in environments ranging from inner
80 shelf/shoreface to outer shelf and basinal settings. Importantly, nearly all samples have
81 experienced low to moderate thermal metamorphism despite their age (see Table 1), with the
82 majority being subject to burial diagenesis only. The samples were collected from drillcores,
83 except for those from the Chuar Group and three Ediacaran/Cambrian shales from Svalbard.
84 Previous work has shown that Chuar shales have primary $\delta^{13}\text{C}$ values, well-preserved Fe-
85 speciation chemistry, and preserved biomarker molecules (Summons et al., 1988; Dehler et al.,
86 2005; Johnston et al., 2008), suggesting that late stage alteration/oxidative weathering was
87 minimal.

88 For bulk quantitative mineralogical analyses, hand selected shale samples were lightly
89 pre-crushed in an aluminum mortar and pestle; 10 wt. % reagent grade ZnO (Alfa Aesar;
90 confirmed to be pure Zincite by powder XRD) was added to each sample (0.1111g ZnO per
91 gram of sample) as an internal standard for quantitative analyses. Samples were then ground in a
92 Spex (#8507) hardened steel shatterbox container and swing mill (at 1 minute intervals), with
93 Vertrel XF fluorocarbon used as a grinding aid to attain particle sizes below 10 μm . The
94 shatterbox was cleaned with ultra-pure quartz and “pre-contaminated” by grinding a small
95 amount of sample prior to treatment.

96 For separation and powder XRD analysis of clay-mineral fractions, we used a modified
97 procedure after Moore & Reynolds (1997) to separate the <2 μm particle size fraction. Isolation

98 of the $<2\ \mu\text{m}$ particle size fraction was performed using separate bulk rock samples (that were
99 disaggregated by hand) than those used for bulk mineralogical analyses.

100 Acquisition of powder X-ray diffraction patterns (XRD) was performed with a Scintag
101 XDS 2000 diffractometer (Cu $K\alpha$ radiation). Data were collected in step sizes of $0.02^\circ\ 2\Theta$ with
102 counting time ranging from 2-4 seconds for bulk powders and clay-sized fractions. Background
103 stripping, indexing of diffraction peaks and mineral identification was performed using
104 Crystallographica Search-Match software (Oxford Cryosystems). Divergent slit sizes of 1 and
105 2mm, and receiving slit sizes of 0.5 and 0.3 mm were used for all analyses.

106 Randomly-oriented powder mounts were prepared for bulk mineralogical analyses using
107 a modified back-drift method as described in Moore & Reynolds (1997). For the analysis of
108 oriented clay fractions ($<2\ \mu\text{m}$ particle size), samples were prepared on glass slides following a
109 millipore filter-peel technique (Drever, 1973). Treatment with ethylene glycol involved sealing
110 prepared slides in a glass desiccator containing ethylene glycol liquid overnight at 65°C .

111 After initial mineral phases were identified, quantitative abundances were determined
112 with RockJock software (Eberl, 2003). The program compares integrated X-ray intensities for
113 minerals present in a sample with that of the internal standard (ZnO) and weight percentages are
114 calculated using previously measured peak intensity factors (Eberl, 2003). The RockJock
115 quantitative calculations have been checked for accuracy using predetermined mineral mixtures
116 and generally give values to within a precision of 1 to 2%. In addition, abundances for each
117 mineral are calculated independently with respect to the internal ZnO standard and so a total
118 value of close 100 wt. % serves as an independent check on the accuracy of calculations. We
119 only accepted calculations that yielded a “degree of fit” less than 0.11. For the determination of
120 clay mineral abundances, the program excludes peaks at 2Θ angles less than 20° (Cu $K\alpha$) and

121 instead uses high angle 060 reflections, which are less sensitive to preferred orientation effects
122 resulting from imperfect sample preparation (Srodon et al., 2001; Eberl, 2003). Each sample scan
123 was analyzed using the 20°-65° 2 Θ range and the auto-background correction feature, allowing
124 mineral standards to be slightly shifted in 2 Θ to maximize the degree of fit. The program is
125 freely available from the USGS at: <ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/>. Results from
126 Crystallographica Search-Match and RockJock analyses were compared to analyses on oriented
127 (and glycolated) clay size fractions as a check for consistency.

128 The RockJock software generally produces accurate results when quantifying major
129 groups of clay minerals (i.e., kaolinite, 2:1 dioctahedral clays and chlorites). However,
130 quantitative assignment of polytypes (and species within these groups) is less reliable, and in
131 some cases the software produces false positive identification of phases and polytypes. For this
132 reason, where possible, ZnO-free randomly oriented powder XRD patterns were analyzed to
133 verify 1*M* (possibly including 1*M*_d) and 2*M*₁ illite polytypes using *hkl* reflections at 32.1 (2*M*₁)
134 and 24.3 degrees 2 Θ (Cu K α) and the 2.58Å band, which is common to all illite polytypes
135 (Grathoff and Moore, 1996). The identification and estimate of 1*M* and 1*M*_d illite polytypes is
136 complicated by the fact that their specific *hkl* reflections often overlap. Thus an approximate
137 estimate for polytype percentage independent of RockJock software involves dividing the area of
138 the 32.1° peak over the total area of the 2.58Å band (Grathoff and Moore, 1996; see electronic
139 annex). This analysis could not be done for all samples because of the difficulty in detecting
140 these weak polytype specific peaks, especially in cases where 2*M*₁ illite abundances were low.
141 Where it was possible, however, this allowed a check on RockJock determined polytype
142 assignments. Some inaccuracy is inescapable, but the stratigraphic coherence of large differences
143 found within our sample set suggests our data reflect real differences in clay content.

144 In addition, for some samples, RockJock fits were slightly improved by the inclusion of
145 discrete smectite phases (Table 2). However, discrete smectite was not identified in any of the
146 oriented aggregate specimens analyses of the $<2\mu\text{m}$ size fraction, and so these quantities suggest
147 an effective detection limit for our RockJock analyses of ~ 5 wt. %.

148 For ethylene glycol treated oriented aggregates, the full width at half maximum of the
149 10\AA peak was measured using WINFIT, a program for XRD profile fitting and size/strain
150 analysis (Krumm, 1996). For all peak decomposition analyses, line shapes were specified as
151 symmetrical and Gaussian. For oriented aggregates solvated with ethylene glycol, peak positions
152 were used to estimate the proportion of expandable smectite layers within illite found in our
153 samples. We follow Srodon (1980) and Moore & Reynolds (1997) for approximating the
154 smectite component present in our analyses using the $\Delta 2\Theta$ between the illite 001 / EG-smectite
155 002 reflection and the illite 002 / EG-smectite 003 reflection.

