

Geochronology Manuscript Comments from Referee

1:

Subarkah et al. have investigated the links between burial history, palaeo-temperature evolution, illite formation age, illite crystallinity and organic matter maturation in Proterozoic shales from the McArthur Basin, Australia, by combining a literature study with novel petrographic analysis, thermal modelling of the effect of a dolerite intrusion and in-situ Rb–Sr dating of authigenic illitic clays via LA-ICP-MS/MS. The authors argue that the illite Rb–Sr system is stable at temperatures around the oil window but tends to be reset at higher temperatures around or above the gas window. The manuscript is well structured and the outcome is of potential interest for the geochemical society. Nonetheless, I have identified numerous (mostly minor) problems and inaccuracies that must be included before the manuscript can be accepted for publication. The present work would greatly benefit, if the authors:

1) Can provide vitrinite reflectance data for a direct temperature assessment?

Vitrinite is plant-derived and is only found in rocks from the Silurian and younger. There is no vitrinite in the Mesoproterozoic, and as such, this is not a tool at our disposal. However, we are able to calculate modelled Vitrinite Reflectance equivalents from our Tmax data following Jarvie et al., (2001). We will also be able to do this from new bitumen reflectance, methyl phenanthrene distribution factor and methyl phenanthrene ratio data collated from Jarret et al., (2019). We will include this as a new figure to show that the four thermal maturation indicators reflect the same elevated patterns down-hole and can also use this for a direct temperature assessment.

2) Could provide in-situ Rb–Sr glauconite ages (arguably the earliest diagenetic product) and compare with burial diagenetic illite formation ages?

Unfortunately, this is outside the scope of this study. More importantly, glauconite in samples here is also be a very minor component (1-2 wt. %), such that a laser spot target the phase will inherently incorporate the illite matrix within its vicinity. Furthermore, the illite-derived thermal constraints compiled in the study may also not reflect the formation of the glauconite phase in the samples.

3) Consider and discuss the possibility of a second pulse of illite growth associated with the dolerite intrusion rather than a simple reset of the pristine signature of an inherited illite phase (pedogenic or early burial diagenetic), which would explain the decreasing Kübler indices with depth and the different illite morphologies.

Done. Some illite morphologies in the reset samples do look recrystallised and can be interpreted as a secondary growth. This description will be discussed further for further clarity.

4) Can identify (if possible) a relation between illite type (pore growth vs. lamellar), host rock lithology (shale vs. sandstone) and illite age (pristine vs. reset vs. newly formed). It looks like the sandstone-associated illite ages are reset (or represent illite neo-formation) while the shale-associated illite ages are true depositional or burial diagenetic ages. Is there a correlation between rock porosity, permeability, fluid transport and illite mineralization vs. resetting events?

We apologise for the mistake shown in Figure 2 as the samples are shown from the wrong depths here. The reset ages are samples from the Lower and Middle Velkerri Formation with a relatively rise in the gamma-ray well log which signify a relative increase in the grain size in

comparison to the Upper and Middle Velkerri Formation. However, the density and neutron well logs show similar values which represent similar porosity and permeability between the different formation intervals. Additionally, all of the samples analysed for Rb-Sr dating are shales, therefore we can corroborate that there are no distinguishing differences in lithology between the shale samples.

5) Can provide XRD patterns of illite and clay assemblages) to prove the absence of interstratified I-S in their samples?

Done.

Taking all these aspects together, I recommend publication of the manuscript after some moderate revision with the aforementioned points in mind.

Other minor and major issues:

L20: "Hydrothermal" implies interaction of rocks with hot fluids generated from a cooling magma – better change to "thermal sensitivity".

We disagree with the reviewer here, as hydrothermal only means "hot water" and does not suggest where that fluid comes from. We use the term "hydrothermal sensitivity" as the system is susceptible to fluid and heat. Changing this to "thermal sensitivity" would be incorrect and misleading on our behalf.

L22: Worthy to say that the study site is located in Australia...

Done.

L27-29: There is something wrong with the sentence structure, please check.

Done.

L39: "thermal systems absent of fluids" – this is extremely simplified; fluids are always present in shales given that hydrous phyllosilicates and organic matter are present.

This will be rewritten for clarity.

L46-47: Worthy to say that distinctions between detrital and authigenic (plus resetting events) mineral phases must be made.

Done.

