



# Clay Mineralogy, Organic Carbon Burial, and Redox Evolution in Proterozoic Oceans

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

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12  
13  
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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub> 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 O<sub>2</sub>.

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 $\mu\text{m}$ . 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  $\mu\text{m}$  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  $65^\circ\text{C}$ .

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  $2\Theta$  angles less than  $20^\circ$  (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 $\Theta$  range and the auto-background correction feature, allowing  
124 mineral standards to be slightly shifted in 2 $\Theta$  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*<sub>d</sub>) and 2*M*<sub>1</sub> illite polytypes using *hkl* reflections at 32.1 (2*M*<sub>1</sub>)  
134 and 24.3 degrees 2 $\Theta$  (Cu K $\alpha$ ) 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*<sub>d</sub> 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*<sub>1</sub> 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  $\sim 5$  wt. %.

148 For ethylene glycol treated oriented aggregates, the full width at half maximum of the  
149  $10\text{\AA}$  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  $105^{\circ}\text{C}$  and  
158 heating to  $550^{\circ}\text{C}$ . 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  $\text{Al}_2\text{O}_3$ -( $\text{CaO}^*$ + $\text{Na}_2\text{O}$ )- $\text{K}_2\text{O}$  ternary plot (here, referred to as A-CN-K) of molar oxide  
244 proportions, where  $\text{CaO}^*$  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  $\text{Al}_2\text{O}_3$  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 ( $\text{Al}_2\text{O}_3$ ) 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  $10\text{\AA}$  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  $10\text{\AA}$  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  $10\text{\AA}$  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  $10\text{\AA}$  peak correlates strongly ( $r_s = 0.598$ ,  $P =$   
364  $2.3 \times 10^{-4}$ ) 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  $6.8 \times 10^{-4}$ ; 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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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 |

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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> |
|----------------------|------------|-----------|------------------|------------------------|------------|--------------|-------------|---------------|------------|-----------|------------|-----------------|--------------|---------------|-----------------|
| <b>GKPO1 248.09</b>  | 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   |
| <b>GKPO1 483.90</b>  | 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   |
| <b>GKPO1 385</b>     | 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   |
| <b>GKPO1 1017</b>    | 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   |
| <b>ABDP-9 149.30</b> | 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   |
| <b>ABDP-9 178.60</b> | 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   |
| <b>ABDP-9 147.30</b> | 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   |
| <b>ABDP-9 174.67</b> | 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   |
| <b>A82/5-97</b>      | 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   |
| <b>MANTAI-277</b>    | 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   |
| <b>A82/2-473</b>     | 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   |
| <b>A82/3-512</b>     | 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   |
| <b>A82/3-328</b>     | 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   |
| <b>U5-412</b>        | 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   |
| <b>U5-130</b>        | 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   |
| <b>GG1-266</b>       | 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   |
| <b>BR1-229</b>       | 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   |
| <b>RS-4</b>          | 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   |
| <b>RS-22</b>         | 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   |
| <b>RS-18</b>         | 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   |
| <b>RS-13</b>         | 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   |
| <b>RS-21</b>         | 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   |
| <b>AK10-60-6</b>     | 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        |
| <b>AK10-60-21</b>    | 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        |
| <b>SP12 69 8</b>     | 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        |
| <b>SP12 63 22</b>    | 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        |
| <b>SP12 69 4</b>     | 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        |
| <b>SP12 53 4</b>     | 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        |
| <b>SP14 63 12</b>    | 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        |
| <b>SP14 53 17</b>    | 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        |
| <b>SP12 63 4</b>     | 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        |
| <b>SP12 53 7</b>     | 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        |

|                    |      |      |      |      |      |      |      |      |      |     |     |      |      |     |                  |
|--------------------|------|------|------|------|------|------|------|------|------|-----|-----|------|------|-----|------------------|
| <b>40 2358</b>     | 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         |
| <b>46 2398</b>     | 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         |
| <b>55 2504</b>     | 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         |
| <b>61 2606</b>     | 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         |
| <b>74 2688</b>     | 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         |
| <b>83 2779</b>     | 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         |
| <b>94 2821</b>     | 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         |
| <b>TO 320</b>      | 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      |
| <b>K05-M-4</b>     | 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     |
| <b>PIN 5079/61</b> | 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     |
| <b>96-Ko-41</b>    | 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 |
| <b>96-Ko-31</b>    | 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 |
| <b>95-Ko-4E</b>    | 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 |
| <b>TSES 4275</b>   | 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     |
| <b>TSES 5150</b>   | 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     |
| <b>OMR 003</b>     | 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         |
| <b>OMR 021</b>     | 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         |
| <b>OMR 022</b>     | 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         |
| <b>OMR 002</b>     | 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         |
| <b>OMR 017</b>     | 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         |
| <b>OMR 010</b>     | 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         |
| <b>HU 61483</b>    | 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?         |
| <b>AE 1845</b>     | 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.