156 TOC analyses were conducted on powdered bulk rock samples using the loss on ignition
157 (LOI) method outlined in Heiri et al. (2001), which involved drying overnight at 105°C and
158 heating to 550°C . Most samples were run in duplicate as a check on reproducibility and the
159 averages of multiple analyses are reported in Table 2, and, in an effort to improve precision,
160 sample weights, heating temperatures, heating duration and oven placement were invariant for all
161 analyses (Heiri et al., 2001). Although using the LOI method as a measure of TOC in our
162 samples is subject to interference from structural water loss from hydrated clay minerals (Heiri et
163 al., 2001), the consistent lithology of our samples (fine-grained siliciclastic sediments with low
164 carbonate abundances) eliminates the effect of mineralogical heterogeneity and allows for more
165 reliable inter-sample comparison of TOC content. Although some water loss may be expected to
166 contribute to the overall LOI signal from hydrated mineralogy, for the most part these effects are

167 anticipated to be small. For example, assuming an average of 50 wt % illite and using
168 unpublished data on illite structural water loss upon ignition ([http://www-](http://www-usr.rider.edu/~hsun/carbon.pdf)
169 [usr.rider.edu/~hsun/carbon.pdf](http://www-usr.rider.edu/~hsun/carbon.pdf)) the effects are expected to exhibit minor interference with only
170 the lowest TOC samples (<1-2 wt%).

171 Bulk chemical analyses were performed using a Bruker S4 Pioneer wavelength dispersive
172 X-ray fluorescence spectrometer. Powdered bulk rock samples were pressed into pellets in a
173 cellulose matrix and analyses were performed using internal X-ray fluorescence standards.

174

175 **3. Mineralogy and Geochemistry of Proterozoic Shales**

176 *3.1 Clay mineralogy through the Proterozoic Eon*

177 Many clay minerals occur at the Earth's surface, but the hallmark of Precambrian shales
178 is illite (Weaver, 1989). Illite forms under a variety of conditions and crystallizes in different
179 forms, or polytypes, that differ only in their crystallographic structure (Srodon and Eberl, 1984).
180 Most shales contain a mixture of illite polytypes. Commonly, illite in shales forms by the
181 diagenetic or metamorphic transformation of smectite and/or kaolinite (Srodon, 1999). With
182 temperature and/or time, this reaction progresses through mix-layered (e.g., illite/smectite)
183 species to clays that contain a high percentage of illite layers (~85-95% illite) and few
184 smectite/kaolinite layers. This diagenetic illite consists almost exclusively of the $1M$ and $1M_d$
185 polytypes (referred to herein as $1M/1M_d$ illite) (Srodon, 1999). Thus, distinction can be made
186 between these polytypes and the $2M_1$ mica-illite polytype (including muscovite) that generally
187 reflects clays formed by igneous and high-grade metamorphic processes and typically introduced
188 to sediments as detrital particles. The identification of $1M/1M_d$ illite polytypes, then, allows a
189 first-order estimate of the contribution of originally weathering-derived smectite and/or kaolinite

190 to the mineral assemblage. However, clays derived from weathering in the regolith are not the
191 only source of $1M/1M_d$ illite. Volcanic material deposited in the ocean and/or on land rapidly
192 alters to smectite and this contribution could overprint a soil-borne clay component especially
193 when integrated over the significant timescales captured by our sample set (Weaver, 1989). That
194 noted, we know of no distribution of volcanic components, either in the shales we collected or in
195 the basins we sampled, that could explain the stratigraphic distribution $1M/1M_d$ illites reported
196 below. Clay formed from diagenetic reactions, in authigenic pore-filling cements from
197 sandstones and previously illitized mudstones may also complicate a weathering signal preserved
198 in ancient sedimentary rocks (Weaver, 1989; Meunier and Velde, 2004).

199 Quantitative analysis of illite polytypes in our samples shows that a significant proportion
200 of the clay fraction (to a maximum of ~70 wt. %) occurs as $1M$ or $1M_d$ illite. Analyses of
201 ethylene-glycolated mineral separates further show that, with few exceptions, the percentage of
202 illite in mixed layered materials ranges from 85 to >95%, and discrete smectite is negligible or
203 non-existent. This suggests that, in nearly all samples illitization has reached an advanced stage.

204 Our samples also contain a significant component of $2M_1$ illite (which, as discussed here,
205 includes muscovite; Figure 1; Table 2). As this mineral forms at temperatures well above any
206 experienced by all but the oldest of our sample set (e.g., >275°C; Table 1), its origin in nearly all
207 cases must be detrital. Other clays in our samples typically include glauconite, chlorite, and
208 minor amounts of kaolinite (Table 2). “Glauconite”, as used here, is defined operationally based
209 on the position of the 060 XRD peak and decomposition of 001 peaks; it includes not only true
210 glauconites, but those species which can be collectively classified as Fe-rich 2:1 clays (Srodon et
211 al., 2001).

212 Glauconite was identified in most samples (Table 2; Fig. 2). Glauconite is generally
213 thought to form by the recrystallization of a precursor material (usually Fe-rich) under typically
214 reducing conditions, and this reaction must occur near the sediment-water interface in contact
215 with seawater derived K to allow K_2O incorporation and the formation of glauconitic mica
216 (Rousset et al., 2004; Meunier and El Albani, 2007). The precursor may form as an intermediate
217 phase during early diagenesis and glauconitization, or it may be composed of detrital material
218 that reacted with ambient chemistry in the sediment. Nevertheless, the origins of glauconite
219 most clearly represent specific physical/chemical conditions (i.e., reducing, seawater K diffusion
220 and low sedimentation rate) during early diagenesis (Velde, 2003; Rousset et al., 2004).

221 The most noticeable changes in clay mineralogy occur among samples from late
222 Neoproterozoic basins (Figures 1 & 2). Compared to samples from the late Archean and
223 Mesoproterozoic, most late Neoproterozoic samples show a significant increase in the proportion
224 of $2M_1$ illite (including muscovite) in the clay fraction (Figure 1). The proportion of $1M/1M_d$
225 illite and glauconite shows a corresponding decrease within the same basins (Figure 2), reflecting
226 an effective switch in the dominant phyllosilicate phase in these late Neoproterozoic samples,
227 with total clay content remaining more or less constant.

228 In our samples, smectites are essentially undetectable; however, a major fraction of
229 $1M/1M_d$ illite in our samples probably represents the transformation of pre-existing smectite
230 and/or kaolinite in the original clay assemblage. Thus, non-detection of smectite most likely
231 reflects burial diagenesis and not original absence. From this, we conclude that clay-rich
232 weathering products were common throughout the Proterozoic Eon, in line with previous studies
233 of Precambrian shales that also report significant diagenetic $1M/1M_d$ illite (Reynolds, 1963, 1965;
234 Weaver, 1967, 1989; Eslinger and Sellars, 1981).