L56: instruments // techniques

'Instruments' is correct, as this is said in reference to the application of similar methods using different instruments such as a Multi-Collector.

L58: Define "reactive gas". // a LA-ICP-MS/MS system

Done.

L62: I agree, but its worthy to mention that LA spot sizes (typically 50 or 75 μm) limit the area of investigation and that nm or μm sized mineral intergrowths of different origin are problematic, as they give mixed ages that need to be deconvoluted.

Done.

L68: Clay minerals present in shales are barely visible with naked eyes, please re-phrase.

Done.

L71: ...the samples analysed and of the fluids involved.

Done.

L72: has been

Done.

L78: Most clay mineral reactions take place under far-from-equilibrium conditions, especially in diagenetic settings, where, for instance, smectite matures to illite through mixed-layer I-S. This process can proceed over millions of years depending on T, K content, subsidence rate, fluid composition etc. (see Hower et al., 1976), and is never ever in equilibrium. Also, the term “water-column” is misleading here, as the seawater-derived fluids are always modified during diagenesis; better change to “burial fluids” or “formation waters” (or a similar phrase).

Done.

L81: ...and erosion of soils and unstable parent rocks”.

Done.

L90-98: I agree. However, it is worthy to say that illite maturation in shales via I-S formation is not an event-driven mineral reaction. Indeed, this process takes time (~Myr) and it is, until now, unclear how the Rb-Sr system in illite and I-S is affected during this continuous alteration process.

Done.

L99-101: Hard to follow, please simplify.

Done.

L102: Which type of clays is involved, illite, chlorite?

Illite.

L133: The saline Black Sea is characterized by a strong water-column redox stratification, while the Baltic Sea is brackish and mostly oxygenated (except for very deep basin parts, like Landsort deep). Perhaps the modern Black Sea is a better analogue for the Roper Group?

Both comparisons have been previously made in literature as seen in Ahmad and Munson (2013), Yang et al., (2020), and Cox et al., (2022).

L145: have been deposited? The U-Pb age of a detrital zircon cannot be used to establish a minimum age of a formation, because the zircons can record any age. However, I agree that the intrusion must be younger than the depositional age of the shale, so better say that the Kyalla Formation is somewhat older than 1313 Ma.

We disagree with the reviewer here. The Kyalla Formation cannot be older than the youngest detrital zircon age and is younger than the age of the intrusion. Therefore, the deposition window for the Kyalla Formation is bracketed between these two constraints.

L149: Depositional age or diagenetic age, given that we look at authigenic clays?

This was in relation to the Re-Os age referenced in literature, which has been interpreted as the depositional age. We will rewrite this for clarity.

L171: ... which provide important complementary data to supplement this study, such as...

Done.

L182: Use of the word "sands". Isn't it sandstone or weakly consolidated sandstone, given that metamorphic rocks (shale) are involved?

Done.

L188: collated // collected

Done.

L190: were // where

Done.

L191: at depths of

Done.

L195: Adelaide Microscopy – is this correct?

Yes.

L196: ...acceleration voltage. MLA maps were collected

Done.

L199: Which chemical criteria were chosen to distinguish between smectite, illite and I-S, or between different chlorite minerals? How good are the MLA quantifications compared to the bulk XRD data? Note here that Rafiei et al. (2020) report good data comparability for fine sized samples.

The minerals were identified through a comparison of the analysed spectra with a universal library provided by the Bruker AMICS software. The machine and program used by Rafiei et al. (2020) is different to the one used in this study and may result in a slight disparity.

L199-205: Were the Sr initials calculated from the isochrons or assumed to reflect Proterozoic seawater?

Calculated from the isochrons.

L214: The GLO age should be somewhat older (~100 Ma), because the host rock is of lower Cenomanian age. Please comment on this.

The age that we obtained (96 +/- 4 Ma) is accurate and within error to the published solution age of GL-O which is 94 +/- 1 Ma (Charbit et al., 1998 and Derkowski et al., 2009). This is noted as younger than a tuff-horizon U-Pb age for the unit dated at 113 +/- 0.3 Ma (Selby, 2009). As such, the ages obtained from GL-O have been proposed to instead either be indicative of the formation of glauconite in the host rock or the timing of isotopic closure of the mineral, occurring 4-5 m.y. after deposition (Selby, 2009 and Redaa et al., 2022). We will discuss this in the manuscript for clarity.

