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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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 2M₁ 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**

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

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

1. Introduction

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

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

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

2. Sample set and methods

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

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

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

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

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

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

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

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

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

The RockJock software generally produces accurate results when quantifying major groups of clay minerals (i.e., kaolinite, 2:1 dioctahedral clays and chlorites). However, quantitative assignment of polytypes (and species within these groups) is less reliable, and in some cases the software produces false positive identification of phases and polytypes. For this reason, where possible, ZnO-free randomly oriented powder XRD patterns were analyzed to verify $1M$ (possibly including $1M_d$) and $2M_1$ illite polytypes using hkl reflections at 32.1 ($2M_1$) and 24.3 degrees 2Θ (Cu $K\alpha$) and the $2.58\text{\AA}$ band, which is common to all illite polytypes (Grathoff and Moore, 1996). The identification and estimate of $1M$ and $1M_d$ illite polytypes is complicated by the fact that their specific hkl reflections often overlap. Thus an approximate estimate for polytype percentage independent of RockJock software involves dividing the area of the 32.1° peak over the total area of the $2.58\text{\AA}$ band (Grathoff and Moore, 1996; see electronic annex). This analysis could not be done for all samples because of the difficulty in detecting these weak polytype specific peaks, especially in cases where $2M_1$ illite abundances were low. Where it was possible, however, this allowed a check on RockJock determined polytype assignments. Some inaccuracy is inescapable, but the stratigraphic coherence of large differences found within our sample set suggests our data reflect real differences in clay content.

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

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

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

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

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

3. Mineralogy and Geochemistry of Proterozoic Shales

3.1 Clay mineralogy through the Proterozoic Eon

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

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

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

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

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

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

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

3.2 *Paleo-weathering indices and K-metasomatism*

Chemical weathering leaches and subsequently depletes the soluble elements Ca, Na and K relative to Al and, in some cases, Fe. Mineralogically, progressive Al-enrichment is reflected by the formation of smectite and Al-bearing clay minerals in the residual weathered materials (Nesbitt and Young, 1989; Nesbitt and Markovics, 1997). The net effect of chemical weathering, then, is the conversion of feldspar to smectite and, with continued and/or more intense leaching, Al-rich clays such as gibbsite and kaolinite. These changes are most effectively uncovered using a Al_2O_3 -($\text{CaO}^* + \text{Na}_2\text{O}$)- K_2O ternary plot (here, referred to as A-CN-K) of molar oxide proportions, where CaO^* is silicate CaO only (the CaO correction includes removal of carbonate-associated Ca, as well as phosphate-associated CaO. More details of the correction can be found in Fedo et al. (1995)). The chemical trends of modern and ancient weathering profiles are indistinguishable to those predicted from thermodynamic and kinetic data (Nesbitt and Young, 1984; Nesbitt et al., 1997). This relationship requires that the predicted chemical weathering trend of a given source rock composition on the A-CN-K diagram evolve along a path parallel to the A-CN join (see Figure 3). With continued and/or more intense weathering, after intersection with the A-K join, the trend continues to the Al_2O_3 apex where the soil mineralogy is dominated by aluminous phases (Figure 3). Quantitatively, the degree of weathering is expressed by the chemical index of alteration (CIA), where:

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

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

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

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

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

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

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

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

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

4. Mineralogical and geochemical associations with organic carbon

4.1 Paleo-CIA and TOC

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

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

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

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

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

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

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

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

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

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

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

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

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

5. Physical and chemical weathering through the Neoproterozoic Era

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

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

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

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

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

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

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

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

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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	Vychevda	Russia	DC	f
46 2398	ca 600-560	Vychevda	Russia	DC	f
55 2504	ca 600-560	Vychevda	Russia	DC	f
61 2606	ca 600-560	Vychevda	Russia	DC	f
74 2688	ca 600-560	Vychevda	Russia	DC	f
83 2779	ca 600-560	Vychevda	Russia	DC	f
94 2821	ca 600-560	Vychevda	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.

670

671

672

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 K₂O 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)*: Vychegda 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.