235

236 *3.2 Paleo-weathering indices and K-metasomatism*

237 Chemical weathering leaches and subsequently depletes the soluble elements Ca, Na and
238 K relative to Al and, in some cases, Fe. Mineralogically, progressive Al-enrichment is reflected
239 by the formation of smectite and Al-bearing clay minerals in the residual weathered materials
240 (Nesbitt and Young, 1989; Nesbitt and Markovics, 1997). The net effect of chemical weathering,
241 then, is the conversion of feldspar to smectite and, with continued and/or more intense leaching,
242 Al-rich clays such as gibbsite and kaolinite. These changes are most effectively uncovered using
243 a Al_2O_3 -(CaO^* + Na_2O)- K_2O ternary plot (here, referred to as A-CN-K) of molar oxide
244 proportions, where CaO^* is silicate CaO only (the CaO correction includes removal of
245 carbonate-associated Ca, as well as phosphate-associated CaO. More details of the correction can
246 be found in Fedo et al. (1995)). The chemical trends of modern and ancient weathering profiles
247 are indistinguishable to those predicted from thermodynamic and kinetic data (Nesbitt and
248 Young, 1984; Nesbitt et al., 1997). This relationship requires that the predicted chemical
249 weathering trend of a given source rock composition on the A-CN-K diagram evolve along a
250 path parallel to the A-CN join (see Figure 3). With continued and/or more intense weathering,
251 after intersection with the A-K join, the trend continues to the Al_2O_3 apex where the soil
252 mineralogy is dominated by aluminous phases (Figure 3). Quantitatively, the degree of
253 weathering is expressed by the chemical index of alteration (CIA), where:

$$254 \quad \text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] * 100$$

255 On the A-CN-K diagram, the CIA is simply a projection on the vertical (Al_2O_3) axis (Figure 3).
256 Unweathered feldspar-rich source rocks display CIA values near 50 and the value increases with
257 the intensity of chemical weathering.

258 The effects of burial metamorphism and metasomatism obscure these primary weathering
259 trends. Upon burial diagenesis and heating, the predominant chemical change is K-
260 metasomatism in two forms: (1) K-addition to aluminous products -- for example, the addition of
261 K to kaolinite/smectite to produce metamorphic illite, and (2) the substitution of K for Ca or Na
262 in plagioclase (Fedo et al., 1995). On the A-CN-K diagram, the net effect of these reactions is to
263 drive each weathered sample toward the K_2O apex in the case of K-addition to aluminous
264 products, or to drive the sample horizontally to the A-K join in the case of K-substitution (Figure
265 3). Aside from K, diagenetic processes have been shown to cause the redistribution of Ca, Mg,
266 Na, Fe, Si and possibly Al, but the scale at which these elements are mobile and the degree to
267 which such systems can be considered open remains unresolved (McLennan et al., 2003).
268 Nevertheless, the bulk of fine-grained siliciclastics that have been analyzed in A-CN-K ternary
269 space show that illitization results in a net offset toward the K_2O axis (Fedo et al., 1995, 1996,
270 1997; Bloch et al., 2006). This suggests that K may be considered highly mobile in fine-grained
271 illitization systems at the basinal scale (e.g., Furlan et al., 1996) -- more so than Al, which is
272 redistributed through isomorphic substitution and limited to exchange between primary and
273 secondary mineral phases.

274 Given these relationships, if source composition is known or can be inferred, a predicted
275 “pre-metamorphic” weathering trend can be calculated. The effects of K-metasomatism can then
276 be removed by extending a vector from the K_2O apex through each sample to the predicted
277 chemical weathering trend (Fedo et al., 1995). Thus, the present day CIA value is corrected for
278 metamorphic effects and a “paleo-CIA” value can be estimated for a given sample (Figure 3).

279 Our late Archean and Mesoproterozoic samples plot close to the A-K join on an array
280 that extends away from a portion of the A-CN join defined by smectite-kaolinite mixing (Figure

281 4). None of the late Archean or Mesoproterozoic basins define a trend that is subparallel to a
282 predicted chemical weathering pathway. Assuming a pre-weathered source composition
283 equivalent to average late Archean upper crust (Condie, 1993; Fedo et al., 1995), we can define a
284 weathering trend for samples unaffected by K-metasomatism (Figure 4). Applying corrections to
285 each sample from the K_2O apex to the predicted late Archean upper crustal weathering trend, we
286 have estimated paleo-CIA values for each sample (Figure 4; Table 2). The assumption of an
287 upper crustal source composition and the observed positions of our late Archean and
288 Mesoproterozoic samples on Figure 4 requires a significant degree of K-enrichment.
289 Mineralogical evidence suggests that these samples could have experienced the highest degrees
290 of K-addition; $1M/1M_d$ illite abundances (and glauconite) are among the highest measured in our
291 sample set (Table 2). In addition, the illite 001 XRD peaks are among the broadest measured;
292 this is inconsistent with illite derivation largely from magmatic processes and points to K-
293 addition to chemical weathering and/or diagenetic products.

294 Late Archean samples yield paleo-CIA values of 81-86+ (with one exception, 68),
295 consistent with intense weathering and leaching. Our results are, thus, in agreement with a
296 number of studies that report high paleo-CIA values for siliciclastics of this age (Fedo et al.,
297 1996; Bhat and Ghosh, 2001; Condie et al., 2001; Hessler and Lowe, 2006). In fact, it has long
298 been recognized that Archean shales are enriched in K_2O relative to estimates of average upper
299 crust (McLennan et al., 1983). The consistently high paleo-CIA of Archean and Paleoproterozoic
300 rocks (see Condie et al. (2001) for a compilation; Fig. 6) reflect intense leaching and weathering
301 processes perhaps driven by elevated pCO_2 (Holland, 1984; Hessler and Lowe, 2006). In such an
302 environment, residual Al-rich species such as kaolinite and gibbsite would have dominated the
303 clay assemblage. For our Mesoproterozoic shales from Northern Australia, we calculate paleo-

304 CIA values of 71-85, reflecting more moderate weathering involving metal retention and
305 concomitant pH increase, a regime that typically favors smectite production.

306 Neoproterozoic samples are significantly more scattered than late Archean and
307 Mesoproterozoic samples (Figure 5). In addition, inferred source rock compositions are more
308 diverse and complex, ranging from granodioritic (roughly equivalent to the average Upper
309 Neoproterozoic crust) to more K-enriched charnockitic. Some Neoproterozoic and early
310 Cambrian sample suites define a clear trend from an unweathered source composition, but in
311 others such a trend is difficult to discern. For these latter samples we choose unweathered source
312 compositions based on mineralogical constraints as much as possible (see electronic annex for a
313 sample-by-sample discussion), but we also record corresponding “maximum” paleo-CIA values
314 relative to an average crustal source in Table 2. It should be noted that the choice of a more
315 mafic crustal source is incompatible with the mineralogical characteristics measured in most
316 Neoproterozoic samples. In short, samples from most of the Neoproterozoic basins sampled in
317 this study exhibit lower paleo-CIA values than those collected from Mesoproterozoic and late
318 Archean basins (Figure 6), even when maximum estimates based purely on an upper crustal
319 source composition (Table 2) are used. This is consistent with the marked change in clay
320 mineralogy seen in these same samples.