L229: Is there any mineralogical evidence for the assumed temperature of the sill, such as high-T mineral assemblages?

Sills of the Derim Derim Dolerite commonly comprise of plagioclase, clinopyroxene, hornblende, magnetite and minor quartz, although detailed analysis of the intrusion temperatures has not been conducted and is beyond the scope of this study. Sills are however interpreted as extracted from a mantle plume below the region (Yang et al., 2020; Nixon et al., 2021), and estimates of melt temperatures extracted from this source type have been used to constrain sill temperature (Wang et al., 2012).

L247: Tmax results compiled in this study range

Done.

L253: The Kübler Index is extremely high for true illite. Provide XRD patterns at EG-solvated state to determine the potential presence of I-S intermediates. If chlorite is present in the samples it is worthy to report the Archai Index as well, and cross-check with the Kübler Index data.

Done.

L257: If the temperature is > 120 °C kaolinite will change into dickite, please verify. Also, Mnt is not stable under these burial conditions. The only possibility of having Mnt in the samples is more recent sub-surface weathering (of for example feldspar).

Some clay phases have been identified as products of alteration of detrital feldspar. This is discussed in the Supplementary Material but we will discuss this further in the next iteration of the manuscript for clarity.

L260: Clinochlore is a Mg-rich chlorite – what is the difference between chlorite and clinochlore here?

The SEM instrument used here has differentiated between chlorite and clinochlore. Chlorite and clinochlore will be combined in the next iteration of the manuscript for clarity.

L263: XRD is not a destructive method by definition, but samples need to be crushed to obtain fine powders so that fabric information are lost, please revise.

Crushing the rock into powder for analysis destroys the petrographic relationship of the sample. After the sample is crushed for XRD, it cannot be reused for in situ analysis. We will rewrite this for clarity.

L264: Worthy to say that 1) MLA is often localized on small areas or layers that are not always representative for the bulk rock, 2) MLA assumes ideal mineral compositions and densities for mineral quantification and 3) MLA is based on 2D information. These aspects can make comparison with XRD datasets enigmatic.

Done.

L265: bulk XRD and MLA mapping results are summarized...

Done.

L271: Why is the age uncertainty so high in case of the shale samples investigated?

This is discussed in lines 272-278. Some samples simply do not have a wide range in Rb/Sr ratios, or are not abundant in Rb.

Table 1: The correlation between XRD and MLA datasets is OK (good) but far away from being consistent or excellent, as indicated by the authors. For example, kaolinite, montmorillonite and quartz are off by >10 wt.% in many cases, please clarify. Clinocllore is the Mg member of the chlorite family.

This is discussed in lines 260-265.

L313: Kübler index (KI) is determined by the 001-reflection of illite

Done.

L316: Vitrinite reflectance data can provide absolute formation temperatures.

As previously discussed, vitrinite is not present in the rock record during the Proterozoic. However, we will calculate vitrinite reflectance equivalents based on several maturity indicators such as Tmax, bitumen reflectance and aromatic hydrocarbon data in the next iteration of the manuscript.

L319: such as changes in heating rate

Done.

L335: ...or possibly due to the presence of I-S in the samples? Provide XRD patterns for confirmation.

Done.

L376: formed within the host sediment during burial diagenesis

Done.

L377: A minor component of illite also replaces micas and feldspars...

Done.

L383: suggesting that the majority of illite formed relatively soon after sediment deposition.

Done.

L403: Unclear meaning of "more crystalline morphologies", re-phrase

Done.

L429: ...recrystallized the former mineral assemblage or induced a second mineralization of clays.

Done.

L431-449: This is largely repetition, delete.

This paragraph is a summary of the discussions mentioned in the section and is used to conclude the argument. Hence, some points will be reiterated. However, we will rewrite this for clarity.

L456: Re-phrase: "which as intersected at present day depth 1696 m."

Done.

L463: or induced a second mineralization event?

Done.

L496: crystalline illite morphologies

Done.

Figure 2: Why has TOC a negative value?

Done. Fixed figure.

Figure 5: Mineral coding is difficult to read, i.e. change mineral colors on the maps.

Done.

Figure 6: Can the authors explain the differences in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ values among the sample set, i.e. ranging from radiogenic to seawater-type?

This is calculated from the isochrons. Each samples have a different spread in data, and as such, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ value calculated from each isochron (i.e. the y-intercept) will differ.

Best regards