321

322 **4. Mineralogical and geochemical associations with organic carbon**

323 *4.1 Paleo-CIA and TOC*

324 It is tempting to ask whether an increase in the proportion of igneous phyllosilicates seen
325 in our late Neoproterozoic samples could lead to more efficient burial and sequestration of
326 organic carbon. However, we observe no correlation between the amount of igneous

327 phyllosilicates (i.e., muscovite, $2M_1$ illite) and TOC. On the other hand, paleo-CIA shows a weak
328 positive correlation with TOC (Spearman rank correlation coefficient (r_s) = 0.208, $P = 0.063$;
329 Figure 7). As discussed above, the chemical weathering conditions that lead to efficient smectite
330 production do not necessarily correlate with weathering intensity, or paleo-CIA; the CIA values
331 that correspond to the highest potential smectite abundances instead lie between 70 and 82 (see
332 Fig. 3). Indeed, our highest TOC samples lie within this range; they are the most likely to have
333 been influenced by moderate paleo-weathering conditions and efficient smectite generation
334 (Figure 7). With increasing weathering intensity beyond the smectite-dominated range, leaching
335 begins to dominate and smectite minerals are destabilized, giving way to aluminous products.
336 Samples residing at this end of the CIA values generally show decreased TOC content, but two
337 of the highest TOC samples also have the highest paleo-CIA, suggesting that aluminous clay
338 mineralogy does not preclude high OM content upon burial (Figure 7). Although a robust metric
339 for the quantity and type of clays derived from chemical weathering is difficult to derive for such
340 a sample suite, this correlation suggests that the characteristics of smectite-rich soils may have
341 increased the effectiveness of organic carbon burial (e.g., Mayer, 1994; Ransom et al., 1998).

342 Additionally, our highest TOC (and the most intensely weathered) samples are pre-
343 Ediacaran in age. Although our sample set is biased toward high TOC, this observation is in
344 broad agreement with TOC compilations among shales spanning the Proterozoic; a survey of
345 ~1800 shales showed that average TOC is highest among Paleo- and Mesoproterozoic samples
346 (10.3 and 13.4 mg/g, respectively) and decreases into the Neoproterozoic (4.7 mg/g) (Strauss et
347 al. (1992)).

348

349

350 4.2 Illite crystallinity: Constraints on the physical association between clays and OM

351 Empirical measures of illite “crystallinity” (IC) have been widely used as indicators of
352 thermal history (Srodon and Eberl, 1984; Meunier, 2005), but they may contain additional
353 information on clay-OM interactions. Illite “crystallinity,” measured by 10\AA XRD peak widths,
354 reflects a combination of three mineral components: $2M_1$ mica-illite, $1M/1M_d$ illite (including
355 mixed layer I/S) and glauconite. The full width at half-maximum (FWHM) of the 10\AA peak is
356 controlled mainly by: (1) crystallite-size distribution, (2) the number of expandable layers
357 present in the illite and (3) any structural defects or distortions present in the crystals (Eberl and
358 Velde, 1989). Because almost all of our samples are composed of illite that contains only a small
359 proportion of expandable smectite layers (5-15% maximum), we can discount any significant
360 contribution of I/S expandability to the FWHM of the 10\AA peak (Eberl and Velde, 1989; Suchy
361 et al., 2007). Accordingly, the larger FWHM values can be taken to be representative of a greater
362 proportion of smaller or poorly crystalline illite crystallites.

363 Analyses show that the FWHM of the 10\AA peak correlates strongly ($r_s = 0.598$, $P =$
364 2.3×10^{-4}) with total organic carbon (TOC) content (Figure 8). Because several basins each
365 contain samples spanning almost the entire range of this correlation, we can eliminate any
366 thermal effects of diagenesis or metamorphism on this relationship. In fact, samples from the Mt.
367 McRae shale span 30 m of drill core (and so have an imperceptible metamorphic gradient), but
368 encompass the entire range of this correlation.

369 The principal controls on IC are not straight-forward, but the metric weakly correlates
370 with increasing amounts of the illite $1M$ and $1M_d$ polytypes and glauconite ($r_s = 0.551$, $P =$
371 6.8×10^{-4} ; see electronic annex). There is also a weak negative correlation between IC and $2M_1$
372 illite content ($r_s = -0.158$, $P = 0.37$), indicating that increasing amounts of coarse (detrital) $2M_1$

373 illite probably play a small role in decreasing the overall width of the 10Å illite XRD peak (see
374 electronic annex). The IC-TOC association is significant because the $1M/1M_d$ illite polytypes
375 mainly occur through the transformation of smectite/kaolinite precursors. On the other hand,
376 detrital $2M_1$ mica-illite seems to have little direct association with organic matter, implicating
377 weathering-derived (but since transformed) clays in OM burial.

378 Studies of OM association with clays in modern marine settings offer insight into
379 mechanisms responsible for the IC-TOC association in our samples. Detailed HR-TEM analyses
380 of continental margin sediments off of the California coast have revealed that the physical
381 association between OM and smectite initially occurs through the formation of OM-clay flocs
382 (Ransom et al., 1997, 1998). Upon deposition in seawater, fine clay crystals tend to flocculate
383 and form aggregates that incorporate significant amounts of OM (Ransom et al., 1998). In the
384 aggregates, the OM tends to be irregularly distributed, occurring as blebs and smears intimately
385 associated with clays (Ransom et al., 1997; Curry et al., 2007). The result of OM incorporation is
386 a significant decrease in permeability, in part from a greater percentage of pore space being
387 occupied by OM and the subsequent creation of inaccessible micro-porosity (Curry et al., 2007).
388 This physical association has been suggested to lead to greater preservation potential of OM
389 matter by inhibiting enzymatic breakdown; the enzyme-controlled degradation becomes
390 diffusion limited and much of the OM occupies pore space inaccessible to the reactants (Ransom
391 et al., 1998; Rothman and Forney, 2007). Causality may run in more than one direction, however;
392 OM physically interferes with the illite formation process, preserving small crystallite size.
393 Although there are few data in the literature that report both illite crystallinity and TOC, positive
394 relationships are observed for both Proterozoic and Phanerozoic rocks, but only when TOC
395 concentrations extend beyond ~1 wt. % (Underwood et al., 1989; Yang and Hesse, 1991; Sucha

396 et al., 1994; Uysal et al., 2004). Further evaluating potential IC-TOC relationships involves
397 making the distinction between primary and diagenetic influences by ruling out any possible
398 thermal effects, as discussed above.

399 Illitization is thought to occur by a number of different mechanisms, but three have
400 gained acceptance: (1) solid-state transformation (SST) of smectite layers to illite layers, (2)
401 smectite dissolution and illite crystallization (DC), and (3) Ostwald ripening (Altaner and Ylagan,
402 1997). The dominant mechanism(s) for illitization in a given setting is thought to be a function of
403 sediment permeability (Altaner and Ylagan, 1997; Srodon, 1999). For example, sandstones are
404 typically characterized by the DC mechanism whereas illitization in lower permeability
405 bentonites proceeds by the SST mechanism. Shales and other fine-grained siliciclastic rocks have
406 been shown to exhibit both SST and DC mechanisms, which reflects the variable mineralogy,
407 burial conditions and hydrothermal reactions experienced after deposition. The most important
408 feature of these two mechanisms, however, is that the SST mechanism preserves parent crystal
409 size, morphology and polytype (Altaner and Ylagan, 1997). In contrast, the DC mechanism
410 results in larger crystals and destruction of parent crystal morphology and polytype. In other
411 words, illitization by SST is largely a function of sediment permeability. Based on these
412 observations, higher OM content is likely to interfere with illitization by lowering local
413 permeability, fostering the probability of solid-state illitization. The final result is the
414 preservation of small crystallite size, largely determined by the original mode of flocculation and
415 aggregation of OM-clay particles, and later by burial and compaction.

416 The suggestion that OM may have inhibited recrystallization of illite during diagenesis is
417 not a new one. In fact, Jackson (1977) found that his sample set (comprised of a number of fine-
418 grained siliciclastics spanning the Proterozoic) displayed a positive correlation between illite

419 crystallinity and the degree of OM humification. The original interpretation was that although
420 burial diagenesis is known to increase OM condensation (leading to a decrease in aliphatic and
421 polar groups), the variations were primary, or pre-determined by OM-clay interactions, perhaps
422 leading to an interference of OM on illitization. In the end, the correlation between illite
423 crystallinity and TOC may reflect *both* the facilitation of OM sequestration by poorly crystalline
424 illite with high surface area (Bock and Mayer, 2000) and the impedance of diagenetic illitization
425 by OM incorporation.

426

427 **5. Physical and chemical weathering through the Neoproterozoic Era**

428 Most siliciclastic successions display marked chemical variation, reflecting the dynamic
429 interplay of chemical weathering, physical erosion and diagenetic/metamorphic processes
430 (McLennan et al., 1993; Nesbitt et al., 1997). In particular, the balance between rates of chemical
431 weathering and physical erosion exerts a major control on the geochemistry and mineralogy of
432 siliciclastic rocks (Nesbitt et al., 1997). The general consistency of paleo-CIA values over a
433 billion years of Late Archean through Mesoproterozoic time, thus, suggest long term balance in
434 weathering and erosion rates. Low paleo-CIA values obtained for two early Neoproterozoic
435 Chuar Group shales might simply identify outliers in a statistical distribution like that of earlier
436 intervals. Paleo-CIA values for Ediacaran to basal Cambrian shales, however, cannot be
437 explained this way. These samples are statistically different from older shales ($p = 9.4 \times 10^{-9}$;
438 Student's t-test), requiring perturbation in the rates of chemical weathering and/or physical
439 erosion in response to climatic shifts or tectonism (Nesbitt et al., 1997).

440 Lower paleo-CIA values could reflect Ediacaran increases in rates of erosion and
441 (concomitantly) sediment accumulation. For example, Squire et al. (2006) have hypothesized

442 that sediment accumulation rates increased in response to large-scale Pan-African uplift (Squire
443 et al., 2006). Increased physical erosion of uplifted terrains would tend to drive CIA lower,
444 allowing for a greater proportion of igneous/detrital clay relative to clay formed through
445 weathering in the regolith.

446 In contrast, hypotheses of increased chemical weathering on Ediacaran continents are at
447 odds with our data (Kennedy et al., 2006). The increasing weathering hypothesis was based on
448 the XRD analyses of siliciclastic rocks spanning the latest Neoproterozoic; Kennedy et al. (2006)
449 supported their hypothesis by reporting the Schultz Ratio, a ratio of the 020 XRD peak ($19.8^\circ 2\Theta$;
450 $\text{CuK}\alpha$), which all phyllosilicates (weathering-derived, detrital or igneous) exhibit, to the 100
451 XRD peak ($20.8^\circ 2\Theta$; $\text{CuK}\alpha$), which only quartz exhibits. Although our results clearly show an
452 increase in the *proportional abundance* of mica and $2M_1$ illite in the clay fraction of Ediacaran
453 and basal Cambrian shales, we observe no increase in *absolute* clay mineral content (see
454 electronic annex). Thus, at the sample level, increased detrital contributions appear to be
455 compensated by decreased input from chemical weathering products. The relative abundance of
456 quartz in the non-clay fraction also decreases markedly in our latest Neoproterozoic samples (see
457 electronic annex). This is consistent with an influx of chemically immature sediments, but may
458 not be directly reflective of this because XRD analysis cannot differentiate between sedimentary
459 quartz and later cements.

460 Figure 9 shows the Schultz ratio from our samples plotted as a function of age. A
461 proportional decrease in quartz and concomitant increase in igneous and metamorphic
462 phyllosilicates (i.e., muscovite and $2M_1$ illite) readily accounts for the observed increase in the
463 Schultz ratio (note that igneous clays and quartz strongly diffract X-rays in powder X-ray
464 diffraction; Moore and Reynolds, 1997). Moreover, Figure 10 shows that, regardless of any

465 secular decrease in quartz, $2M_1$ illite and mica minerals are the principal controls on Schultz ratio
466 in all of our samples (with the exception of chlorite-rich late Archean shales). Although the $2M_1$
467 illite observed in our samples might be blamed on original clay-rich weathering products that
468 were transformed in a prior rock cycle, major element geochemistry shows that these samples
469 were relatively unweathered at the time of sedimentation.

470 In total, then, the mineralogy and geochemistry of our sample set are consistent with the
471 analyses reported by Kennedy et al. (2006), but we suggest that decreased weathering, probably
472 tied to increased rates of uplift and physical erosion, can account for observed secular variation
473 without invoking any change in land vegetation or increased rates of chemical weathering.

474 To summarize, relative to chemical weathering, physical erosion dominates samples
475 across the Proterozoic-Cambrian boundary leading to a significant influx of detritally borne (and
476 relatively unweathered) micaceous clay-bearing sediment. Mesoproterozoic samples provide
477 multiple lines of evidence for moderate chemical weathering conditions (CIA = 70-85) that were
478 the most conducive to smectite mineral generation; and late Archean samples show more intense
479 weathering and leaching conditions (CIA = 90+) leading to residual enrichment of Al-rich
480 products before burial metamorphism. Whereas clay minerals undoubtedly played a role in OM
481 burial throughout Earth history, our data provide little support for the idea that *changes* in the
482 rate of clay formation in the regolith were principal drivers of Proterozoic oxygenation.

483

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493

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663 **Table 1:** Ages, formations, geographic locations, and thermal histories of samples discussed in
 664 this study.

<i>Sample ID</i>	<i>Age (Ma)</i>	<i>Formation</i>	<i>Location</i>	<i>Sample Type</i>	<i>Thermal</i>
GKPO1 248.09	2520-2500	Kleine Naute	S. Africa	DC	a, d, e
GKPO1 483.90	2600-2520	Nauga	S. Africa	DC	a, d, e
GKPO1 385	2600-2520	Nauga	S. Africa	DC	a, d, e
GKPO1 1017	2650-1600	Monteville	S. Africa	DC	a, d, e
GKPO1 893.1	ca 2600	Reivilo	S. Africa	DC	a, d, e
ABDP-9 149.30	2510-2500	Mt. McRae	W. Australia	DC	b, e
ABDP-9 178.60	2510-2500	Mt. McRae	W. Australia	DC	b, e
ABDP-9 147.30	2510-2500	Mt. McRae	W. Australia	DC	b, e
ABDP-9 174.67	2510-2500	Mt. McRae	W. Australia	DC	b, e
A82/5-97	1636	Lynnot	N. Australia	DC	a
MANTAI-277	1636	Barney Creek	N. Australia	DC	a
A82/2-473	1609	Dungaminnie	N. Australia	DC	c, e
A82/3-512	1492	Mainoru	N. Australia	DC	c, e
A82/3-328	1492-ca 1400	Crawford	N. Australia	DC	c, e
U5-412	1492-ca 1400	Jalboi	N. Australia	DC	c, e
U5-130	1492-ca 1400	Jalboi	N. Australia	DC	c, e
GG1-266	1492-ca 1400	Corcoran	N. Australia	DC	c, e
BR1-229	1492	Mainoru	N. Australia	DC	c, e
RS-4	1492-ca 1400	Velkerri	N. Australia	DC	c, e
RS-22	1492-ca 1400	Velkerri	N. Australia	DC	c, e
RS-18	1492-ca 1400	Velkerri	N. Australia	DC	c, e
RS-13	1492-ca 1400	Velkerri	N. Australia	DC	c, e
RS-21	1492-ca 1400	Velkerri	N. Australia	DC	c, e
AK10-60-6	ca 800-740	Kwagunt	N. America	OC	c, e
AK10-60-21	ca 800-740	Kwagunt	N. America	OC	c, e
SP12 69 8	ca 800-740	Galeros	N. America	OC	c, e
SP12 63 22	ca 800-740	Galeros	N. America	OC	c, e
SP12 69 4	ca 800-740	Galeros	N. America	OC	c, e
SP12 53 4	ca 800-740	Galeros	N. America	OC	c, e
SP14 63 12	ca 800-740	Galeros	N. America	OC	c, e
SP14 53 17	ca 800-740	Kwagunt	N. America	OC	c, e
SP12 63 4	ca 800-740	Galeros	N. America	OC	c, e
SP12 53 7	ca 800-740	Galeros	N. America	OC	c, e
SP14 53 15	ca 800-740	Kwagunt	N. America	OC	c, e
40 2358	ca 600-560	Vycheгда	Russia	DC	f
46 2398	ca 600-560	Vycheгда	Russia	DC	f
55 2504	ca 600-560	Vycheгда	Russia	DC	f
61 2606	ca 600-560	Vycheгда	Russia	DC	f
74 2688	ca 600-560	Vycheгда	Russia	DC	f
83 2779	ca 600-560	Vycheгда	Russia	DC	f
94 2821	ca 600-560	Vycheгда	Russia	DC	f
TO-320	635-ca580	Dracoisen	Svalbard	OC	c, e
OMR 010	<600-550	Shuram	Oman	DC	a
PIN-5079/61	ca 550	Redkino	Russia	OC	c, e
K05-M-4	ca 550	Redkino	Russia	OC	c, e
TSES-4275	549-545	Schwarzrand	Namibia	DC	a
TSES-5150	549-545	Nudaus	Namibia	DC	a
OMR 002	550-547	Buah	Oman	DC	a
OMR 017	550-547	Buah	Oman	DC	a

OMR 003	541	Thuleilat shale	Oman	DC	a
OMR 021	541	Thuleilat shale	Oman	DC	a
OMR 022	541	Thuleilat shale	Oman	DC	a
96-Ko-41	ca 545-543	Kotlin	Estonia	OC	c, e
96-Ko-31	ca 545-543	Kotlin	Estonia	OC	c, e
HU-61483	ca 540-530	Tokammane	Svalbard	OC	c, e
AE-1845	ca 540-530	Tokammane	Svalbard	OC	c, e

665

666 a. Below greenschist facies equivalent (<200°C max.); b. Prehnite-pumpellyite facies equivalent
667 to <300°C; c. Burial diagenesis to ~75°C; d. Fabric retentive diagenetic dolomite; e. Minimum
668 deformation fabric; f. Burial diagenesis to 120-150°C max; OC: outcrop sample; DC: drillcore
669 sample.

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673 **Table 2:** Mineralogical and geochemical characteristics of samples discussed in this study. All
674 mineral abundances and TOC are in wt. %. TOC: total organic carbon, SR: Schultz ratio, CIA:
675 chemical index of alteration (see text).

<i>Sample</i>	<i>TOC</i>	<i>SR</i>	<i>paleo CIA</i>	<i>CIA (Meso. UC)*</i>	<i>Qtz</i>	<i>Kspar</i>	<i>Plag</i>	<i>Glauc.</i>	<i>2M1</i>	<i>1M</i>	<i>1Md</i>	<i>Chlorite</i>	<i>Kaol.</i>	<i>Smect.</i>	<i>Source**</i>
GKPO1 248.09	8.4	0.20	82.1	--	19.5	34.8	0.0	0.0	11.5	0.0	0.0	16.3	0.0	0.0	L. Archean UC
GKPO1 483.90	6.6	2.43	68.6	--	7.1	0.0	0.0	0.0	24.1	7.1	0.0	0.0	0.0	0.0	L. Archean UC
GKPO1 385	1.11	1.93	81.4	--	0.0	18.4	0.0	9.7	38.1	19.7	11.6	5.6	0.0	0.0	L. Archean UC
GKPO1 1017	2.67	1.22	84.1	--	19.1	0.0	0.0	0.0	33.0	32.5	0.0	12.1	0.0	0.0	L. Archean UC
ABDP-9 149.30	12.09	0.21	85.4	--	17.7	40.0	0.0	7.8	14.4	6.8	0.0	6.5	0.0	0.0	L. Archean UC
ABDP-9 178.60	4.87	0.07	85.4	--	26.1	36.9	0.9	0.0	8.3	3.6	0.0	14.0	0.0	0.0	L. Archean UC
ABDP-9 147.30	12.6	0.13	86.1	--	32.4	31.5	0.0	5.4	6.6	7.6	0.0	10.8	0.3	0.0	L. Archean UC
ABDP-9 174.67	2.92	0.02	85.1	--	25.4	28.8	0.0	0.0	2.5	0.0	0.0	19.8	0.0	0.0	L. Archean UC
A82/5-97	4.5	0.10	83.0	--	30.8	26.9	0.0	14.8	4.0	0.0	0.0	4.7	0.0	0.0	L. Archean UC
MANTAI-277	3.9	0.33	85.3	--	32.2	14.2	0.0	16.6	19.1	3.6	3.6	7.1	1.2	0.0	L. Archean UC
A82/2-473	2.45	0.43	83.8	--	21.3	0.0	0.0	12.8	40.6	12.0	4.5	7.3	0.0	0.0	L. Archean UC
A82/3-512	2.1	0.09	74.6	--	47.4	3.8	5.6	5.7	17.3	2.9	0.0	10.3	0.0	0.0	L. Archean UC
A82/3-328	3.1	0.33	83.8	--	18.2	3.7	0.0	15.8	36.2	15.5	5.7	6.4	0.0	0.0	L. Archean UC
U5-412	2.5	0.27	81.9	--	41.2	6.5	0.0	16.4	15.6	0.0	0.0	17.6	0.0	0.0	L. Archean UC
U5-130	1.5	0.12	81.3	--	66.0	0.0	0.1	5.8	14.5	11.8	3.6	0.8	0.0	0.0	L. Archean UC
GG1-266	3.3	0.82	83.5	--	28.4	0.0	0.0	13.6	46.7	0.0	0.0	8.0	0.0	0.0	L. Archean UC
BR1-229	2.5	0.04	78.4	--	62.4	8.1	2.6	0.0	15.1	0.0	0.0	6.5	0.0	0.0	L. Archean UC
RS-4	12.4	0.14	72.0	--	53.1	2.1	3.9	14.1	8.7	13.4	6.4	2.4	0.0	0.0	L. Archean UC
RS-22	12.6	0.24	74.7	--	45.9	4.8	2.4	14.0	10.1	10.7	6.8	1.4	0.0	0.0	L. Archean UC
RS-18	11.3	0.20	70.7	--	43.0	3.8	4.8	19.8	5.6	14.5	6.3	3.7	0.0	0.0	L. Archean UC
RS-13	7	0.21	73.6	--	56.1	0.7	2.9	8.6	12.1	15.0	10.9	2.4	0.0	0.0	L. Archean UC
RS-21	5.7	0.24	78.2	--	47.2	5.3	1.8	11.9	9.3	19.2	9.4	2.4	0.0	0.0	L. Archean UC
AK10-60-6	6.6	0.55	81.9	85.9	29.2	0.0	0.0	2.7	35.4	0.0	0.0	2.4	27.0	0.0	Granitic
AK10-60-21	8.9	0.34	78.7	82.4	34.7	0.9	0.0	15.5	18.1	19.1	11.7	0.5	5.0	0.0	Granitic
SP12 69 8	4.68	0.62	79.7	83.7	26.2	0.0	0.0	4.2	22.3	15.7	15.6	1.0	11.5	0.0	Granitic
SP12 63 22	3.89	0.18	81.4	85.4	37.1	1.6	0.1	1.5	18.4	17.4	0.0	0.1	19.4	0.0	Granitic
SP12 69 4	0.31	1.33	77.3	81.1	21.6	0.0	0.0	10.3	29.6	28.3	1.5	0.9	1.4	0.0	Granitic
SP12 53 4	4.92	0.05	58.3	61.4	65.8	8.5	11.1	0.8	5.9	1.1	0.0	3.3	0.0	0.0	Granitic
SP14 63 12	0.08	0.27	80.3	84.1	59.9	0.0	0.0	1.2	18.2	9.4	0.1	1.0	7.6	0.0	Granitic
SP14 53 17	4.91	0.52	80.9	84.9	29.3	0.4	0.0	11.8	20.8	5.8	6.1	2.0	18.8	0.9	Granitic
SP12 63 4	4.96	0.20	75.1	78.8	55.5	0.6	3.2	1.7	12.0	7.5	1.0	0.4	14.0	1.8	Granitic
SP12 53 7	4.97	0.17	76.4	79.1	24.4	1.2	1.6	0.8	6.7	0.0	0.0	8.4	0.7	8.2	Granitic

40 2358	2.37	0.45	59.0	60.9	29.4	2.5	21.3	11.5	12.1	3.4	2.3	11.6	0.8	0.0	Granitic
46 2398	4.62	0.71	58.5	59.2	13.4	2.7	38.7	6.8	10.1	4.6	0.0	16.6	0.0	0.0	Granitic
55 2504	2.57	0.12	61.4	67.8	48.4	5.8	8.6	4.4	15.1	1.7	5.1	1.0	2.2	0.0	Granitic
61 2606	5.03	0.55	62.7	69.2	28.7	1.4	10.3	14.6	21.7	2.8	0.0	6.8	1.7	1.2	Granitic
74 2688	4.14	0.23	61.0	67.3	37.1	4.1	10.9	14.1	16.0	1.3	0.0	7.3	0.0	0.0	Granitic
83 2779	2.59	0.38	58.5	64.3	32.3	8.1	15.0	5.0	20.9	4.4	0.0	4.1	0.0	0.0	Granitic
94 2821	2.7	0.11	66.8	73.2	65.5	6.4	3.7	4.5	6.8	3.0	0.0	5.7	0.0	0.0	Granitic
TO 320	5.8	0.38	84.9	85.1	15.2	18.1	0.0	12.6	26.9	0.2	0.2	2.5	17.2	0.0	Neoprot. UC
K05-M-4	3.1	0.65	55.8	63.3	18.8	0.0	13.1	16.3	36.6	0.0	0.0	7.0	0.0	0.0	Charnockitic
PIN 5079/61	3.4	0.43	60.9	68.9	22.2	3.2	9.5	22.7	22.9	1.7	0.6	10.5	0.4	0.0	Charnockitic
96-Ko-41	2.9	0.26	59.0	83.2	35.0	11.2	0.0	0.5	36.0	0.0	0.0	4.5	1.0	0.0	Potassic granite
96-Ko-31	2.9	0.23	58.9	83.5	38.6	13.2	0.0	8.4	23.2	2.2	2.2	5.0	1.3	0.0	Potassic granite
95-Ko-4E	3.45	0.44	58.7	84.0	32.2	12.6	0.0	11.2	27.1	2.6	0.0	4.0	6.5	0.0	Potassic granite
TSES 4275	3.1	1.10	55.9	72.4	16.7	0.0	6.2	0.0	59.0	0.0	0.0	9.1	0.0	0.0	Charnockitic
TSES 5150	3.5	0.73	62.7	81.6	24.5	0.0	0.4	7.0	47.0	2.7	0.0	10.5	0.0	0.0	Charnockitic
OMR 003	8	0.20	79.0	87.5	46.0	3.2	0.0	0.0	7.0	4.2	0.0	0.0	4.1	1.0	Granitic
OMR 021	6.4	0.19	75.0	80.3	59.4	2.0	1.0	0.0	6.4	1.7	0.0	0.0	6.6	0.0	Granitic
OMR 022	2.5	0.34	74.0	82.4	23.1	3.5	1.3	0.0	4.8	8.6	0.1	0.9	3.5	0.0	Granitic
OMR 002	1.6	0.18	49.5	54.9	47.7	5.3	13.0	2.4	9.5	4.4	1.6	0.3	0.0	0.0	Granitic
OMR 017	2.3	0.11	50.0	55.8	55.3	4.7	7.9	1.6	3.5	6.1	0.0	0.0	1.4	0.0	Granitic
OMR 010	2.5	0.22	64.4	71.5	38.2	1.3	4.6	0.3	9.6	3.3	0.2	1.8	1.3	0.0	Granitic
HU 61483	3	0.41	55.7	83.5	4.0	48.4	0.0	2.8	29.9	0.0	0.0	2.8	3.7	0.0	Granite?
AE 1845	5.5	0.27	72.0	72.8	25.5	8.4	4.8	1.7	35.7	0.0	0.0	4.3	0.0	0	Granite?

*Paleo-CIA values recalculated in reference to average upper crust at the Mesoproterozoic/Neoproterozoic transition. Although for most samples the source composition can be constrained, average upper crust represents a low-K source and, in cases where few constraints on the source composition exist, serves to estimate “maximum” paleo-CIA values.

**Source composition used to estimate paleo-CIA values listed in the “paleo-CIA” column and shown in Figure 6.

Figure Captions:

Figure 1: Proportion of $2M_1$ illite (including muscovite) in the clay fraction in Proterozoic samples. Averages for each basin indicate that $2M_1$ mica-illite dominates the clay mineralogy in across Neoproterozoic samples.

Figure 2: Proportion of $1M/1M_d$ illite and glauconite in the clay fraction in Proterozoic samples. Averages for each basin indicate that these phases are minor components in Neoproterozoic samples.

Figure 3: A-CN-K molar ternary diagram with mineral compositions plotted for reference. Unweathered source rock compositions lie along the plagioclase-K-feldspar join, with mafic compositions plotting toward the A-CN join, and more potassic compositions plotting toward the A-K join. Chemical weathering of a given unaltered source rock composition is indicated by the blue line. K-metasomatism in the form of K-addition to aluminous clay minerals is indicated by the red line. K-substitution in plagioclase is indicated by the green line. Correction for K-metasomatism allows estimates of pre-metamorphosed CIA values (shown on left hand vertical axis). Mineralogical and/or petrographic information is required to infer whether samples have become weathered and subsequently enriched in K, or whether simple K-substitution in feldspar is responsible for its position on this diagram.

Figure 4: A-CN-K molar ternary diagram plotting late Archean and Mesoproterozoic samples analyzed in this study. All samples plot on an array extending from a region of the A-CN join consistent with smectite-kaolinite mixing. Relative to average upper Archean upper crust, all

samples have been significantly affected by K-metasomatism upon diagenesis and metamorphism. *Circles*: Late Archean; *triangles (down)*: Lynnot, Barney Creek and Dungaminnie Fmn.; *squares*: Mainoru, Crawford, Jalboi, Corcoran, Velkerri Fmn.

Figure 5: A-CN-K molar ternary diagram plotting Neoproterozoic samples analyzed in this study. These samples reflect various degrees of feldspar weathering, source compositions and K-metasomatism. All samples are enriched in K_2O relative to average upper crust at the Mesoproterozoic/Neoproterozoic transition, but in most cases source compositions are constrained by best fits to sample suites combined with mineralogical analyses. *Filled circles*: Kwagunt and Galeros Fmn.; *triangles (down)*: Vycheгда Fmn.; *squares*: Dracoisen Fmn.; *diamonds*: Redkino, Schwarzrand and Nudaus Fmn.; *triangles (up)*: Kotlin Fmn.; *empty circles*: Shuram, Buah, Thuleilat Fmn.; *hexagons*: Tokammane Fmn.

Figure 6: Estimated paleo-CIA values for each sample derived from constraints on source composition (discussed in text) and correction for K-metasomatism. Late Archean through Mesoproterozoic samples reflect moderate to intense weathering. Neoproterozoic samples generally exhibit lower paleo-CIA values, which are controlled by the contribution of immature (relatively unweathered) sediment. Values from Condie et al. (2001) represent formation averages.

Figure 7: Total organic carbon (in wt. %) as a function of estimated paleo-CIA value. The highest TOC samples occur at CIA values which correspond to weathering conditions most conducive to smectite genesis (shaded field). The majority of more intensely weathered samples

exhibit lower TOC values under conditions where smectites become destabilized by intense leaching. *Grey circles*: Late Archean; *empty triangles (down)*: Lynnot, Barney Creek and Dungaminnie Fmn.; *empty squares*: Mainoru, Crawford, Jalboi, Corcoran, Velkerri Fmn.; *filled circles*: Kwagunt and Galeros Fmn.; *filled triangles (down)*: Vychegda Fmn.; *filled squares*: Dracoisen Fmn.; *diamonds*: Redkino, Schwarzrand and Nudaus Fmn.; *triangles (up)*: Kotlin Fmn.; *empty circles*: Shuram, Buah, Thuleilat Fmn.; *hexagons*: Tokammane Fmn.

Figure 8: Total organic carbon (in wt. %) as a function of “illite crystallinity”, expressed by the full width at half maximum of the 10Å illite 001 peak. A larger FWHM corresponds to finer crystallite size. The 10Å peak represents the contribution of $2M_1$, $1M$ and $1M_d$ illite and glauconite present in the sample. The highest TOC samples are associated with the finest illite crystallite size, which is likely the product of physical aggregation and the interference of OM with the illitization reaction. This potential interference preserves illite polytype and crystal size, but could lead to the association of high surface area with high TOC content observed in ancient siliciclastic rocks. *Grey circles*: Late Archean; *triangles (down)*: Lynnot, Barney Creek and Dungaminnie Fmn.; *squares*: Mainoru, Crawford, Jalboi, Corcoran, Velkerri Fmn.; *filled circles*: Kwagunt and Galeros Fmn.; *diamonds*: Redkino, Schwarzrand and Nudaus Fmn.; *triangles (up)*: Kotlin Fmn.

Figure 9: Schultz ratio measured in Proterozoic samples. The Schultz ratio is an empirical measurement of the relative peak intensities between all phyllosilicates (including all illite polytypes, chlorite, muscovite and weathering-derived clays) and quartz. Schultz ratios are variable across all samples, with Neoproterozoic samples exhibiting, on average, higher values

than more ancient samples. However, the contribution of later generations of quartz cement cannot be distinguished with XRD data alone.

Figure 10: Schultz ratio as a function of $2M_1$ illite (including muscovite) content (in wt. %). The strong correlation shows that Schultz ratios in our samples are strongly controlled by igneous/detrital clays, with Neoproterozoic samples exhibiting the highest values. Late Archean samples that contain appreciable chlorite exhibit some of the highest Schultz ratios measured.